NITRO COMPOUNDS DETECTION SUBSTRATE AND METHODS OF USING THE SAME

CROSS-REFERENCE TO RELATED APPLICATION

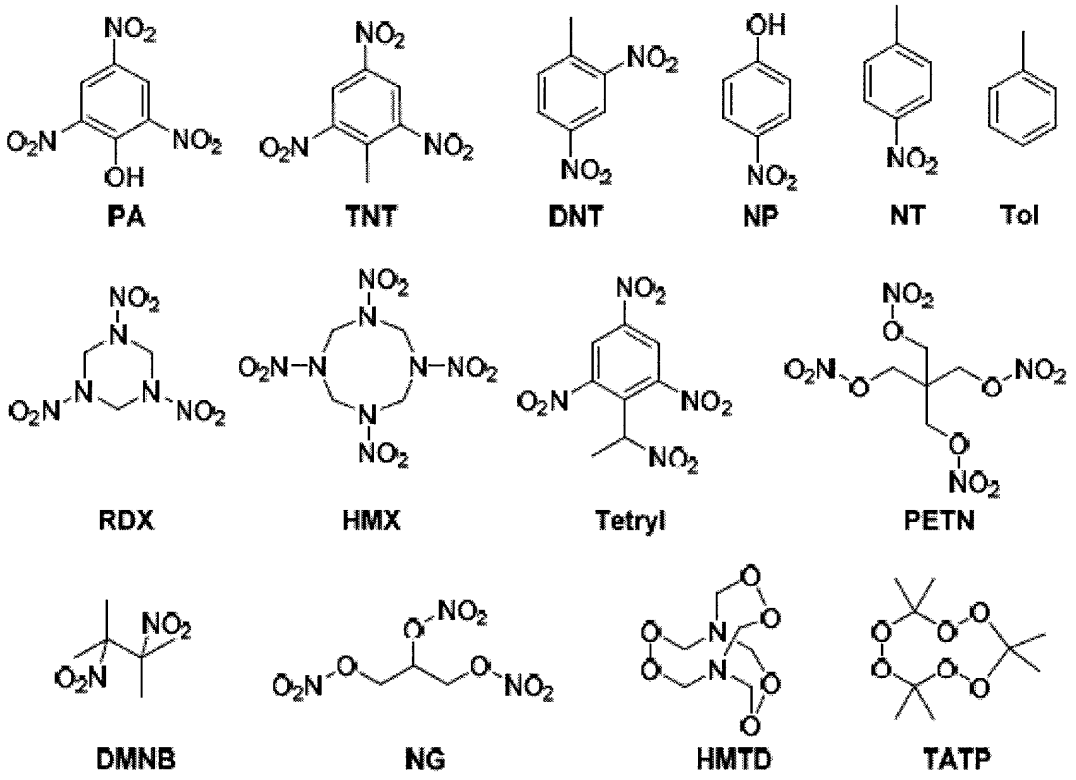
[0001] This application claims the benefit of priority of Singapore application No. 10201601232X, filed February 19, 2016, the contents of it being hereby incorporated by reference in its entirety for all purposes.

FIELD OF INVENTION

[0002] The present disclosure generally relates to polymeric nanoparticles comprising an aromatic backbone connected with ethylene bridges. The conjugated polymer nanoparticles exhibit fluorescence which is quenched in the presence of nitro compounds. The polymeric nanoparticles of the present disclosure therefore are useful as detection substrates for nitro compounds. The present disclosure also relates to a device for the detection of nitro compounds, a method of fabricating such as device, a method for detection of nitro compounds, use of the polymeric nanoparticle for the detection of nitro compounds and a method of preparing the polymeric nanoparticles.

BACKGROUND

[0003] Detection of explosives has become a crucial task for the anti-terrorism efforts and homeland security. Nitro-substituted organic compounds are a common class of highly explosive compounds. Typically, nitro-aromatics (Scheme 1), such as 2,4,6-trinitrotoluene (TNT) and plastic explosives are the primary military explosives and also the principal components in the unexploded landmines worldwide.



Scheme 1: *Structural illustration of explosives and examples, including PA (picric acid), TNT (2,4,6-trinitrotoluene), DNT (2,4-dinitrotoluene), NT (4-nitrotoluene), Tol (toluene), RDX (1,3,5-Trinitro-1,3,5-triazacyclohexane), HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), Tetryl (2,4,6-Trinitrophenylmethylnitramine), PETN (Pentaerythritol tetranitrate), DMNB (2,3-Dimethyl-2,3-dinitrobutane), NG (Nitroglycerin), HMTD (Hexamethylene triperoxide diamine) and TATP (Triacetone triperoxide).*

[0004] Traditionally, various instrumental analytical techniques have been employed for the detection of explosives, such as chromatography with ultraviolet absorption detector, mass spectrometry, Raman spectroscopy, X-ray imaging, thermal neutron analysis, electrochemical assay, and ion mobility spectroscopy. The EPA protocol SW-846 Method 8330a involves reverse-phase HPLC with UV detection. However, these detection methods are always highly costly and more importantly, not portable at all for on-site detection.

[0005] Fluorescence based sensing has provided an alternative detection approach, which is highly sensitive, convenient and cost-effective. Fluorescent conjugated polymers exhibiting efficient exciton migration along the polymer chains have been applied as thin-film sensing materials for the vapor detection of nitro compounds. However, the performance of most fluorescent sensory materials is limited by film thickness due to the

fact that diffusion of analyte vapor in low-porous rigid films is slow. A spin-coated conjugated polymer film is reported to achieve its optimum quenching efficiency towards TNT vapor with an ultra-thin film (ca. 2.5 nm) and experiences a sharp drop in quenching efficiency at films thicker than 25 nm. To reduce the dependence of sensing performance on film thickness, a sensor based on a highly nanostructured film with a large surface-to-volume ratio, inherent high porosity, and easy accessibility of sensing materials is needed.

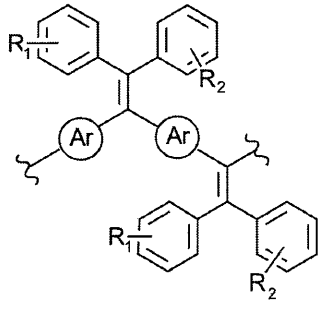
[0006] Another issue to overcome is the aggregation-caused quenching (ACQ) of fluorescence commonly observed in fluorescent conjugated polymers in solid state, which has undermined their potential as solid state sensors or probes for explosive detections. Recently, aggregation induced emission (AIE) materials in the areas of optoelectronics and sensory systems have attracted increasing interest as they countered problems faced by materials exhibiting ACQ properties.

[0007] In a previous work, it was shown that porous films by electrospinning AIE active copolymers showed strong response to vapor of nitro-compounds. Unlike fluorescent conjugated polymers, the porous AIE polymer films showed less dependence of fluorescence response to nitro compounds on film thickness even though they have thickness as high as 560±60 nm.

[0008] It is therefore an object of the present disclosure to provide a substrate for the detection of nitro compounds on a fluorescence quenching basis. Preferably the sensing performance of this substrate would be independent of the film thickness. It is a further object of the present disclosure to provide a substrate wherein quenching of the fluorescence is not observed in the solid or aggregated state in the absence of a nitro compound.

