Electronic Supplementary Information for Signal Enhancement of Sensing Nitroaromatics Based On Highly Sensitive Polymer Dots

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Contents

1. Materials and Instrument.

1.1 Materials

9,9'-((2,7-dibromo-9*H*-fluorene-9,9-diyl)bis(decane-10,1-diyl))bis(9*H*-carbazole) and 9,9-didecyl-2,7-diethynyl-9*H*-fluorene were prepared according to our reported procedures[1]. 4,7-bis(2-bromothiophenyl)benzo[c][1,2,5]thiadiazole (98%), bis(triphenylphosphine) palladium (II) chloride (98%), cuprous iodide (99%) and 4,7-dibromobenzo[c][1,2,5]thiadiazole (98%) were purchased from TCI (Shanghai) Chemical Industry Development Co., Ltd. A comb-like polymer, polystyrene graft ethylene oxide functionalized with carboxy groups (PS-PEG-COOH, main chain M_n = 6500 Da, graft chain M_n = 4600 Da, total chain M_n = 36500 Da, polydispersity 1.3), was purchased from Polymer Source Inc. (Quebec, Canada). TNP and TNT (2,4,6-trinitrotoluene) were supplied by Xiya Reagent and were recrystallized with ethanol before use. Other nitroaromatics were purchased from Aladdin Chemistry Co., Ltd. (China). The nitroaromatics were dissolved in the mixed solvent of ethanol and acetonitrile (volume ratio of 4:1) to obtain

1mg/mL stock solutions before use. All organic solvents were purchased from commercial sources and were carefully dried and distilled prior to use.

1.2 Instrument

1.2.1 Characterization Compounds.

Infrared spectra were obtained with a Bruker VECTOR 22 Fourier-transform infrared (FT-IR) spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded in trichloromethane-d using tetramethylsilane as internal standard on a Bruker 500 (500 MHz). Elemental Analysis data were obtained using a CHN-O-Rapid elemental analyzer (Foss. Heraeus, Germany). Molecular weight of polymers was measured on gel permeation chromatography (GPC) apparatus equipped with UV-vis detection and Waters 1515 HPLC pump. Tetrahydrofuran was used as a carrier solvent at a flow rate of 1.0 mL/min at 25 °C. A calibration curve was made to determine M_n and M_w/M_n values with polystyrene standards, $M_w＝900～1.74×10^6$ g/mol, $D＜1.1$. Simultaneous TG-DTA Netzsch STA 449F3 was used to investigate the thermal stability of the polymers in nitrogen atmosphere from ambient temperature to 700 °C at a heating rate of 10 °C min^{-1}.

1.2.2 Morphological Characterizations.

Transmission electron microscopy (TEM) images were taken by a JEM-1011 electron microscope (JEOL, Japan) at an accelerating voltage of 100 kV. Dynamic light scattering (DLS) result was obtained by a Malvern MasterSizer 2000. Scanning electron microscope (SEM) images were taken by Hitachi S-4800 at an accelerating voltage of 10 kV, 10 UA current, and the working distance was 8.1 mm. 15 nm thick layers of gold plating were obtained on the sample surface by SCD-500 (BAL-TEC) vacuum sputtering coating machine with 15 mA current gold-plated 100 s, in order to reduce the charged phenomenon in the process of scanning electron microscope observation.

1.2.3 Spectral Measurements.

Ultraviolet-visible (UV-vis) absorption spectra of the obtained polymers solution were carried on a UV-1800 (PC) UV-vis spectrophotometer (Mapada, China). All solution fluorescence spectra of the compound were measured with a FluoroMax-4 spectrofluorometer (HORIBA Scientific, Japan) with slit width of 5 nm for both excitation and emission. The solid state emission spectra were recorded on a FluoroMax-4 spectrofluorometer using a front face sample holder with slit width of 5 nm for excitation and slit width of 2 nm for emission. The photoluminescence QYs were determined on the spectrophotometer (FP-6600, Jasco Inc.) with an integrating sphere (ISF-513).

2. The Synthesis and Characterization Compounds and Pdots

2.1 The Synthesis and Characterization of Polymers

The synthesis of ***P1***. 9,9-didecyl-2,7-diethynyl-9*H*-fluorene (124 mg, 0.25 mmol), 9,9'-((2,7-dibromo-9*H*-fluorene-9,9-diyl)bis(decane-10,1-diyl))bis(9*H*-carbazole) (234 mg, 0.25 mmol), tetrakis(triphenylphosphine) palladium(0) (6 mg, 2 mol %), copper iodide (3 mg, 5 mol %), *N*,*N*-diisopropylamine (3 mL), and toluene (6 mL) were added into a Schlenk flask in a nitrogen-filled glove box. After stirring at 80 °C for 48 h, the mixture was filtered and precipitated into methanol. The solid was then filtered and washed in a Soxhlet extractor with methanol followed by acetone to remove residual catalyst and low-molecular-weight material. The yield was 76% as an orange solid. $M_w = 4.29\times10^4$, $M_n = 1.64\times10^4$, PDI = 2.62, (GPC, polystyrene); FT-IR (cm^{-1}, KBr): 2923, 2852 (s; CH), 2142 (w; C≡C), 1627, 1604, (m; Ar); ^1H NMR (500 MHz, $CDCl_3$, δ): 8.08 (br, Ar–H), 7.66–7.38 (br, Ar–H), 7.21 (br, Ar–H), 4.25 (br, N–CH_2), 1.95–0.58 (br, $(CH_2)_{10}$ and $(CH_2)_9CH_3$).

The general procedure for ***P2*** and ***P3*** synthesis.

