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(54) Title: SEMICONDUCTOR NANOPARTICLE CAPPING AGENTS

(57) Abstract: Semiconductor nanoparticle capping ligands, their production and use. An aspect of the present invention provides a ligand having the formula (I) : wherein m ranges from approximately 8 to approximately 45. A further aspect provides a method of forming a compound of the formula (II), the method comprising the steps of providing a first starting material comprising poly(ethyleneglycol) and reacting the first starting material with a second starting material comprising a functional group for chelating to the surface of a nanoparticle.



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## **SEMICONDUCTOR NANOPARTICLE CAPPING AGENTS**

The present invention relates to semiconductor nanoparticle capping ligands, their production and use in preparing functionalized semiconductor nanoparticles.

The size of a semiconductor nanoparticle dictates the electronic properties of the material; the bandgap energy is inversely proportional to the size of the semiconductor nanoparticle as a consequence of quantum confinement effects. In addition, the large surface area to volume ratio of the nanoparticle has a profound impact upon the physical and chemical properties of the nanoparticle.

Single-core nanoparticles that comprise a single semiconductor material usually have relatively low quantum efficiencies. These low quantum efficiencies arise from non-radiative electron-hole recombinations that occur at defects and dangling bonds at the surface of the nanoparticle.

Core-shell nanoparticles typically comprise a single semiconductor core material that has a shell of a second semiconductor material grown epitaxially on the surface of the core. The shell material usually has a wider bandgap and similar lattice dimensions to the core semiconductor material. The intention of adding the shell is to eliminate defects and dangling bonds from the surface of the core, and thereby confine charge carriers within the core and away from surface states that may function as centers for non-radiative recombination.

Still, the surfaces of core, core-shell, and core-multishell nanoparticles may have highly reactive dangling bonds. These can be passivated by capping the surface atoms with organic ligand molecules which inhibit aggregation of particles, protect the particle from its surrounding chemical environment, and (at least in the case of core nanoparticles) provide electronic stabilization. The capping ligand compound may be the solvent that is employed in the core growth and/or shelling of the nanoparticles. Alternatively, the capping ligand may be dissolved in an inert solvent and then used in the core growth and/or shelling of the nanoparticles. Either way, the ligand compound caps the surface of

the nanoparticle by donating lone-pair electrons to the surface metal atoms of the nanoparticle.

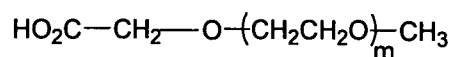
Nanoparticles are typically synthesized in the presence of a lipophilic ligand compound, resulting in nanoparticles that are soluble in non-polar media. To decrease or eliminate this solubility, the ligand compound may be exchanged for a different ligand compound of greater polarity; however, the quantum yield of the nanoparticles diminishes as a result.

The resulting semiconductor nanoparticles may be used in a range of different applications, in which the nanoparticles are externally excited by photo-excitation, electro-excitation, or another form of excitation, leading to electron-hole recombination and subsequent emission of photons in the form of light of a predetermined wavelength, e.g. visible light. The use of surface functionalized nanoparticles in such applications has so far, however, been limited by the loss in quantum yield upon surface functionalisation.

An object of the present invention is to obviate or mitigate one or more of the above problems with current methods for producing surface functionalized semiconductor nanoparticles.

The present invention relates to the fabrication of capping ligands for semiconductor nanoparticles as well as the precursors of the capping ligands. The capping ligands disclosed herein are preferably utilized in and during the synthesis of the nanoparticles, resulting in nanoparticles of high quantum yield and polarity. The resulting semiconductor nanoparticles may be used in a range of different applications, such as display applications whereby the semiconductor nanoparticles are incorporated into a device or transparent material; incorporation into polar solvents (e.g. water and water-based solvents). The resulting nanoparticles may also be incorporated into inks, polymers or glasses; or attached to cells, biomolecules, metals, molecules and the like. The present invention thus overcomes the problems with prior art methods for the surface functionalisation of semiconductor nanoparticles which have previously hindered the use of surface functionalized nanoparticles in such applications.

In an aspect, embodiments of the invention feature the preparation and use of a compound of the following formula in the production and capping of quantum dot nanoparticles:



where  $m$  is between 0 and approximately 4500, or more preferably, between 0 and approximately 450, or even between 0 and approximately 17. In particular embodiments,  $m$  is approximately 8, approximately 13, approximately 17, or approximately 45. These compounds are suitable for use as a ligand compound (i.e., a capping agent) for core growth and/or shelling of quantum dot nanoparticles.

