Supporting information for

Solution-Dispersed Porous Hyperbranched Conjugated Polymer Nanoparticle for Fluorescent Sensing of TNT with Enhanced Sensitivity

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Experimental section

Measurement and Characterization. ^1H and ^{13}C NMR spectra were recorded on Bruker AV-300 with $CDCl_3$ as solvents. The ^{13}C {^1H} CP MAS spectra were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm starndard bore CPM AS probe head whose X channel was tuned to 100.62 MHz for ^{13}C and the other channel was tuned to 400.18 MHz for broad band 1H decoupling, using a magnetic field of 9.39 T at 297 K. The dried and finely powder samples were packed in the ZrO_2, rotor closed with Kel-F cap which were spun at 12 KHz rate. The $\pi/2$ pulse for proton and carbons were found to be 11.3 μs and 4 μs at power levels of 120 dB and 8 dB, respectively. The experiments were conducted at a contact time of 2 ms. A total of 5000scans were recorded with 5 s recycle delay for each sample. All ^{13}C CP MAS chemical shifts are referenced to the resonances of adamantine ($C_{10}H_{16}$) standard (δ_{CH2}=38.5). IR spectra were obtained on FT-IR Bruker Vertex 70 spectrometer at a nominal resolution of 2 cm^{-1}. The power samples were prepared by adding model compounds and polymers into KBr and the mixture was ground to a fine power and pressed to form disk. Molecular mass spectra of model compound and its precursor were recorded on LDI-1700 MALDI-TOF mass spectroscopy. Elemental analysis was performed by Bio-Rad elemental analysis system. Molecular weight and polydispersity of the polymers were determined by gel permeation chromatography (GPC) on a Waters 410 instrument with polystyrene as standards and THF as eluent. A commercial LLS spectrometer (ALV CGS-3), equipped with a multi-τ digital time correlation (ALV7000) and a cylindrical 22 mW He_Ne laser (λ = 632.8 nm, Uniphase) as light source, was used for dynamic light scattering. The samples were measured at 25 °C with a scattering angle of 90 degrees. Field-emission scanning electron microscopy (FE-SEM) imaging was performed on a Philips-FEI XL30 microscopy at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) imaging was operated on a Philips-FEI Tecnai F20 microscopy (Philips, The Netherlands) at an accelerating voltage of 200 kV. Nitrogen sorption experiments were conducted at 77K on a Quadrasorb machine from Quantachrome Instruments. Before measurement, the samples were degassed in vacuum at 160 °C for more than 10 h.

Data analysis was performed using the QuadraWin software from Quantachrome Instruments. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. UV–visible absorption measurements were carried out on Perkin-Elmer Lambda 35 UV-vis spectrometer, with a scan rate of 500 nm /min. Fluorescence emission spectra were recorded on a Perkin-Elmer LS 50B luminescence spectrometer with Xenon discharge lamp excitation.

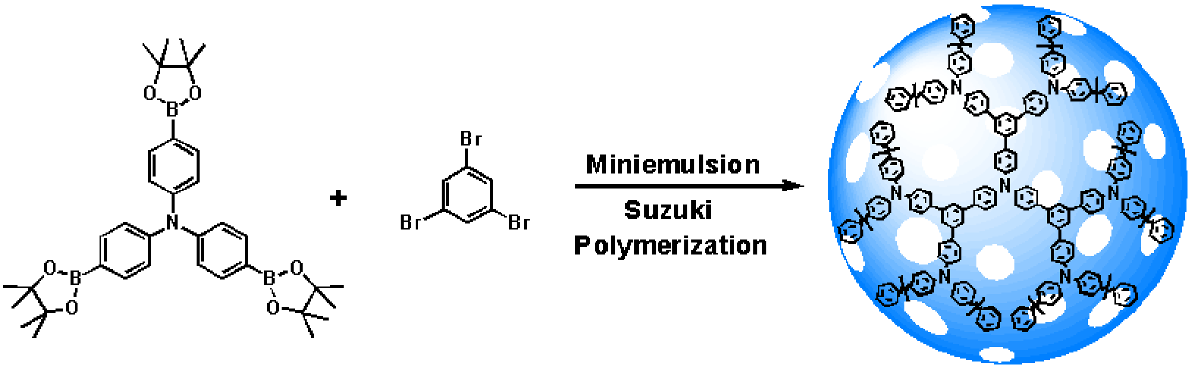
Material. All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to standard procedures. Monomer 9,9-dioctyl-2,7-dibromofluorene[1], 9,9-dioctylfluorene-2,7-bis(trimethylene boronate) [2], Tris(4-bromophenyl)amine[3], Tris{4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane)phenyl}amine[3], N,N-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline[4] were synthesized as previously described.