9,9-didecyl-2,7-diethynyl-9*H*-fluorene (124 mg, 0.25 mmol), 9,9'-((2,7-dibromo-9*H*-fluorene - 9,9-diyl)bis(decane-10,1-diyl))bis(9*H*-carbazole) (187 mg, 0.20 mmol), dibromo comonomer (BT and DBT) (0.05 mmol), tetrakis(triphenylphosphine) palladium (0) (6 mg, 2 mol %), copper iodide (3 mg, 5 mol %), *N*,*N*-diisopropylamine (3 mL), and toluene (6 mL) were added into a Schlenk flask in a nitrogen-filled glove box. After stirring at 80 °C for 48 h, the mixture was filtered and precipitated into methanol. The solid was then filtered and washed in a Soxhlet extractor with methanol followed by acetone to remove residual catalyst and low-molecular-weight material.

P2. Yield was 71% as a yellow solid. $M_w = 1.63\times10^4$, $M_n = 9.72\times10^3$, PDI = 1.68, (GPC, polystyrene); FT-IR (cm^{-1}, KBr): 2946, 2871 (s; CH), 2135 (w; C≡C), 1681, 1597, (m; Ar); ^1H NMR (500 MHz, $CDCl_3$, δ): 8.01 (br, Ar–H), 7.81–7.32 (br, Ar–H), 7.13 (br, Ar–H), 4.18 (br, N–CH_2), 1.92–0.54 (br, $(CH_2)_{10}$ and $(CH_2)_9CH_3$).

P3. Yield was 63% as a red solid. $M_w = 2.95\times10^4$, $M_n = 1.30\times10^4$, PDI = 2.27, (GPC, polystyrene);

FT-IR (cm^{-1}, KBr): 2939, 2866 (s; CH), 2129 (w; C≡C), 1662, 1615, (m; Ar); ^1H NMR (500 MHz, $CDCl_3$, δ): 8.07 (br, Ar–H), 7.81–7.36 (br, Ar–H), 7.20 (br, Ar–H), 4.27 (br, N–CH_2), 1.97–0.59 (br, $(CH_2)_{10}$ and $(CH_2)_9CH_3$).

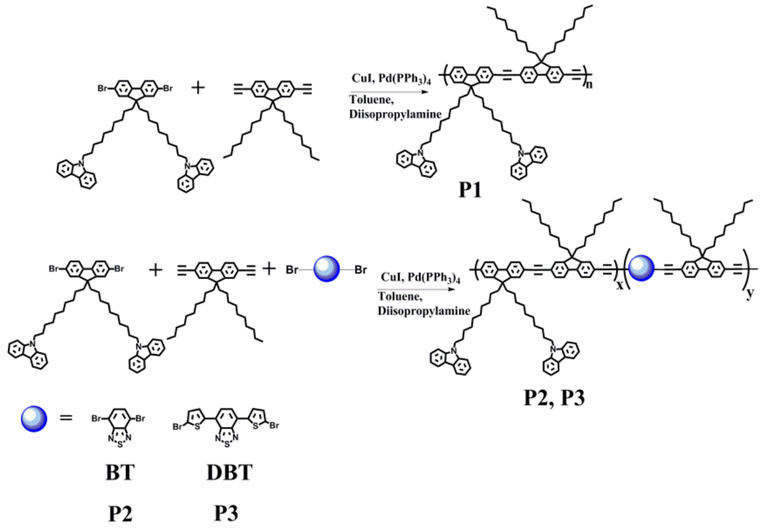

Figure S1. Synthesis of semiconducting conjugated emissive polymers.

2.1.1 Calculation of the actual composition in the main chain of polymers

The proportion of 9,9-didecyl-2,7-diethynyl-9*H*-fluorene and 9,9'-((2,7-dibromo-9*H*-fluorene-9,9-diyl)bis(decane-10,1-diyl))bis(9*H*-carbazole) copolymer unit (FC), 9,9-didecyl-2,7-diethynyl-9*H*-fluorene and benzothiadiazole copolymer unit (FB) of P2 and P3 could be measured by ^1H NMR. The characteristic peak **b** at about 4.20 ppm belongs to -CH_3, and the characteristic peak **c** at about 0.85 ppm is attributed to -NCH_2 (see Figure S3 and S4). Therefore, the proportion of FC and FB could be calculated by the integration area ratio of **b** and **c** peak. The X values were calculated according to the given equation:

$$\mathbf{X+Y=1, \qquad I_b/I_c = 4X/(6X+6Y) = 2X/3}$$

"X" refers to the proportion of FC copolymer unit in the main chain of polymers, and "Y" refers to the proportion of FB copolymer unit in the main chain of polymers. "$\mathbf{I_b/I_c}$" is the integration area ratio of **b** and **c** peak in the ^1H NMR spectra of **P2** or **P3**. The calculation results were listed in the following table.

Table S1. The actual composition in the main chain of polymers

Polymer	The integration area ratio of **b** and **c** peak (I_b/I_c)	The actual proportion FC copolymer unit in the main chain of polymers	X and Y value
P1	0.606	1	/
P2	0.441	0.662	X = 0.662, Y = 0.338
P3	0.476	0.714	X = 0.714, Y = 0.286