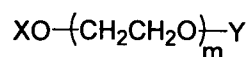
An aspect of the present invention provides a ligand having the formula  $\text{HO}_2\text{C}-\text{CH}_2-\text{O}-\left(\text{CH}_2\text{CH}_2\text{O}\right)_m-\text{CH}_3$ , wherein  $m$  ranges from approximately 8 to approximately 45.

In a preferred embodiment, the ligand may be disposed proximate a core of a nanoparticle, said core preferably comprising at least one semiconductor material.

In a further preferred embodiment, the ligand may be disposed proximate a shell of a nanoparticle, the shell optionally comprising at least one semiconductor material.

The ligand may be disposed within a solvent, in which case it is preferred that the solvent further comprises at least one nanoparticle precursor material.

In another aspect, embodiments of the invention feature methods of synthesizing a compound of formula:



where  $m$  is as defined above, X includes or consists essentially of H,  $-\text{CH}_3$ , or  $-\text{CH}_2\text{CO}_2\text{H}$ , and Y includes or consists essentially of *p*-toluene sulphonate, carboxyl (e.g.  $-\text{CH}_2\text{CO}_2\text{H}$  or  $-\text{PhCO}_2\text{H}$ ),  $-\text{SiPh}_2\text{tBu}$ , phenyl (e.g.  $-\text{CH}_2\text{Ph}$ ), thiol, amino, dithiocarbamate, phosphonic acid, phosphinic acid, vinyl, acetylene, aryl, heteroaryl, and the like.

Another aspect of the present invention provides a method of forming a compound of the

formula  $\text{XO}-(\text{CH}_2\text{CH}_2\text{O})_m-\text{Y}$ , the method comprising the steps of:

- providing a first starting material comprising poly(ethyleneglycol); and
- reacting the first starting material with a second starting material comprising a functional group for chelating to the surface of a nanoparticle.

Preferably the first starting material comprises a terminal hydroxyl group and the second starting material comprises a leaving group and the step of reacting the first and second starting materials comprises detaching the leaving group.

It is preferred that the method further comprises capping at least one nanoparticle with the compound. Accordingly, a further aspect of the present invention relates to a method for producing capped nanoparticles comprising carrying out the method described above and then capping at least one nanoparticle with the resulting compound of formula

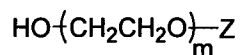
$\text{XO}-(\text{CH}_2\text{CH}_2\text{O})_m-\text{Y}$  as defined above. Moreover, a still further aspect provides nanoparticles capped with a compound of formula  $\text{XO}-(\text{CH}_2\text{CH}_2\text{O})_m-\text{Y}$  as defined above.

There is further provided in another aspect a display device comprising a plurality of nanoparticles, each capped with a ligand having the formula  $\text{HO}_2\text{C}-\text{CH}_2-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_m-\text{CH}_3$ , disposed within a material substantially transparent to light.

In a preferred embodiment the display device further comprises means for exciting the plurality of nanoparticles such that the nanoparticles emit visible light. Moreover, preferably each of the plurality of nanoparticles comprises:

- a core comprising a first semiconductor material; and
- a shell comprising a second semiconductor material different from the first semiconductor material.

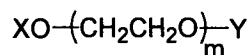
The above defined methods preferably include the steps of coupling, to an appropriately functionalized molecule of the formula X-W, the hydroxyl functionality of a poly(ethyleneglycol) starting material having the formula:



where m is as defined above, and Z includes or consists essentially of H or -CH<sub>3</sub>. X includes or consists essentially of a leaving group such as a halogen, *p*-toluene sulphonate, mesyl (CH<sub>3</sub>-S(O)<sub>2</sub>-O-) or a nucleophile such as OH, and W includes or consists essentially of a suitable functional group to chelate to the surface of a nanoparticle, such as a carboxyl or thio group.