SUMMARY

[0009] In a first aspect, there is provided polymeric nanoparticles having a unit structure represented by formula (I),



(I)

wherein

R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, cyano, formyl, alkyl carbonyl, carboxylic acid, alkyl carboxylic acid, carboxylic ester, alkyl carboxylic ester, alkylaldehyde, and ketone;

is selected from the group consisting of substituted or unsubstituted aromatic rings and substituted or unsubstituted heteroaromatic rings, wherein the substituents are independently selected from the group consisting of C_{1-12} alkyl and wherein the heteroatom is independently selected from the group consisting of N, S, and O; and

$\wr$ indicates the attachment point of the next unit.

[00010] Advantageously, the polymeric nanoparticles possess aggregation induced emission. As such, they exhibit fluorescence in the solid or aggregated state (for example, while being immobilized on a device). This fluorescence is quenched in the presence of nitro compounds. It has been shown that the quenching of fluorescence does not occur for phenol and toluene alone. Accordingly, and further advantageously, the quenching is selective for nitro compounds. It has also been shown that in some embodiments, the nitro compounds are detected in a concentration of less than 5 ppb. Accordingly, and further advantageously, there is a high sensitivity for the detection of nitro compounds. It has also been shown that the fluorescence quenching is not reduced by a bigger film thickness (by applying a higher concentrated solution of the polymeric nanoparticle).

[00011] In a second aspect, there is provided a device for the detection of nitro compounds, comprising polymeric nanoparticles as described above.

[00012] In a third aspect, there is provided a method for fabricating a device as described above, comprising the steps of:

a) preparing a dispersion of polymeric nanoparticles as described above in a mixture of tetrahydrofuran (THF)/H_2O;

b) applying the dispersion of step a) to a support; and

c) drying of the support obtained in step b).

[00012] In a fourth aspect, there is provided a method for the detection of nitro compounds, comprising the steps of:

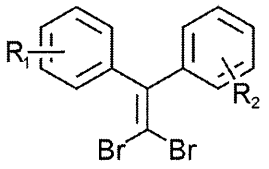
a) contacting the device as described above with a sample;

b) exposing the sample contaminated device obtained in step a) to UV radiation; and

c) determining the presence of nitro compounds in the sample by observing fluorescence quenching on the device.

[00013] In a fifth aspect, there is provided use of polymeric nanoparticles as described above for the detection of nitro compounds.

[00014] In a sixth aspect, there is provided a method for preparing the polymeric nanoparticles as described above, comprising reacting a compound of formula (II)

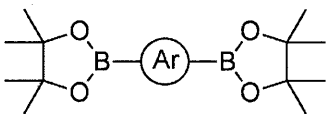


(II)

with a compound of formula (III)

$(OH)_2B$-(Ar)-$B(OH)_2$ (III)

or formula (IIIa)



(IIIa)

wherein R_1, R_2 and (Ar) are defined as described above

in a Suzuki coupling reaction in the presence of (i) a base, preferably K_2CO_3 or Cs_2CO_3, and (ii) a palladium catalyst, preferably $Pd(PPh_3)_4$.

BRIEF DESCRIPTION OF THE DRAWINGS

[00015] The disclosure will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

[00016] Fig. 1 represents a schematic embodiment of the reaction sequence utilized in order to prepare the polymers. A compound of Formula (II) is reacted in a Suzuki cross-

coupling reaction with an optionally substituted (hetero-)aromatic group (Ar), substituted with a di-boronic acid or a di-boronic pinacol ester, to give the polymer of Formula (I).

[00017] Fig. 2 shows the fluorescence spectra of the polymer in THF/H_2O mixtures with different H_2O contents (λ_{ex} = 332 nm, [PTPE-A] = 100.0 μg•mL^{-1}).

[00018] Fig. 3 shows the normalized UV and fluorescence spectra of polymer nanoparticles in THF/H_2O mixtures, [PTPE-A] = 100.0 μg•mL^{-1}, H_2O content = 90%.

[00019] Fig. 4 shows photographs of solutions taken under UV illumination (λ_{ex} = 365 nm).

[00020] Fig. 5 shows the particle size (d) of polymer in THF/H_2O mixtures measured by dynamic light scattering. Turbidity data measured as a function of absorbance at 633 nm, [PTPE-A] = 100.0 μg•mL^{-1}.

[00021] Fig. 6 shows the fluorescence intensity of polymer nanoparticles in THF/H_2O (1:9 v/v) mixture via time. Samples were stored at 4 °C, [PTPE-A] = 100.0 μg•mL^{-1}.

[00022] Fig. 7 shows the enlarged image (a) and fluorescent image (b) of polymer particles. The samples are prepared from polymer in THF/H_2O (1:9 v/v) mixture, [PTPE-A] = 100.0 μg•mL^{-1}. The fluorescent image of polymer nanoparticles is taken under a fluorescence microscope with a 337 nm excitation.

[00023] Fig. 8 shows the images of paper sensor under UV light illumination (365 nm), formed by spray coating polymer nanoparticles in THF/H_2O (1:9 v/v) mixture onto filter paper, with an approximate concentration of: (a) 2.0 μg/cm^2; (b) 1.0 μg/cm^2; (c) 0.5 μg/cm^2; (d) 0.25 μg/cm^2; (e) 0.125 μg/cm^2; (f) 0 μg/cm^2.

[00024] Fig. 9 shows the concentration-dependent fluorescence quenching of polymer nanoparticles by nitro compounds. [PTPE-A] = 100.0 μg•mL^{-1} in THF/H_2O (1:9 v/v) mixture.

[00025] Fig. 10 shows the demonstration for nitro compound vapors detection. (a) The bright image of filter paper contaminated by nitro compound (left). The right image shows the paper sensor fabricated by spray coating polymer nanoparticles in THF/H_2O (1:9 v/v) mixture onto filter paper, with an approximate concentration of 1.0 μg/cm^2. (b) The demonstration for DNT vapor detection using paper sensor.

[00026] Fig. 11 shows the fluorescence quenching of paper sensor upon exposure to DNT saturated vapor for different times: (a) 0 min, (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min. The images of paper sensor are under UV light illumination (365 nm).

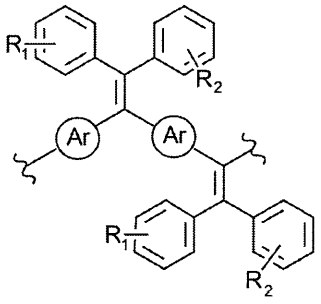
[00027] Fig. 12 shows the fluorescence quenching of paper sensor upon exposure to nitro compounds vapors, the fluorescent images of paper sensor are checked by naked eyes after 30 min. (a) The image of paper sensor under UV light illumination (365 nm) without nitro compound. Figure b, c, d and e are the images of paper sensor under UV light illumination (365 nm) after contacting with PA, TNT, DNT and NT, respectively.

[00028] Fig. 13 shows the detection limit of paper sensor on nitro compounds. The image of paper sensor under UV light illumination (365 nm) depicted the effectiveness of paper sensor in present disclosure. The nitro compounds are PA, TNT, DNT and NT. The weight amounts used of those nitro compounds are 1 μg, 100 ng, 10 ng and 1 ng.