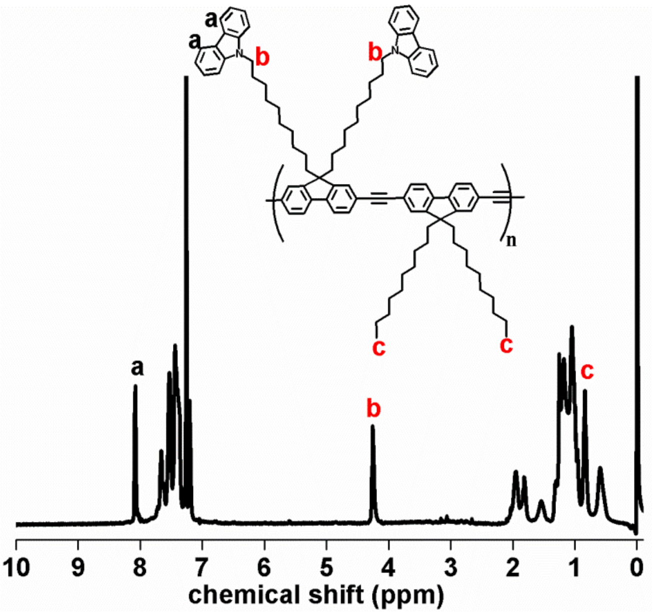

Figure S2. The ^{1}H NMR spectrum of P1. (500 MHz, $CDCl_3$)

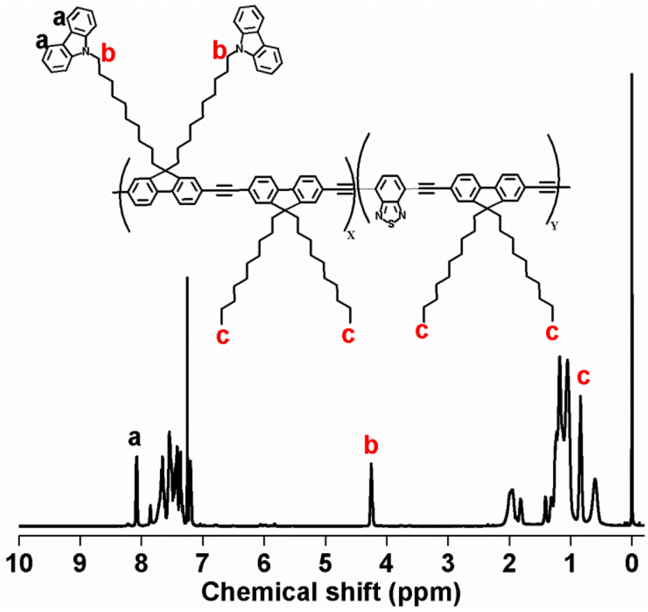

Figure S3. The ^{1}H NMR spectrum of P2. (500 MHz, $CDCl_3$)

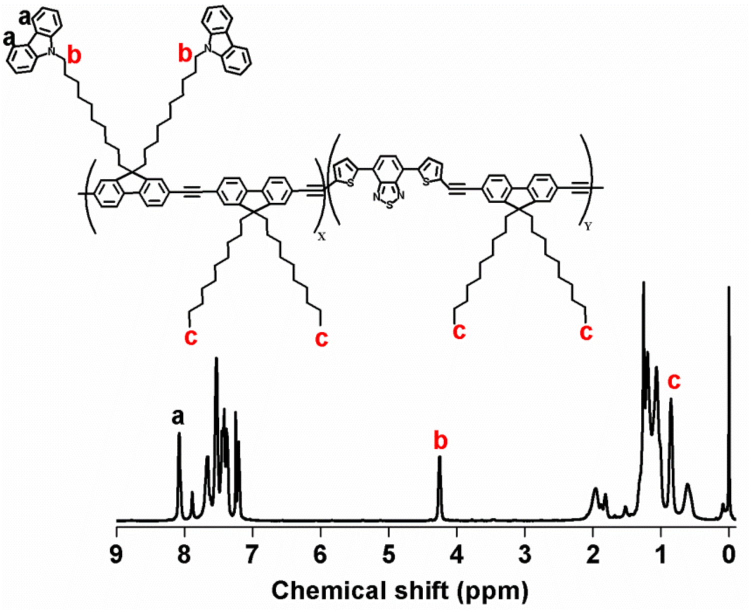

Figure S4. The ^{1}H NMR spectrum of P3. (500 MHz, $CDCl_3$)

2.2 Thermal stability of P1~P3

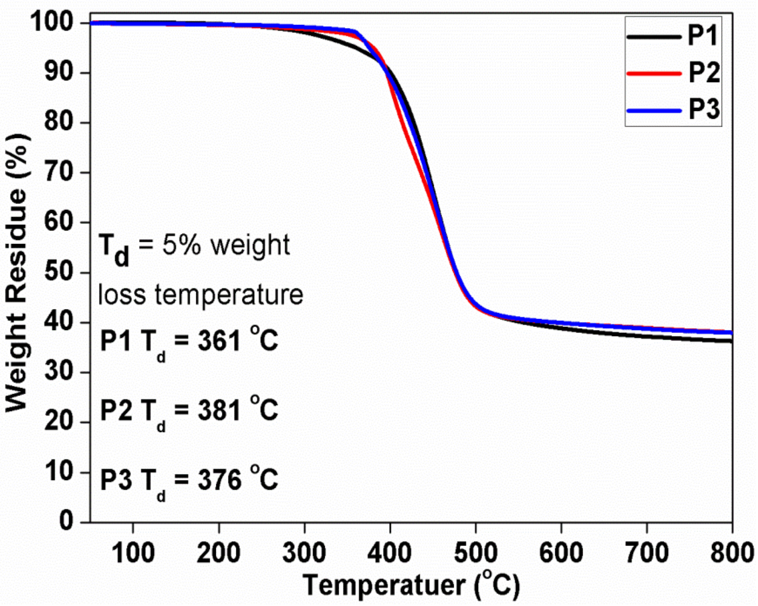

Figure S5. TGA thermograms of P1~P3 at a ramp rate of 10 °C/min in nitrogen flow.

