



(12) 发明专利

(10) 授权公告号 CN 113004255 B

(45) 授权公告日 2023. 08. 01

(21) 申请号 201911322687.X

(22) 申请日 2019.12.20

(65) 同一申请的已公布的文献号  
申请公布号 CN 113004255 A

(43) 申请公布日 2021.06.22

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(51) Int. Cl.

- C07D 405/04 (2006.01)
- C07D 405/10 (2006.01)
- C07D 405/14 (2006.01)
- C07D 407/04 (2006.01)

C07D 407/08 (2006.01)

C07D 471/04 (2006.01)

C07D 491/048 (2006.01)

H10K 85/60 (2023.01)

H10K 50/11 (2023.01)

H10K 50/18 (2023.01)

H10K 50/16 (2023.01)

(56) 对比文件

CN 102870248 A, 2013.01.09

CN 103189368 A, 2013.07.03

CN 110963969 A, 2020.04.07

ACS.RN 2133447-09-1等.STN

Registry.2017,1-6.

审查员 金英

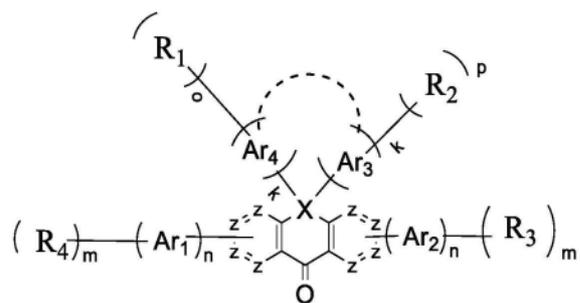
权利要求书9页 说明书30页 附图1页

(54) 发明名称

一种以杂蒽酮为核心的化合物及其应用

(57) 摘要

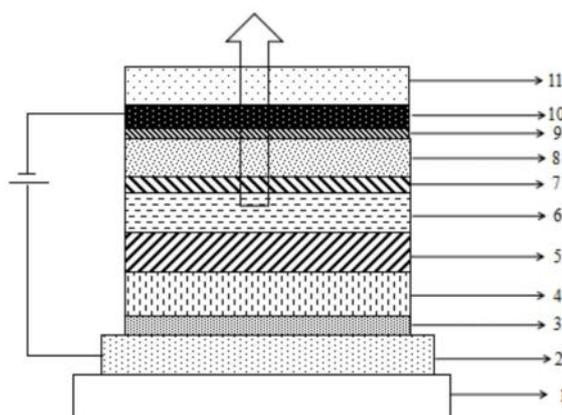
本发明公开了一种以杂蒽酮为核心的化合物及其应用,属于半导体技术领域。本发明提供的化合物的结构如通式(1)所示:



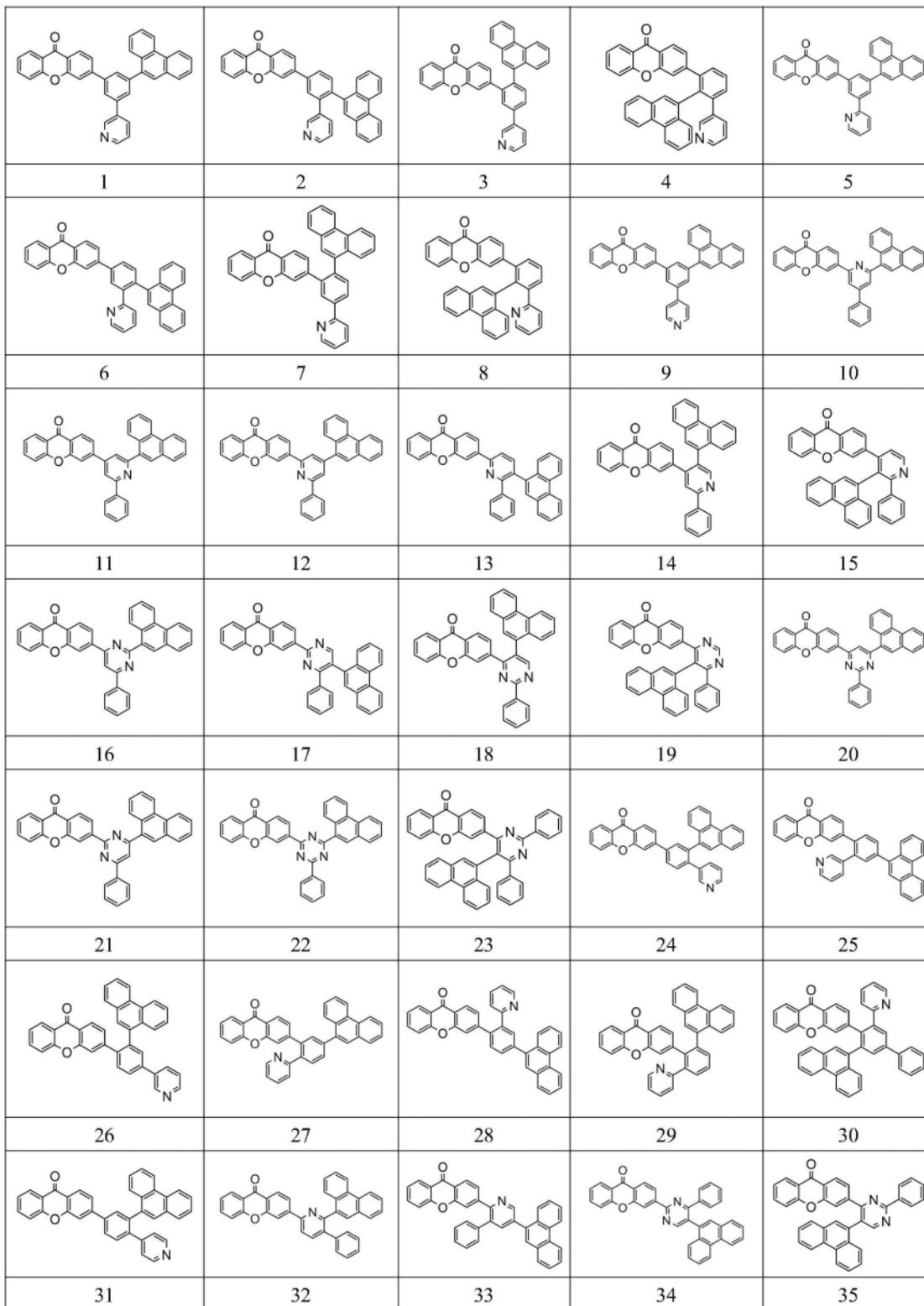
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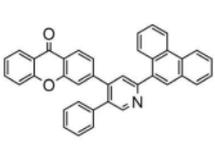
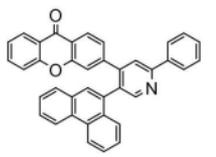
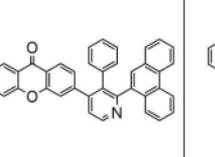
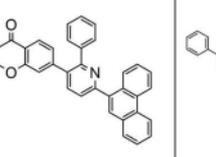
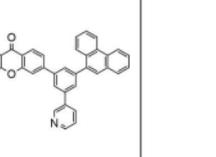
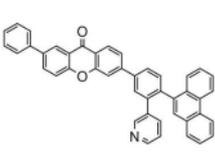
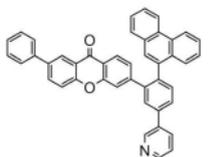
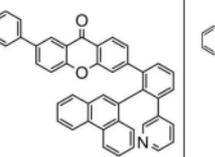
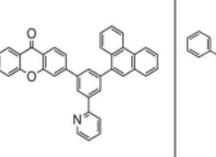
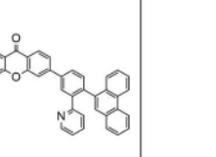
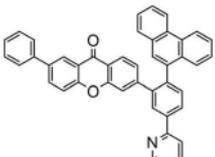
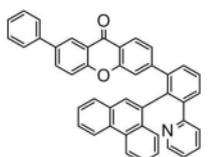
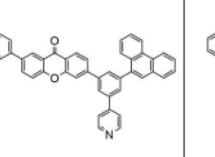
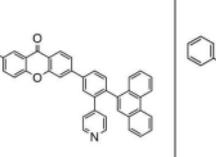
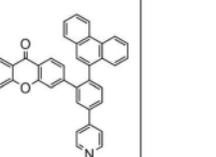
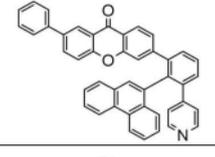
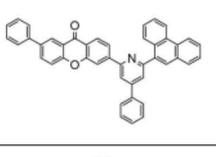
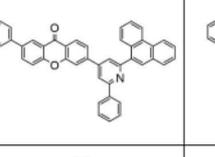
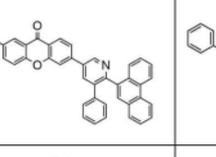
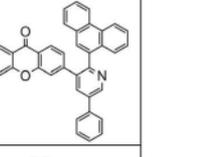
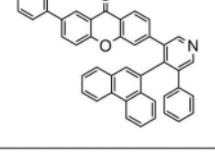
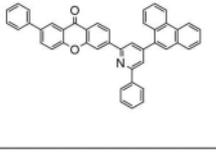
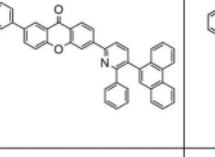
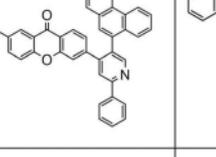
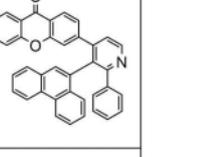
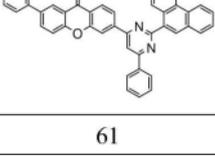
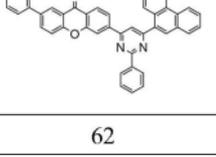
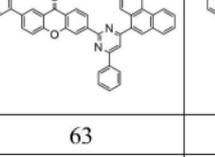
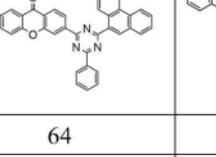
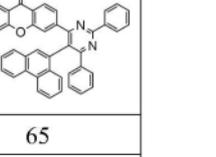
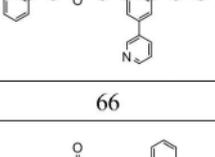
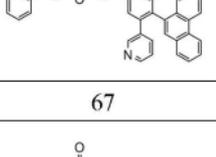
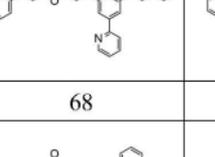
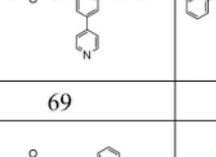
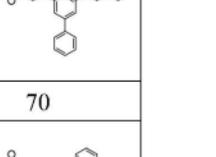
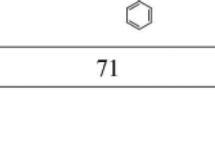
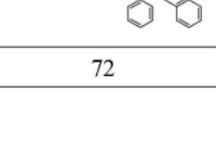
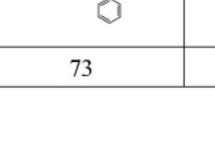
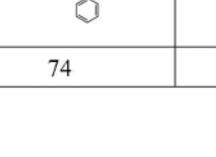
本发明的化合物含有杂蒽酮类母核结构,具有合适的HOMO和LUMO能级,较高的Eg和三线态能级(T1)。本发明提供的化合物还具有较高的玻璃化温度和分子热稳定性;作为OLED发光器件的发光层或空穴阻挡或电子传输层材料使用时,搭配本发明范围内的支链可有效提高该类结构立体性;

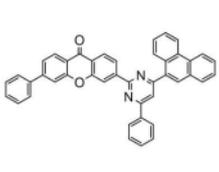
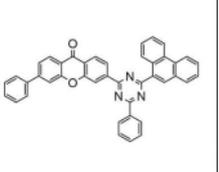
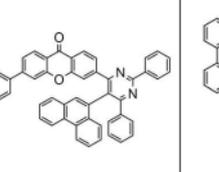
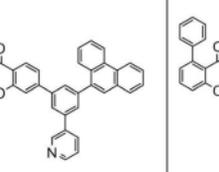
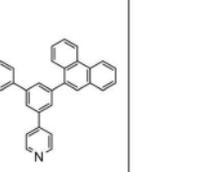
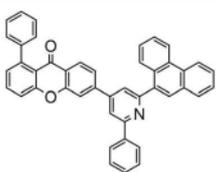
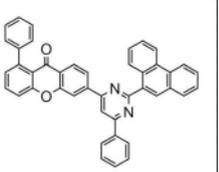
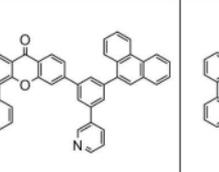
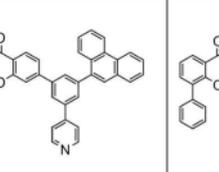
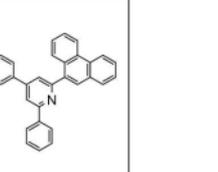
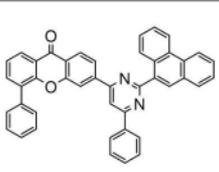
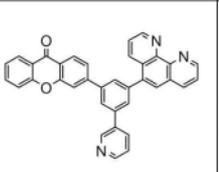
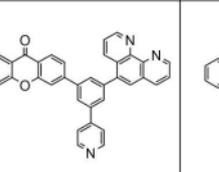
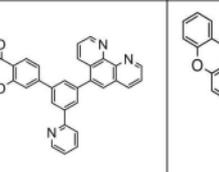
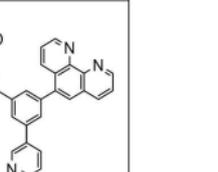
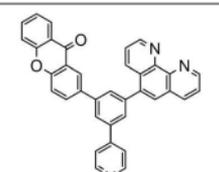
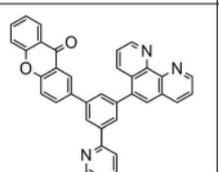
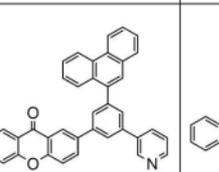
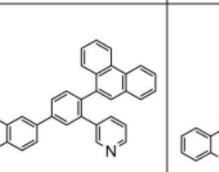
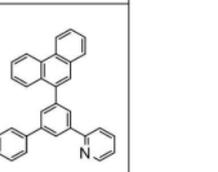
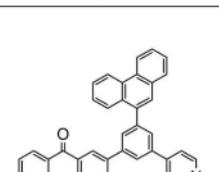
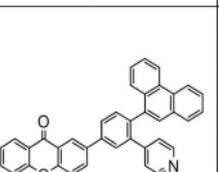
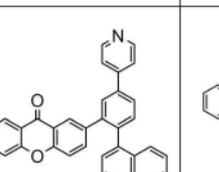
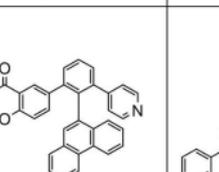
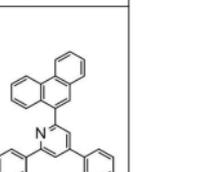
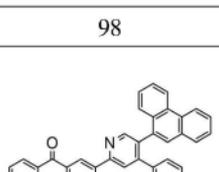
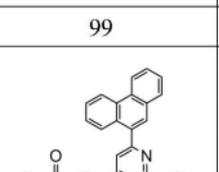
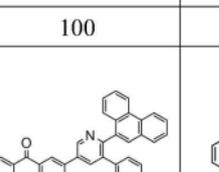
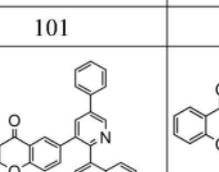
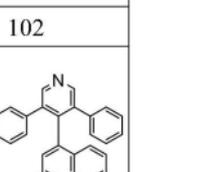
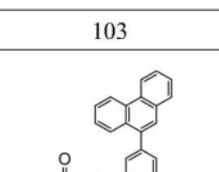
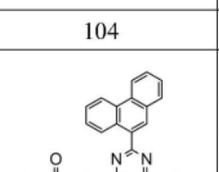
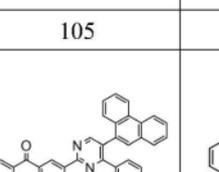
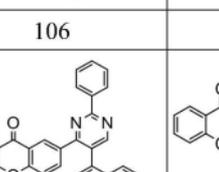
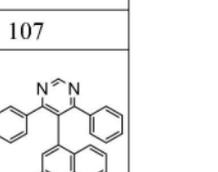
分子整体空间位阻大,不易转动,提高了材料化学稳定性。因此,本发明化合物应用于OLED器件后,可有效提升器件的发光效率及使用寿命。

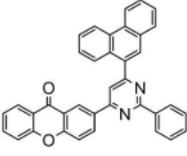
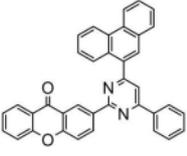
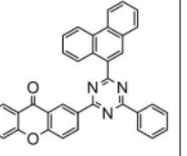
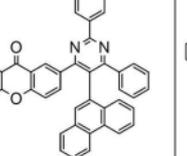
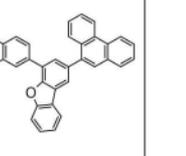
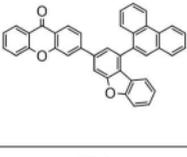
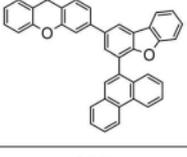
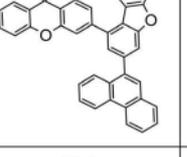
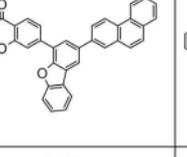
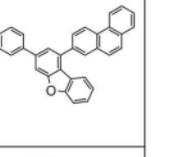
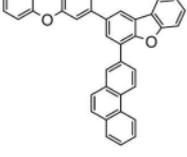
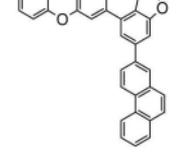
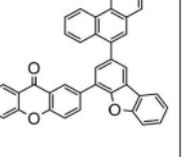
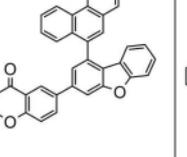
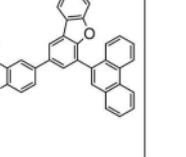
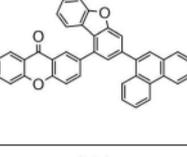
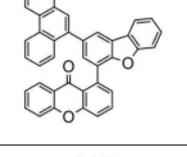
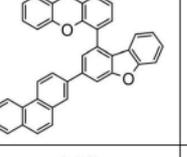
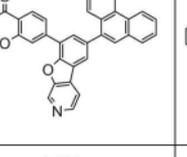
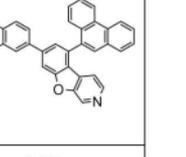
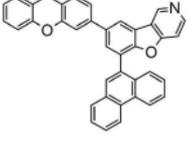
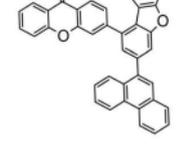
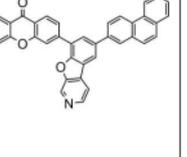
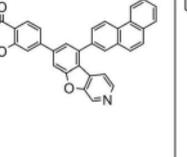
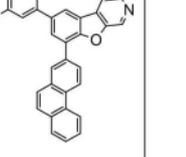
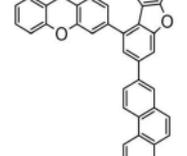
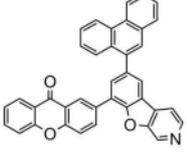
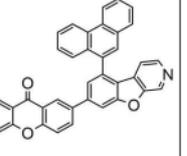
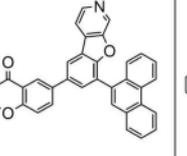
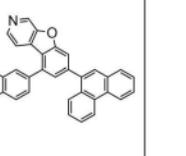
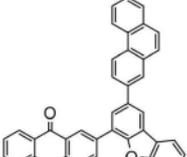
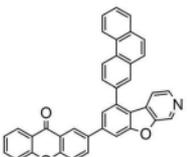
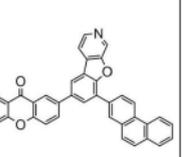
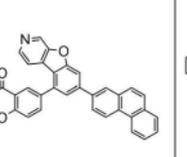
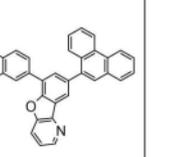