Preparation of PHCPN by miniemulsion Suzuki polymerization. Tris{4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane)phenyl}amine (249.2 mg,0.4 mmol), 1,3,5-tribromobenzene (126 mg , 0.4 mmol) and $Pd(PPh_3)_4$ (2.4mg) were dissolved in degassed toluene (10mL). Under argon atmosphere, the mixture solution was injected to a solution of cetyltrimethylammonium bromide (CTAB) (15.6 g, 42.8 mmol) in degassed deionized water (300 mL) with a syringe. The mixture was stirred and then ultrasonicated in an ultrasonic bath at 65°C for 10 min. A solution of 2 M aqueous K_2CO_3 (5 mL) was added under this condition. After ultrasonicating for 20 min, clear and transparent emulsion was formed. The reaction emulsion was stirred in oil bath at 80°C for 48 h under argon atmosphere. The phenylboronic acid and bromobenzene as end-capped agents was added in turn. The resulting mixture poured into saturated NaCl solution, and THF, dichloromethane and ethanol were added. The organic layer was separated, and the most of solvents were removed. The residue was precipitated in methanol. The resulting suspension was separated by centrifugation. The precipitated solid was placed into methanol and ultrasonicated for 20 min, and the suspension was separated by centrifugation. This procedure was repeated for several times. The obtained solid was extracted by Soxhlet with methanol and acetone for 1 day respectively, and dried at 100 °C under vacuum for 24 h, to afford the product with a yield of 55% (70 mg). ^{13}C CP/MAS NMR: δ(ppm): 147.3, 142.8, 127.9. FT-IR (cm^{-1}): 3031, 2922, 2852, 1715, 1595, 1506, 1427, 1359, 1318, 1284, 1181, 1105, 1014, 825, 741, 695, 650.

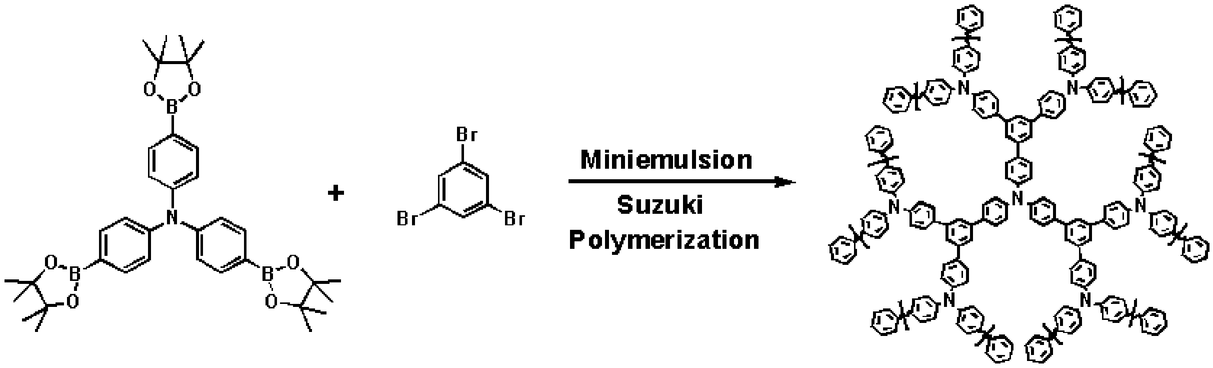
Synthesis of CMP by conventional Suzuki polymerization. A mixture of tris{4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane)phenyl}amine (311.5 mg, 0.5 mmol), 1,3,5-tribromobenzene and $Pd(PPh_3)_4$ (2.3mg) were added and degassed for 30 min. Then a solution of 2 M aqueous K_2CO_3 (3 mL) and toluene (8 mL) was added and the reaction mixture was degassed and stirred at 95 °C for 24 h under argon atmosphere. The phenylboronic acid and bromobenzene as end-capped agents was added in turn. After cooling to room temperature, the resulting mixture was poured into H_2O. After filtration, the residue was washed with H_2O, MeOH, THF and CH_2Cl_2, extracted by Soxhlet with methanol, acetone, and THF for 1 day, respectively, and dried at 100 °C under vacuum for 24 h to afford the product with a yield of 73% (232 mg). ^{13}C CP/MAS NMR: δ(ppm): 147.4, 142.7, 127.9. FT-IR (cm^{-1}): FT-IR (cm^{-1}): 3029, 2919, 2849, 1716, 1595, 1504, 1440, 1358, 1316, 1263, 1181, 1105, 1014, 823, 734, 695, 649.