2.3 Optical properties of P1~P3

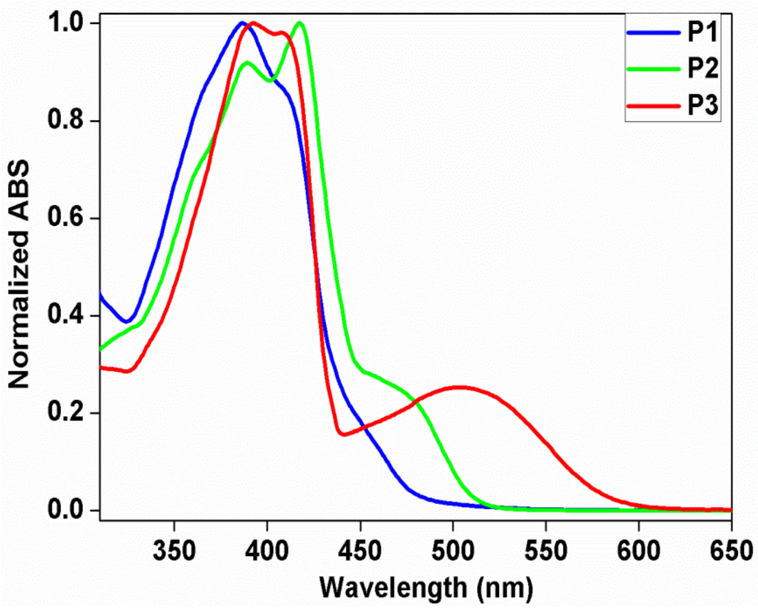

Figure S6. The absorption spectra of P1~P3 in THF solutions.

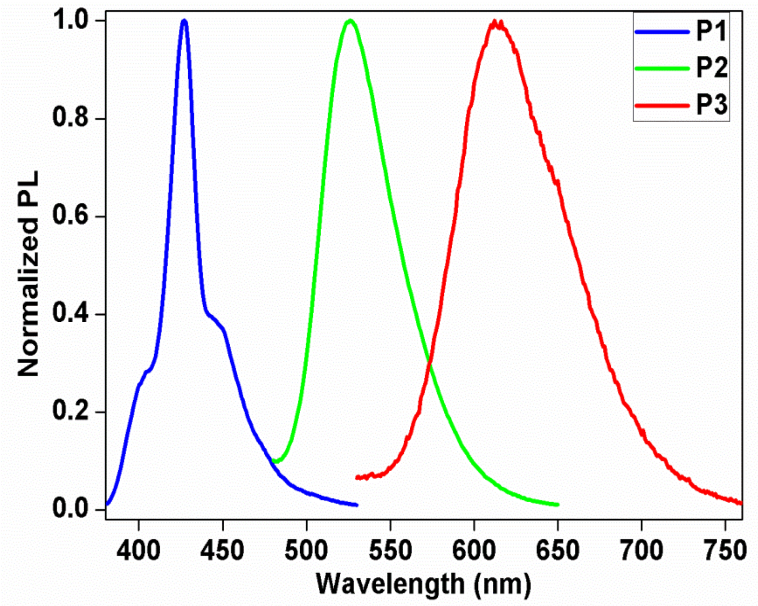

Figure S7. The emission spectra of P1~P3 in THF solutions.

2.4 Functionalization of semiconducting polymer dots.

Functionalized Pdots in aqueous solution were prepared by using a modified nano-precipitation method.[2] Semiconducting polymers (P1~P3) and PS-PEG-COOH were firstly dissolved in tetrahydrofuran (THF) to make a stock solution with a concentration of 1 mg/mL solution, respectively. The three polymer solutions were diluted and mixed with THF to produce a mixture solution according to Table S2. Four kinds of Pdots were then prepared. Later, the mixtures were sonicated to form homogeneous solutions. 10 mL of the as-prepared solutions were quickly added to 12 mL of MilliQ water in a vigorous bath sonicator, which were concentrated by continuous nitrogen stripping to 10 mL at 70 ºC, followed by filtration through 0.22 micron filters. In the process of concentrating, a small amount of Pdots would aggregate, so it was necessary to remeasure the actual mass concentrations of Pdots in the solution by freeze-drying method. The Pdots actual mass concentrations were given in Table S2.

Table S2. The mass concentrations of polymers in THF solution and the actual mass concentrations of Pdots in aqueous solution.

Sample	P1 (μg/mL)	P2 (μg/mL)	P3 (μg/mL)	PS-PEG-COOH (μg/mL)	Pdots (μg/mL)
*(P1+P2+P3)Pdots-614	250	150	200	150	600
*(P1+P2)Pdots-530	250	150	/	100	380
(P2+P3)Pdots-621	/	150	200	100	300
(P1+P3)Pdot-609	250	/	200	100	360
(P2)Pdots-530	/	250	/	100	210
(P3)Pdots-610	/	/	250	100	220