[00029] Fig. 14 demonstrates the detection of nitro compound contamination. The fluorescent images were checked by naked eyes immediately after finger printing, wherein a finger was contaminated by nitro compounds as a solid in trace scale. Paper sensors are fabricated by spray coating polymer nanoparticles in THF/H_2O (1:9 v/v) mixture onto filter paper, with an approximate concentration of 1.0 μg/cm^2. (a) The bright image of paper sensor with clean finger and contaminated finger printing. (b) The image of paper sensor under UV light illumination (365 nm) without nitro compound. Figures c, d, e and f are the images of paper sensor under UV light illumination (365 nm) after finger printing with PA, TNT, DNT and NT, respectively.

DESCRIPTION

[00030] Polymeric nanoparticles have been developed according to various embodiments. The polymeric nanoparticle according to the disclosure may comprise or substantially consist of a polymer, which possesses aggregation induced emission. Hence, the polymer may exhibit fluorescent activity and its fluorescent behaviour may be depending on whether the polymer is in solution or in an aggregated state. Accordingly, in a first aspect, there is provided polymeric nanoparticles having a unit structure represented by formula (I),



(I)

wherein

R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, cyano, formyl, carboxylic acid, alkyl carbonyl, alkyl carboxylic acid, carboxylic ester, alkyl carboxylic ester, alkylaldehyde, and ketone;

(Ar) is selected from the group consisting of substituted or unsubstituted aromatic rings and substituted or unsubstituted heteroaromatic rings, wherein the substituents are independently selected from the group consisting of C_{1-12} alkyl and wherein the heteroatom is independently selected from the group consisting of N, S, and O; and

$\sim$ indicates the attachment point of the next unit. (Ar), at each occurrence, may be the same or different.

[00031] The term "polymeric nanoparticles" in this application is to be interpreted broadly to include nano size particles of one or more polymers. The size of said nanoparticles is dependent on the solvent mixture they are present in. While in a purely organic solvent (for example THF) the one or more polymers may be completely dissolved, i.e. the nanoparticle may not be present, the nanoparticle starts to form upon decreasing polarity of said solvent mixture (for example by adding water). The one or more polymers starts to conglobate or aggregate and eventually forms said nanoparticles. The degree of aggregation is dependent on the polarity. Hence, the size of the nanoparticle may be bigger when the polarity of the solvent mixture is not very high, and decrease with increase in polarity of the solvent mixture. Mixtures of the polymer and the solvent mixture THF/water are macroscopically homogenous and visually transparent without observing any precipitates. The size of the polymeric nanoparticle is dependent of the polarity of the solvent mixture and may be measured by dynamic light scattering.

The polymer used for forming the nanoparticle according to the disclosure may exhibit aggregated induced emission. Hence, in a dissolved state (for example in pure THF solution), the polymer may not exhibit fluorescent activity. However, upon increasing polarity (increasing the water content in the THF/water solvent mixture) the polymer forms said polymeric nanoparticle and emits fluorescence. The fluorescence intensity may increase with increased polarity, for example, for a 1:9 THF/water mixture the fluorescence may be 200 times higher than for a 9:1 THF/water mixture.

[00032] "Alkyl" as a group or part of a group refers to a linear or branched aliphatic hydrocarbon group, preferably a C_{1-25} alkyl, more preferably a C_{1-12} alkyl, most preferably C_{1-4} unless otherwise noted. Examples of suitable straight and branched C_{1-25} alkyl substituents include methyl, ethyl, n-propyl, 2-propyl, n-butyl, sec-butyl, t-butyl, hexyl, and the like. The group may be a terminal group or a bridging group.

[00033] "Aromatic ring" as a group or part of a group denotes (i) an optionally substituted monocyclic, polycyclic, or fused polycyclic aromatic carbocycle (ring structure having ring atoms that are all carbon) preferably having from 5 to 18 atoms per ring. The terminology also includes a system wherein a monocyclic ring may be connected to another monocyclic ring via a triple bond. Examples of aromatic rings include phenyl, naphthyl, benzene, 1,1'-biphenyl, 1,2-diphenylethyne, fluorine, terphenyl and the like; (ii) an optionally substituted partially saturated polycyclic aromatic carbocyclic moiety in which at least one phenyl and a C_{5-7} cycloalkyl or C_{5-7} cycloalkenyl group are fused together to form a cyclic structure, such as tetrahydronaphthyl, indenyl, indanyl or fluorene. The group may be a terminal group or a bridging group. Typically an aromatic ring is a C_{3-18} aryl group.

[00034] "Heteroaromatic ring" either alone or part of a group refers to groups containing an aromatic ring (preferably a 5 or 6 membered aromatic ring) having one or more heteroatoms as ring atoms in the aromatic ring with the remainder of the ring atoms being carbon atoms. Suitable heteroatoms include nitrogen, oxygen and sulphur. Examples of heteroaromatic rings include thiophene, benzothiophene, benzofuran, benzimidazole, benzoxazole, benzothiazole, benzisothiazole, naphtho[2,34j]thiophene, furan, isoindolizine, xantholene, phenoxatine, pyrrole, imidazole, pyrazole, pyridine, pyrazine, pyrimidine, pyridazine, tetrazole, indole, isoindole, 1H-indazole, purine, quinoline, isoquinoline, phthalazine, naphthyridine, quinoxaline, cinnoline, carbazole, phenanthridine, acridine, phenazine, thiazole, isothiazole, phenothiazine, oxazole,

isooxazole, furazane, phenoxazine, 2-, 3- or 4- pyridyl, 2-, 3-, 4-, 5-, or 8- quinolyl, 1-, 3-, 4-, or 5- isoquinolinyl 1-, 2-, or 3- indolyl, benzo[c][1,2,5]thiadiazole, 2,2'-bithiophene, benzo[c]thiophene and 2-, or 3-thienyl. A heteroaromatic ring is typically a heteroaryl group. The group may be a terminal group or a bridging group. Typically a heteroaromatic ring is a 3 to 18 membered group.

[00035] It is understood that included in the family of compounds of Formula (I) are isomeric forms including diastereoisomers, enantiomers, tautomers, and geometrical isomers in "trans" or "cis" configurational isomer or a mixture of E and Z isomers. It is also understood that some isomeric forms such as diastereomers, enantiomers, and geometrical isomers can be separated by physical and/or chemical methods and by those skilled in the art.

[00036] Some of the compounds of the disclosed embodiments may exist as single stereoisomers, racemates, and/or mixtures of enantiomers and /or diastereomers. All such single stereoisomers, racemates and mixtures thereof, are intended to be within the scope of the subject matter described and claimed.

[00037] Additionally, Formula (I) is intended to cover, where applicable, solvated as well as unsolvated forms of the compounds. Thus, each formula includes compounds having the indicated structure, including the hydrated as well as the non-hydrated forms.