Synthesis of HCPN by miniemulsion Suzuki polymerization. Tris(4-bromophenyl)amine (96.4 mg,0.2 mmol), 9,9-dioctylfluorene-2,7-bis(trimethylene boronate) (167.5 mg , 0.3 mmol) and $Pd(PPh_3)_4$ (1.4mg) were dissolved in degassed toluene (1.5 mL). Under argon atmosphere, the mixture solution was injected to a solution of cetyltrimethylammonium bromide (CTAB) (2.9 g, 8.0 mmol) in degassed deionized water (45 mL) with a syringe. The mixture was stirred and then ultrasonicated in an ultrasonic bath at 65°C for 10 min. A solution of 2 M aqueous K_2CO_3 (1.2 mL) was added under this condition and ultrasonicated for 20 min. The reaction emulsion was stirred in oil bath at 80°C for 48 h under argon atmosphere. The phenylboronic acid and bromobenzene as end-capped agents was added in turn. The resulting mixture poured into saturated NaCl solution, and dichloromethane and ethanol were added. The organic layer was separated, and the most of solvents were removed. The residue was precipitated in methanol. The resulting suspension was separated by centrifugation. The precipitated solid was placed into methanol and ultrasonicated for 20 min, and the suspension was separated by centrifugation. This procedure was repeated for two times. The obtained solid was extracted by Soxhlet with methanol and acetone for 1 day respectively, and dried at 100 °C under vacuum for 24 h, to afford the product with a yield of 50% (82.6 mg). ^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm): 7.74 (m, 2H), 7.60-7.55 (m, 8H), 7.32-7.21 (m, 8H), 2.04 (br,4H), 1.09 (br, 20H), 0.77 (m, 10H). FT-IR (cm^{-1}): 3030, 2923, 2851, 1739, 1599, 1511, 1485, 1464, 1314, 1260, 1183, 1182, 1108, 1071, 1009, 889, 812,739.

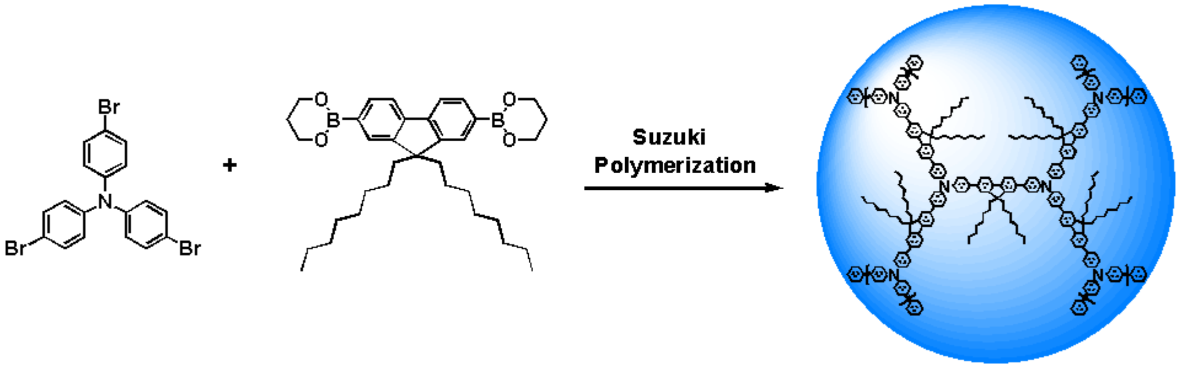
Synthesis of LCP. A mixture of N,N-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (248 mg, 0.5 mmol), 9,9-dioctyl-2,7-dibromofluorene (274 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (2.3 mg) were added and degassed for 30 min. Then a solution of 2 M aqueous K_2CO_3 (2 mL) and toluene (6 mL) was added and the reaction mixture was degassed and stirred at 80 °C for 48 h under argon atmosphere. The phenylboronic acid and bromobenzene as end-capped agents was added in turn. After cooling to room temperature, dichloromethane was diluted in dichloromethane. The solution was washed with brine and deionized water. The separated organic layer was dried with anhydrous Na_2SO_4. After filtration, the solvent was removed, and the residue was redissolved with a minimum amount of dichloromethane and precipitated in methanol. The resulting polymers were obtained after drying in vacuum with a yield of 86% (270 mg). ^{1}H NMR ($CDCl_3$, 300 MHz): δ(ppm): 7.74 (d, 2H, J = 7.7 Hz), 7.60-7.55 (m, 8H), 7.32-7.21 (m, 8H), 7.07-7.02 (m, 1H), 2.01 (br,4H), 1.05 (br, 20H), 0.77 (m, 10H). FT-IR (cm^{-1}): 3030, 2925, 2853, 1595, 1512, 1492, 1465, 1317, 1280, 1183, 1108, 1014, 814, 753, 695. GPC (THF, polystyrene standard), Mn=1.89 $\times 10^4$, PDI=3.54.