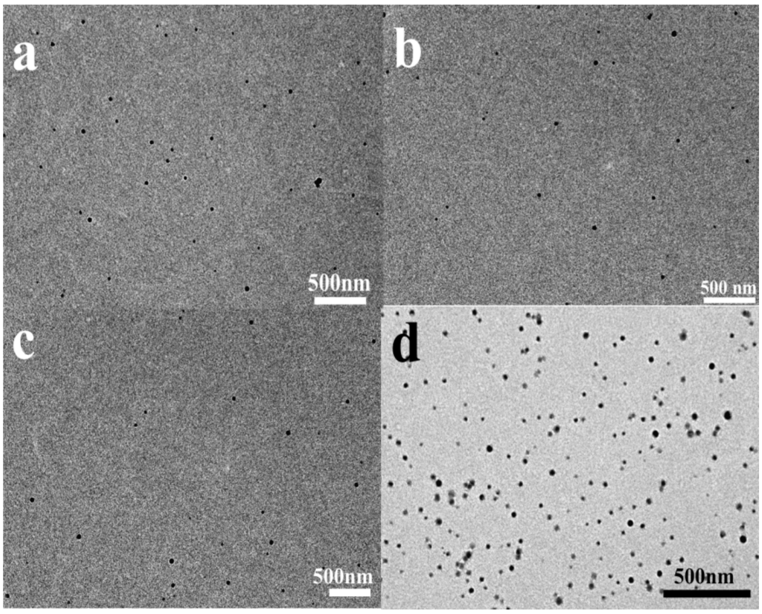

Figure S8. The TEM images (scale bar = 500 nm) of Pdots-614 (a), Pdots-530 (b), Pdots-621 (c) and Pdots-609 (d).

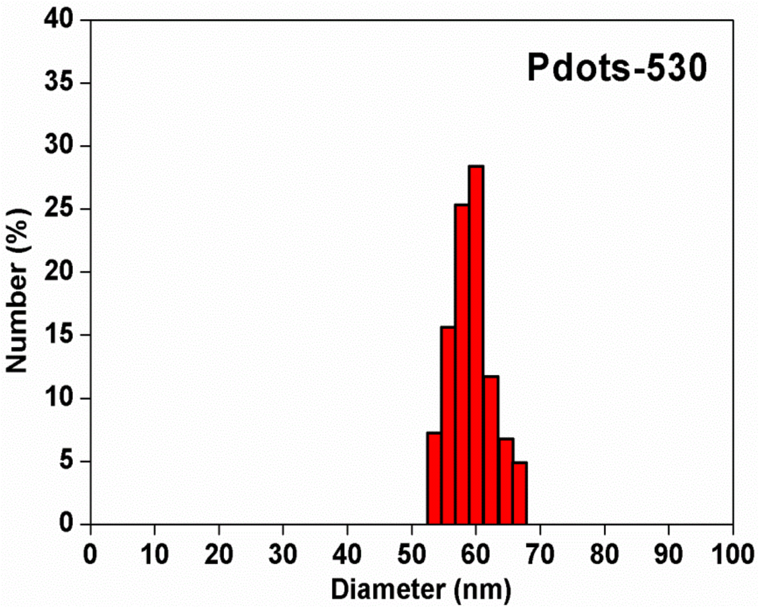

Figure S9. The hydrodynamic diameter of Pdots-530 measured by dynamic light scattering.

2.5 Fluorescence Quantum Yield (Ø) Measurements

Fluorescence quantum yields (Ø) of P1~P3 and Pdots were obtained by the following steps. 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyran (DCM) was dissolved in acetonitrile (literature quantum yield 0.60 at 430 nm) as reference for P3, Pdots-614, Pdots-620 and Pdots-609.[3] Fluorescein was dissolved in methanol (literature quantum yield 0.79 at 425 nm) as reference for P2 and Pdots-530.[4] Quinine sulfate was dissolved in 0.1 M sulphuric acid (literature quantum yield 0.54 at 360 nm) as reference for P1.[5] Then UV-vis absorption and PL emission spectra were measured for P3, Pdots-614, Pdots-620 and Pdots-609 with 430 nm excitation, P2 and Pdots-530 with 425 nm excitation, and P1 with 360 nm excitation, respectively. The accurate Ø values were calculated according to the given equation:

$$\emptyset_{sam} = \emptyset_{ref}\frac{\mathbf{I}_{\mathbf{sam}} A_{ref}\ n_{sam}^{2}}{I_{ref} A_{sam} n_{ref}^{2}}$$

“Sam” and “ref” refer to sample and reference respectively. “Ø” means quantum yield. “I” is the integrated emission intensity, and could be calculated from the emission spectra at 430 nm for P3, Pdots-609, Pdots-614 and Pdots-621 or 425 nm for P2 and Pdots-530 or 360 nm for P1 excitation. “A” represents UV-vis absorbance at 430 nm or 425 nm or 360 nm and was control under 0.1 in the 10 mm quartz to avoid re-absorption effect. “n” is the refractive index.

Table S3. Fluorescence quantum yield (Ø) calculation of Pdots.

Sample	Integrated emission intensity (I)	UV Absorbance (A)	Refractive index of solvent (n)	Fluorescence quantum yield (Ø)	Maximum emission wavelength (nm)
DCM	94076775	0.0654	1.344	60.0%	/
Fluorescein	247510290	0.0391	1.361	79.0%	/
Quinine sulfate	277489460	0.0258	1.332	54.0%	/
P1	393604360	0.0311	1.407	70.9%	426
P2(Polymer-528)	210611250	0.0459	1.407	61.2%	528
P3(Polymer-614)	49136528	0.0382	1.407	58.8%	614
*(P1+P2+P3)Pdots-614	25739150	0.0694	1.332	15.2%	614
*(P1+P2)Pdots-530	45924487	0.0475	1.332	11.6%	530
(P2+P3)Pdots-621	6960245	0.0535	1.332	5.3%	621
(P1+P3)Pdot-609	3801303	0.0721	1.332	2.2%	609
(P2)Pdots-530	8675964	0.0612	1.332	1.7%	530
(P3)Pdots-610	2526118	0.0527	1.332	2.0%	610