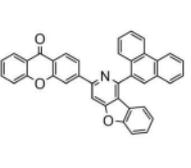
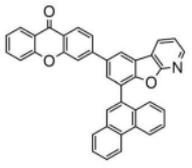
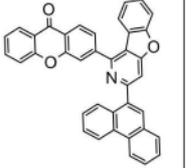
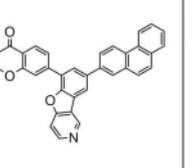
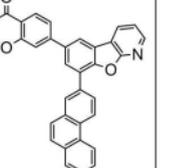
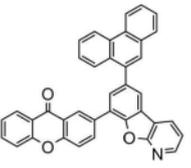
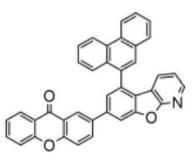
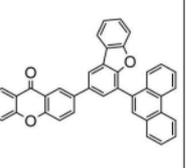
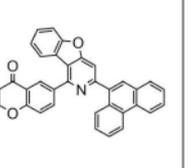
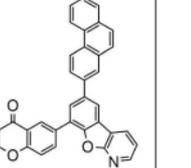
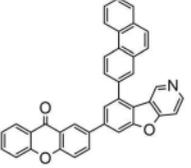
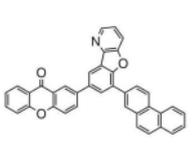
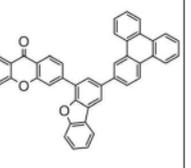
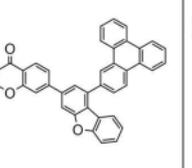
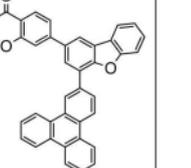
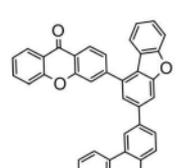
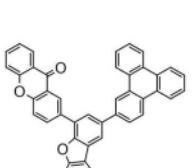
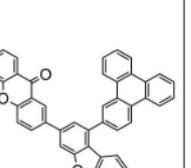
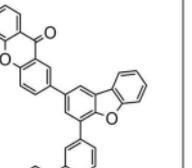
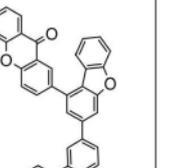
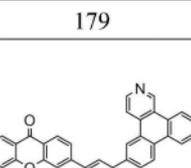
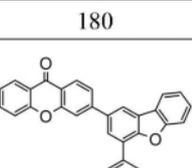
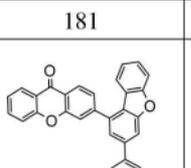
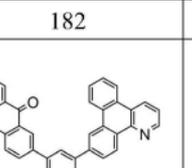
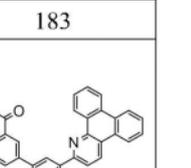
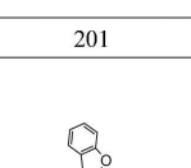
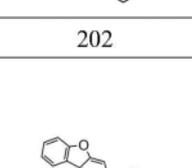
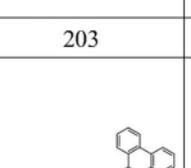
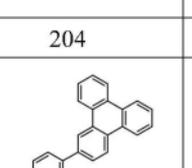
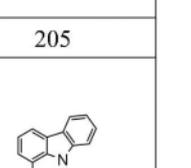
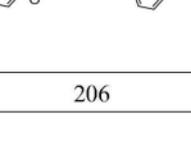
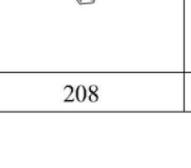
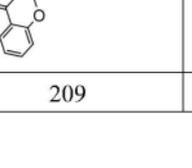
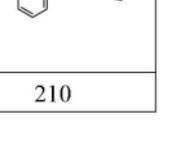
1. 一种以杂蒽酮为核心的化合物,其特征在于,该化合物的具体结构为:

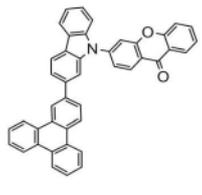
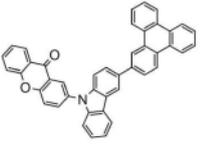
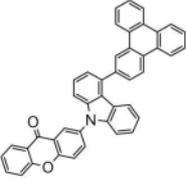
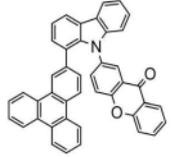
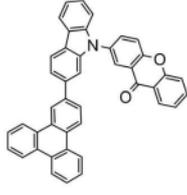
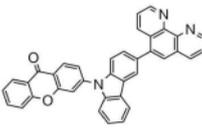
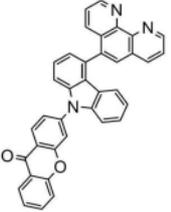
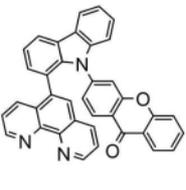
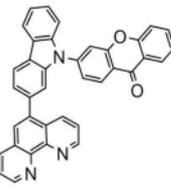
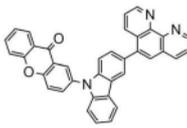
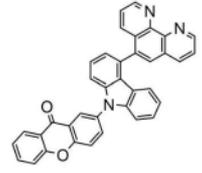
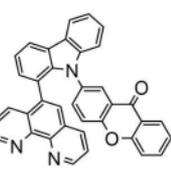
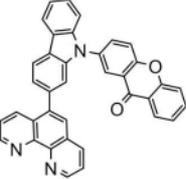
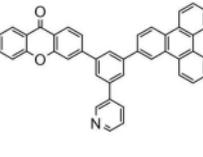
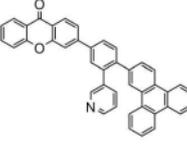
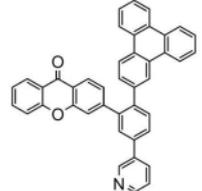
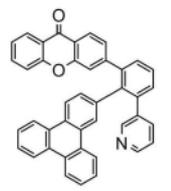
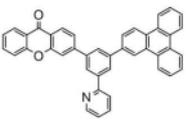
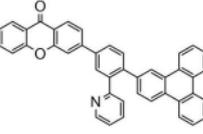
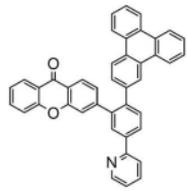
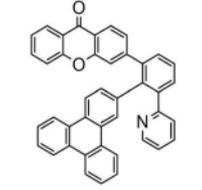
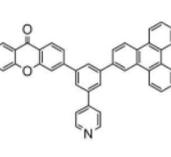
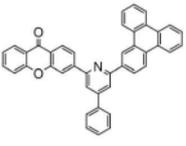
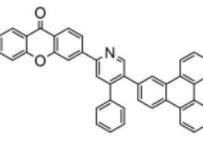
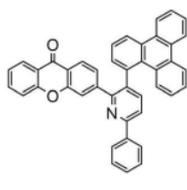
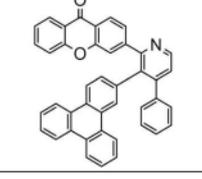
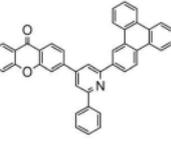
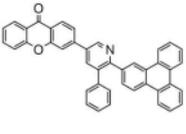
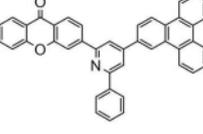
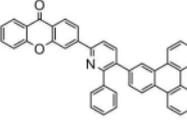


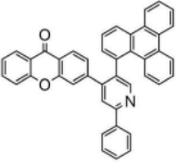
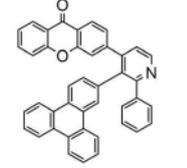
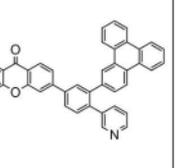
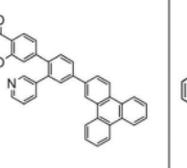
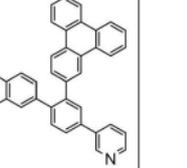
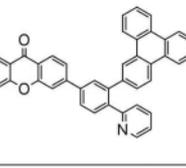
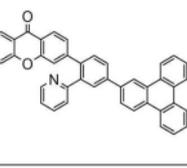
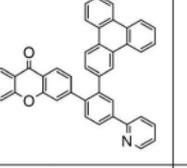
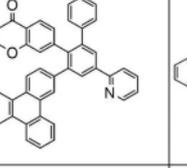
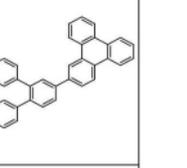
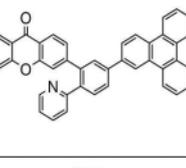
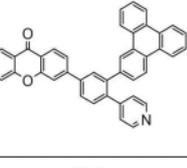
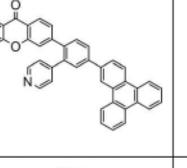
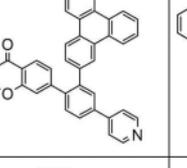
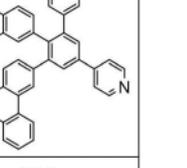
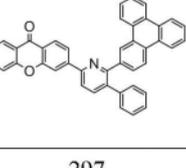
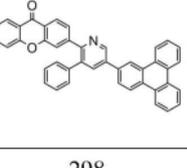
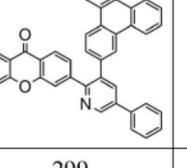
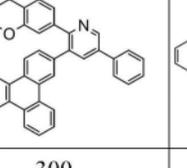
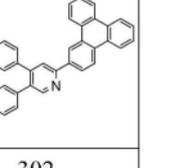
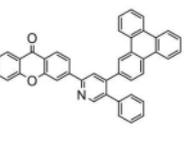
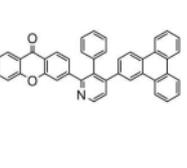
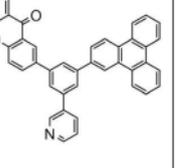
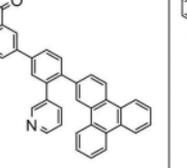
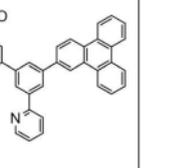
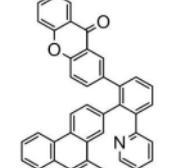
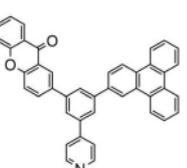
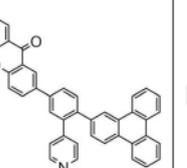
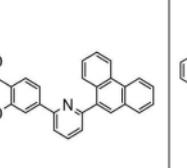
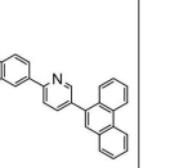
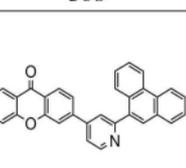
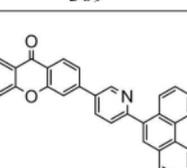
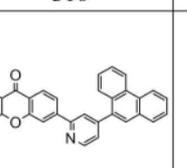
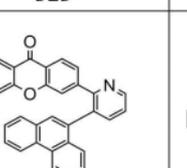
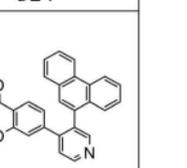
				
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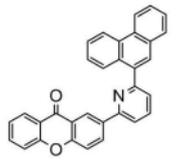
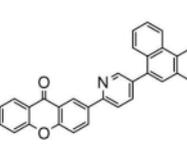
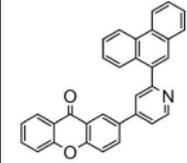
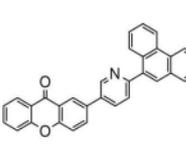
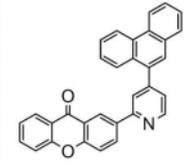
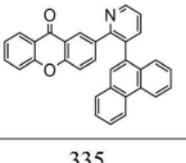
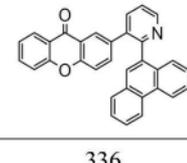
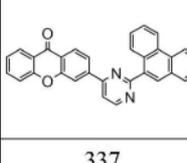
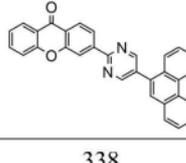
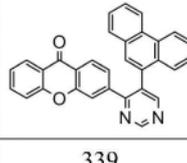
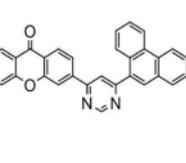
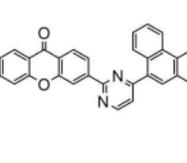
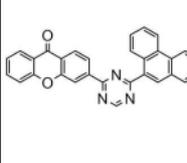
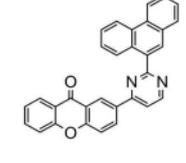
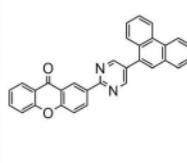
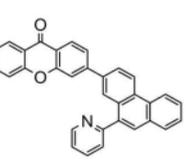
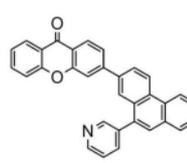
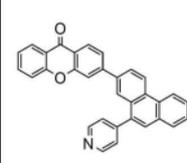
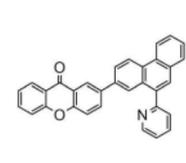
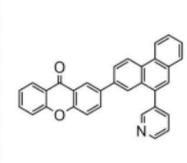
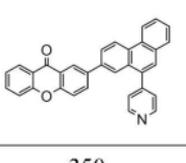
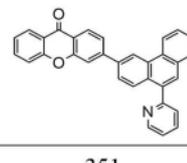
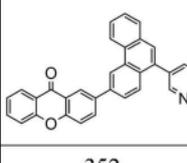
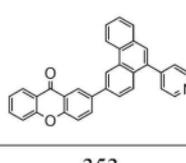
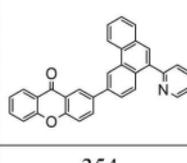
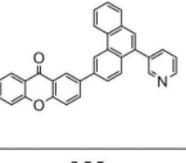
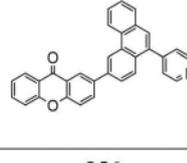
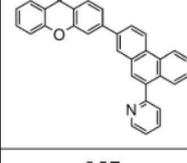
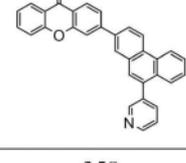
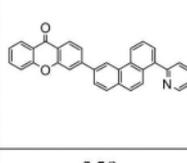
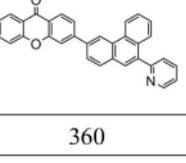
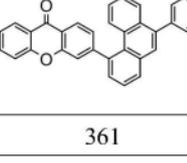
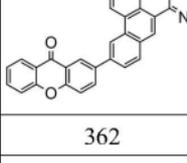
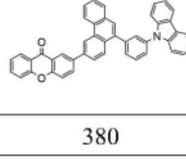
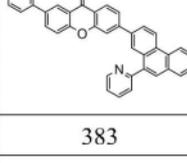
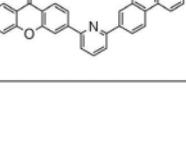
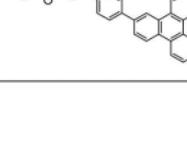
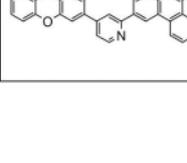
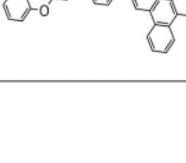
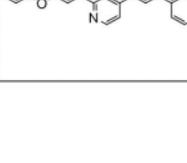
				
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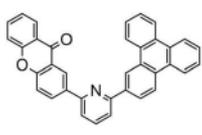
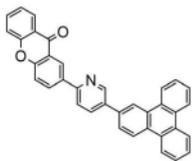
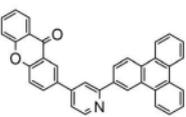
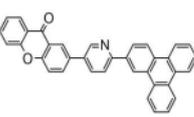
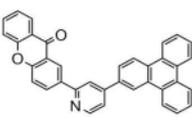
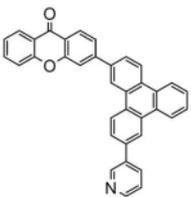
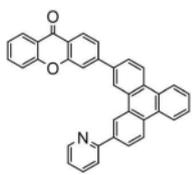
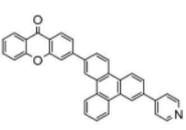
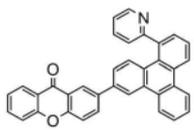
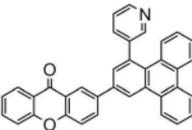
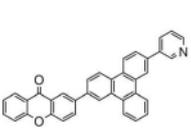
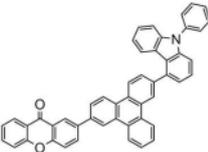
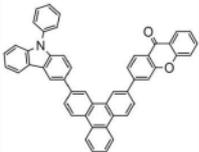
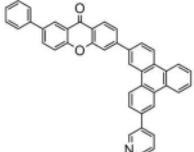
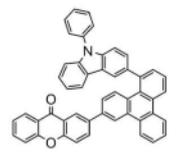
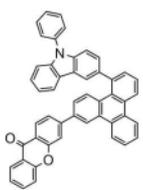
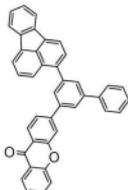
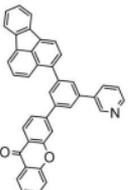
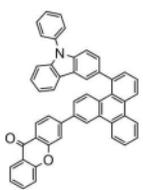
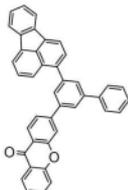
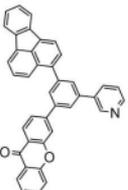
				
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422	428	429		
				

中的任一种。

2. 一种有机电致发光器件, 包括阳极、阴极和功能层, 所述功能层位于阳极和阴极之间, 其特征在于, 所述有机电致发光器件中的至少一层功能层含有权利要求1所述的以杂蒽酮为核心的化合物。

3. 根据权利要求2所述的有机电致发光器件, 所述功能层包括发光层, 其特征在于, 所述发光层含有权利要求1所述的以杂蒽酮为核心的化合物。

4. 根据权利要求2所述的有机电致发光器件, 所述功能层包括空穴阻挡层或电子传输层, 其特征在于, 所述空穴阻挡层或电子传输层含有权利要求1所述的以杂蒽酮为核心的化合物。