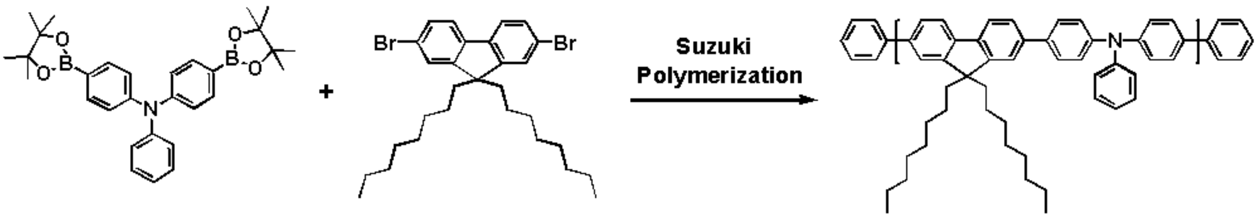
PHCPN



CMP



HCPN



LCP

Fig. S1 Solid-state ^{13}C CP/MAS NMR spectra of PHCPN. The asterisks denote the spinning sidebands.

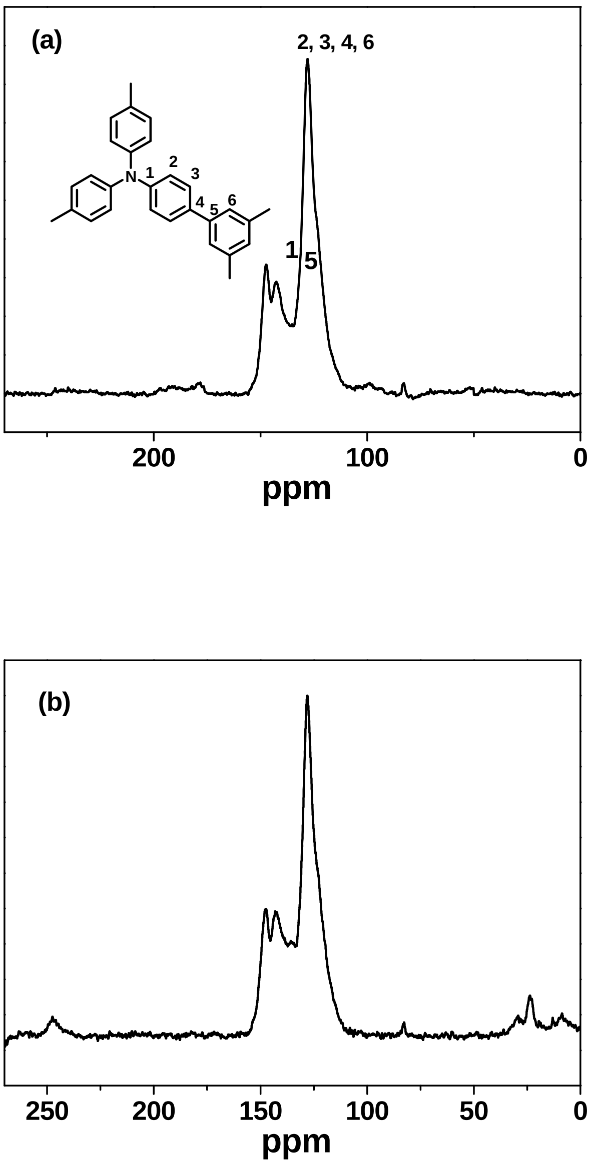


Fig. S2 FT-IR spectra of PHCPN (a) and CMP (b).

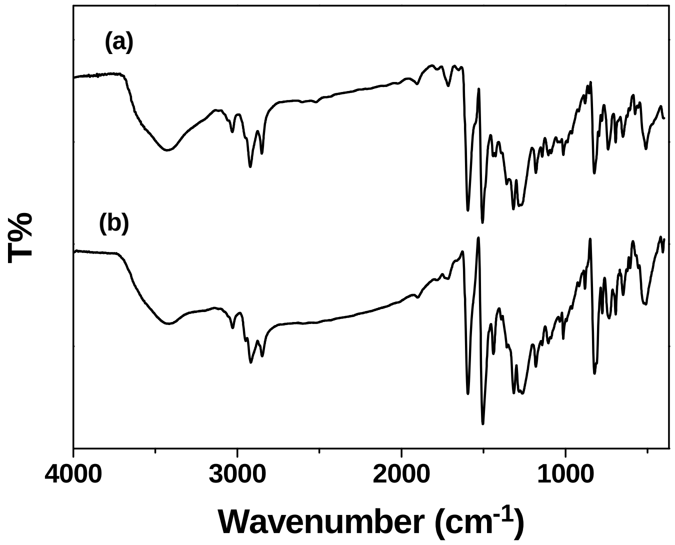


Table S1. Comparison of C, H, N contents of PHCPN and CMP.