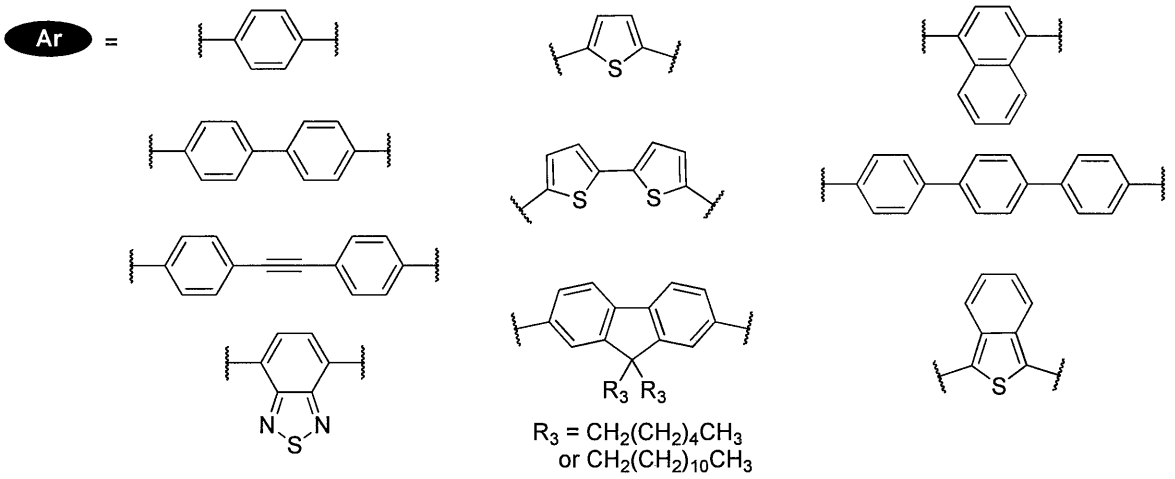
[00038] Advantageously, the polymeric nanoparticle comprises a conjugated pi system which functions as a luminophore. Further advantageously, the polymeric nanoparticle may comprise optionally substituted alkyl substituents R_1 and R_2 which may fine-tune the required polarity for aggregation in the THF/water mixture.

[00039] Hence, R_1 and R_2 of formula (I) may be independently selected from the group consisting of hydrogen, cyano, $C_{1\text{-}12}$ alkyl, -C(O)H, -$C_{1\text{-}12}$ alkyl-C(O)H, -$C(O)CH_3$, -$C_{1\text{-}12}$ alkyl-$C(O)CH_3$, -C(O)OH, -$C_{1\text{-}12}$ alkyl-C(O)OH, -$C(O)OCH_3$ and -$C_{1\text{-}12}$ alkyl-$C(O)OCH_3$.

[00040] (Ar) of formula (I) is selected from the group consisting of benzene, 1,1'-biphenyl, 1,2-diphenylethyne, benzo[c][1,2,5]thiadiazole, thiophene, 2,2'-bithiophene, fluorene, 9,9-dihexyl-fluorene, 9,9-didodecyl-fluorene, naphthalene, terphenyl, and benzo[c]thiophene. Advantageously, two (Ar) groups are bound to the same carbon of the tetrasubstituted double bond of Formula (I), which may result in the polymer to exhibit AIE active properties, or it may improve the AIE active property. The fluorescence

emission wavelength of polymer may be changed through introduction of different (Ar) groups into polymer. Nevertheless, the adjustment for band gap, LUMO and HOMO of polymers may optimize the fluorescence quenching driving force of polymeric nanoparticle to nitro compounds, resulting in improved fluorescence response of polymeric nanoparticles. Compared to the similar polymers in the prior art, the polymeric nanoparticle fabricated from those polymers in this disclosure displays higher fluorescence quenching efficiency when contacted with nitro compounds, which may be due to their structural differences.

[00041] The connectivity of the group (Ar) to the remaining parts of Formula (I) may be as depicted in the following Scheme 2:



Scheme 2: *Optional connectivity of the group (Ar) in Formula (I) of the present disclosure*

[00042] The polymeric nanoparticles according to the present disclosure may exhibit fluorescent activity, preferably when dissolved or present in a solution of tetrahydrofuran (THF) / H_2O, wherein the volume ratio of THF and H_2O is in the range from about 9:1 to about 1:9. The fluorescent activity may be dependent on the ratio of the solvent mixture. Accordingly, the fluorescent activity may increase with an increased water content in the THF/water solvent mixture. As such, the fluorescent activity may be about 150 to about 400 times higher, or about 200 to about 300 times higher, or about 250 times higher in a 1:9 THF/water mixture than in a 9:1 THF/water mixture. Additionally, the fluorescent activity may be about 2 to about 8 times higher, or about 3 to about 6 times higher, or

about 4 times higher in a 1:9 THF/water mixture than in a 1:1 THF/water mixture. The polymeric nanoparcticles may be very stable in the THF/H_2O solution, and as such, their fluorescence does not change when they are stored at 4 °C for 36 weeks. The formed dispersion displays a strong fluorescent emission with an emission peak at 480 nm and wide spectrum ranging from 400 nm to 600 nm, which is quite obvious by naked eyes under UV illustration at 365 nm. The term "fluorescent activity" in this application is to be interpreted broadly to include an activity wherein a molecule emits light of one wavelength after absorbing light of a different wavelength.

[00043] The mean particle size of the polymeric nanoparticles may be in the range from about 50 nm to about 1500 nm, preferably from about 100 nm to about 1300 nm, more preferably from about 200 nm to about 1200 nm, preferably when dissolved in a solution of THF/H_2O, wherein the volume ratio of THF and H_2O is in the range from about 9:1 to about 1:9. The mean particle size of the polymeric nanoparticles may be dependent on the ratio of the solvent mixture and may roughly follow an inversely proportional behavior, measured against increasing water content (Fig. 5). Accordingly, the mean particle size of the polymeric nanoparticles may decrease with an increased water content in the THF/water solvent mixture. As such, the mean particle size of the polymeric nanoparticles may be about 200 to about 500 nanometers, or about 250 to about 400 nanometers, or about 300 nanometers in a 1:9 THF/water mixture (90% water content). Additionally, the mean particle size of the polymeric nanoparticles may be about 400 to about 1000 nanometers, or about 600 to about 800 nanometers, or about 700 nanometers in a 1:1 THF/water mixture (50% water content).

[00044] The polymeric nanoparticles may exhibit aggregation-induced emission (AIE) properties. The term "aggregated-induced emission" in this application is to be interpreted broadly to include a process wherein an organic compound possesses a plurality of freely rotating groups which act as luminophores. The luminophores may consist of conjugated pi systems, which are excited in solution and promote radiation-less decay via a non-radiative channel. When these luminophores aggregate, the intramolecular free rotation of those groups is restricted in the aggregated state and light emission is turned on. Hence, in the aggregated state, the photoluminescence efficiency (i.e. quantum yield) becomes higher than in the solution phase

[00045] In a second aspect, there may be provided a device for the detection of nitro compounds, comprising polymeric nanoparticles as described above. The term "nitro

compound" in this application is to be interpreted broadly to include a compound comprising at least one terminal nitro moiety. The total weight of the compound may not exceed 200 g/mol. The nitro moiety may be covalently bound to an aromatic, heterocyclic or heteroaliphatic moiety. Examples for a nitro compound with the nitro moiety covalently bound to an aromatic moiety comprise of picric acid (PA), 2,4,6- trinitrotoluene (TNT), 2, 4-dinitrotoluene (DNT), 4-nitrotoluene (NT), 4-nitrophenol (NP) and styphnic acid.