5. 一种照明或显示元件, 其特征在于, 所述照明或显示元件包括权利要求2~4任一所述的有机电致发光器件。

## 一种以杂蒽酮为核心的化合物及其应用

### 技术领域

[0001] 本发明涉及一种以杂蒽酮为核心的化合物及其应用,属于半导体技术领域。

### 背景技术

[0002] 有机电致发光(Organic Light Emission Diodes,OLED)器件技术既可以用来制造新型显示产品,也可以用于制作新型照明产品,有望替代现有的液晶显示和荧光灯照明,应用前景十分广泛。OLED发光器件犹如三明治的结构,包括电极材料膜层以及夹在不同电极膜层之间的有机功能材料,各种不同功能材料根据用途相互叠加在一起共同组成OLED发光器件。OLED发光器件作为电流器件,当对其两端电极施加电压,并通过电场作用有机层功能材料膜层中的正负电荷时,正负电荷进一步在发光层中复合,即产生OLED电致发光。

[0003] 当前,OLED显示技术已经在智能手机,平板电脑等领域获得应用,进一步还将向电视等大尺寸应用领域扩展,但是,和实际的产品应用要求相比,OLED器件的发光效率和使用寿命等性能还需要进一步提升。目前对OLED发光器件提高性能的研究包括:降低器件的驱动电压、提高器件的发光效率、提高器件的使用寿命等。为了实现OLED器件的性能的不断提升,不但需要从OLED器件结构和制作工艺的创新,更需要OLED光电功能材料不断研究和创新,创制出更高性能的OLED功能材料。

[0004] 应用于OLED器件的OLED光电功能材料从用途上可划分为两大类,分别为电荷注入传输材料和发光材料。进一步,还可将电荷注入传输材料分为电子注入传输材料、电子阻挡材料、空穴注入传输材料和空穴阻挡材料,还可以将发光材料分为主体发光材料和掺杂材料。

[0005] 为了制作高性能的OLED发光器件,要求各种有机功能材料具备良好的光电性能,譬如,作为电荷传输材料,要求具有良好的载流子迁移率,高玻璃化转化温度等,作为发光层的主体材料具有良好双极性,适当的HOMO/LUMO能阶等。

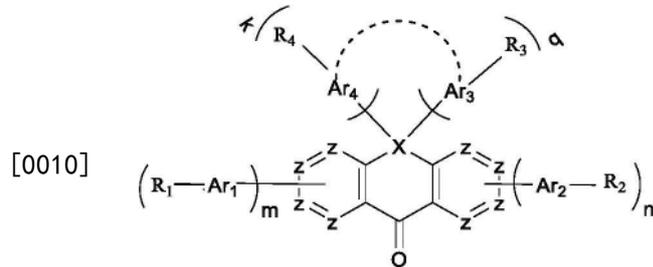
[0006] 构成OLED器件的OLED光电功能材料膜层至少包括两层以上结构,产业上应用的OLED器件结构则包括空穴注入层、空穴传输层、电子阻挡层、发光层、空穴阻挡层、电子传输层、电子注入层等多种膜层,也就是说应用于OLED器件的光电功能材料至少包括空穴注入材料、空穴传输材料、发光材料、电子传输材料等,材料类型和搭配形式具有丰富性和多样性的特点。另外,对于不同结构的OLED器件搭配而言,所使用的光电功能材料具有较强的选择性,相同的材料在不同结构器件中的性能表现也可能完全迥异。

[0007] 因此,针对当前OLED器件的产业应用要求以及OLED器件的不同功能膜层,器件的光电特性需求,必须选择更适合、性能更高的OLED功能材料或材料组合,才能实现器件的高效率、长寿命和低电压的综合特性。就当前的OLED显示照明产业的实际需求而言,目前OLED材料的发展还远远不够,落后于面板制造企业的要求,作为材料企业开发更高性能的有机功能材料显得尤为重要。

## 发明内容

[0008] 本发明的目的之一,是提供一种以杂蒽酮为核心的化合物。本发明的化合物具有较高的玻璃化温度和分子热稳定性,合适的HOMO、LUMO能级,以及高的载流子迁移率,可有效提升OLED器件的光电性能以及OLED器件的寿命。

[0009] 一种以杂蒽酮为核心的化合物,该化合物的结构如通式(1)所示:



通式(1)

[0011] 通式(1)中,X表示为O、S或C;m、n、k和q分别表示0或1,且 $m+n+k+q \geq 1$ ;

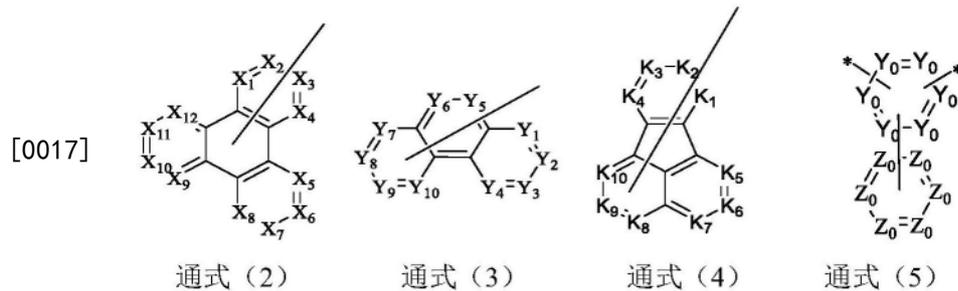
[0012] 当X表示为O原子或S原子时, $k=q=0$ ;

[0013] 当X表示为C原子时, $k=q=1$ ;

[0014] 通式(1)中,所述Z表示为氮原子或C(Ra),Z每次出现相同或者不同;

[0015] 所述 $Ar_1-Ar_4$ 表示为单键、取代或未取代的5至30元亚杂芳基或通式(5)所示结构;当 $X_1-X_{12}$ 或 $Y_1-Y_{10}$ 全部表示为CH时, $Ar_1-Ar_4$ 表示为杂芳基;

[0016] 所述 $R_1-R_4$ 分别独立地表示为氢原子、通式(2)、通式(3)或通式(4)所示结构;且 $R_1-R_4$ 至少一个表示为通式(2)、通式(3)或通式(4)所示结构;



[0018] 通式(2)、通式(3)和通式(4)中,所述 $X_1-X_{12}$ 或 $Y_1-Y_{10}$ 、 $K_1-K_{10}$ 各自独立地表示为N、C或C- $R_b$ ,所述 $X_1-X_{12}$ 每次出现相同或不同,所述 $Y_1-Y_{10}$ 每次出现相同或不同,所述 $K_1-K_{10}$ 每次出现相同或不同;

[0019] 通式(5)中, $Y_0$ 表示为C(R);

[0020]  $Z_0$ 每次出现相同或不同地表示为N或C( $R_0$ ),且至少有一个 $Z_0$ 表示为N;

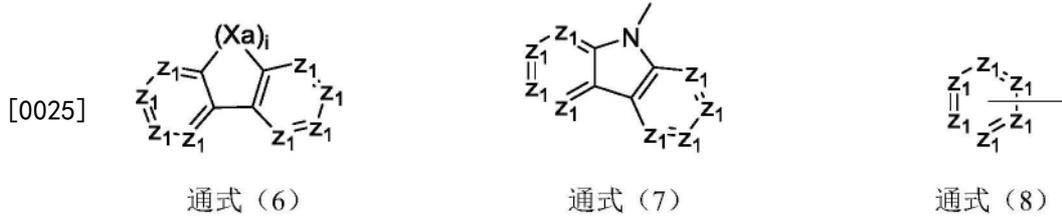
[0021] 所述R、 $R_0$ 、 $R_a$ 、 $R_b$ 分别独立地表示为氢原子、卤素、氰基、C1-10的烷基、取代或未取代的C6-30的芳基、含有一个或多个杂原子的取代或未取代的5-30元杂芳基;

[0022] 所述可被取代基团的取代基任选自氰基、卤素、C1-20烷基、C2-20烯基、C6-30芳基、5-30元杂芳基中的一种或几种;

[0023] 所述杂芳基和亚杂芳基中杂原子任选自氧原子、硫原子或氮原子中的一种或几种。

[0024] 作为本发明的进一步改进, $R_b$ 、R分别独立地表示为:氢原子或通式(6)、通式(7)和

通式(8)所示结构:



[0026] 通式(6)、通式(7)、通式(8)中,所述Xa表示为-O-、-S-、-C(R<sub>c</sub>)(R<sub>d</sub>)-或-N(R<sub>e</sub>)-,i表示0或1;

[0027] 所述Z<sub>1</sub>表示为氮原子或C(R<sub>f</sub>),Z<sub>1</sub>每次出现相同或者不同;

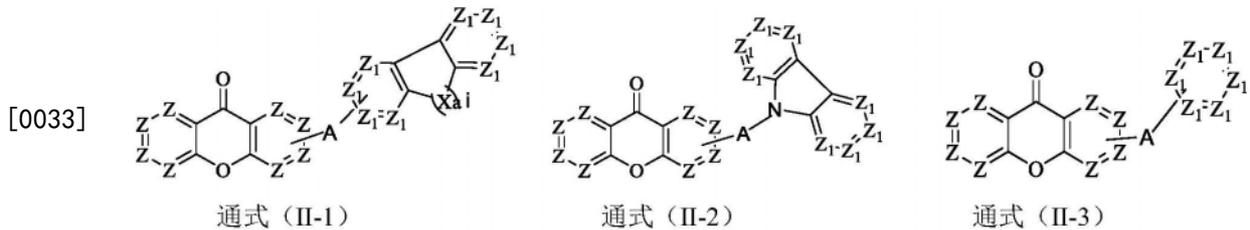
[0028] R<sub>c</sub>、R<sub>d</sub>、R<sub>e</sub>分别独立地表示为氢原子、C1-20烷基、C2-20烯基、C6-30芳基、5-30元杂芳基中的一种或几种;

[0029] R<sub>f</sub>表示为氰基、卤素、C1-20烷基、C2-20烯基、C6-30芳基、5-30元杂芳基中的一种或几种。

[0030] 作为本发明的进一步改进,通式(2)、通式(3)以及通式(4)有且仅有一个R<sub>b</sub>表示为通式(6)、通式(7)或通式(8)所示结构,其余R<sub>b</sub>表示为氢原子。

[0031] 通式(5)中有且仅有一个R表示为通式(6)、通式(7)或通式(8)所示结构,其余R表示为氢原子。

[0032] 作为本发明的进一步改进,当Ar<sub>1</sub>-Ar<sub>4</sub>表示为单键时,当Ar<sub>1</sub>-Ar<sub>4</sub>表示为单键时,所述化合物结构通过以下通式(II-1)至通式(II-3)表示:



[0034] 通式(II-1)、通式(II-2)、通式(II-3)中,Z具有权利要求1中所定义的含义;

[0035] 所述A表示为通式(2)、通式(3)或通式(4)所示结构;

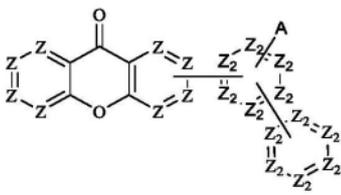
[0036] 所述Xa表示为-O-、-S-、-C(R<sub>c</sub>)(R<sub>d</sub>)-或-N(R<sub>e</sub>)-,i表示0或1;

[0037] 所述Z<sub>1</sub>表示为氮原子或C(R<sub>f</sub>),Z<sub>1</sub>每次出现相同或者不同;

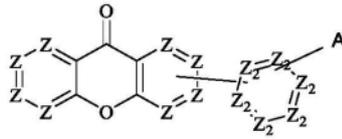
[0038] R<sub>c</sub>、R<sub>d</sub>、R<sub>e</sub>分别独立地表示为氢原子、C1-20烷基、C2-20烯基、C6-30芳基、5-30元杂芳基中的一种或几种;

[0039] R<sub>f</sub>表示为氰基、卤素、C1-20烷基、C2-20烯基、C6-30芳基、5-30元杂芳基中的一种或几种。

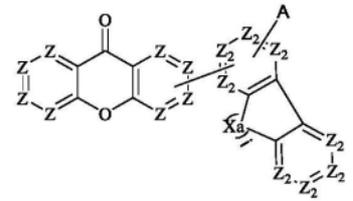
[0040] 作为本发明的进一步改进,所述化合物结构通过以下通式(III-1)至通式(III-5)表示:



通式 (III-1)

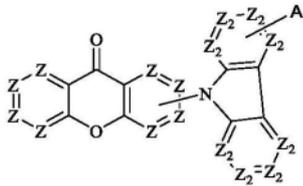


通式 (III-2)

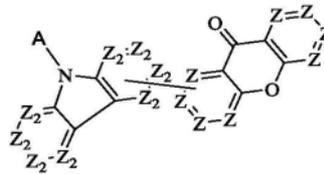


通式 (III-3)

[0041]



通式 (III-4)



通式 (III-5)

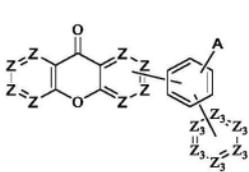
[0042] 通式 (III-1) 至通式 (III-5) 中, 符号 Z、A、Xa 和 i 具有权利要求 1 和 2 中所定义的含义;

[0043] 所述 Z<sub>2</sub> 表示为氮原子或 C(R<sub>g</sub>), Z<sub>2</sub> 每次出现相同或者不同;

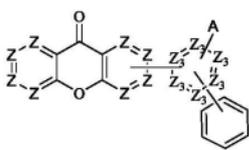
[0044] R<sub>g</sub> 表示为氰基、卤素、C1-20 烷基、C2-20 烯基、C6-30 芳基、5-30 元杂芳基中的一种或几种;

[0045] 通式 (III-1) 中, 至少有一个 Z<sub>2</sub> 表示为 N 原子。

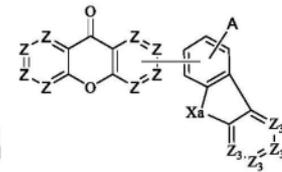
[0046] 作为本发明的进一步改进, 所述化合物结构通过通式 (IV-1) 至通式 (IV-15) 表示:



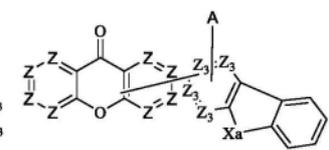
通式 (IV-1)



通式 (IV-2)

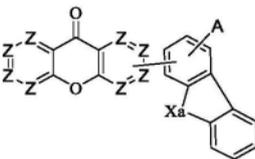


通式 (IV-3)

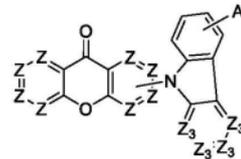


通式 (IV-4)

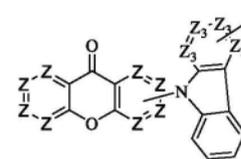
[0047]



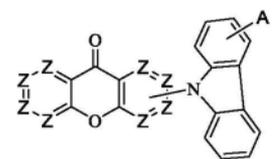
通式 (IV-5)



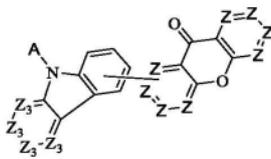
通式 (IV-6)



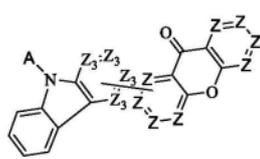
通式 (IV-7)



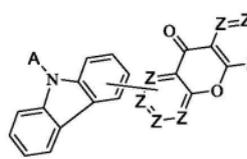
通式 (IV-8)



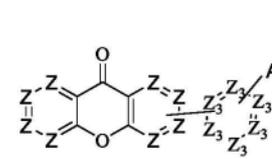
通式 (IV-9)



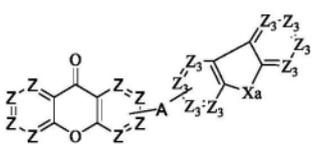
通式 (IV-10)



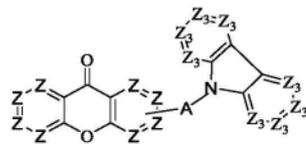
通式 (IV-11)



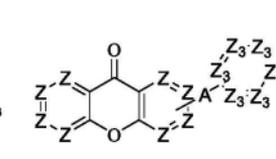
通式 (IV-12)



通式 (IV-13)



通式 (IV-14)



通式 (IV-15)

[0048] 通式 (IV-1) 至通式 (IV-15) 中, 符号 Z、A、Xa 和 i 具有权利要求 1 和 2 中所定义的含义;

[0049] 所述 Z<sub>3</sub> 表示为氮原子或 C(R<sub>h</sub>), Z<sub>3</sub> 每次出现相同或者不同;

[0050]  $R_h$ 表示为氰基、卤素、C1-20烷基、C2-20烯基、C6-30芳基、5-30元杂芳基中的一种或几种；

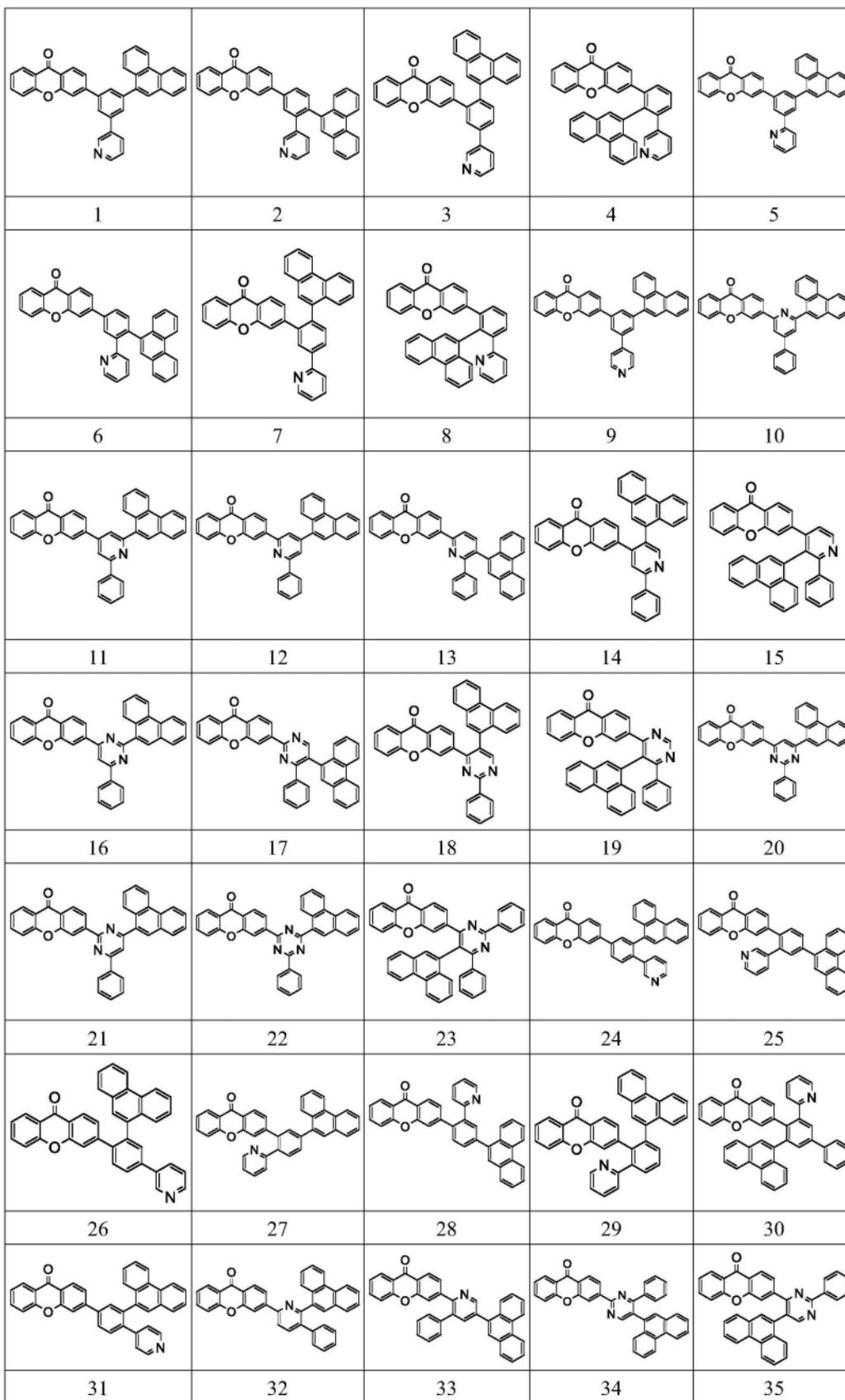
[0051] 通式(IV-1)和通式(IV-2)中,至少有一个 $Z_3$ 表示为N原子。