	C (%)	**N (%)**	**H (%)**
PHCNP	**79.02**	**3.23**	**5.07**
CMP	**67.81**	**3.15**	**3.94**

Fig. S3 TGA curves recorded under N2 for PHCPN and HCPN.

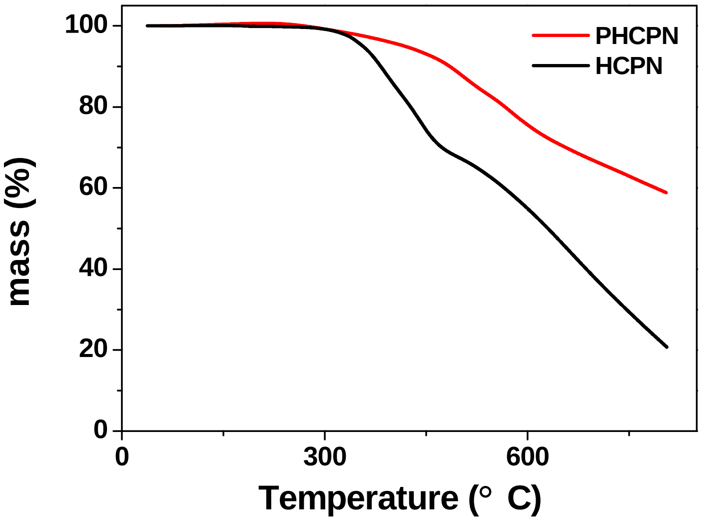


Fig. S4 Hydrodynamic radii of PHCPN (a) and HCPN (b) in THF, as measured by dynamic light scattering (DLS).

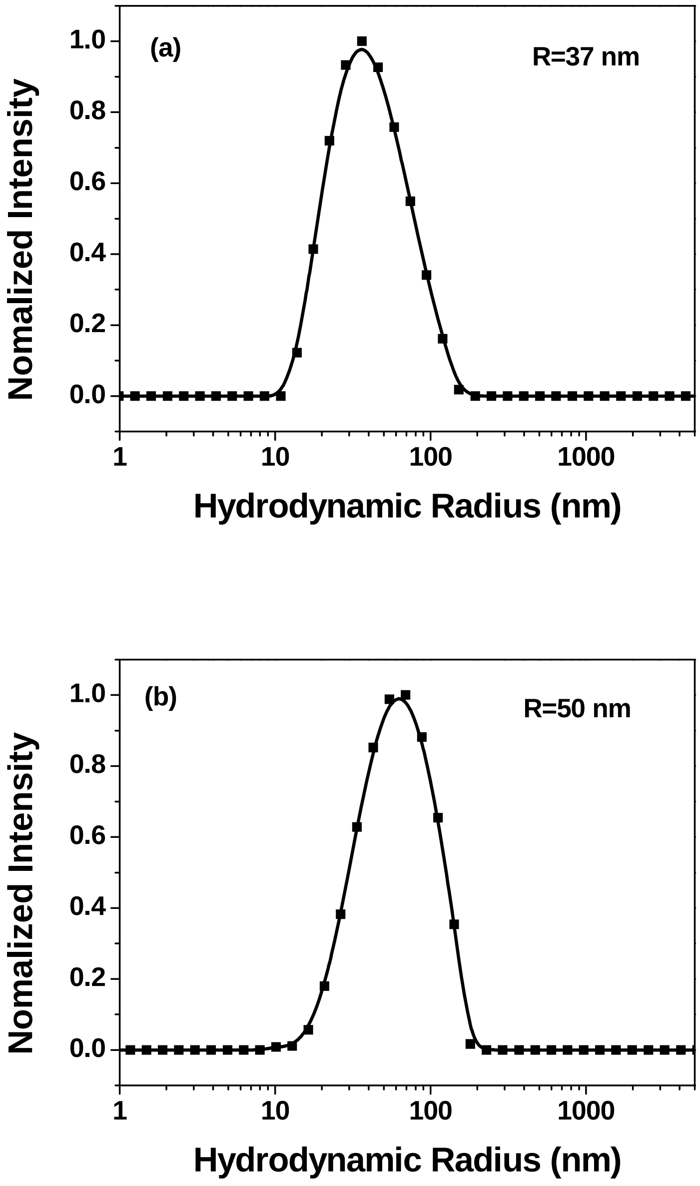


Fig. S5 SEM images by drop-casting PHCPN in THF onto Si wafer.