[00046] The nitro compounds according to the present disclosure may contain nitro moieties, which lower the LUMO (lowest occupied molecular orbital) energy of the compound. Thus, the nitro compounds according to the disclosure may be characterized by a relatively low LUMO energy. This may increase the likelihood of an electron in its excited state to be accepted. The electron in its excited state may be provided by the polymeric nanoparticle. The device may comprise a solid surface, upon which the polymeric nanoparticle is deposited. The solid surface may be glass or paper.

[00047] In one embodiment, the device may comprise paper. Using paper in the device may be advantageous as it can be easily impregnated with the polymeric nanoparticle. It is further advantageous to use paper as it is a relatively light, inexpensive material, which can be easily discarded after use. For example, the paper may be filter paper.

[00048] The polymeric nanoparticles may be located on the surface of the device. In one embodiment, the polymeric nanoparticle may be located on the surface of a piece of paper. For example, it may be impregnated on the paper. The surface concentration of the polymeric nanoparticles is in the range from about 0.1 $\mu g/cm^2$ to about 5 $\mu g/cm^2$, preferably from about 0.5 $\mu g/cm^2$ to about 2 $\mu g/cm^2$, more preferably from about 0.8 $\mu g/cm^2$ to about 1.5 $\mu g/cm^2$. The polymeric nanoparticle may appear 'scattered' on the surface. Hence, the density of the polymeric nanoparticle on the substrate may not be homogenous.

[00049] The mean particle size of the polymeric nanoparticles on the device may be in the range from about 50 nm to about 1500 nm, preferably from about 100 nm to about 1300 nm, more preferably from about 200 nm to about 1200 nm. This is generally dependent on the ratio of the solvent mixture, as outlined further above.

[00050] In a third aspect, there is provided a method for fabricating a device as disclosed above, comprising the steps of:

a) preparing a dispersion of polymeric nanoparticles as described above in a mixture of THF/H_2O;

b) applying the dispersion of step a) to a support; and

c) drying of the support obtained in step b).

[00051] The concentration of polymeric nanoparticles in the dispersion prepared in step a) is in the range from about 50 μg/ml to about 200 μg/ml, or from about 70 μg/ml to about 150 μg/ml, or about 100 μg/ml.

[00052] In step a), the volume ratio of THF and H_2O may be in the range from about 9:1 to about 1:9. The mean particle size may be decreased by using larger amounts of water in the solvent mixture. Accordingly, fluorescence activity may be increased by using larger amounts of water in the solvent mixture. Preferably, a volume ratio comprising at least 50 vol.-% of water may be used, more preferably at least 70 vol.-% of water, most preferably at least 90 vol.-% of water.

[00053] The applying of step b) may be performed by drop coating, spin coating, dip coating, spray coating or vapor deposition. For application on paper, the preferred method of application may be spray coating. The coating may result in a surface concentration of the polymeric nanoparticles from about 0.05 μg/cm^2 to about 5 μg/cm^2, or from about 0.1 μg/cm^2 to about 3 μg/cm^2, or from about 0.125 μg/cm^2 to about 2 μg/cm^2. The term 'vapor' or 'vaporized' is to be interpreted broadly to include a gaseous phase of the compound. As used herein, it refers to the gaseous phase of the nitro compound.

[00054] The support of step b) may be paper. More preferably filter paper.

[00055] The drying of step c) may be performed by natural air drying, indirect drying, such as vacuum drying, or application of hot air. The sample would be considered as "dry' when it is substantially free of the THF/water mixture, or of any other solvent which may have been used previously.

[00056] In a fourth aspect, there is provided a method for the detection of nitro compounds, comprising the steps of:

a) contacting the device as described above with a sample;

b) exposing the sample contaminated device obtained in step a) to UV radiation; and

c) determining the presence of nitro compounds in the sample by observing fluorescence quenching on the device.

[00057] The term "fluorescence quenching" in this application is to be interpreted broadly to include an activity wherein a previously existing fluorescence, which is visible

to the naked eye, is extinguished, which is also visible to the naked eye. The extinction, as used herein, may occur as a consequence of a nitro compound which is brought into contact with the fluorescing material (the polymeric nanoparticle, as used herein).

[00058] The contacting of step a) may be exposure of the device to sample vapor, direct application of sample onto the surface of the device or dipping of the device into a solution of the sample.

[00059] The duration of contacting of step a) is in the range from about 1 sec to about 45 min, preferably from about 30 sec to about 30 min, more preferably from about 1 min to about 10 min. While in general solutions containing the nitro compound may be used as a sample, in a preferred embodiment the sample is a solid. Advantageously, this resembles more closely a situation in 'real world', i.e. at border control or airports.

[00060] The UV radiation used for detection may be in the range of about 100 to about 400 nm (UVGA, UVB and UVC), more preferably in the range of about 280 to about 400 nm (UVA and UVB), most preferably in the range of about 315 to about 400 nm (UVA), for example at about 365 nm.

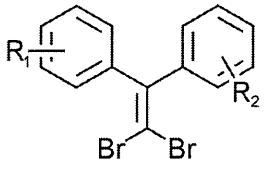
[00061] The concentration of the nitro compounds in the sample may be at least 2 ppb, or at least 5 ppb.

[00062] The method may further comprise the step of e) comparing the fluorescence quenching on the sample contaminated device with a suitable non-contaminated control. This comparison may be done by the naked eye. Hence, no extra device may be needed in order to detect the presence of a nitro compound. The term "non-contaminated control" in this application is to be interpreted to include a sample which essentially does not contain a nitro compound or does not emit a vapor comprising a nitro compound.

[00063] The nitro compounds to be detected may comprise nitrotoluene, dinitrotoluene, trinitrotoluene, picric acid, styphnic acid, and combinations thereof.

[00064] In a fifth aspect, there is provided use of polymeric nanoparticles as described above for the detection of nitro compounds. The nitro compounds may comprise nitrotoluene, dinitrotoluene, trinitrotoluene, picric acid, styphnic acid, and combinations thereof.

[00065] In a fifth aspect, there is provided a method for preparing the polymeric nanoparticles as described above, comprising reacting a compound of formula (II)

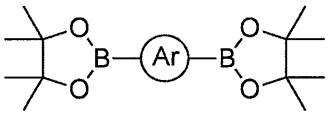


(II)

with a compound of formula (III)

$(OH)_2B$-Ar-$B(OH)_2$ (III)

or formula (IIIa)



(IIIa)

wherein R_1, R_2 and Ar are defined as above

in a Suzuki coupling reaction in the presence of (i) a base, preferably K_2CO_3 or Cs_2CO_3, and (ii) a palladium catalyst, preferably $Pd(PPh_3)_4$.

[00066] A method for preparing the compound of Formula (I) as defined above may comprise the steps of: providing the compound of Formula (II) as defined above; and contacting the compound of Formula (II) as defined above with a compound having the formula (III) or (IIIa) in the presence of a palladium catalyst. The palladium catalyst may be selected from [1,1′-Bis(diphenylphosphino)ferrocene]dichloropalladium(II), complex with dichloromethane, and Tetrakis(triphenylphosphine)palladium(0).