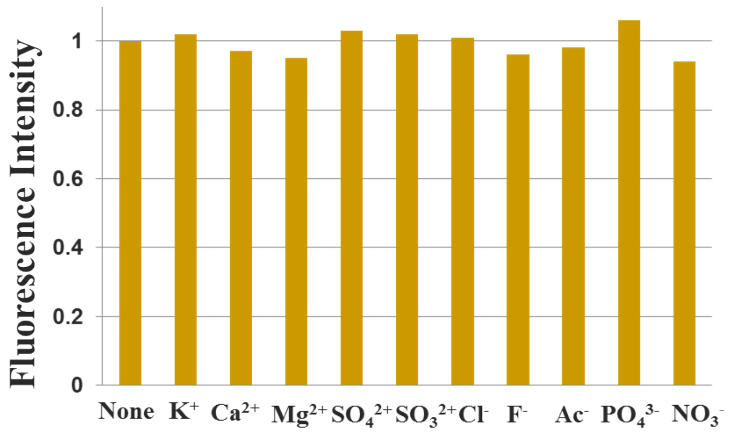

Figure S10. The influence of common anions for the fluorescence intensity of Pdots-614 (ion concentration 1 mmol/L)

3. The Pdots-based Detection for Nitroaromatics in Solution

3.1 Nitroaromatics Analysis in Solution.

100 μL of the Pdots-614 aqueous solutions (0.6 mg/mL) were mixed with 40 μL of the stock solution of nitroaromatics (1 mg/mL), which were then diluted to 2.0 mL with Na_2CO_3−$NaHCO_3$−NaOH (pH, 9.0, 0.02 mol/L) buffer solution. The fluorescence spectra of the mixture solution were measured using an excitation wavelength of 430 nm for Pdots-614. The Pdots-530 as a fluorescent sensor for the detection of nitroaromatics was also tested according to above-mentioned method (excitation wavelength 425 nm). As the control groups, the corresponding polymers (Polymer-614 and Polymer-528) were used to detection nitroaromatics in THF solution. Firstly, the THF solution of Polymer-614 was prepared. The mass concentration was the same as that of the aqueous solution of Pdots-614 (600 μg/mL), and so was the THF solution of Polymer-528 (380 μg/mL). Later, 100 μL of Polymer-614 or Polymer-528 THF solutions and 40 μL of stock solutions of nitroaromatics (1 mg/mL) were mixed, which were then diluted to 2.0 mL with THF. The concentrations of nitroaromatics were 20 μg/mL. The Polymers-mixture-614 (P1+P2+P3+PS-PEG-COOH) and the Polymers-mixture-528 (P1+P2+PS-PEG-COOH) were also applied on the detection of nitroaromatics in organic phase in the same way. The mass concentrations of Polymers-mixture-614 and Polymers-mixture-528 THF solutions were 600 μg/mL and 380 μg/mL respectively, which were the same as those of Pdots-614 and Pdots-530 aqueous solutions. The constituents of Polymers-mixture-528 and Polymers-mixture-614 in THF solution, which were based on the constituents for the synthesis of Pdots, were shown in Table S4

Table S4. The constituents of Polymers-mixture-528 and Polymers-mixture-614 in THF solution.

Sample	P1 (μg/mL)	P2 (μg/mL)	P3 (μg/mL)	PS-PEG-COOH (μg/mL)	Concentration (μg/mL)
Polymers-mixture-528	190	114	/	76	380
Polymers-mixture-614	200	120	160	120	600

3.2 Quantitative Analysis of TNP and PNP in Aqueous Solutions.

100 μL of the Pdots-614 aqueous solutions (0.6 mg/mL) were mixed with different volumes of the stock solution of TNP and PNP (1 mg/mL), which were then diluted to 2.0 mL with Na_2CO_3−$NaHCO_3$−NaOH (pH, 9.0, 0.02 mol/L) buffer solutions. The fluorescence spectra of the mixture solution were measured within 30 second using an excitation wavelength of 430 nm for Pdots-614.

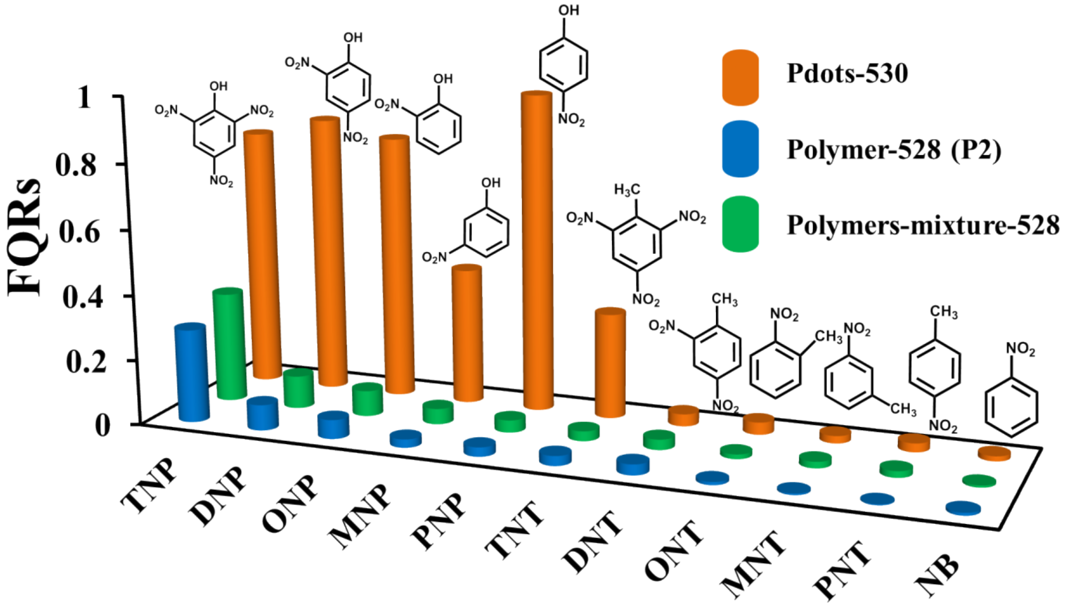

Figure S11. Comparison of the FQRs of Pdots-530 (30.0 μg/mL) in the aqueous solution, Polymer-528 (30.0 μg/mL) in THF solution and Polymers-mixture-528 (30.0 μg/mL) in THF solution, in the presence of nitroaromatics (20.0 μg/mL).