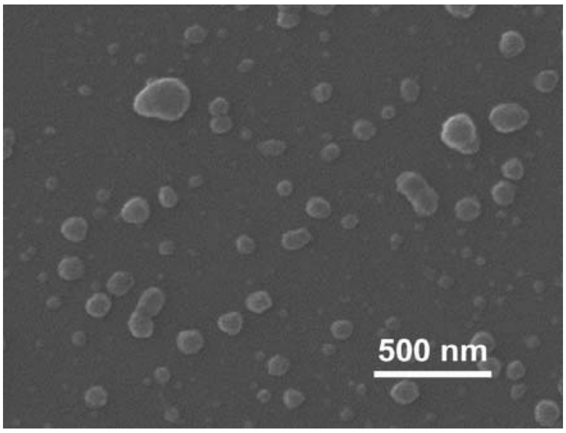


Fig. S6 SEM images of solid powder of PHCPN (a), HCPN (b) and CMP (c).

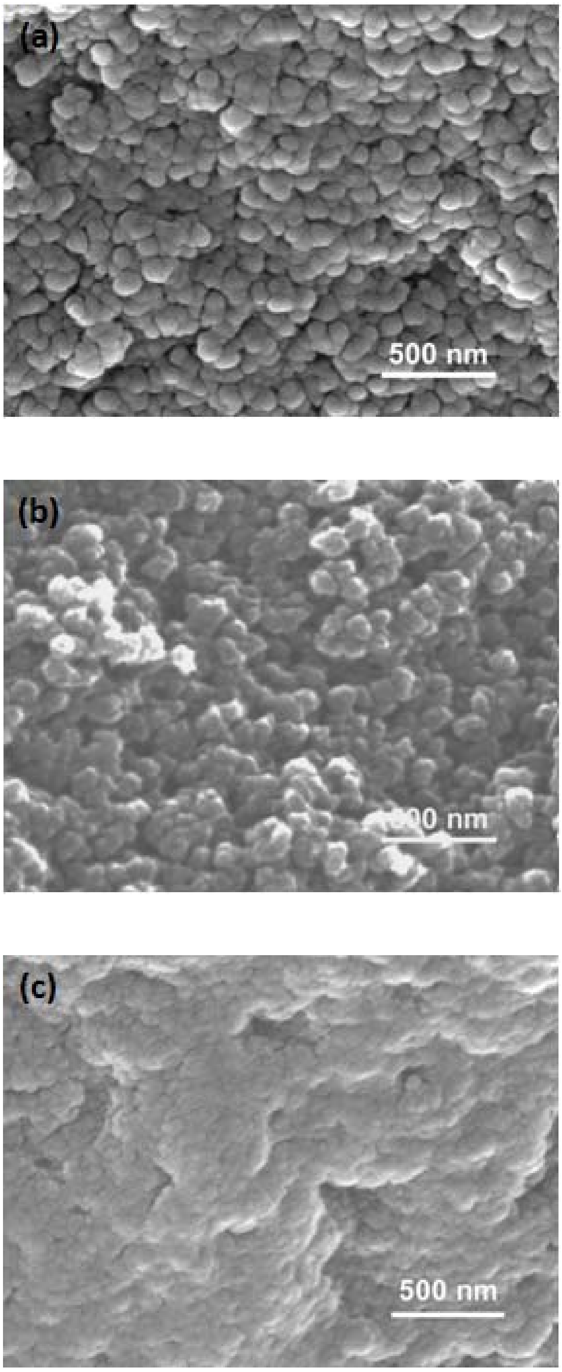


Table S2. Optical properties of PHCNP, HCPN and LCP in THF.

	λ_{abs} (nm)	**λ_{PL} (nm)**	**Φ_{PL}（%）**
PHCPN	356	438	11
HCPN	383	435	44
LCP	387	429	65

Fig.S7 The PL spectral stability of PHCPN dispersion in THF.

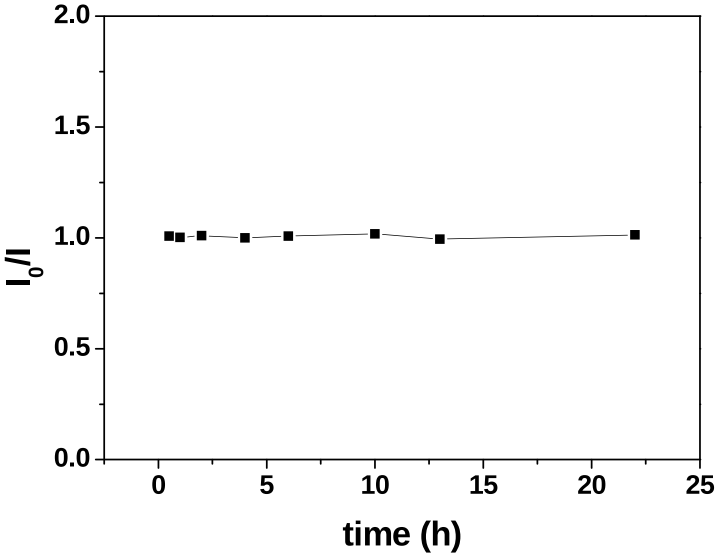


Fig. S8 The image of PHCPN (left), HCPN(middle) and LCP (right) dispersed in THF under the sunlight (a) and UV lamp (b).