Z may be pre-functionalized to include a head group to afford the desired solubility to nanoparticles capped with the ligand produced as a result of the reaction of X-W with HO-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>m</sub>-Z, or Z may be subject to post-reaction modification so that incorporates the desired head group, such as, but not limited to *p*-toluene sulphonate, carboxyl (e.g. -CH<sub>2</sub>CO<sub>2</sub>H or -PhCO<sub>2</sub>H), -SiPh<sub>2</sub><sup>t</sup>Bu, phenyl (e.g. -CH<sub>2</sub>Ph), thiol, amino, dithiocarbamate, phosphonic acid, phosphinic acid, vinyl, acetylene, aryl, heteroaryl, and the like.

In a preferred embodiment, the ligand has the formula:



where X includes or consists essentially of -CH<sub>3</sub> and m is approximately 8 in both the poly(ethyleneglycol) methyl ether (~350) starting material and ligand compound. Y includes or consists essentially of H in the poly(ethyleneglycol) methyl ether (having a molecular weight of approximately 350) starting material and Y includes or consists essentially of -CH<sub>2</sub>CO<sub>2</sub>H in the ligand compound.

In further preferred aspects there are provided semiconductor quantum dot nanoparticles incorporating the capping ligands defined above and methods for producing the same employing standard synthetic methods for binding such ligands to the nanoparticle surface.

The semiconductor material comprised in the nanoparticles capped with the above defined capping ligands according to the present invention may incorporate ions from any one or more of groups 2 to 16 of the periodic table, including binary, ternary and quaternary materials, that is, materials incorporating two, three or four different ions respectively. By way of example, the nanoparticles may incorporate a core semiconductor material, such as, but not limited to, CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, InP, InAs, InSb, AlP, AlS, AlAs, AlSb, GaN, GaP, GaAs, GaSb, PbS, PbSe, Si, Ge and combinations thereof. Nanoparticles preferably possess cores with mean diameters of less than around 20 nm, more preferably less than around 15 nm and most preferably in the range of around 2 to 5 nm.

As mentioned above, in order to at least partially address issues related to non-radiative electron-hole recombinations that occur at defects and dangling bonds at the nanoparticle surface resulting in undesirably low quantum efficiencies, nanoparticle cores may be at least partially coated with one or more layers (also referred to herein as "shells") of a different material to the core, for example a semiconductor material. Thus, the nanoparticles capped using ligands according to the present invention may incorporate one or more shell layers. The material comprised in the or each shell may incorporate ions from any one or more of groups 2 to 16 of the periodic table. Where a nanoparticle comprises two or more shells, each shell is preferably formed of a different material. In an exemplary core/shell material, the core is formed of one of the materials specified above and the shell is comprised of a semiconductor material of larger band-gap energy and similar lattice dimensions to the core material. Example shell materials include, but are not limited to, ZnS, MgS, MgSe, MgTe and GaN. The confinement of charge carriers within the core and away from surface states provides quantum dots of greater stability and higher quantum yield. It will be appreciated that where two materials are provided in adjacent layers of a semiconductor nanoparticle whose lattice structures do not correspond closely, it may be appropriate to ease any lattice strain that exists at the interface of the two materials by introducing a graded layer in between the two layers of material. The graded layer would typically include most, if not all, of the ions in each of the two adjacent layers but the proportions of the ions would vary from the core to the shell. The region of the graded layer adjacent to the core would comprise a majority of at least one of the ions in

the core material and the region of the graded layer adjacent to the shell would comprise a majority of the at least one of the ions in the shell material.

The mean diameter of quantum dot nanoparticles, which may be capped using the ligands of the present invention, may be varied to modify the emission-wavelength. The energy levels and hence the frequency of the quantum dot fluorescence emission can be controlled by the material from which the quantum dot is made and the size of the quantum dot. Generally, quantum dots made of the same material have a more pronounced red emission the larger the quantum dot. It is preferred that the quantum dots have diameters of around 1 to 15 nm, more preferably around 1 to 10 nm. The quantum dots preferably emit light having a wavelength of around 400 to 900 nm, more preferably around 400 to 700 nm.

Typically, as a result of the core and/or shelling procedures employed to produce the core, core/shell or core/multishell nanoparticles, the nanoparticles are at least partially coated with a surface binding ligand, such as myristic acid, hexadecylamine and/or trioctylphosphineoxide. Such ligands are typically derived from the solvent in which the core and/or shelling procedures were carried out. While ligands of this type can increase the stability of the nanoparticles in non-polar media, provide electronic stabilisation and/or negate undesirable nanoparticle agglomeration, as mentioned previously, such ligands usually prevent the nanoparticles from stably dispersing or dissolving in more polar media, such as aqueous solvents.