[0052] 作为本发明的进一步改进, $R_c$ 、 $R_d$ 、 $R_e$ 分别独立地表示为甲基、乙基、丙基、异丙基、叔丁基、戊基、取代或未取代的苯基、取代或未取代的萘基、取代或未取代的萘啶基、取代或未取代的吡啶基、取代或未取代的二联苯基、取代或未取代的三联苯基、取代或未取代的二甲基苄基、取代或未取代的二苯基苄基、取代或未取代的咪唑基、取代或未取代的二苯并咪唑基、取代或未取代的二苯并噻吩基、取代或未取代的氮杂咪唑基中的一种；

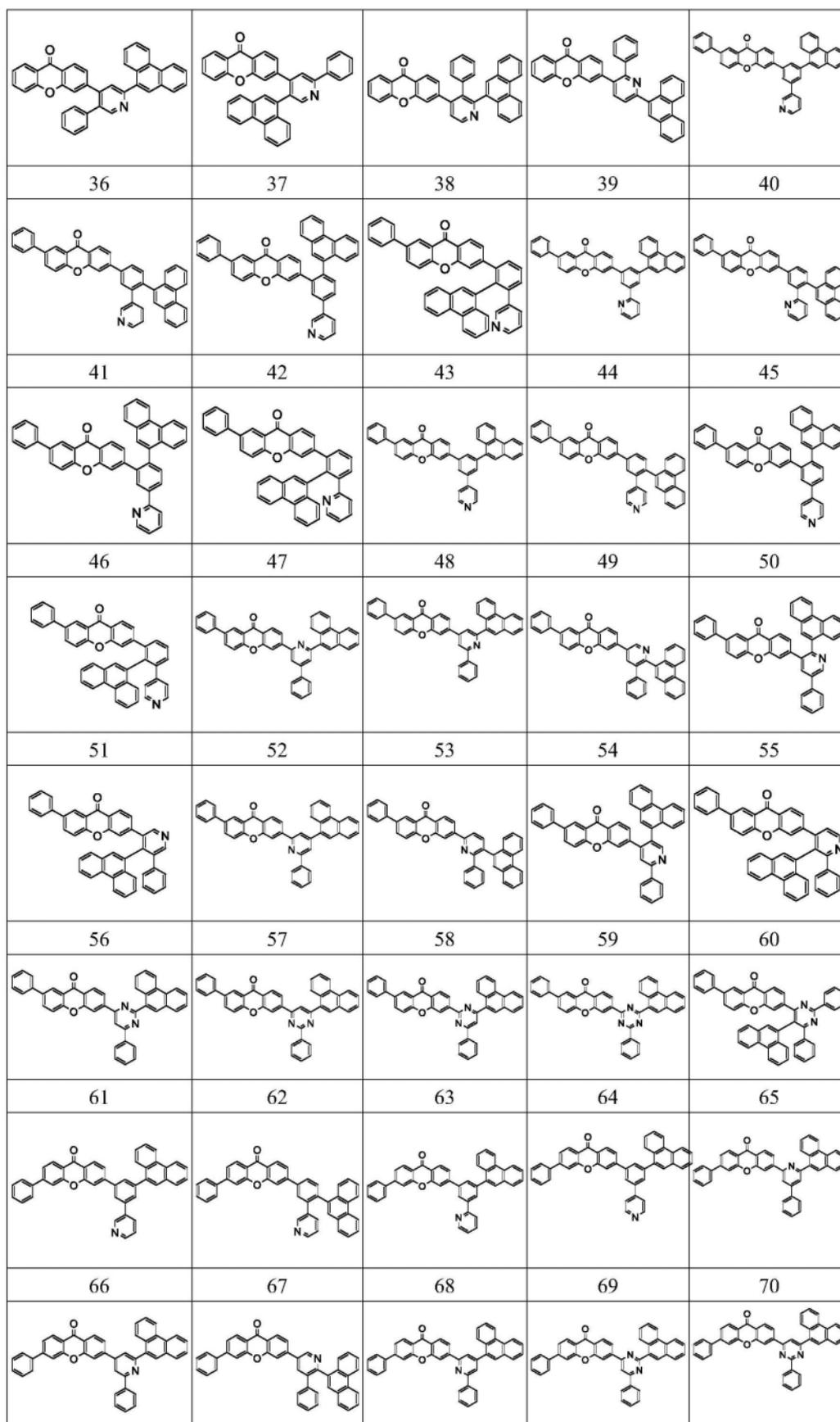
[0053]  $R$ 、 $R_0$ 、 $R_a$ 、 $R_b$ 、 $R_f$ 、 $R_g$ 和 $R_h$ 分别独立地表示为氢原子、氘原子、氟原子、氰基、甲基、乙基、丙基、异丙基、叔丁基、戊基、取代或未取代的苯基、取代或未取代的萘基、取代或未取代的萘啶基、取代或未取代的吡啶基、取代或未取代的二联苯基、取代或未取代的三联苯基、取代或未取代的二甲基苄基、取代或未取代的二苯基苄基、取代或未取代的咪唑基、取代或未取代的二苯并咪唑基、取代或未取代的二苯并噻吩基、取代或未取代的氮杂咪唑基中的一种。

[0054] “取代或未取代的”上述基团的取代基任选自甲基、乙基、丙基、异丙基、叔丁基、戊基、苯基、萘基、萘啶基、二联苯基、三联苯基、咪唑基、二苯并咪唑基、咪唑基或吡啶基中的一种或几种。

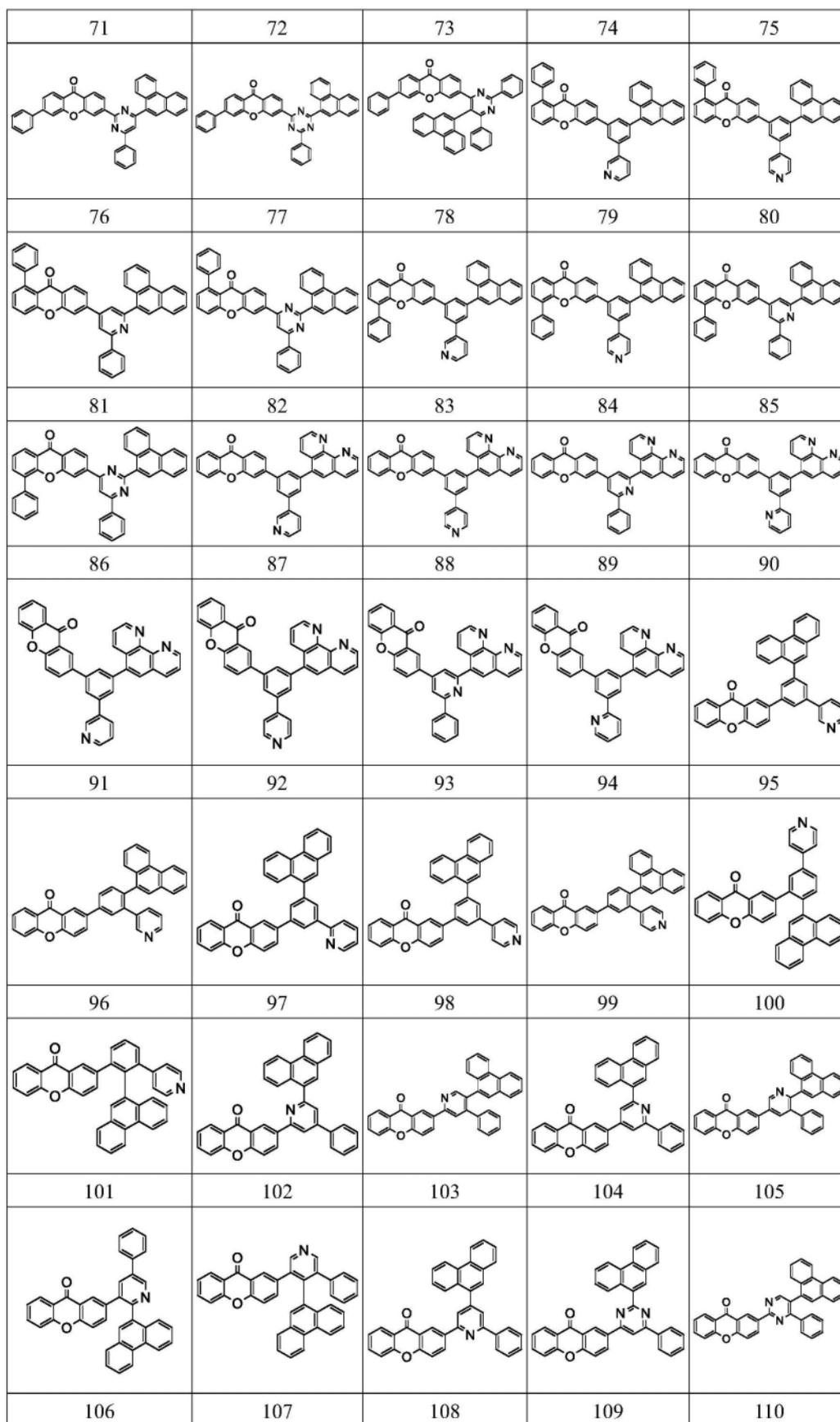
[0055] 作为本发明的进一步改进,所述化合物的具体结构为:



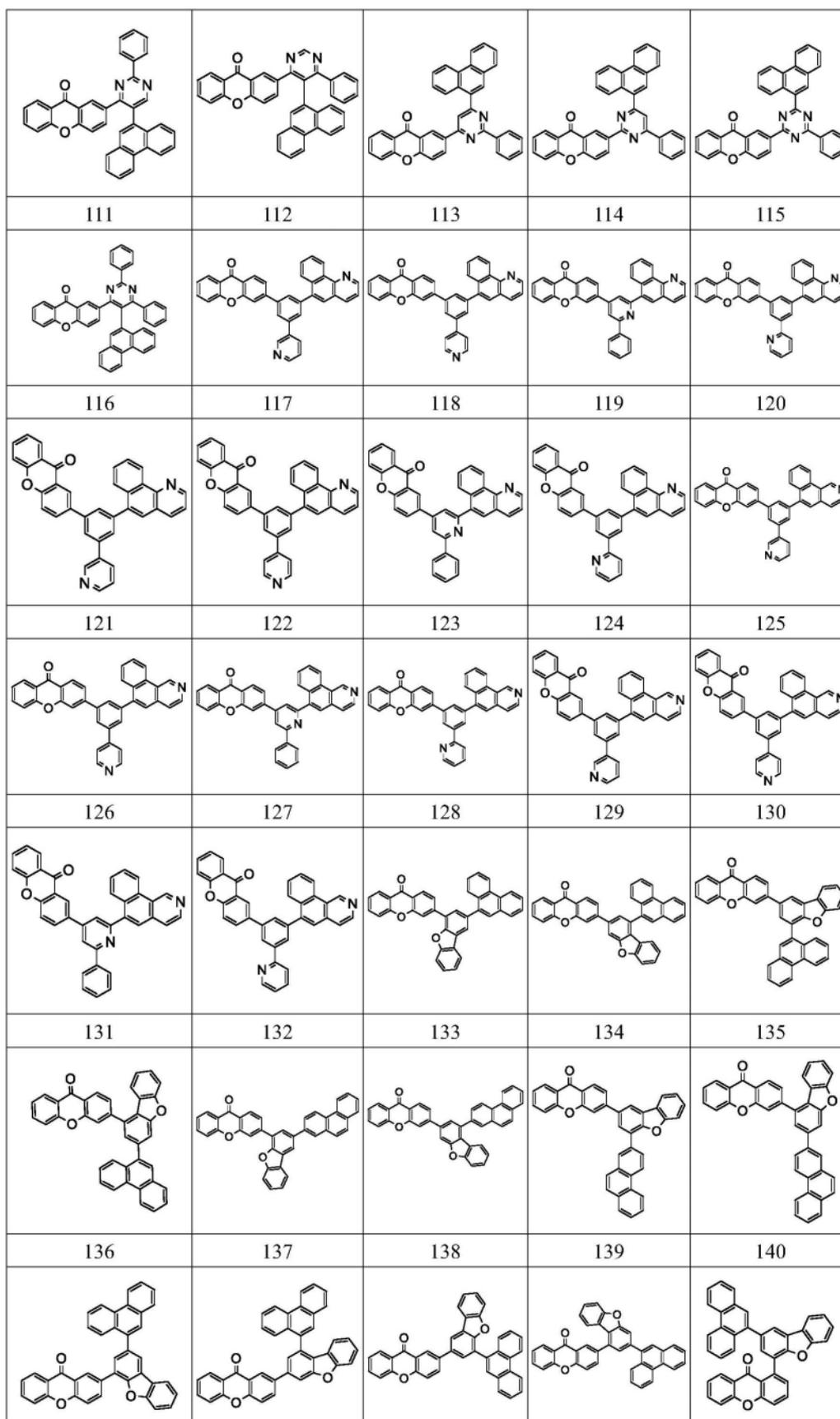
[0056]



[0057]



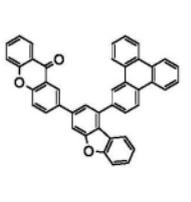
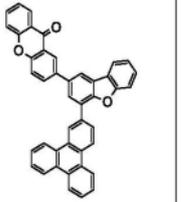
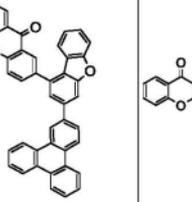
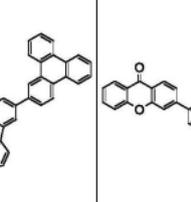
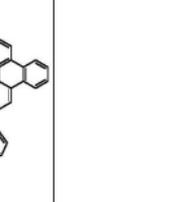
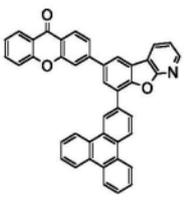
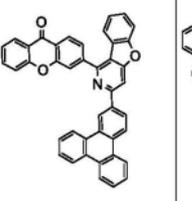
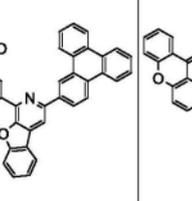
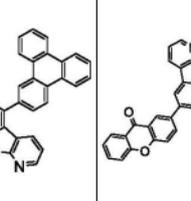
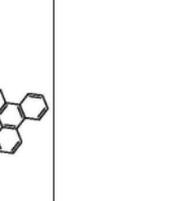
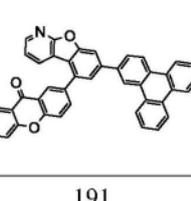
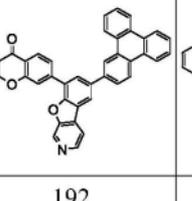
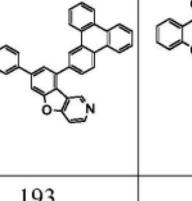
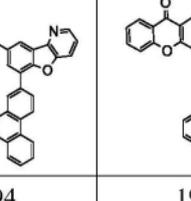
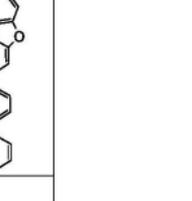
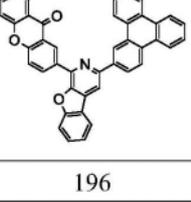
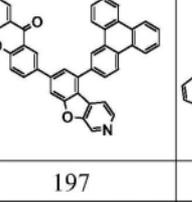
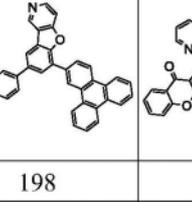
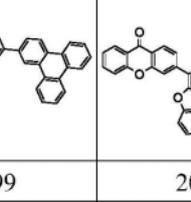
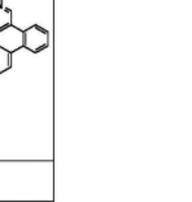
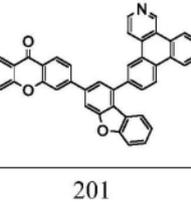
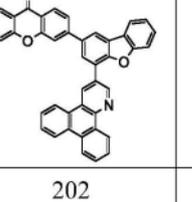
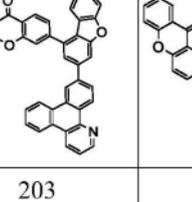
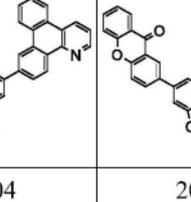
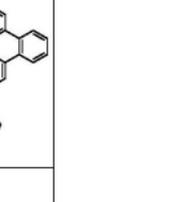
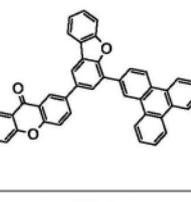
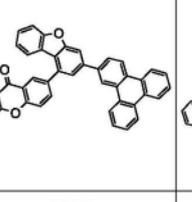
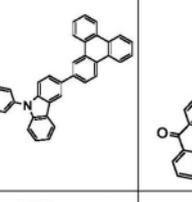
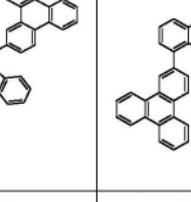
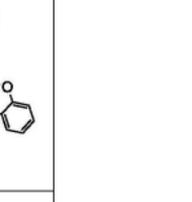
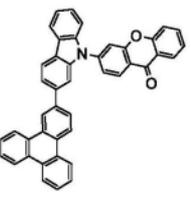
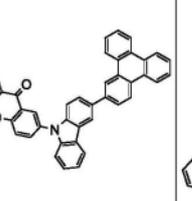
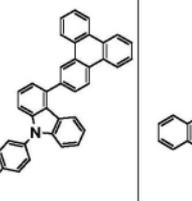
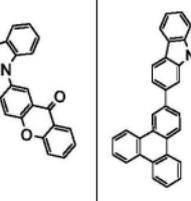
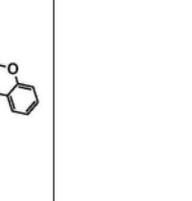
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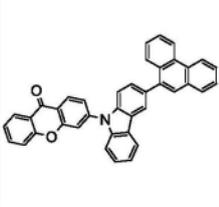
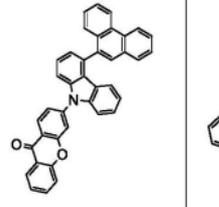
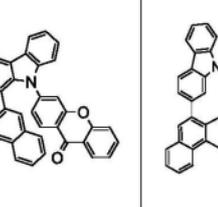
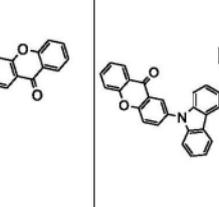
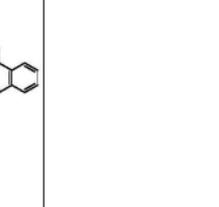
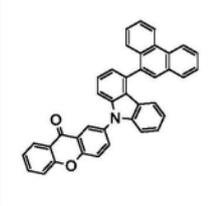
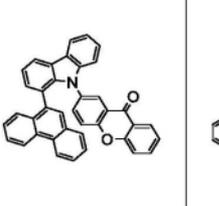
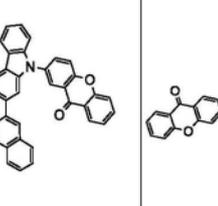
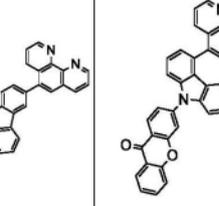
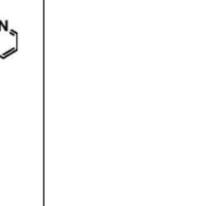
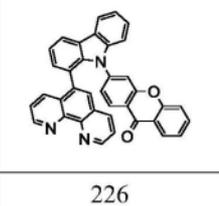
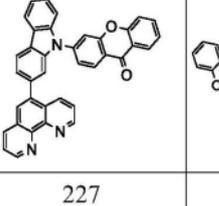
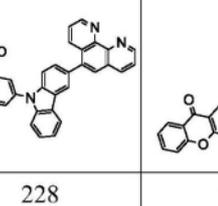
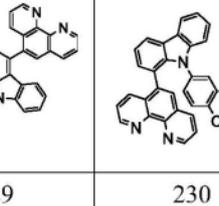
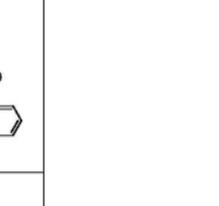
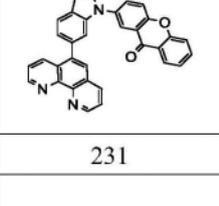
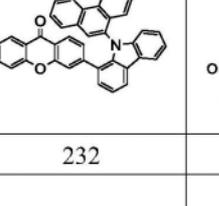
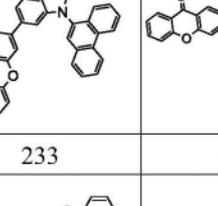
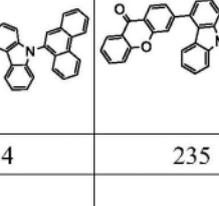
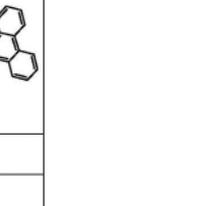
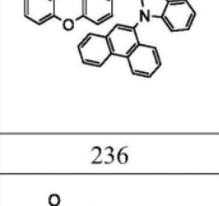
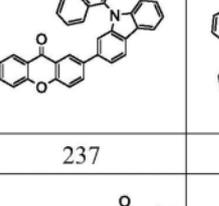
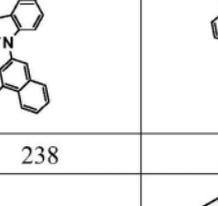
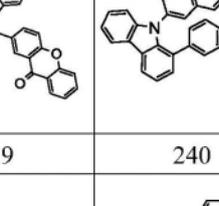
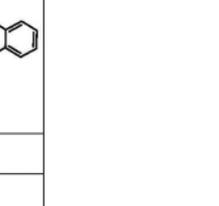
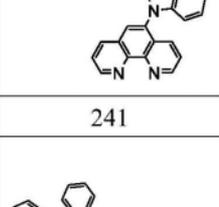
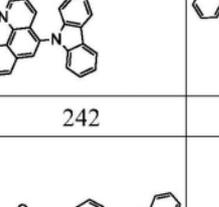
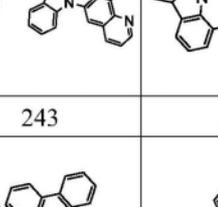
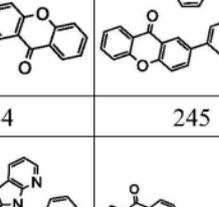
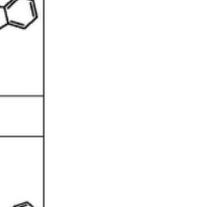
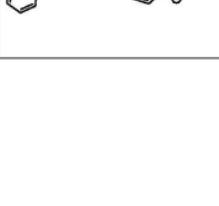
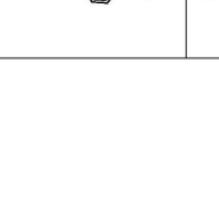
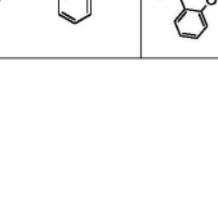
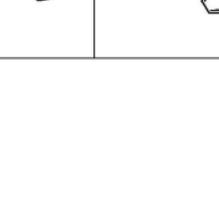
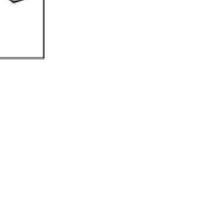
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[0060]