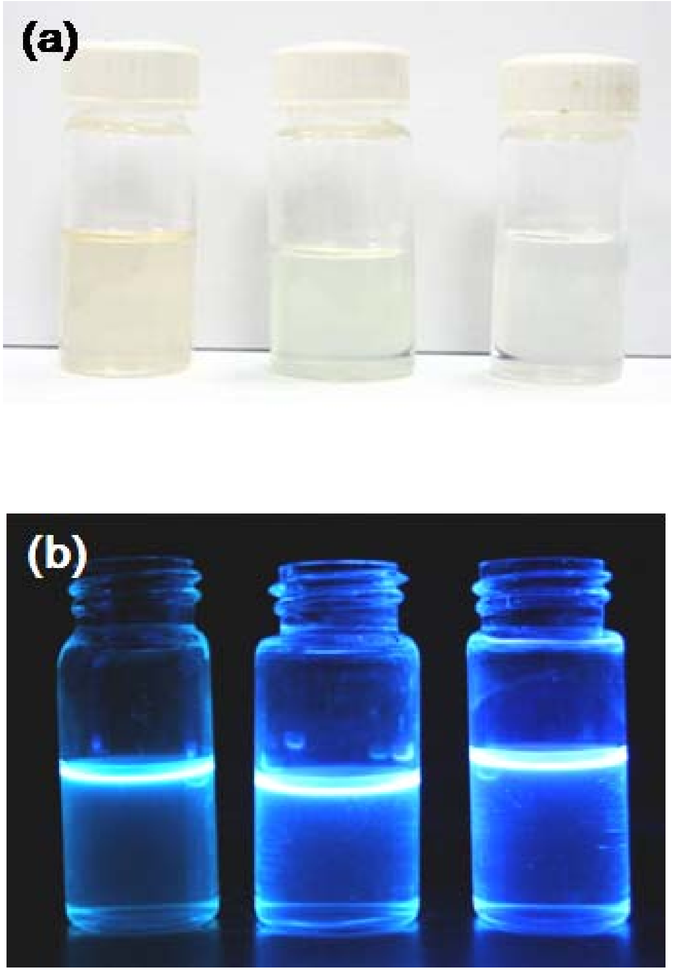
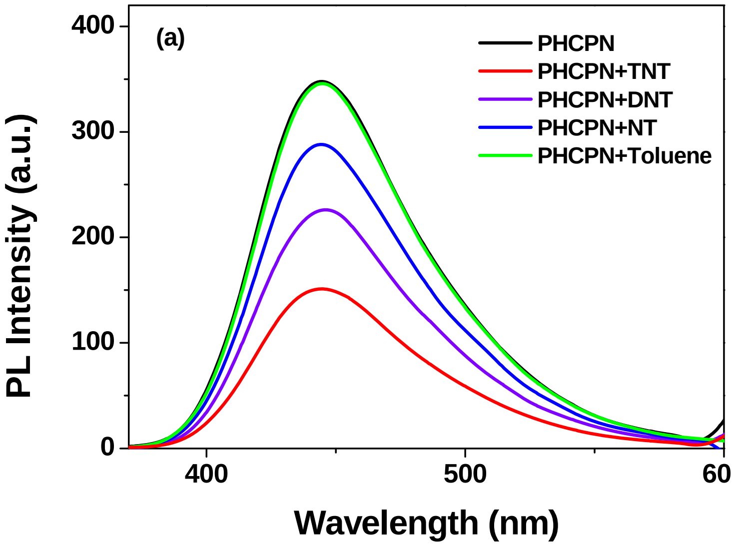


Table S3. Surface areas and pore volumes of PHCPN, HCPN and LCP.

	S_{BET} (m^2/g)^a	$S_{Langmuir}$ (m^2/g)^b	$MPV_{0.1}$ (cm^3/g)^c	$PV_{0.8}$ (cm^3/g)^d
PHCNP	133	220	0.04	0.14
HCNP	13	42	0.002	0.013
LCP	0	0	-	-

a) Surface areas calculated from the N_2 adsorption isotherms using BET method; b) Surface areas calculated from the N2 adsorption isotherms using Langmiurmethod c) Micropore volume determined from the adsorption isotherm at a relative pressure P/P_0 of 0.1; d) Total pore determined from the adsorption isotherm at a relative pressure P/P_0 of 0.80.[5]

Fig. S9 (a) Fluorescence spectra of PHCPN dispersion in THF before and after adding TNT, DNT, NB and toluene of 1 mM, respectively. (b) Changes in fluorescence intensity of PHCPN dispersion in THF upon the addition of various analytes of 1 mM. TNT=1,3,5-Trinitrotoluene, DNT= 2,4-Dinitrotoluene, NB=Nitrobenzene, TOL=Toluene, PhOH=Phenol, BQ=Benzoquinone, CB=Chlorobenzene, BB=Bromobenzene, MeOH=Methanol, NM= Nitromethane, EtOH=Ethanol.