In preferred embodiments, the present invention provides quantum dots that are aqueous compatible, stable, small and of high quantum yield. Where lipophilic surface binding ligand(s) are coordinated to the surface of the quantum dots as a result of the core and/or shelling procedures (examples include hexadecylamine, trioctylphosphineoxide, myristic acid), such ligands may be exchanged entirely or partially with ligands according to the present invention using standard methods known to the skilled person, or the ligands of the invention may interchelate with the existing lipophilic surface binding ligands, again using standard methods.

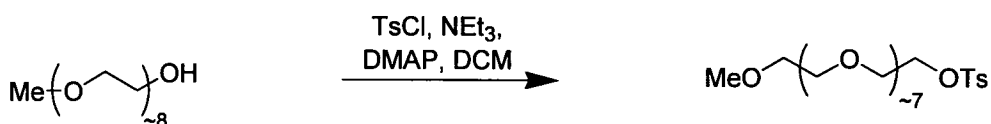


The invention will now be further described, by way of example only, with reference to the following non-limiting Figures and Example:

Figure 1 shows a schematic diagram of a quantum dot nanoparticle.

**EXAMPLE**

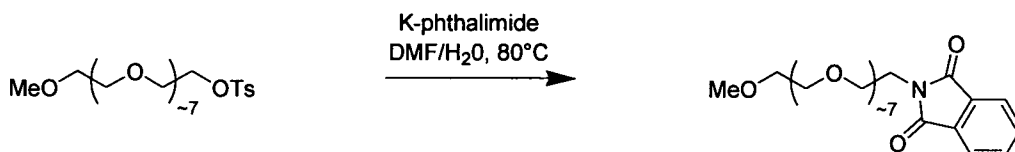
Glassware was dried (120 °C) in an oven overnight. Dichloromethane (“DCM”) and triethylamine (“TEA”) were distilled from calcium hydride after heating at reflux for at least 1 hour. Tetrahydrofuran was distilled Na/benzophenone after heating at reflux for at least 1 hour. Poly(ethylene glycols) were heated at 120 °C under high vacuum for 1 hour. All other reagents were used as received from a commercial supplier. All reaction mixtures were stirred magnetically and conducted under an atmosphere of dinitrogen gas.

**Synthesis of poly(oxyethylene glycol)<sub>350</sub> monomethyl ether *p*-toluene sulfonate**

Scheme 1: Synthesis of Poly(oxyethylene glycol)<sub>350</sub> monomethyl ether *p*-toluene sulfonate.

A solution of TsCl (27.792 g, 143.00 mmol) in DCM (80 mL) was added drop-wise over 2 hours to an ice-cooled solution of poly(oxyethylene glycol)<sub>350</sub> monomethyl ether (50.000 g, 143.00 mmol), triethylamine (40.30 mL, 290.0 mmol), and DMAP (0.177 g, 1.4 mmol) in DCM (75 mL), and the resultant mixture was left to stir overnight while warming to room temperature. The reaction mixture was washed with distilled water (2 × 200 mL), saturated sodium bicarbonate solution (2 × 100 mL), saturated citric acid solution (2 × 100 mL), dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure to give yellow-colored oil. This oil was dissolved in hexane (3 × 200 mL) and the unreacted TsCl was separated from the reaction mixture by filtration. The filtrate was concentrated under reduced pressure to provide poly(oxyethylene glycol)<sub>350</sub> monomethyl ether *p*-toluene sulfonate as a pale yellow-colored oil.

### Synthesis of monomethyl ether poly(oxyethylene glycol)<sub>350</sub> phthalimide



Scheme 2: Synthesis of monomethyl ether poly(oxyethylene glycol)<sub>350</sub> phthalimide.

Potassium phthalimide (2.679 g, 14.48 mmol) was added to a solution of poly(oxyethylene glycol)<sub>350</sub> monomethyl ether p-toluene sulfonate (5.000 g, 9.65 mmol) in DMF (45 mL)/water (6 mL) and then stirred overnight (80 °C).