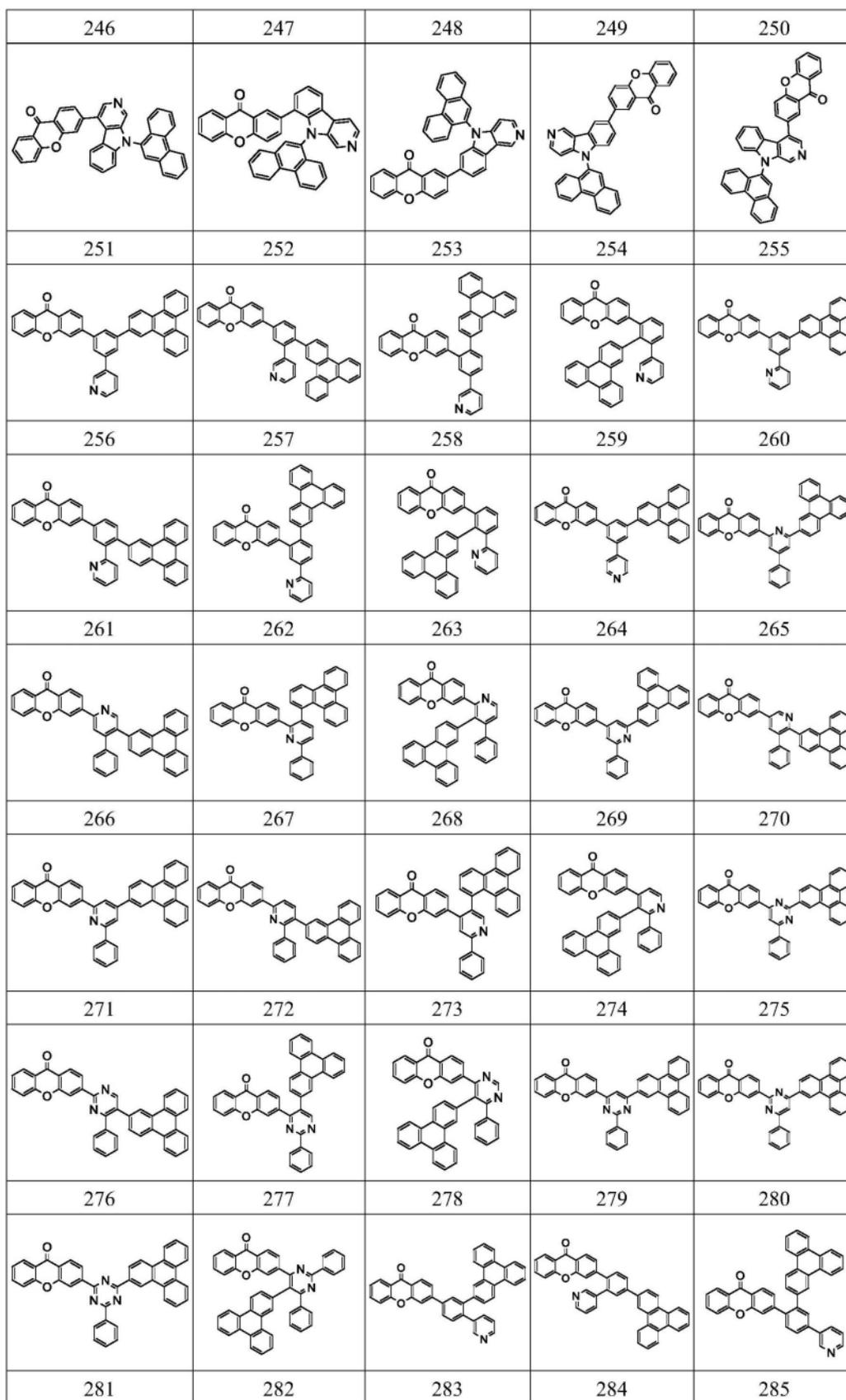
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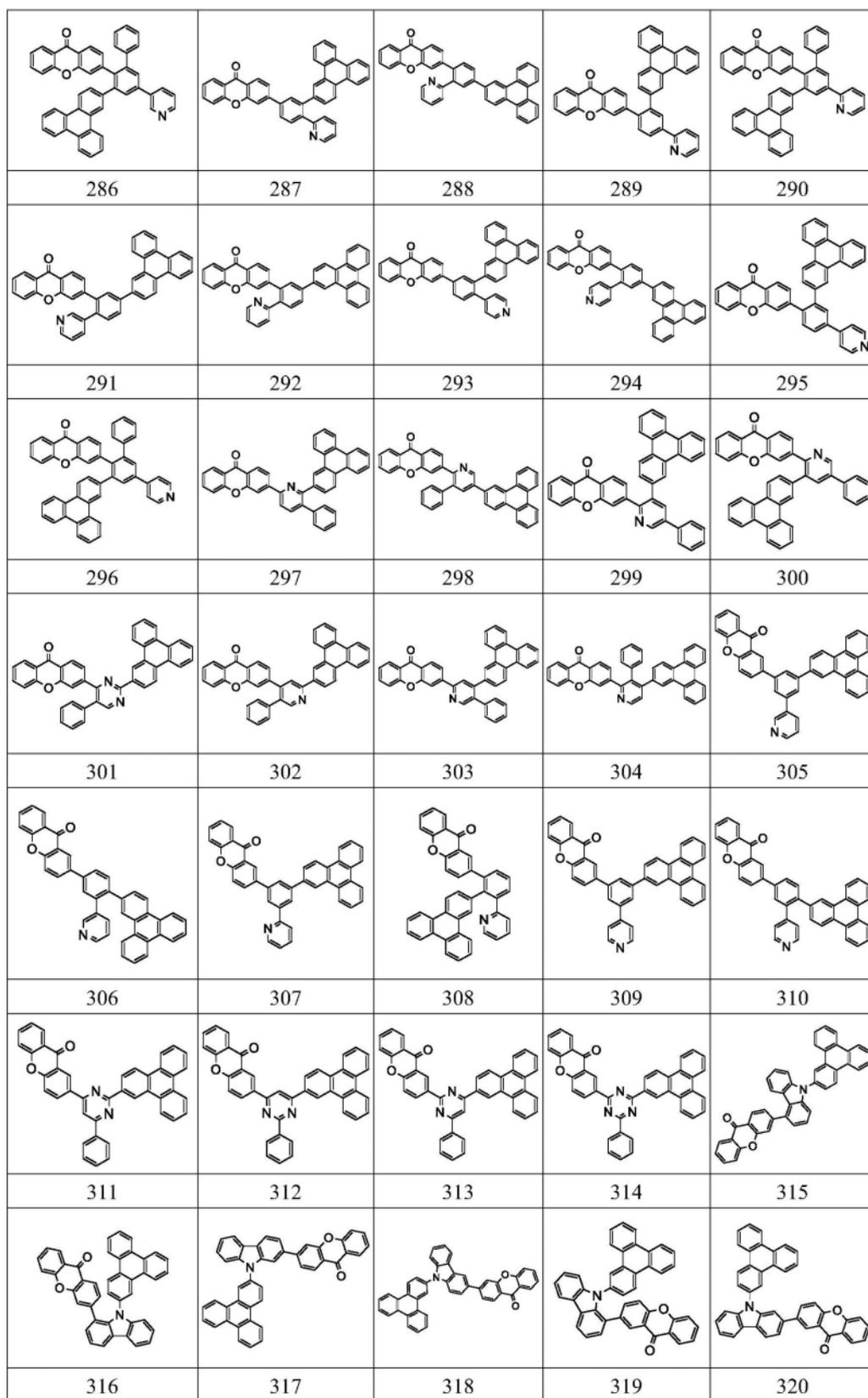
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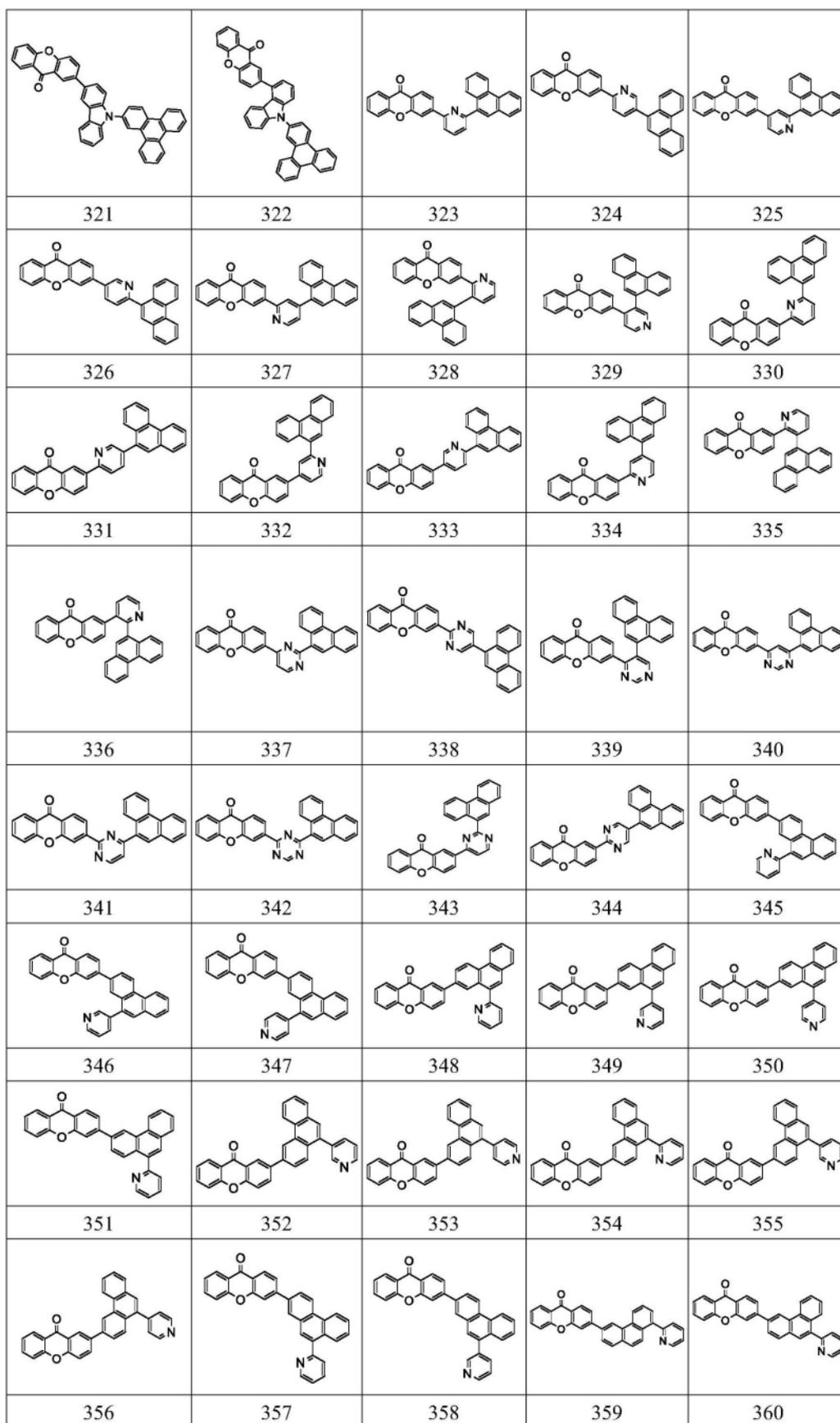
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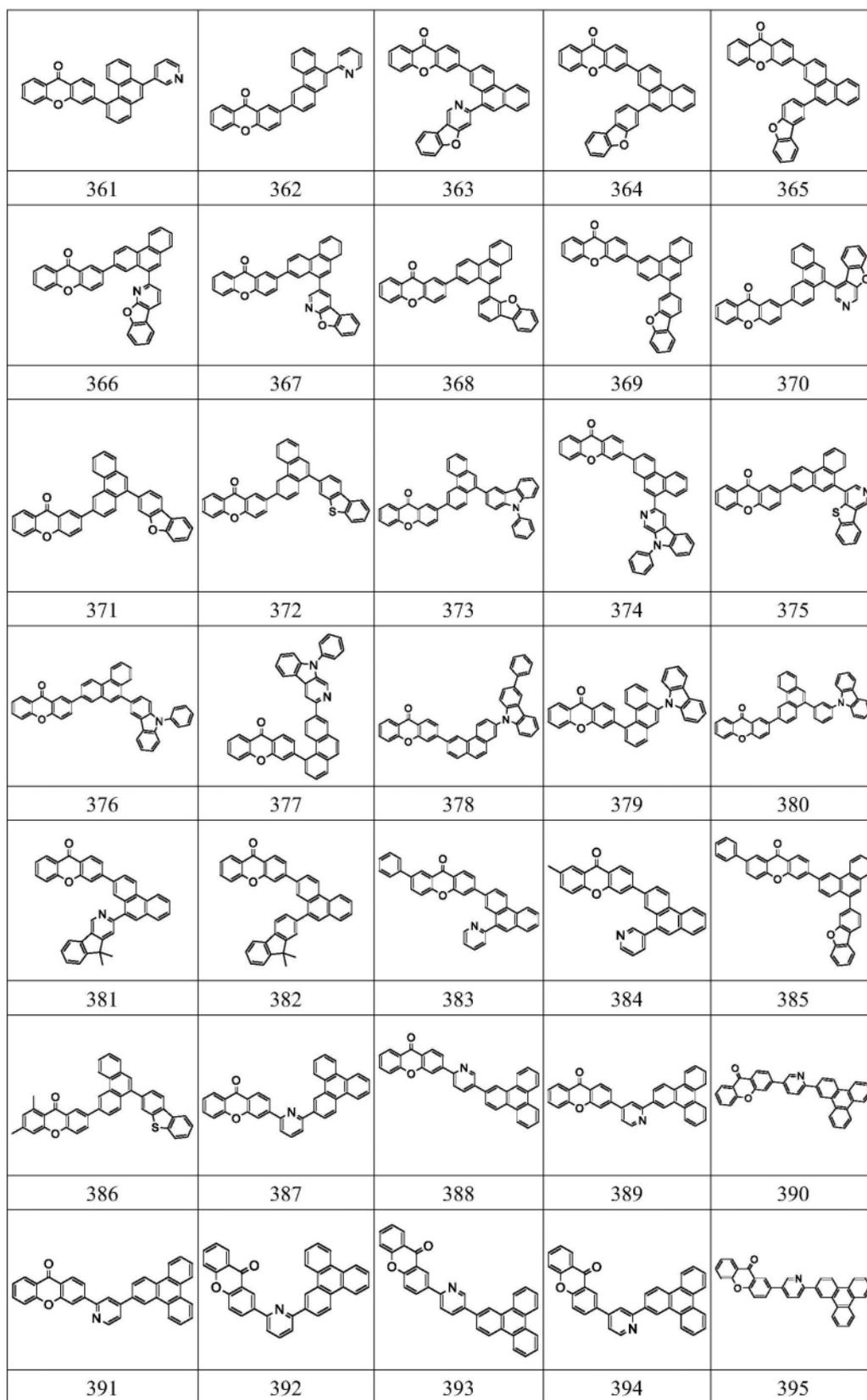
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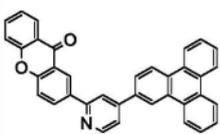
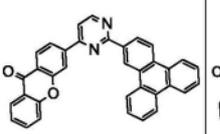
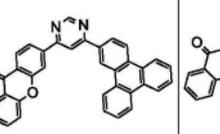
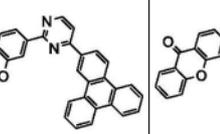
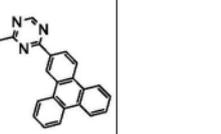
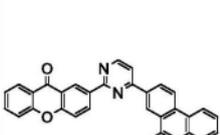
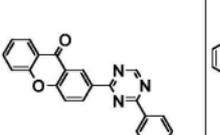
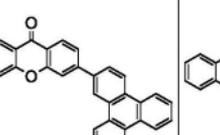
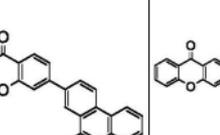
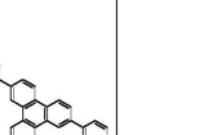
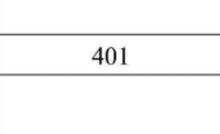
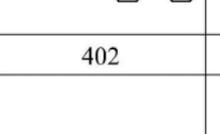
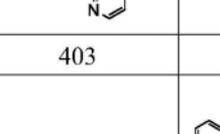
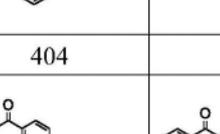
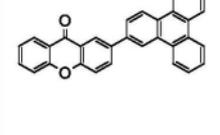
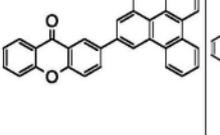
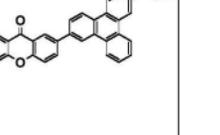
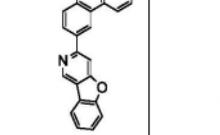
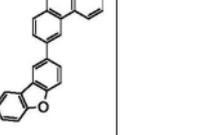
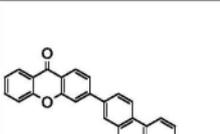
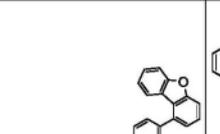
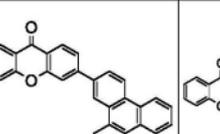
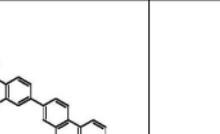
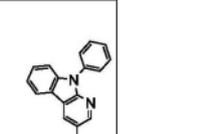
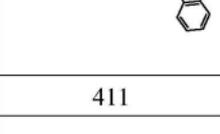
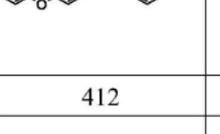
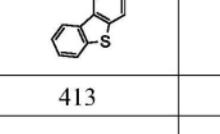
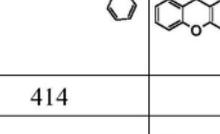
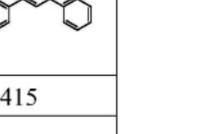
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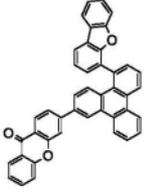
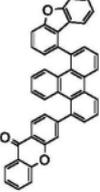
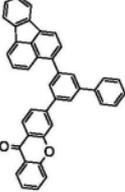
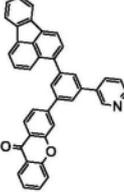
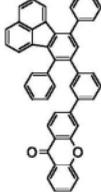
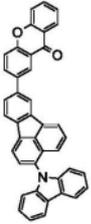
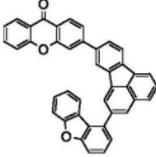
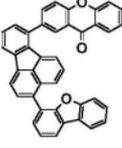
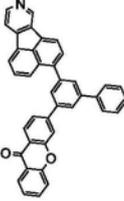
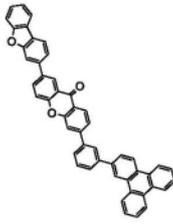
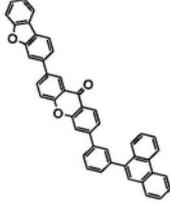
[0065]