4. The Pdots-based Detection for Nitroaromatics with Pdots/Fiber Composite Fluorescence Test Strips

4.1 Preparation of Composite Fluorescence Test Strips

Filter papers (40 mm × 40 mm) were immerged in the Pdots aqueous solution for 30 second. The filter papers were then removed from the solution and dried at 80 °C for 20 min. Under the irradiation of 365 nm with a UV lamp, the Pdots-614/fiber composite test strip emitted strong red fluorescence, and Pdots-530/fiber composite test strip emitted yellow fluorescence. As the control groups, Polymer-614/fiber, Polymers-mixture-614/fiber, Polymer-528/fiber and Polymers-mixture-528/fiber composite fluorescent test strips were prepared. Taking Polymer-614/fiber and Polymers-mixture-614/fiber composite fluorescent test strips as examples, filter papers were soaked in the THF solution of the Polymer-614 or Polymers-mixture-614 for 30 second, and then the solvent was evaporated under 60 °C for 5 min. The control groups of Pdots-530 were prepared according to the aforementioned method.

4.2 Qualitative Detection of Nitroaromatic by Emission Quenching with Test Strips.

The test strips were dipped into the nitroaromatic analyte solution (20 μg/mL, 40 μL stock solution of nitroaromatic in 1.96 mL aqueous solution, PH=9), and the solvents were allowed to evaporate. The emission spectra were collected by a front face technique using a film sample holder. The emission spectrum of a blank sample was monitored by dipped into the water alone. And then fluorescence quenching rates were calculated.

4.3 Contact Mode Visual Detection of Nitroaromatics.

The analyte solutions (0.01 μg/mL, 1 μg/mL and 10 μg/mL, PH=9) of TNP (2,4,6-trinitrophenol), TNT (2,4,6-trinitrotoluene), PNP (*p*-nitrophenol), NB (nitrobenzene) as ink were spotted onto the test strips, respectively (4 μL of the analyte were dropped onto the test strips with a spot area of 0.5 cm^2). After solvent evaporation, the emission was collected by a front face technique using a film sample holder.

4.4 Quantitative Detection of TNP by Emission Quenching with Test Strips.

The TNP analyte solution (0 ~ 20 μg/mL, PH = 9) as ink were spotted on the filter paper with contact mode detection method (4 μL of the TNP analyte solution were dropped onto the test strips with a spot area of 0.5 cm^2). After solvent evaporation, the emission spectra were collected by a front face technique using a film sample holder. And the emission spectrum of a blank sample was monitored by the addition of solvent alone. The luminescent photos were taken by a digital camera under the 365 nm UV illumination with a UV lamp. The detection limits were calculated from the lowest concentration of the explosive referring to the previous literature.[6]

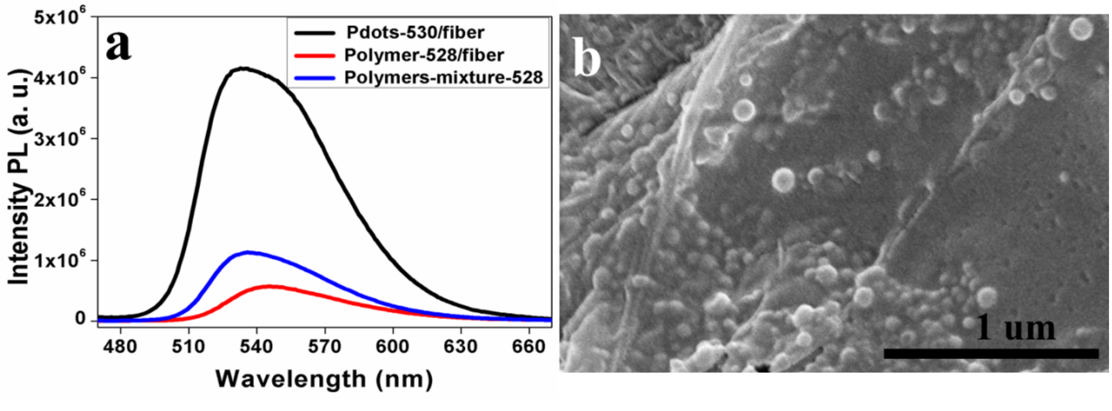

Figure S12. (a) The emission spectra of Pdots-530/fiber, Polymer-528/fiber and Polymers-mixture-528/fiber composite fluorescent test strips. (b) The SEM image of Pdots-530/fiber composite fluorescent test strips.