The reaction mixture was allowed to cool to room temperature, dissolved in DCM (100 mL) and washed sequentially with, distilled water (6 × 500 mL), saturated brine (6 × 500 mL) (Removes DMF), distilled water (500 mL), dried over anhydrous magnesium sulphate, filtered and concentrated under reduced pressure. The resultant oil was dissolved in the minimum volume of DCM, filtered, and then concentrated under reduced pressure to give monomethyl ether poly(oxyethylene glycol)<sub>350</sub> phthalimide.

The phthalimide group of the monomethyl ether poly(oxyethylene glycol)<sub>350</sub> phthalimide compound is an example of a terminal functional group which can be conveniently converted into another group (such as an amino group, e.g. -NH<sub>2</sub>, when treated with a base) to confer to the resulting ligand the ability to bind to the surface of nanoparticles and/or the ability to modify the solubility of nanoparticles to which the ligand is bound.

### Synthesis of poly(oxyethylene glycol)<sub>350</sub> monomethyl ether acetic acid

A solution of bromoacetic acid (162.83g, 1.1719 moles) in tetrahydrofuran (500 mL) was added dropwise to a suspension of sodium hydride (93.744g, 2.3436 moles) in tetrahydrofuran (500 mL) that was stirred and cooled (0°C). Poly(oxyethylene glycol)<sub>350</sub> monomethyl ether that had previously been dried (120°C, high vacuum, 1 hour) was dissolved in tetrahydrofuran (150 mL) and added dropwise to the reaction mixture. The reaction mixture was stirred while warming to room temperature overnight.

The reaction mixture was poured over ice, acidified (pH=1) and then concentrated under reduced pressure to give a white solid suspended in a yellow-colored oil. The oil was dissolved in  $\text{CH}_2\text{Cl}_2$  (2.5 L) and the white solid was separated by filtration. The filtrate was washed with saturated  $\text{NaHCO}_3$  ( $5 \times 50$  mL) and then concentrated under reduced pressure to give a yellow-colored oil. The oil was dissolved in water (2L) and washed with diethylether ( $5 \times 50$  mL). The aqueous phase (pH of approximately 3) was acidified with 1M  $\text{HCl}_{(\text{aq})}$  to pH of approximately 1 and washed with diethylether (50mL). The aqueous phase was concentrated under reduced pressure to give a colorless oil (298.78g).

### **Capping of Quantum Dots**

Representative quantum-dot materials compatible with embodiments of the invention include CdSe, GaAs, InAs, InP,  $\text{CuInS}_2$ ,  $\text{CuInSe}_2$ , and  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ . Nanoparticle synthesis may be carried out using techniques described, for example, in U.S. Patent No. 6,379,635 and copending U.S. Patent Application Serial Nos. 11/579,050 and 11/588,880. The nanoparticles may be characterized by any conventional technique (e.g., XRD, UV/Vis/Near-IR spectrometry, SEM, TEM, EDAX, photoluminescence spectrometry, elemental analysis).

QDs can be capped with the ligands described above (e.g. poly(oxyethylene glycol)<sub>350</sub> monomethyl ether acetic acid) using any one of a number of suitable methods known to the skilled person, which may optionally include ligand exchange and/or ligand interchelation methodologies.

**CLAIMS**

1. A ligand having the formula  $\text{HO}_2\text{C}-\text{CH}_2-\text{O}-\left(\text{CH}_2\text{CH}_2\text{O}\right)_m-\text{CH}_3$ , wherein m ranges from approximately 8 to approximately 45.
2. The ligand of claim 1 disposed proximate a core of a nanoparticle.
3. The ligand of claim 2, wherein the core of the nanoparticle comprises at least one semiconductor material.
4. The ligand of claim 1 disposed proximate a shell of a nanoparticle.
5. The ligand of claim 4, wherein the shell of the nanoparticle comprises at least one semiconductor material.
6. The ligand of claim 1 disposed within a solvent, the solvent further comprising at least one nanoparticle precursor material.
7. A method of forming a compound of the formula  $\text{XO}-\left(\text{CH}_2\text{CH}_2\text{O}\right)_m-\text{Y}$ , wherein X is an atom or chemical group, Y is an atom or chemical group and m is an integer, the method comprising the steps of:
  - providing a first starting material comprising poly(ethyleneglycol); and
  - reacting the first starting material with a second starting material comprising a functional group for chelating to the surface of a nanoparticle.
8. The method of claim 7, wherein the first starting material comprises a terminal hydroxyl group, the second starting material comprises a leaving group, and reacting the first and second starting materials comprises detaching the leaving group.
9. The method of claim 7 or 8, further comprising capping at least one nanoparticle with the compound.