[0066]

				
396	397	398	399	400
				
401	402	403	404	405
				
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[0067]

					
	426	427	428	429	430
[0068]					
	431	432	433	434	435
					
	436	437			

[0069] 中的任一种。

[0070] 本发明的目的之二,是提供一种有机电致发光器件。本发明的化合物在应用于OLED器件时,通过器件结构优化,可保持高的膜层稳定性,可有效提升OLED器件的光电性能以及OLED器件的寿命,具有良好的应用效果和产业化前景。

[0071] 本发明解决上述技术问题的技术方案如下:一种有机电致发光器件,包括阳极、阴极和有机功能层,所述有机功能层位于阳极和阴极之间,所述有机功能层含有所述的以杂蒽酮骨架为核心的化合物。

[0072] 在上述技术方案的基础上,本发明还可以做如下改进。

[0073] 进一步,所述有机功能层为发光层和/或空穴阻挡和/或电子传输层,所述发光层和/或空穴阻挡/电子传输层含有所述的以杂蒽酮骨架为核心的化合物。

[0074] 本发明的目的之三,是提供一种照明或显示元件。本发明的有机电致发光器件可以应用在照明或显示元件,使器件的电流效率,功率效率和外量子效率均得到很大改善;同时,对于器件寿命提升非常明显,在OLED发光器件中具有良好的应用效果,具有良好的产业化前景。

[0075] 本发明解决上述技术问题的技术方案如下:一种照明或显示元件,包括上述有机电致发光器件。

[0076] 本发明的有益效果是:

[0077] 本发明的化合物均以杂蒽酮为骨架,与稠环类支链相连,分子整体刚性较强,不易转动,使得本发明化合物材料的立体结构更加稳定。本发明化合物作为OLED的空穴阻挡/电子传输层使用时,合适的LUMO能级能够有效地实现电子传输,提升激子在发光层中的复合效率,减少了能量损失,使发光层主体材料能量充分传递至掺杂材料,从而提升材料应用于

器件后的发光效率。

[0078] 本发明的化合物作为发光层主体材料使用时,使得电子和空穴在发光层的分布更加平衡,在恰当的LUMO能级下,提升了电子的注入和传输性能;作为OLED发光器件的发光功能层材料使用时,以杂蒽酮为骨架的母核搭配本发明范围内的支链可有效提高激子利用率和高荧光辐射效率,降低高电流密度下的效率滚降,降低器件电压,提高器件的电流效率和寿命。

[0079] 本发明的化合物中 $\pi$ 共轭效应和支链良好的平面刚性使得其有很强的电子传输能力,高的电子迁移率能够降低器件的起始电压,提高有机电致发光器件的效率。

[0080] 本发明化合物在杂蒽酮骨架上进行设计,增加取代基团后,材料Tg温度升高、活泼C-H键得到钝化,提高了材料的稳定性;取代基团的加入使得材料分子量增加,但在实际应用过程中,材料的蒸镀温度反而降低,材料加工温度和分解温度之间的温度区间变宽,提高了材料的使用加工窗口。

[0081] 本发明化合物基团刚性较强,具有分子间不易结晶、不易聚集、具有良好成膜性的特点,具有高的玻璃化温度及热稳定性,所以,本发明化合物应用于OLED器件时,可保持材料成膜后的膜层稳定性,提高OLED器件使用寿命。本发明所述化合物作为有机电致发光功能层材料应用于OLED器件后,器件的电流效率,功率效率和外量子效率均得到很大改善;同时,对于器件寿命提升非常明显,在OLED发光器件中具有良好的应用效果,具有良好的产业化前景。

## 附图说明

[0082] 图1为本发明所列举的材料应用于OLED器件的结构示意图;

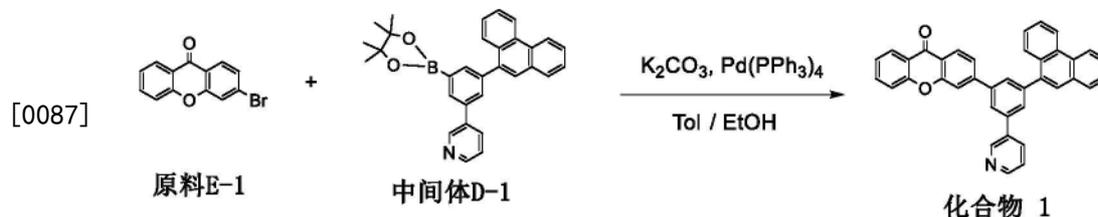
[0083] 其中,1为透明基板层,2为阳极层,3为空穴注入层,4为空穴传输层,5为电子阻挡层,6为发光层,7为空穴阻挡层,8为电子传输层,9为电子注入层,10为阴极层。

## 具体实施方式

[0084] 以下结合附图对本发明的原理和特征进行描述,所举实例只用于解释本发明,并非用于限定本发明的范围。

[0085] 下述实施例中所有原料均采购于烟台万润精细化工股份有限公司。

[0086] 实施例1化合物1的合成:

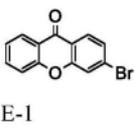
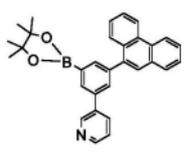
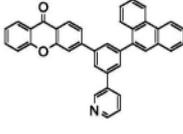
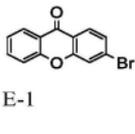
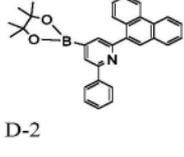
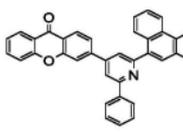
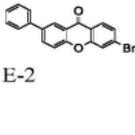
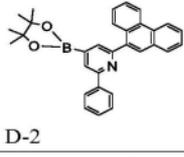
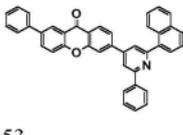
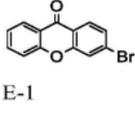
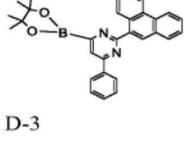
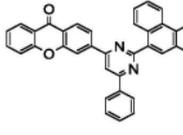
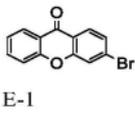
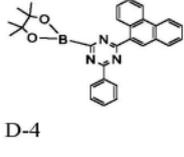
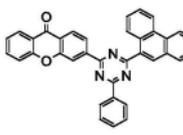
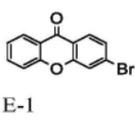
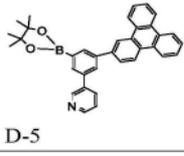
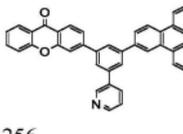
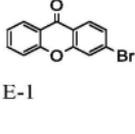
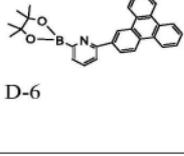
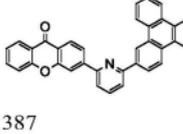
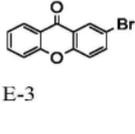
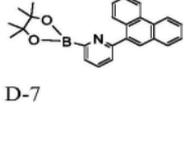
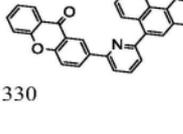
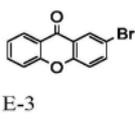
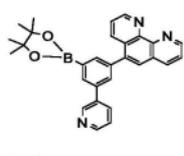
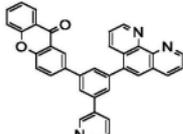


[0088] 将0.01mol的中间体D-1与0.012mol的原料E-1加至120mL的甲苯:乙醇=2:1的混合溶剂中,加入0.02mol的碳酸钾,除氧后加入0.0002mol  $\text{Pd}(\text{PPh}_3)_4$ ,在氮气的氛围下110°C反应48小时,取样点板,待反应物反应完全后,冷却、过滤,将滤液旋蒸除去溶剂,粗产品过硅胶柱,得到化合物1。

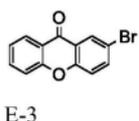
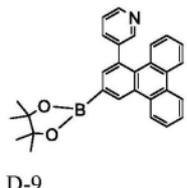
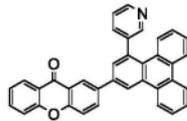
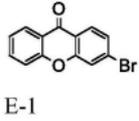
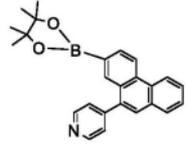
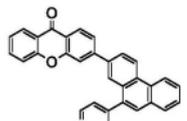
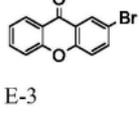
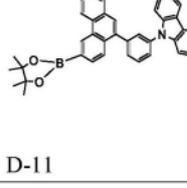
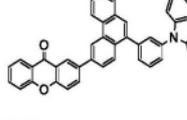
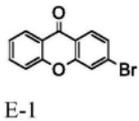
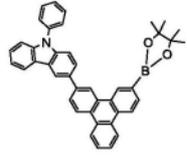
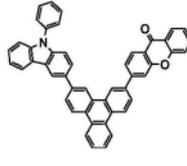
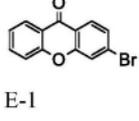
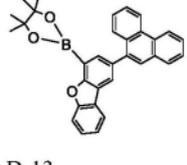
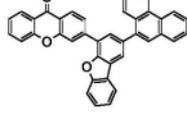
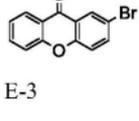
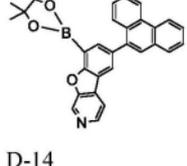
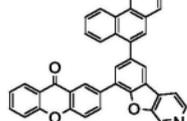
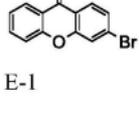
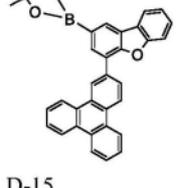
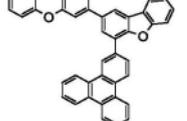
[0089] 重复实施例1的制备过程合成实施例1-实施例19的目标化合物,反应条件相同,不

同之处在于使用下表1中所列出的中间体D和原料E;

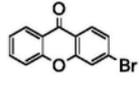
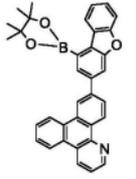
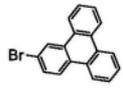
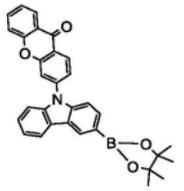
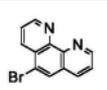
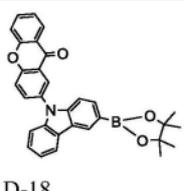
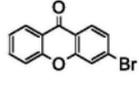
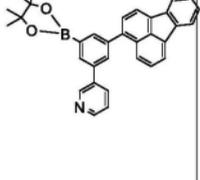
[0090] 表1

编号	原料 E	中间体 D	目标化合物	测试结果
[0091] 实施例 1	 E-1	 D-1	 1	HPLC 纯度 99.84%，收率 84.8%；元素分析结构 (C <sub>38</sub> H <sub>23</sub> NO <sub>2</sub> ) 理论值：C, 86.84; H, 4.41; N, 2.66; 测试值：C, 86.87; H, 4.45; N, 2.68。LC-MS：理论值：525.17，实测值：525.24
实施例 2	 E-1	 D-2	 11	HPLC 纯度 99.79%，收率 85.2%；元素分析结构 (C <sub>38</sub> H <sub>23</sub> NO <sub>2</sub> ) 理论值：C, 86.84; H, 4.41; N, 2.66; 测试值：C, 86.83; H, 4.44; N, 2.67。LC-MS：理论值：525.17，实测值：525.22
实施例 3	 E-2	 D-2	 53	HPLC 纯度 99.82%，收率 79.4%；元素分析结构 (C <sub>44</sub> H <sub>27</sub> NO <sub>2</sub> ) 理论值：C, 87.83; H, 4.52; N, 2.33 测试值 C, 87.88; H, 4.53; N, 2.35。LC-MS：理论值：601.20，实测值：601.22
实施例 4	 E-1	 D-3	 16	HPLC 纯度 99.85%，收率 82.8%；元素分析结构 (C <sub>37</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> ) 理论值：C, 84.39; H, 4.21; N, 5.32; 测试值：C, 84.41; H, 4.27; N, 5.34; LC-MS：理论值：526.17，实测值：526.19
实施例 5	 E-1	 D-4	 22	HPLC 纯度 99.85%，收率 84.6%；元素分析结构 (C <sub>36</sub> H <sub>21</sub> N <sub>3</sub> O <sub>2</sub> ) 理论值：C, 81.96; H, 4.01; N, 7.96 测试值：C, 81.98; H, 4.06; N, 7.97。LC-MS：理论值：527.16，实测值：527.20
[0092] 实施例 6	 E-1	 D-5	 256	HPLC 纯度 99.91%，收率 86.2%；元素分析结构 (C <sub>42</sub> H <sub>25</sub> NO <sub>2</sub> ) 理论值：C, 87.63; H, 4.38; N, 2.43; 测试值：C, 87.64; H, 4.43; N, 2.42。LC-MS：理论值：575.19，实测值：575.23
实施例 7	 E-1	 D-6	 387	HPLC 纯度 99.63%，收率 82.1%；元素分析结构 (C <sub>36</sub> H <sub>21</sub> NO <sub>2</sub> ) 理论值：C, 86.55; H, 4.24; N, 2.80; 测试值：C, 86.52; H, 4.29; N, 2.82。LC-MS：理论值：499.16，实测值：499.19
实施例 8	 E-3	 D-7	 330	HPLC 纯度 99.62%，收率 80.3%；元素分析结构 (C <sub>32</sub> H <sub>19</sub> NO <sub>2</sub> ) 理论值：C, 85.50; H, 4.26; N, 3.12 测试值：C, 85.52; H, 4.29; N, 3.15。LC-MS：理论值：449.14，实测值：449.16
实施例 9	 E-3	 D-8	 91	HPLC 纯度 99.89%，收率 84.7%；元素分析结构 (C <sub>36</sub> H <sub>21</sub> N <sub>3</sub> O <sub>2</sub> ) 理论值：C, 81.96; H, 4.01; N, 7.96 测试值：C, 81.98; H, 4.03; N, 7.95。LC-MS：理论值：527.16，实测值：527.13

[0093]