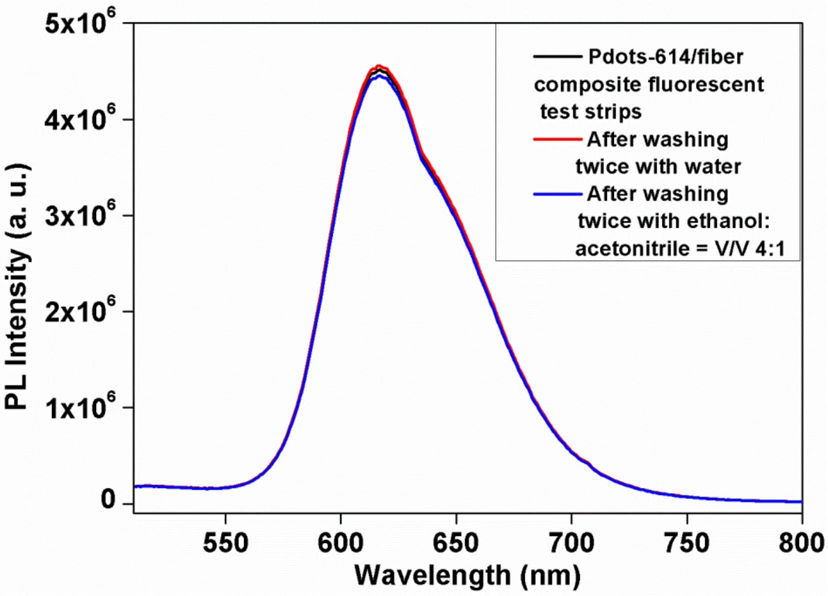

Figure S13. The emission spectra of Pdots-614/fiber composite fluorescent test strips, after washing twice with water and then twice with ethanol: acetonitrile = V/V 4:1.

5. Proof of the mechanism via hydrogen bonding interaction between Pdots and nitroaromatics

In this system, hydrogen bond was derived from -COOH in PS-PEG-COOH, which not only contributed to recognize nitrophenol, but also enhanced the stability of the Pdots in water. To clarify the influence of hydrogen bond on the Pdots based nitroaromatic sensors, the PS-PEG-$COCH_3$ was synthesized (Figure S14a). The PS-PEG-COOH could be reacted with thionyl chloride in the methanol solution at 70 °C for 4h. Pdots-red was then composited with PS-PEG-$COCH_3$, which was referred to the synthesis of Pdots-614. It was found that Pdots-red was instable in water, and could easily aggregate and form large particles (Figure S14b). Next the Pdots-red was applied on sensing TNP at PH=9. The results were shown in the Figure S15. Compared with Pdots-614, the FQRs (fluorescence quenching rates) of Pdots-red were greatly reduced. The result could further confirm the proposed mechanism.

In addition, the mechanism of interaction between Pdots-614 sensor and nitroaromatic was similar to that of interaction between *p*-phenyl-enevinylene based sensor and nitroaromatic, which was reported in the previous literature (Figure S16).[7]

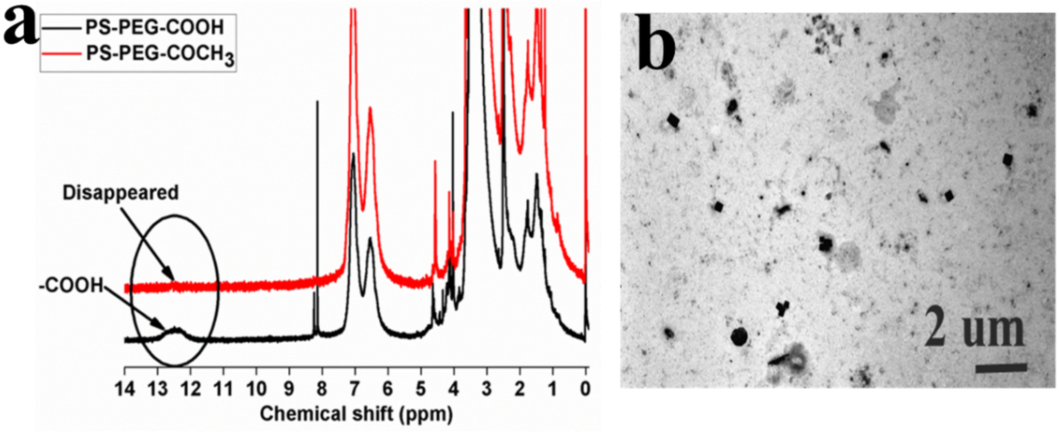

Figure S14. (a) The ^{1}H NMR spectra of PS-PEG-COOH and PS-PEG-COCH$_3$ (500 MHz, DMSO-d_6), (b) The TEM of "Pdots-red" prepared with PS-PEG-COCH$_3$.

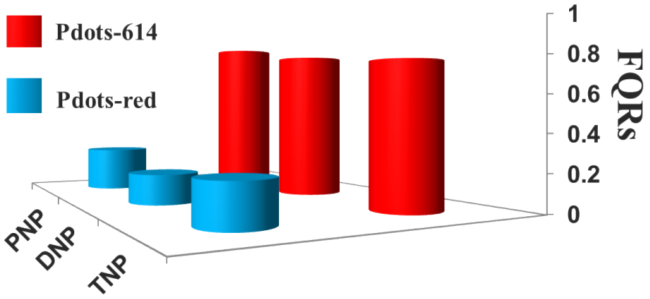

Figure S15. The FQRs (fluorescence quenching rates) of Pdots-614 and Pdots-red in the aqueous solution, in the presence of TNP, DNP and PNP (20.0 μg/mL)

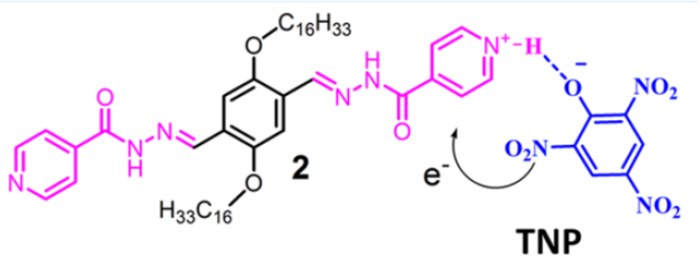

Figure S16. The scheme of the molecular level interaction, the figure from the literature: ACS Appl. Mater. Interfaces 2013, 5, 8394−8400.

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