10. A method for producing capped nanoparticles comprising capping at least one nanoparticle with a compound of formula  $\text{XO}-(\text{CH}_2\text{CH}_2\text{O})_m-\text{Y}$ , wherein X is an atom or chemical group, Y is an atom or chemical group and m is an integer.

11. The method of any one of claims 7 to 10, wherein X comprises at least one of H,  $\text{CH}_3$ , or  $-\text{CH}_2\text{CO}_2\text{H}$ .

12. The method of any one of claims 7 to 11, wherein Y comprises at least one of *p*-toluene sulphonate, carboxyl,  $-\text{CH}_2\text{CO}_2\text{H}$ ,  $-\text{PhCO}_2\text{H}$ ,  $-\text{SiPh}_2\text{tBu}$ , phenyl,  $-\text{CH}_2\text{Ph}$ , thiol, amino, dithiocarbamate, phosphonic acid, phosphinic acid, vinyl, acetylene, aryl, heteroaryl, and the like.

13. The method of any one of claims 7 to 12, wherein m ranges from approximately 8 to approximately 45.

14. The method of any one of claims 7 to 13, wherein the at least one nanoparticle comprises at least one semiconductor material.

15. Nanoparticles capped with a compound of formula  $\text{XO}-(\text{CH}_2\text{CH}_2\text{O})_m-\text{Y}$  wherein X is an atom or chemical group, Y is an atom or chemical group and m is an integer.

16. Nanoparticles according to claim 15, wherein X comprises at least one of H,  $\text{CH}_3$ , or  $-\text{CH}_2\text{CO}_2\text{H}$ .

17. Nanoparticles according to claim 15 or 16, wherein Y comprises at least one of *p*-toluene sulphonate, carboxyl,  $-\text{CH}_2\text{CO}_2\text{H}$ ,  $-\text{PhCO}_2\text{H}$ ,  $-\text{SiPh}_2\text{tBu}$ , phenyl,  $-\text{CH}_2\text{Ph}$ , thiol, amino, dithiocarbamate, phosphonic acid, phosphinic acid, vinyl, acetylene, aryl, heteroaryl, and the like.

18. Nanoparticles according to claim 15, 16 or 17, wherein m ranges from approximately 8 to approximately 45.
19. Nanoparticles according to any one of claims 15 to 18, wherein at least one of the nanoparticle comprises at least one semiconductor material.
20. A display device comprising:  
a plurality of nanoparticles, each capped with a ligand having the formula  $\text{HO}_2\text{C}-\text{CH}_2-\text{O}-\left(\text{CH}_2\text{CH}_2\text{O}\right)_m-\text{CH}_3$ , wherein m is an integer, disposed within a material substantially transparent to light.
21. The display device of claim 20, further comprising means for exciting the plurality of nanoparticles such that the nanoparticles can emit visible light.
22. The display device of claim 21 or 22, wherein each of the plurality of nanoparticles comprises:  
a core comprising a first semiconductor material; and  
a shell comprising a second semiconductor material different from the first semiconductor material.

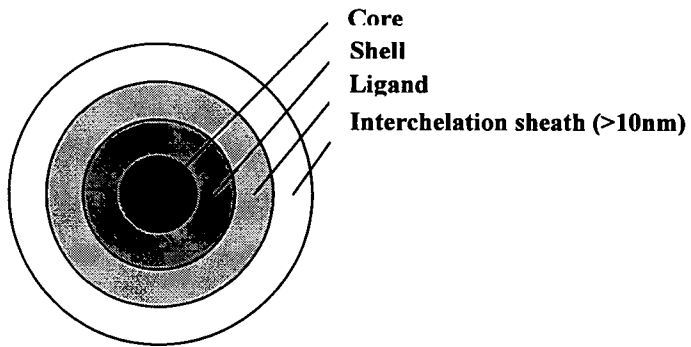


Figure 1



**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/GB2009/000510

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C08G65/332 C08K9/04 H01L21/00 C07C59/125