[00067] The reaction may comprise a base. The base may be a nitrogen base or an inorganic base. The nitrogen base may be selected from pyridine, triethylamine or Huenig's base. The inorganic base may be selected from sodium carbonate, cesium carbonate and potassium carbonate. Preferably, the base may be cesium carbonate or potassium carbonate.

[00068] The method may additionally comprise a solvent. The solvent may be selected from the group consisting of dichloromethane, tetrachloromethane, tetrahydrofuran, dioxane, diphenyl ether, toluene, chlorobenzene, dichlorobenzene,

diemthyl formamide (DMF), xylene and any mixture thereof The solvent may not contain any reactivity towards the reaction mixture.

[00069] The reaction temperature may be in the range of about 40 °C to about 200 °C, about 40 °C to about 60 °C, about 40 °C to about 80 °C, about 40 °C to about 100 °C, about 40 °C to about 120 °C, about 40 °C to about 140 °C, about 40 °C to about 160 °C, about 40 °C to about 180 °C, about 60 °C to about 80 °C, about 60 °C to about 100 °C, about 60 °C to about 120 °C, about 60 °C to about 140 °C, about 60 °C to about 160 °C, about 60 °C to about 180 °C, about 60 °C to about 200 °C, about 80 °C to about 100 °C, about 80 °C to about 120 °C, about 80 °C to about 140 °C, about 80 °C to about 160 °C, about 80 °C to about 180 °C, about 80 °C to about 200 °C, about 100 °C to about 120 °C, about 100 °C to about 140 °C, about 100 °C to about 160 °C, about 100 °C to about 180 °C, about 100 °C to about 200 °C, about 120 °C to about 140 °C, about 120 °C to about 160 °C, about 120 °C to about 180 °C, about 120 °C to about 200 °C, about 140 °C to about 160 °C, about 140 °C to about 180 °C, about 140 °C to about 200 °C, about 160 °C to about 180 °C, about 160 °C to about 200 °C or about 180 °C to about 200 °C. The boiling point of the solvent may be sufficiently high to allow the reaction to proceed. The reaction may be undertaken under conventional heating or alternatively by use of a microwave reactor.

[00070] The duration of reaction may be in the range of about 4 hours to about 24 hours, about 4 hours to about 6 hours, about 4 hours to about 8 hours, about 4 hours to about 10 hours, about 4 hours to about 12 hours, about 4 hours to about 18 hours, about 4 hours to about 24 hours, about 6 hours to about 8 hours, about 6 hours to about 10 hours, about 6 hours to about 12 hours, about 6 hours to about 18 hours, about 6 hours to about 24 hours, about 8 hours to about 10 hours, about 8 hours to about 12 hours, about 8 hours to about 18 hours, about 8 hours to about 24 hours, about 10 hours to about 12 hours, about 10 hours to about 18 hours, about 10 hours to about 24 hours, about 12 hours to about 18 hours, about 12 hours to about 24 hours or about 18 hours to about 24 hours.

[00071] The method of preparing the polymeric nanoparticles may additionally comprise the preparation of a compound of formula (II). The compound of Formula (II) may be prepared from benzophenone and tetrabromomethane.

[00072] Herein, nitro-compound detecting materials were developed through combining three advantages: 1) exciton migration effect of conjugated polymer; 2) AIE property of polymer; 3) porosity of formed substrates. Conjugated polymers were

synthesized though Suzuki coupling reaction and their fluorescence response to nitro compounds was studied. Paper sensors fabricated from the polymeric nanoparticles by spray coating have shown high sensitivity and selectivity for nitro compound vapors or particle contamination.

[00073] Hence, it was possible to achieve outstanding performance on detection of nitro compound vapors and particulate contamination via the above stated approach.

[00074] Throughout this specification, the word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the disclosure.

[00075] Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

[00076] As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

[00077] Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

[00078] Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

EXPERIMENTAL SECTION

[00079] Non-limiting examples of the disclosure will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the disclosure. The synthetic steps are disclosed in a general manner in the following synthetic methods. Variations of these general methods in order to produce the polymers according to the present disclosure are within the ability of the person skilled in the art. Where representative procedures are given, these can be adjusted by the person skilled in the art to other derivatives, if needed.

Example 1 – Synthesis of the polymer

[00080] The synthetic routes leading to the polymers according to the disclosure are shown in Scheme 1. The starting material (2,2-dibromoethene-1,1-diyl)dibenzene was prepared from benzophenone and tetrabromomethane, which reacted with an aromatic compound with di-substituted boronic acid or ester groups via Suzuki coupling reaction to produce polymer with high yield. Polymers were purified by reprecipitation twice in methanol, and further purified by soxhlet extraction with different solvents before use. Those polymers were structurally characterized by various spectroscopic methods and elemental analysis, such as GPC, DSC, ^{1}H-NMR, ^{13}C-NMR, FT-IR and element analysis. In one specific example, the polymer synthesized was PTPE-A: Poly(tetraphenylethene).

Example 2 – Formation of polymeric nanoparticle

[00081] Polymer PTPE-A was synthesized according to Example 1. PTPE-A was non-emissive when dissolved in good solvents, such as THF, dichloromethane, chloroform and toluene. Taking PTPE-A solution in THF as an example (Fig. 2), the fluorescence became obvious when a large amount of H_2O (> 40%) was added into THF solution, indicating that TPE maintained its AIE activity after being incorporated into the polymer structure (Fig. 3 and Fig. 4). Polymer PTPE-A in the mixture of THF/H_2O were in nano-size and the mixtures were macroscopically homogeneous and visually transparent without observing any precipitates, which were confirmed by particle size measurements with dynamic light scattering. In the aggregate state, the restricted intramolecular rotation blocks the non-radiative channel and turns on the light emission of polymers. The particles started to form when the water volume fraction was increased up to 10%, and the sizes of

particles were progressively reduced from 1221 to 314 nm along with the increasing of water volume fraction to 90% (Fig. 5). This is consistent with the fact that the nanoparticle size is getting smaller with continuous increase of water volume fraction and subsequently leads to stronger fluorescence.

[00082] PTPE-A in the mixture of THF/H_2O formed very stable conglobated particles, and their fluorescence did not change stored at 4 °C for 36 weeks (Fig. 6). The samples for microscope were prepared by drop-coating the mixture of PTPE-A in THF/H_2O (1:9 v/v) onto the glass slide. As shown in Fig. 7, the particles showed a bright emission like the stars in the galaxy, which could be clearly observed upon excitation with UV light. The polymer nanoparticles of polymer PTPE-A in THF/H_2O displayed strong fluorescent emission in the range from 400 to 620 nm with an emission maximum of 480 nm.

Example 3 - Fabrication of paper sensor

[00083] Filter papers are widely impregnated with various reagents for use in detection test like pH, pregnancy or diabetes. For the further real application for nitro compounds detecting, a paper sensor was fabricated by spray coating of a polymer nanoparticles solution on the filter papers, wherein polymer nanoparticles was prepared in THF/H_2O (1:9 v/v) mixture. After drying, the formed paper sensor were placed under UV light (λ_{ex} = 365 nm) to excite the polymer fluorescence. Fig. 8 shows the fluorescence images of paper sensor with a surface concentration of polymer nanoparticles approximately as 0.125, 0.25, 0.5, 1.0 and 2.0 $\mu g/cm^2$, respectively.