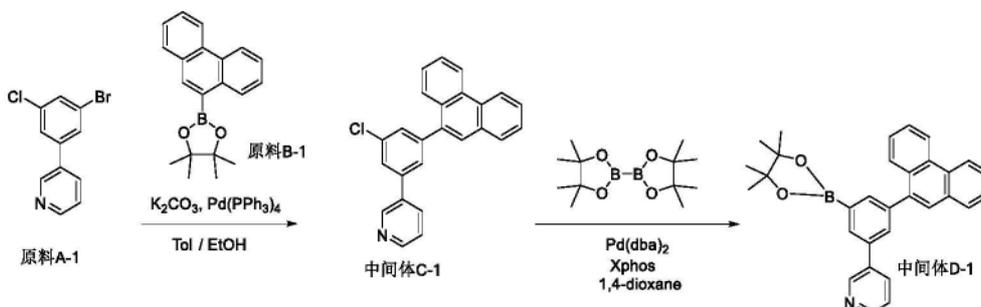
实施例 10	 E-3	 D-9	 407	HPLC 纯度 99.84%，收率 81.2%；元素分析结构 (C <sub>36</sub> H <sub>21</sub> NO <sub>2</sub> ) 理论值：C, 86.55；H, 4.24；N, 2.80 测试值：C, 86.56；H, 4.26；N, 2.82。LC-MS：理论值：499.16，实测值：499.18
实施例 11	 E-1	 D-10	 347	HPLC 纯度 99.80%，收率 86.1%；元素分析结构 (C <sub>32</sub> H <sub>19</sub> NO <sub>2</sub> ) 理论值：C, 85.50；H, 4.26；N, 3.12 测试值：C, 85.55；H, 4.28；N, 3.15。LC-MS：理论值：449.14，实测值：449.16
实施例 12	 E-3	 D-11	 380	HPLC 纯度 99.82%，收率 87.7%；元素分析结构 (C <sub>45</sub> H <sub>27</sub> NO <sub>2</sub> ) 理论值：C, 88.07；H, 4.43；N, 2.28；测试值：C, 88.09；H, 4.48；N, 2.32。LC-MS：理论值：613.20，实测值：613.22
实施例 13	 E-1	 D-12	 417	HPLC 纯度 99.78%，收率 83.2%；元素分析结构 (C <sub>49</sub> H <sub>29</sub> NO <sub>2</sub> ) 理论值：C, 88.67；H, 4.40；N, 2.11；测试值：C, 88.68；H, 4.45；N, 2.13。LC-MS：理论值：663.22，实测值：663.25
实施例 14	 E-1	 D-13	 133	HPLC 纯度 99.83%，收率 81.7%；元素分析结构 (C <sub>39</sub> H <sub>22</sub> O <sub>3</sub> ) 理论值：C, 86.97；H, 4.12 测试值：C, 86.99；H, 4.16。LC-MS：理论值：538.16，实测值：538.19
实施例 15	 E-3	 D-14	 155	HPLC 纯度 99.68%，收率 79.4%；元素分析结构 (C <sub>38</sub> H <sub>21</sub> NO <sub>3</sub> ) 理论值：C, 84.59；H, 3.92；N, 2.60；测试值：C, 84.61；H, 3.94；N, 2.63。LC-MS：理论值：539.15，实测值：539.17
实施例 16	 E-1	 D-15	 178	HPLC 纯度 99.66%，收率 83.2%；元素分析结构 (C <sub>43</sub> H <sub>24</sub> O <sub>3</sub> ) 理论值 C, 87.74；H, 4.11；测试值：C, 87.76；H, 4.15。LC-MS：理论值：588.17，实测值：588.19

[0094]

实施例 17			203	HPLC 纯度 99.82%，收率 87.8%；元素分析结构 (C <sub>42</sub> H <sub>23</sub> NO <sub>3</sub> ) 理论值 C, 85.55; H, 3.93; N, 2.38 测试值 C, 85.57; H, 3.97; N, 2.39; 。LC-MS: 理论值: 589.17, 实测值: 589.19
实施例 18			208	HPLC 纯度 99.68%，收率 92.1%；元素分析结构 (C <sub>43</sub> H <sub>25</sub> NO <sub>2</sub> ) 理论值 C, 87.88; H, 4.29; N, 2.38 测试值 C, 87.89; H, 4.34; N, 2.39 。LC-MS: 理论值: 587.19, 实测值: 587.21
实施例 19			228	HPLC 纯度 99.89%，收率 96.2%；元素分析结构 (C <sub>37</sub> H <sub>21</sub> N <sub>3</sub> O <sub>2</sub> ) 理论值 C, 82.36; H, 3.92; N, 7.79 测试值 C, 82.34; H, 3.96; N, 7.78。LC-MS: 理论值: 539.16, 实测值: 539.16
实施例 20			429	HPLC 纯度 99.74%，收率 90.7%；元素分析结构 (C <sub>40</sub> H <sub>23</sub> NO <sub>2</sub> ) 理论值 C, 87.41; H, 4.22; N, 2.55; 测试值 C, 87.43; H, 4.27; N, 2.57。LC-MS: 理论值: 549.17, 实测值: 549.14

[0095] 其中中间体D-1的合成路线如下:

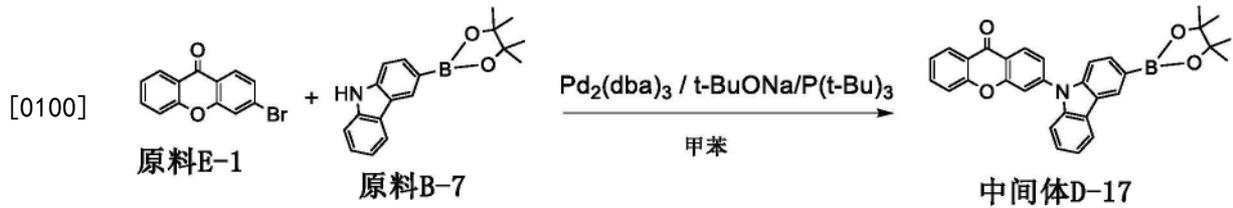
[0096]



[0097] 将0.1mol的原料A-1与0.12mol的原料B-1加至100mL的甲苯:乙醇=2:1的混合溶剂中,加入0.02mol的碳酸钾,除氧后加入0.0002mol Pd(PPh<sub>3</sub>)<sub>4</sub>,在氮气的氛围下110℃反应24小时,取样点板,待反应物反应完全后,冷却、过滤,将滤液旋蒸除去溶剂,粗产品过硅胶柱,得到中间体C-1;

[0098] 将0.1mol所得中间体C-1与0.15mol双联频哪醇硼酸酯加至100mL的1,4-二氧六环中,除氧后加入0.002mol Pd(dba)<sub>2</sub>和0.004mol Xphos(2-二环己基磷-2,4,6-三异丙基联苯),在氮气的氛围下110℃反应24小时,取样点板,待反应物反应完全后,冷却、过滤,将滤液旋蒸除去溶剂,粗产品过硅胶柱,得到中间体D-1;HPLC纯度97.88%,收率78.6%;元素分析结构(C<sub>31</sub>H<sub>28</sub>BN<sub>2</sub>O<sub>2</sub>)理论值:C,81.41;H,6.17;B,2.36;N,3.06;测试值:C,81.43;H,6.19;B,2.35;N,3.08。LC-MS:理论值:457.22,实测值:457.24。

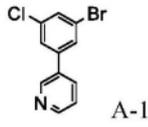
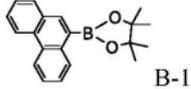
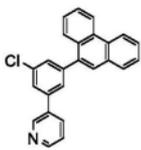
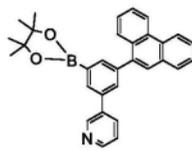
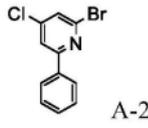
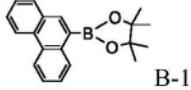
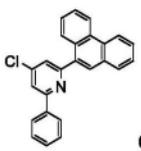
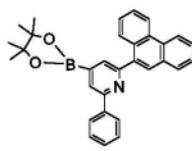
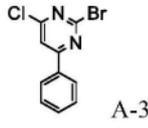
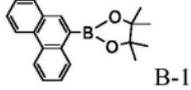
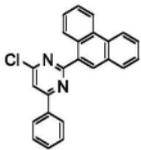
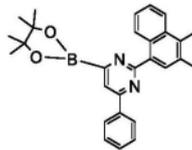
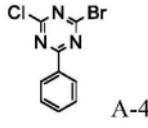
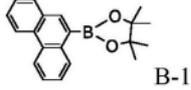
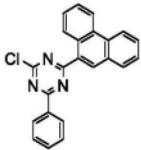
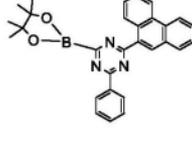
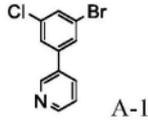
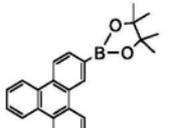
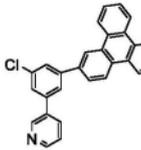
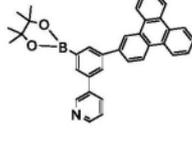
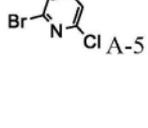
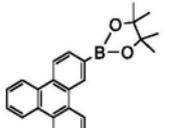
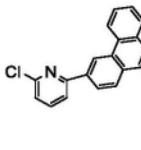
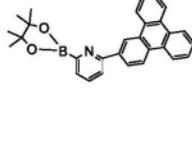
[0099] 中间体D-17的合成路线如下:



[0101] 在250ml的三口瓶中,通氮气保护下,加入0.012mol中间体B-7,0.01mol原料E-1,120ml甲苯搅拌混合,然后加入 $5 \times 10^{-5}$ mol  $\text{Pd}_2(\text{dba})_3$ , $5 \times 10^{-5}$ mol  $\text{P}(\text{t-Bu})_3$ ,0.03mol叔丁醇钠,加热至105℃,回流反应24小时,取样点板,显示无溴代物剩余,反应完全;自然冷却至室温,过滤,滤液旋蒸至无馏分,过中性硅胶柱,得到目标产物。

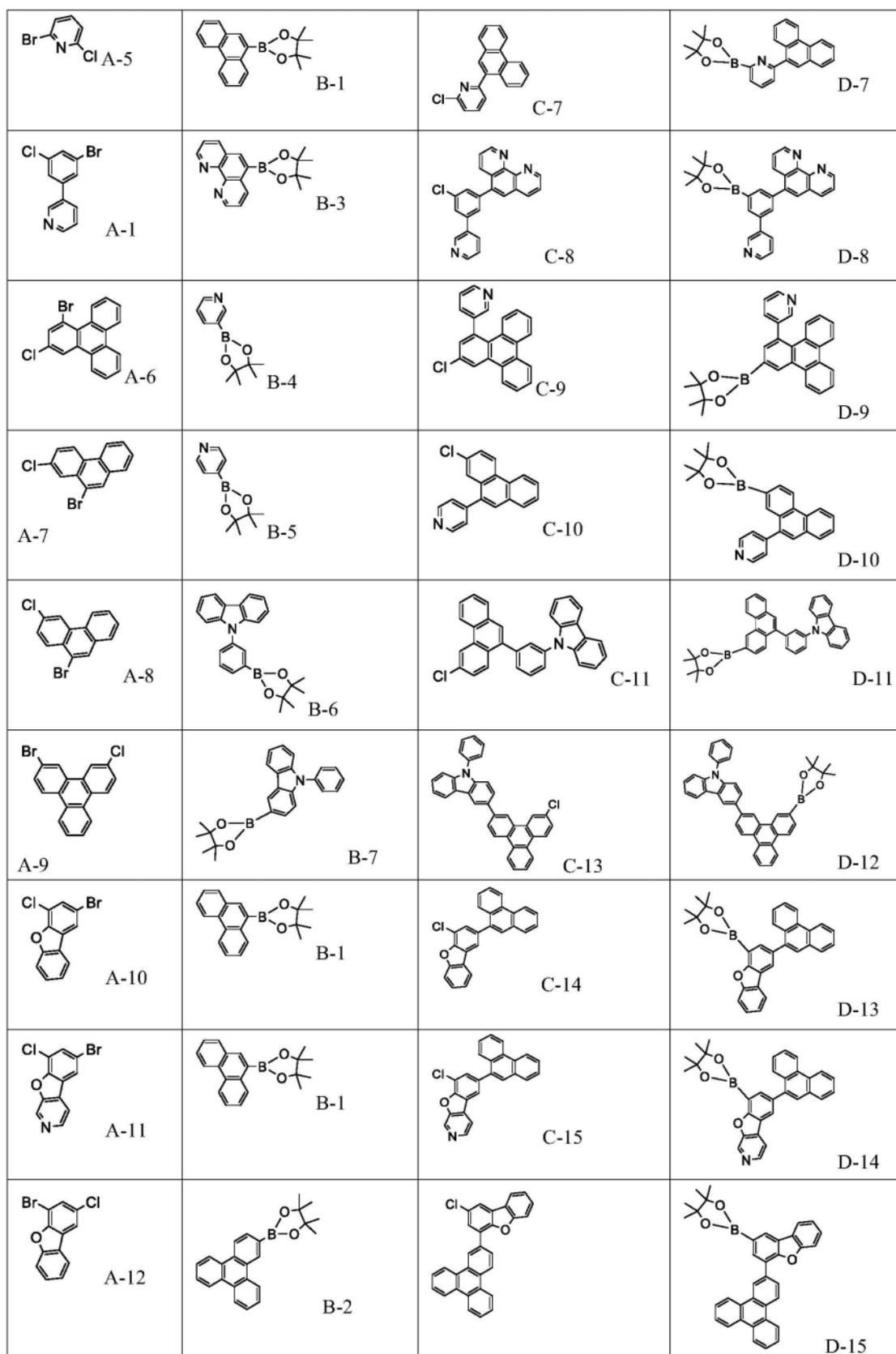
[0102] 重复中间体D-1制备过程合成以下目标化合物D-2至D-16;重复中间体D-17制备过程合成以下目标化合物D-18;反应条件相同,不同之处在于使用下表2中所列出的原料A、原料B、中间体C和原料E;

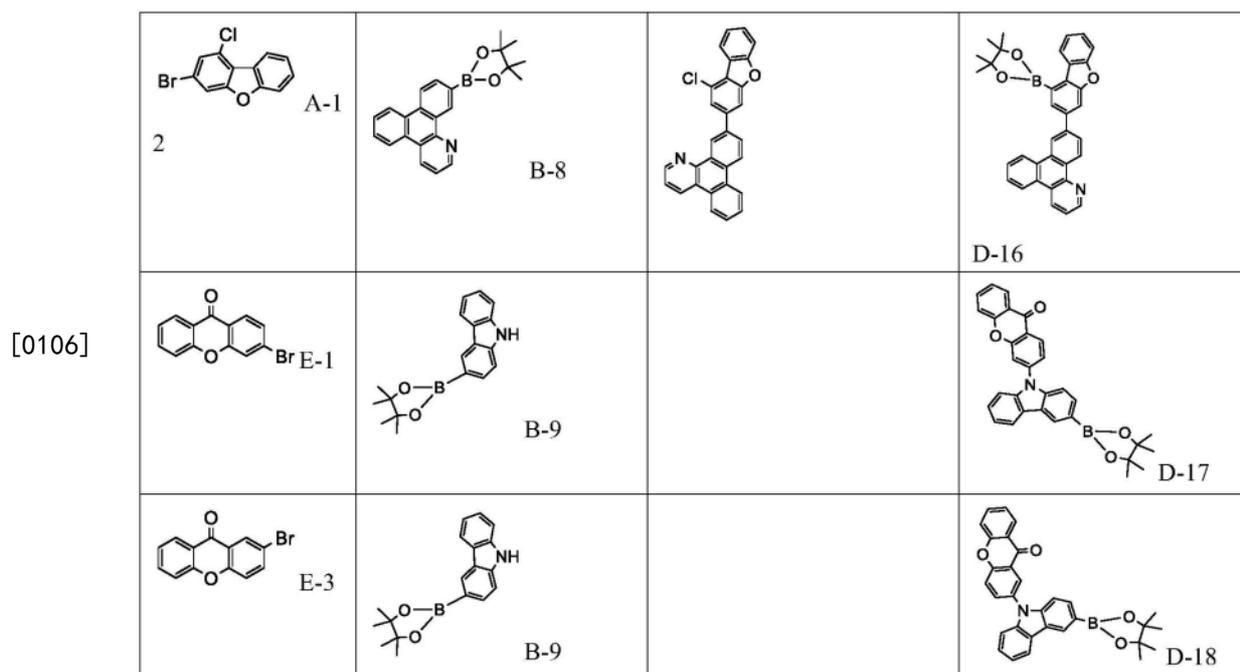
[0103] 表2

原料 A	原料 B	中间体 C	中间体 D
 A-1	 B-1	 C-1	 D-1
 A-2	 B-1	 C-2	 D-2
 A-3	 B-1	 C-3	 D-3
 A-4	 B-1	 C-4	 D-4
 A-1	 B-2	 C-5	 D-5
 A-5	 B-2	 C-6	 D-6

[0104]

[0105]





[0107] 上文所制备化合物的核磁共振氢谱数据如表3所示；

[0108] 表3

[0109]

化合物	<sup>1</sup> H NMR(CDCl <sub>3</sub> , 400MHz)
1	δ 8.86 (d, 1H), 8.63 (dd, 1H), 8.22 – 8.11 (m, 3H), 8.06 (m, 1H), 7.97 (dd, 2H), 7.92 (t, 1H), 7.88 (dd, 3H), 7.83 – 7.74 (m, 1H), 7.64 – 7.47 (m, 5H), 7.47 – 7.37 (m, 3H), 7.37 (t, 1H), 7.07 (d, 1H).
11	δ 8.81 (d, 1H), 8.28 – 8.21 (m, 2H), 8.21 – 8.10 (m, 3H), 8.09 – 8.03 (m, 1H), 8.02 – 7.91 (m, 3H), 7.83 – 7.74 (m, 1H), 7.65 – 7.35 (m, 11H), 7.07 (d, 1H).
53	δ 8.81 (d, 1H), 8.30 – 8.21 (m, 2H), 8.18 (d, 1H), 8.11 (d, 1H), 8.06 (m, 1H), 8.04 – 7.92 (m, 4H), 7.84 – 7.71 (m, 1H), 7.65 – 7.32 (m, 15H), 7.07 (d, 1H).
16	δ 8.30 – 8.25 (m, 1H), 8.25 – 8.19 (m, 2H), 8.17 (s, 1H), 8.14 (dd, 1H), 8.06 (m, 1H), 8.03 – 7.94 (m, 3H), 7.94 – 7.88 (m, 1H), 7.84 – 7.74 (m, 1H), 7.64 – 7.46 (m, 8H), 7.45 – 7.36 (m, 2H), 7.22 (d, 1H).
22	δ 8.61 – 8.51 (m, 2H), 8.32 – 8.27 (m, 1H), 8.15 (dd, 1H), 8.06 (dd, 2H), 8.03 – 7.96 (m, 1H), 7.93 – 7.86 (m, 1H), 7.83 (dd, 1H), 7.79 – 7.73 (m, 1H), 7.64 – 7.37 (m, 10H), 7.22 (d, 1H).
256	δ 9.52 (d, 1H), 8.85 (d, 1H), 8.63 (dd, 1H), 8.29 – 8.21 (m, 1H), 8.21 – 8.16 (m, 1H), 8.14 (dd, 1H), 7.97 (d, 1H), 7.94 – 7.76 (m, 6H), 7.65 – 7.45 (m, 7H), 7.45 – 7.33 (m, 4H), 7.07 (d, 1H).
387	δ 9.89 (d, 1H), 8.27 – 8.11 (m, 3H), 8.02 (dd, 1H), 7.98 (d, 1H), 7.91 – 7.76 (m, 2H), 7.69 – 7.49 (m, 11H), 7.46 – 7.36 (m, 2H).
330	δ 8.48 (dd, 1H), 8.30 (d, 1H), 8.16 (dd, 1H), 8.10 – 8.03 (m, 2H), 8.01 – 7.91 (m, 2H), 7.87 – 7.80 (m, 1H), 7.73 – 7.63 (m, 1H), 7.63 – 7.58 (m, 2H), 7.58 – 7.56 (m, 1H), 7.56 – 7.46 (m, 5H), 7.45 – 7.35 (m, 2H).
91	δ 8.88 – 8.81 (m, 2H), 8.77 (dd, 1H), 8.63 (dd, 1H), 8.28 (m, 1H), 8.26 – 8.17 (m, 2H), 8.15 (m, 2H), 8.04 – 7.95 (m, 2H), 7.88 (m, 2H), 7.66 – 7.59 (m, 2H), 7.59 – 7.51 (m, 1H), 7.50 – 7.33 (m, 5H).
407	δ 9.03 – 8.95 (m, 2H), 8.63 (dd, 1H), 8.37 – 8.30 (m, 1H), 8.22 – 8.11 (m, 2H), 8.02 (d, 1H), 7.92 – 7.82 (m, 2H), 7.77 (d, 1H), 7.67 – 7.36 (m, 11H).
347	δ 8.93 – 8.88 (m, 1H), 8.81 – 8.74 (m, 1H), 8.69 – 8.63 (m, 2H), 8.27 – 8.22 (m, 1H), 8.16 (dd,