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
C08G C08K C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, BEILSTEIN Data, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>W. PETER WUELFING ET AL: "Supporting Information for Nanometer Gold Clusters Protected by Surface Bound Monolayers of Thiolated Poly (ethylene glycol) Polymer Electrolyte" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, [Online] vol. 120, no. 48, 1998, pages S1-S6, XP002529160 Retrieved from the Internet: URL: <a href="http://pubs.acs.org/doi/suppl/10.1021/ja983183m/suppl_file/ja983183m_s.pdf">http://pubs.acs.org/doi/suppl/10.1021/ja983183m/suppl_file/ja983183m_s.pdf</a> [retrieved on 2009-06-05] page S1, lines 10-19</p> <p align="center">----- -/--</p>	10-19

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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/GB2009/000510

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/250745 A1 (OGURA ATSUSHIKO [JP] ET AL) 16 December 2004 (2004-12-16) claim 1 paragraphs [0032], [0039], [0077] -----	7-19
X	EP 1 783 137 A1 (NIPPON SHINYAKU CO LTD [JP]) 9 May 2007 (2007-05-09) page 10, line 45 pages 20-21; example 3 -----	7,8
X	WO 2006/001848 A2 (ADVANCED RES & TECH INST [US]; NAUMANN CHRISTOPH A [US]; YOUNG BRUCE A) 5 January 2006 (2006-01-05) claims 1,6 paragraphs [0029], [0033], [0035] examples 1-5 -----	7-19
X	US 2004/007169 A1 (OHTSU TAKESHI [JP] ET AL) 15 January 2004 (2004-01-15) claims 1,2,11 paragraphs [0122] - [0144] -----	10-19
X	WO 2004/065362 A2 (UNIV MASSACHUSETTS [US]) 5 August 2004 (2004-08-05) claims 1,2,5 page 4 examples 1a,1c,7,8 -----	7-19
X	WO 03/053398 A1 (HENKEL KGAA [DE]; SUS TECH GMBH & CO KG [DE]; KLISS RAINER [DE]; ELSAE) 3 July 2003 (2003-07-03) claims 1-7,12-25 page 6, lines 12-16 page 7, lines 3-9 page 10, lines 24-26 page 11, lines 1-4 page 12 page 31; examples 1,2 page 33; example 4 -----	1-22
X	EP 1 854 792 A1 (CHUGAI PHARMACEUTICAL CO LTD [JP]) 14 November 2007 (2007-11-14) page 202; examples 4-39 page 213; examples 4-57 -----	1,7,8
X	WO 02/24623 A2 (GLAXO GROUP LTD [GB]; LOOKER BRIAN EDGAR [GB]; REDGRAVE ALISON JUDITH) 28 March 2002 (2002-03-28) claim 1 pages 15-17; example 7 -----	1,7,8
X	US 2 769 838 A (MAX MATTER ET AL) 6 November 1956 (1956-11-06) claim 1 examples 2-4 -----	1,7,8

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2009/000510

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2004250745	A1	16-12-2004	JP 4181435 B2 JP 2004300253 A	12-11-2008 28-10-2004
EP 1783137	A1	09-05-2007	WO 2006022325 A1 US 2007244058 A1	02-03-2006 18-10-2007
WO 2006001848	A2	05-01-2006	NONE	
US 2004007169	A1	15-01-2004	NONE	
WO 2004065362	A2	05-08-2004	AU 2003303090 A1	13-08-2004
WO 03053398	A1	03-07-2003	AT 328644 T AU 2002366728 A1 BR 0215155 A CA 2470897 A1 DE 10163256 A1 DK 1455737 T3 EP 1455737 A1 JP 2005519143 T US 2005048010 A1	15-06-2006 09-07-2003 19-10-2004 03-07-2003 10-07-2003 09-10-2006 15-09-2004 30-06-2005 03-03-2005
EP 1854792	A1	14-11-2007	AR 053140 A1 AU 2006216289 A1 CA 2598330 A1 WO 2006090743 A1 KR 20070107139 A US 2009030195 A1	25-04-2007 31-08-2006 31-08-2006 31-08-2006 06-11-2007 29-01-2009
WO 0224623	A2	28-03-2002	AU 9007501 A EP 1318973 A2 JP 2004509159 T US 2004067202 A1	02-04-2002 18-06-2003 25-03-2004 08-04-2004
US 2769838	A	06-11-1956	NONE	