Example 4 - Detection of nitro compounds by polymer nanoparticles in solution

[00084] Fluorescence detection of explosive chemicals was performed through a series of spectrofluorometric experiments using the polymer nanoparticles in THF/H_2O as a probe, and nitroaromatics were used as analytes including picric acid (PA). Fluorescence quenching detection takes advantage of the relatively low LUMO energies of these explosive materials, which can accept an exited state electron from the fluorophore. First, PA was chosen as an analyte in the fluorescence quenching experiment due to its lowest LUMO energy in the common nitroaromatics. As shown in Fig. 9, significant fluorescent quenching for polymer PTPE-A was observed after introducing PA ([PA] = 0 - 100 $\mu g \cdot mL^{-1}$) in the THF/H_2O immediately. The fluorescence quenching efficiency was 97% when

the PA concentration reached to 50 μg•mL-1. When the concentrations of PA were below 40 μg•mL-1, the Stern-Volmer plots of polymers PTPE-A was linear and gave quenching constants of 1.46 × 105.5.

[00085] However, the quenching curves deviated from linearity and bended upward with the continuous increase of PA concentration. In addition, the quenching constants for TNT, DNT and NT were 2.56 × 104, 6.70 × 103 and 6.65 × 103, respectively.

Example 5 - Detection of nitro compounds vapor using paper sensor

[00086] The paper sensor with surface concentration of polymer nanoparticles as 1.0 μ g/cm^2 was used in detecting vapor of nitro compounds. Fig. 10a and 10b are bright field images, which illustrated the vapor detection of nitro-compound using paper sensor. In Fig.10a, the left filter was contaminated by nitro-compound, and the right one was the paper sensor. Fig. 10b shows the fluorescence under UV illustration (365 nm) of the paper sensor, with the paper sensor covering the contaminated filter paper. In order to test the sensing ability, the fluorescence of paper sensor was investigated by exposing to saturated DNT vapors at room temperature. As shown in Fig. 11, fluorescence quenching was observed by exposing paper sensor to saturated DNT vapor for 5 min, and fluorescence of paper sensor was almost quenched by 30 min. Moreover, Fig. 11 shows the fluorescent images of paper sensor exposed to vapor of PA, TNT, DNT and NT, respectively. Dark spots in the paper sensor indicated fluorescence quenching of paper sensor by nitro compounds. Paper sensors show higher sensing ability to NT and DNT vapor which may be due to their higher vapor concentrations (ca. 20 ppm for NT, ca. 100 ppb for DNT) relative to TNT (ca. 5 ppb). Paper sensor's fluorescence was only quenched slightly by PA vapor, while almost no fluorescence response was observed for highly volatile toluene vapor (Fig. 12), demonstrating its good selectivity to nitro-compound vapors.

Example 6 - Detection limit of paper sensor for nitro compounds

[00087] At the beginning, stock solutions of nitro compounds were prepared in toluene, containing nitro-compound of 1 μg, 100 ng, 10 ng and 1 ng, respectively. Aliquots of nitro-compound stock solutions were syringed onto Whatman filter paper (d = 55 mm), and with one aliquot of a toluene blank to serve as control. The spots were between 2 and 5 mm in diameter, to produce a surface concentration ranging from 34-128 ng/cm^2. Finally,

the weights of nitro compounds on the filter paper were controlled as 1 μg, 100 ng, 10 ng and 1 ng, respectively.

[00088] After drying completely, a thin layer of polymer nanoparticles, amounting to surface concentration approximately 1.0 μ g/cm^2 was applied to the contaminated filter paper by spray coating polymer nanoparticles in THF/H_2O (1:9 v/v) mixture (1.0 μg/mL), and allowing it to dry completely. The coated filter paper was placed under UV light (λ_{ex} = 365 nm) to excite the polymer fluorescence. Dark spots in the substrate indicated fluorescence quenching of film by nitro compounds. Illuminated filter papers were examined by an independent observer to determine whether quenching was discernible. Fig. 13 shows the representative image of paper sensor under UV light illustration (365 nm) for the nitro compounds detection. The dark spots were still very obvious even for an analyte weight as low as 1 ng, indicating the good detecting sensitivity of paper sensor to nitro compounds. Detection limits were reported as the lowest amount of explosive necessary for the independent observer to notice quenching visually. The blind detection study was carried out five times for four nitro compounds with paper sensor. Digital images were recorded with a Nikon D5100 megapixel digital camera (Nikon Inc., Tokyo, Japan).

Example 7 - Detection of contamination by nitro compounds

[00089] The nitro compounds detecting were performed at a test range in order to observe the behavior of this technology in experiments closer to what might be expected in the real world. The nitro compounds available at the range are in their used form, rather than in their purified form as used in the laboratory studies, for instance, with impurities, plasticizers, etc., which would be part of the chemical composition of the explosives as they are actually used. In these range experiments, the solid forms of nitro compounds were used to contaminate the paper sensor, not organic solutions of nitro compounds. Therefore, although no quantitative data on the amount of explosive present could be determined, the resultant contamination resembles what might be expected in real-world applications, in terms of surface coverage, particulate size, and size distribution.

[00090] Fig. 14a demonstrates the nitro compounds detecting through pressing finger print with nitro compounds contamination to paper sensor. Trace amounts of nitro compound were analysed as finger print after contacting a solid nitro compound with nitrile gloves. Taking PA detecting for an example, two fingers of left hand were

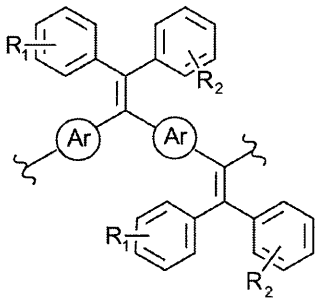
employed, the right finger (nitrile gloved) was rubbed with PA powder and then wiped clean until no visible PA particulates were left, and the left finger was clean. The fingers contaminated by trace amount of PA were then gently pressed (1 s contact time) onto the paper sensor for visualization by naked eyes under a handheld UV light. As a comparison, a clean finger print of the other finger (nitrile gloved) without PA contamination was simultaneously pressed onto the same paper sensor. The fluorescence of contaminated paper sensor was checked immediately under UV illustration (365 nm), and fluorescence quenching was clearly observed by naked eyes in the position pressed by the contaminated finger (Fig. 14c). Moreover, as shown in Fig. 14d-f, all contaminated fingers were positively identified through fluorescence quenching, which were contaminated by TNT, DNT and NT, respectively.

[00091] In this disclosure, polymeric nanoparticles, devices comprising them and methods using them have been presented for quick, inexpensive and highly sensitive detection for nitro compounds. The presented polymeric nanoparticles allow for the detecting of a wide range of nitro compounds. The substrates of present disclosure are based, at least on part, on polymer nanoparticles with AIE properties. Moreover, the paper sensors and methods of the present disclosure are effective in detecting not only higher vapor pressure nitro compounds, such NT, DNT, but also related low vapor pressure nitro compound, such as TNT. The method is capable of detecting a nitro compound in a concentration of less than about 5 ppb. Most importantly, the paper sensors and methods of the present disclosure are highly effective in detecting contamination of nitro compound particulates, such PA, TNT, DNT and NT. In some embodiments, the method is capable detecting a nitro compound in less than 1 ng scale. This technology is able to solve the detection of trace nitro-compounds, such as explosives. It could be used at airports, ports and for border control for detecting the presence of explosives in any explosive-contaminated containers, clothing, clothing, boxes, bags, shoes, etc.