[0110]

	1H), 8.10 – 8.03 (m, 1H), 8.00 – 7.92 (m, 2H), 7.79 (dd, 1H), 7.66 – 7.60 (m, 3H), 7.60 – 7.44 (m, 3H), 7.44 – 7.37 (m, 2H), 7.35 (d, 1H).
380	$\delta$ 9.51 (m, 1H), 8.76 – 8.69 (m, 1H), 8.20 (dd, 1H), 8.19 – 8.12 (m, 3H), 8.12 – 8.02 (m, 2H), 8.01 (d, 1H), 7.91 (t, 1H), 7.68 (dd, 1H), 7.65 – 7.24 (m, 16H).
417	$\delta$ 9.52 (dd, 2H), 8.28 – 8.22 (m, 1H), 8.19 (d, 1H), 8.17 – 8.00 (m, 3H), 7.94 (d, 1H), 7.86 (dd, 1H), 7.84 – 7.76 (m, 2H), 7.68 – 7.18 (m, 17H), 7.07 (d, 1H).
133	$\delta$ 8.19 – 8.10 (m, 3H), 8.05 (m, 2H), 8.00 – 7.93 (m, 3H), 7.87 (d, 1H), 7.83 – 7.74 (m, 1H), 7.65 – 7.49 (m, 6H), 7.48 – 7.35 (m, 5H), 7.30 (d, 1H).
155	$\delta$ 8.67 (d, 1H), 8.52 (s, 1H), 8.14 (m, 3H), 8.06 (m, 1H), 8.00 (t, 2H), 7.96 (dd, 1H), 7.89 – 7.82 (m, 2H), 7.82 – 7.75 (m, 1H), 7.67 (dd, 1H), 7.65 – 7.56 (m, 3H), 7.56 – 7.45 (m, 3H), 7.45 – 7.36 (m, 2H).
178	$\delta$ 9.56 – 9.51 (m, 1H), 8.28 – 8.20 (m, 1H), 8.14 (dd, 1H), 8.10 – 8.00 (m, 2H), 7.94 (d, 1H), 7.91 – 7.78 (m, 4H), 7.64 – 7.35 (m, 13H), 7.07 (d, 1H).
203	$\delta$ 9.55 (d, 1H), 8.85 (dd, 1H), 8.21 – 8.10 (m, 2H), 8.08 – 7.88 (m, 4H), 7.87 – 7.80 (m, 1H), 7.77 (dd, 1H), 7.71 (d, 1H), 7.64 – 7.55 (m, 3H), 7.55 – 7.32 (m, 8H), 7.07 (d, 1H).
208	$\delta$ 9.52 (d, 1H), 9.16 – 9.11 (m, 1H), 8.31 (dd, 1H), 8.28 – 8.21 (m, 1H), 8.18 (d, 1H), 8.13 (dd, 1H), 8.08 (dd, 1H), 7.98 (d, 1H), 7.87 – 7.80 (m, 1H), 7.77 – 7.69 (m, 2H), 7.69 – 7.33 (m, 13H), 7.28 (m, 1H).
228	$\delta$ 9.23 – 9.15 (m, 1H), 8.84 (dd, 1H), 8.77 (dd, 1H), 8.31 – 8.18 (m, 3H), 8.17 – 8.11 (m, 1H), 8.11 – 8.05 (m, 3H), 7.91 (dd, 1H), 7.83 (dd, 1H), 7.67 – 7.51 (m, 3H), 7.49 – 7.23 (m, 6H).
429	$\delta$ 8.86 (d, 1H), 8.63 (dd, 1H), 8.17 – 8.07 (m, 2H), 8.01 – 7.79 (m, 9H), 7.65 – 7.55 (m, 2H), 7.51 (dd, 1H), 7.45 – 7.33 (m, 6H), 7.08 (d, 1H).

[0111] 本发明化合物在发光器件中使用, 具有高的玻璃化转变温度 ( $T_g$ ) 和三线态能级 ( $T_1$ ), 合适的HOMO、LUMO能级, 可作为发光层和空穴阻挡/电子传输层材料使用。对本发明上述实施例制备的化合物分别进行热性能、 $T_1$ 能级以及HOMO能级测试, 结果如表6所示。

[0112] 表6

[0113]

化合物	$T_1$ (eV)	$T_g$ (°C)	HOMO 能级 (eV)	LUMO 能级 (eV)	功能层
化合物 1	2.63	138	-6.15	-2.74	发光层
化合物 11	2.59	144	-6.22	-2.75	发光层
化合物 53	2.79	144	-6.31	-2.72	空穴阻挡层
化合物 16	2.49	140	-6.42	-3.15	电子传输层
化合物 22	2.54	138	-6.47	-3.21	电子传输层
化合物 91	2.46	147	-6.38	-3.14	电子传输层
化合物 256	2.66	150	-5.98	-2.77	发光层
化合物 387	2.68	142	-6.12	-2.9	发光层
化合物 330	2.71	145	-6.07	-2.74	发光层
化合物 407	2.82	142	-6.30	-2.78	空穴阻挡层
化合物 347	2.69	137	-6.06	-2.76	发光层
化合物 380	2.74	143	-6.07	-2.85	发光层
化合物 417	2.70	139	-6.12	-2.88	发光层
化合物 133	2.74	151	-6.09	-3.0	发光层
化合物 155	2.67	146	-6.14	-2.84	发光层
化合物 178	2.77	145	-6.01	-2.74	发光层
化合物 203	2.69	139	-6.14	-2.82	空穴阻挡层

[0114]	化合物 208	2.80	142	-6.16	-2.92	发光层
	化合物 228	2.52	138	-6.41	-3.16	电子传输层
	化合物 429	2.48	144	-6.36	-3.17	电子传输层

[0115] 注：三线态能级T1是由Horiba的Fluorolog-3系列荧光光谱仪测试，材料的测试条件为 $2 \times 10^{-5}$ mol/L的甲苯溶液；玻璃化转变温度T<sub>g</sub>由示差扫描量热法(DSC,德国耐驰公司DSC204F1示差扫描量热仪)测定,升温速率10°C/min;最高占据分子轨道HOMO能级是由电离能量测试系统(IPS-3)测试,测试为大气环境;E<sub>g</sub>通过双光束紫外可见分光光度计(型号: TU-1901)进行测试,LUMO=HOMO+E<sub>g</sub>

[0116] 由上表数据可知,本发明的化合物具有高的玻璃化转变温度,可提高材料膜相态稳定性,进一步提高器件使用寿命;本发明化合物含有强电子受体,和空穴型主体材料搭配,使得应用本发明化合物的OLED器件电子和空穴达到平衡状态,保证了电子和空穴的复合率,从而提升了OLED器件的效率和寿命,本发明材料具有高的三线态能级,可以阻挡发光层能量损失,从而提升器件发光效率。同时本发明材料具有合适的HOMO和LUMO能级可以解决载流子的注入问题,可降低器件电压;因此,本发明的有机材料在应用于OLED器件的不同功能层后,可有效提高器件的发光效率及使用寿命。

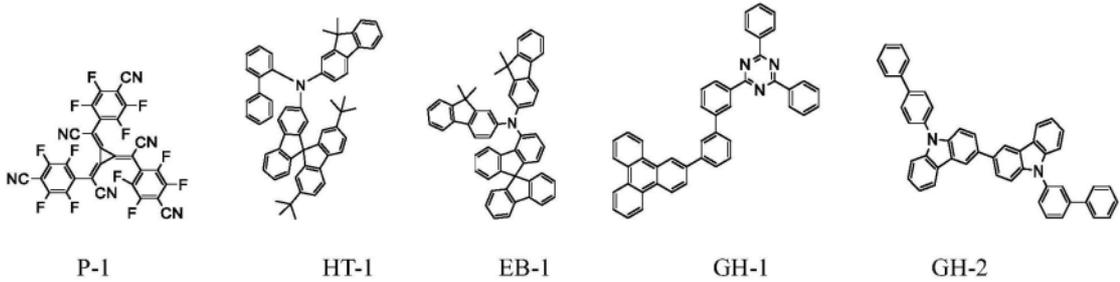
[0117] 下面将通过器件实施例说明本发明的化合物在OLED器件中的应用效果。器件实施例2-30、器件比较例1-4与器件实施例1相比,制作工艺完全相同,并且采用了相同的基板材料和电极材料,电极材料的膜厚也保持一致,所不同的是器件中发光层或空穴阻挡或电子传输层材料发生了改变,各器件每层组成如表4所示,各器件的性能测试结果如表5和表7所示。

[0118] 器件实施例1

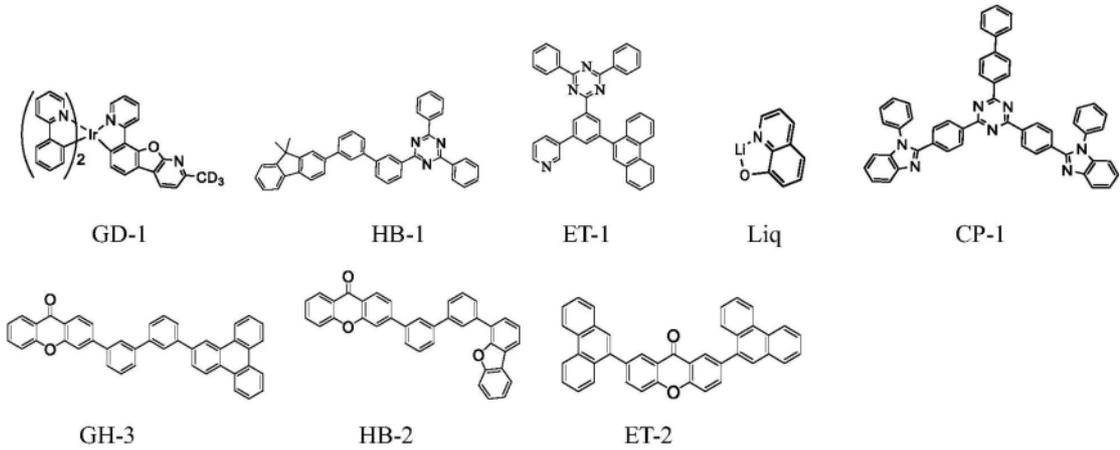
[0119] 如图1所示,透明基板层1为透明PI膜,对阳极层2(ITO(15nm)/Ag(150nm)/ITO(15nm))进行洗涤,即依次进行清洗剂洗涤(SemiClean M-L20)、纯水洗涤、干燥,再进行紫外线-臭氧洗涤以清除阳极层表面的有机残留物。在进行了上述洗涤之后的阳极层2上,利用真空蒸镀装置,蒸镀HT-1和P-1作为空穴注入层3,膜厚为10nm,HT-1和P-1的质量比为97:3。接着蒸镀HT-1作为空穴传输层4,厚度为130nm。随后蒸镀EB-1作为电子阻挡层5,厚度为40nm。上述电子阻挡层材料蒸镀结束后,制作OLED发光器件的发光层6,其结构包括OLED发光层6所使用化合物1和GH-2作为主体材料,GD-1作为掺杂材料,掺杂材料掺杂比例为6%(质量比),发光层膜厚为40nm。在上述发光层6之后,继续真空蒸镀HB-1,膜厚为5nm,此层为空穴阻挡层7。在上述空穴阻挡层7之后,继续真空蒸镀ET-1和Li<sub>q</sub>,ET-1和Li<sub>q</sub>质量比为1:1,膜厚为35nm,此层为电子传输层8。在电子传输层8上,通过真空蒸镀装置,制作膜厚为1nm的Yb层,此层为电子注入层9。在电子注入层9上,通过真空蒸镀装置,制作膜厚为15nm的Mg:Ag电极层,Mg、Ag质量比为1:9,此层为阴极层10使用。在阴极层10上,真空蒸镀CP-1作为CPL层11,厚度为70nm。得到有机电致发光器件1。

[0120] 相关材料的分子结构式如下所示:

[0121]



[0122]



[0123] 表4

器件实施例	空穴注入层/厚度	空穴传输层/厚度	电子阻挡层/厚度	发光层/厚度	空穴阻挡层/厚度	电子传输层/厚度	电子注入层/厚度	阴极层/厚度	CPL层/厚度
1	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 1:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
2	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 11:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
3	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 GH-1:GH-2:GD-1= 47:47:6/40nm	化合物 53/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
4	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 GH-1:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	化合物 16:Liq= 1:1/35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
5	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 GH-1:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	化合物 22:Liq= 1:1/35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
6	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 GH-1:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	化合物 91:Liq= 1:1/35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
7	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 GH-1:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	化合物 228:Liq= =1:1/35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
8	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 256:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
9	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 387:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
10	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 330:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
11	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 GH-1:GH-2:GD-1= 47:47:6/40nm	化合物 407/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)

[0124]

[0125]

12	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 347:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
13	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 380:GH-2:GD-1=47 :47:6/40nm	HB-1/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
14	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 417:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
15	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 133:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
16	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 155:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
17	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 178:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
18	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 GH-1:GH-2:GD-1= 47:47:6/40nm	化合物 203/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
19	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 208:GH-2:GD-1=47 :47:6/40nm	HB-1/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
20	HT-1:P-1 =97:3 10nm	化合物 HT-1 /130nm	化合物 EB-1 /40nm	化合物 GH-1:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	化合物 429:Li <sub>q</sub> =1:1/35 nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
比较 例 1	HT-1:P-1 =97:3 10nm	化合物 HT-1 /60nm	化合物 EB-1 /40nm	GH-1:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
比较 例 2	HT-1:P-1 =97:3 10nm	化合物 HT-1 /60nm	化合物 EB-1 /40nm	GH-3:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
比较 例 3	HT-1:P-1 =97:3 10nm	化合物 HT-1 /60nm	化合物 EB-1 /40nm	GH-1:GH-2:GD-1= 47:47:6/40nm	HB-2/5nm	ET-1:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)
比较 例 4	HT-1:P-1 =97:3 10nm	化合物 HT-1 /60nm	化合物 EB-1 /40nm	GH-1:GH-2:GD-1= 47:47:6/40nm	HB-1/5nm	ET-2:Li q=1:1 /35nm	Yb/1nm	Mg:Ag =1:9 (15nm)	CP-1 (70nm)

[0126] 表5

[0127]

器件实施例	电压 (V)	电流效率 (cd/A)	CIE <sub>x</sub>	CIE <sub>y</sub>	寿命 LT97(Hr)@5000nits
1	3.54	158.6	0.238	0.725	284.8
2	3.60	156.7	0.243	0.718	267.5
3	3.38	155.5	0.237	0.715	281.3
4	3.51	158.2	0.239	0.72	227.4
5	3.46	157.8	0.238	0.719	238.9
6	3.53	152.6	0.243	0.715	251.6
7	3.51	158.4	0.234	0.716	238.0
8	3.52	161.2	0.24	0.721	237.5
9	3.52	162.4	0.244	0.717	240.9

	10	3.57	161.9	0.239	0.72	241.5
	11	3.37	156.7	0.236	0.717	247.2
	12	3.41	170	0.236	0.724	239.3
	13	3.52	167.9	0.24	0.716	271.8
	14	3.58	157.3	0.245	0.723	255.8
	15	3.60	163.1	0.238	0.719	269.1
	16	3.54	169.9	0.247	0.722	280.6
[0128]	17	3.47	166.8	0.246	0.716	271.4
	18	3.39	154.4	0.237	0.718	290.5
	19	3.55	164	0.238	0.715	267.9
	20	3.49	158.7	0.242	0.719	231.4
	比较例1	3.8	144	0.240	0.720	170
	比较例2	3.92	132.8	0.232	0.724	141
	比较例3	3.84	124.7	0.235	0.721	154
	比较例4	3.98	127.4	0.227	0.719	168

[0129] 由表5结果可以看出,本发明制备的以杂蒽酮为核心的化合物可应用于OLED发光器件制作,并且与器件比较例相比,无论是用作发光层或者空穴阻挡层或者电子传输层,效率和寿命均比已知OLED材料获得较大改观,特别是器件的寿命获得较大的提升,且用作空穴阻挡层或电子传输层有降低器件电压的效果。

[0130] 为了比较不同器件在高电流密度下效率衰减的情况,定义了各器件的效率衰减系数 $\Phi$ , $\Phi$ 表示驱动电流为100mA/cm<sup>2</sup>时器件的最大效率 $\mu_{100}$ 与器件的最大效率 $\mu_m$ 之差与最大效率之间的比值, $\Phi$ 值越大,说明器件的效率滚降越严重,反之,说明器件在高电流密度下快速衰减的问题得到了控制。本发明测定了器件实施例1-30,器件比较例1所得器件的效率衰减系数 $\Phi$ ,结果如表7示:

[0131] 表7

器件实施例	效率衰减系数 $\Phi$	器件实施例	效率衰减系数 $\Phi$
1	0.20	13	0.17
2	0.16	14	0.20
3	0.18	15	0.18
4	0.19	16	0.19
5	0.20	17	0.18
6	0.19	18	0.17
7	0.22	19	0.20
8	0.24	20	0.21
9	0.22	比较例1	0.41
10	0.19	比较例2	0.38
11	0.18	比较例3	0.40
12	0.18	比较例4	0.42

[0133] 从表7数据可知,采用本发明的化合物制备的有机发光器件具有较小的效率衰减系数,说明采用本发明的化合物制备的有机电致发光器件能够有效地降低效率滚降。

[0134] 以上所述仅为本发明的较佳实施例,并不用以限制本发明,凡在本发明的精神和原则之内,所作的任何修改、等同替换、改进等,均应包含在本发明的保护范围之内。

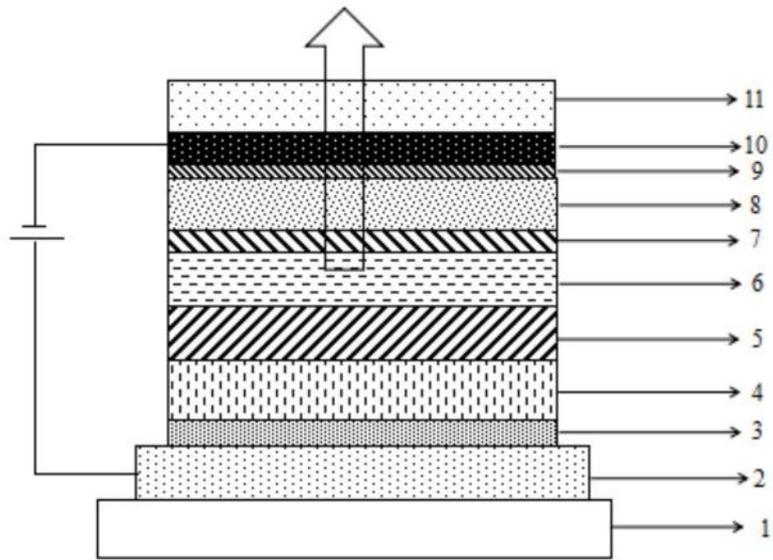


图1