[00092] As reported above, the polymeric nanoparticles as disclosed above may potentially be used in conjunction with other detection methods to broaden the range of detectable explosives to nitrate esters and nitramines, while taking advantage of the high sensitivity of the polymer with respect to nitro compounds. Compared with those sophisticated fluorescence based nitro compounds detection systems, nanofibrous substrates on filter paper prepared by spray coating could be mass-produced with low cost, allowing for large scale application.

CLAIMS

1. Polymeric nanoparticles having a unit structure represented by formula (I),



(I)

wherein

R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, cyano, formyl, alkyl carbonyl, carboxylic acid, alkyl carboxylic acid, carboxylic ester, alkyl carboxylic ester, alkylaldehyde, and ketone;

(Ar) is selected from the group consisting of substituted or unsubstituted aromatic rings and substituted or unsubstituted heteroaromatic rings, wherein the substituents are independently selected from the group consisting of C_{1-12} alkyl and wherein the heteroatom is independently selected from the group consisting of N, S, and O; and

≀ indicates the attachment point of the next unit.

2. The polymeric nanoparticles of claim 1, wherein R_1 and R_2 of formula (I) are independently selected from the group consisting of hydrogen, cyano, C_{1-12} alkyl, -C(O)H, -C_{1-12} alkyl-C(O)H, -$C(O)CH_3$, -C_{1-12} alkyl-$C(O)CH_3$, -C(O)OH, -C_{1-12} alkyl-C(O)OH, -$C(O)OCH_3$ and -C_{1-12} alkyl-$C(O)OCH_3$.

3. The polymeric nanoparticles of claim 1 or 2, wherein (Ar) of formula (I) is selected from the group consisting of benzene, 1,1'-biphenyl, 1,2-diphenylethyne, benzo[c][1,2,5]thiadiazole, thiophene, 2,2'-bithiophene, fluorene, 9,9-dihexyl-fluorene, 9,9-didodecyl-fluorene, naphthalene, terphenyl, and benzo[c]thiophene.

4. The polymeric nanoparticles of any one of claims 1 to 3, wherein the polymeric nanoparticles exhibit fluorescent activity, preferably when present in a solution of tetrahydrofuran (THF) / H_2O, wherein the volume ratio of THF and H_2O is in the range from about 9:1 to about 1:9.

5. The polymeric nanoparticles of any one of claims 1 to 4, wherein the mean particle size of the polymeric nanoparticles is in the range from about 50 nm to about 1500 nm, preferably from about 100 nm to about 1300 nm, more preferably from about 200 nm to about 1200 nm, preferably when present in a solution of THF/H_2O, wherein the volume ratio of THF and H_2O is in the range from about 9:1 to about 1:9.

6. The polymeric nanoparticles of any one of claims 1 to 5, wherein the polymeric nanoparticles exhibit aggregation-induced emission (AIE) properties.

7. A device for the detection of nitro compounds, comprising polymeric nanoparticles of any one of claims 1 to 6.

8. The device of claim 7, wherein the device further comprises paper.

9. The device of claim 7 or 8, wherein the polymeric nanoparticles are located on the surface of the device.

10. The device of claim 9, wherein the surface concentration of the polymeric nanoparticles is in the range from about 0.1 $\mu g/cm^2$ to about 5 $\mu g/cm^2$, preferably from about 0.5 $\mu g/cm^2$ to about 2 $\mu g/cm^2$, more preferably from about 0.8 $\mu g/cm^2$ to about 1.5 $\mu g/cm^2$.

11. The device of any one of claims 7 to 10, wherein the mean particle size of the polymeric nanoparticles is in the range from about 50 nm to about 1500 nm, preferably from about 100 nm to about 1300 nm, more preferably from about 200 nm to about 1200 nm.

12. A method for fabricating a device of any one of claims 7 to 11, comprising the steps of:
    a) preparing a dispersion of polymeric nanoparticles of any one of claims 1 to 6 in a mixture of THF/H_2O;
    b) applying the dispersion of step a) to a support; and
    c) drying of the support obtained in step b).

13. The method of claim 12, wherein the concentration of polymeric nanoparticles in the solution prepared in step a) is in the range from about 50 μg/ml to about 200 μg/ml.

14. The method of claim 12 or 13, wherein, in step a), the volume ratio of THF and H_2O is in the range from about 9:1 to about 1:9.

15. The method of any one of claims 12 to 14, wherein the applying of step b) is performed by drop coating, spin coating, dip coating, spray coating or vapor deposition.

16. The method of any one of claims 12 to 15, wherein the support of step b) is paper.

17. The method of any one of claims 12 to 16, wherein the drying of step c) is performed by natural air drying, indirect drying, vacuum drying, or application of hot air.

18. A method for the detection of nitro compounds, comprising the steps of:
    a) contacting the device of any one of claims 7 to 11 with a sample;
    b) exposing the sample contaminated device obtained in step a) to UV radiation; and
    c) determining the presence of nitro compounds in the sample by observing fluorescence quenching on the device.

19. The method of claim 18, wherein the contacting of step a) is exposure of the device to sample vapor, direct application of sample onto the surface of the device or dipping of the device into a solution of the sample.

20. The method of claim 18 or 19, wherein the duration of contacting of step a) is in the range from about 1 sec to about 45 min, preferably from about 30 sec to about 30 min, more preferably from about 1 min to about 10 min.

21. The method of any one of claims 18 to 20, wherein the concentration of the nitro compounds in the sample is at least 2 ppb.

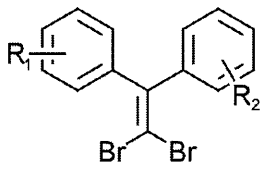
22. The method of any one of claims 18 to 21, wherein the method further comprises the step of d) comparing the fluorescence quenching on the sample contaminated device with a suitable non-contaminated control.

23. The method of any one of claims 18 to 22, wherein the nitro compounds to be detected comprise nitrotoluene, dinitrotoluene, trinitrotoluene, picric acid, styphnic acid, or combinations thereof.

24. Use of polymeric nanoparticles of any one of claims 1 to 6 for the detection of nitro compounds.

25. The use of claim 24, wherein the nitro compounds comprise nitrotoluene, dinitrotoluene, trinitrotoluene, picric acid, styphnic acid, and combinations thereof.

26. A method for preparing the polymeric nanoparticles of any one of claims 1 to 6, comprising reacting a compound of formula (II)

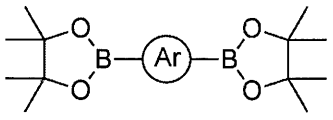


(II)

with a compound of formula (III)

$(OH)_2B$-Ⓐr-$B(OH)_2$ (III)

or formula (IIIa)



(IIIa)

wherein R_1, R_2 and Ⓐr are defined as in claim 1 above

in a Suzuki coupling reaction in the presence of (i) a base, preferably K_2CO_3 or Cs_2CO_3, and (ii) a palladium catalyst, preferably $Pd(PPh_3)_4$.