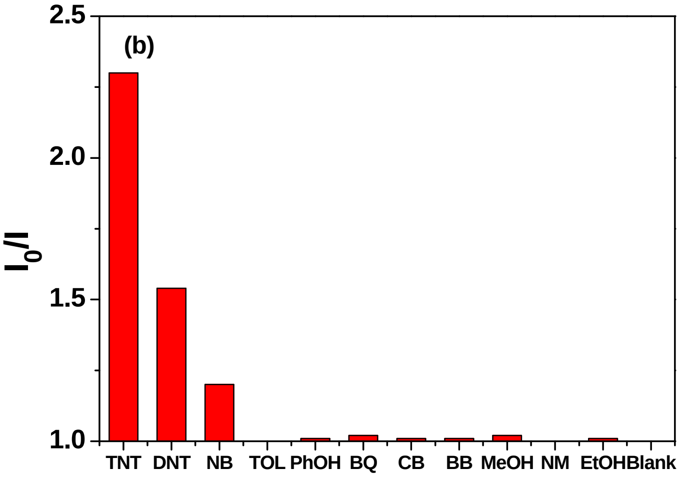


Fig. S10 Fluorescence response profiles of HCPN in THF upon addition of TNT.

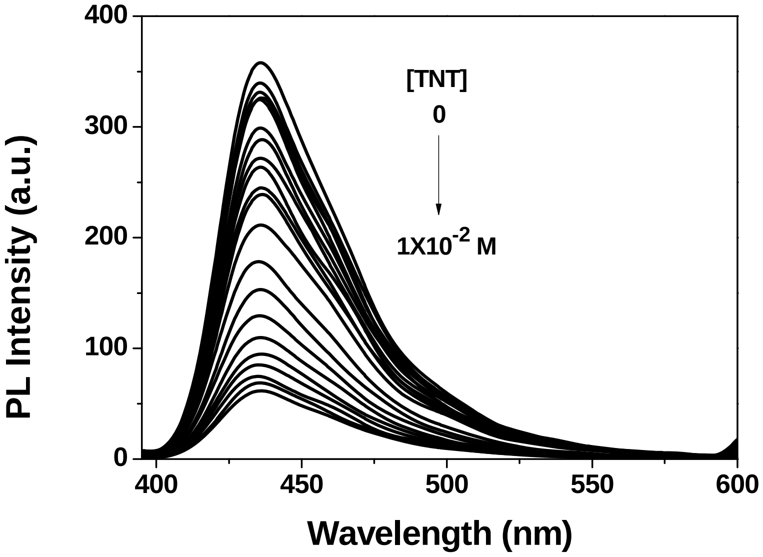


Fig. S11 Fluorescence response profiles of LCP in THF upon addition of TNT.

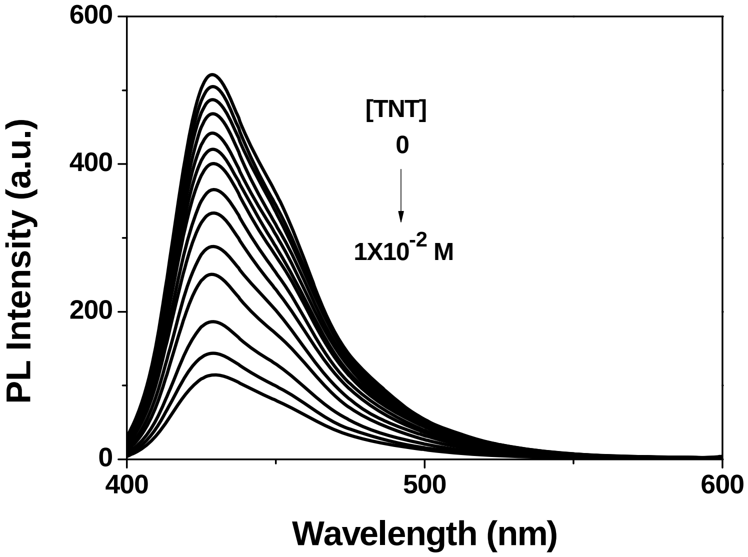


Fig. S12 Fluorescence quenching images of PHCPN (a), HCPN (b) and LCP (c) coated on filter paper by solid particulates of TNT with various amounts (unit: ng/mm^2).

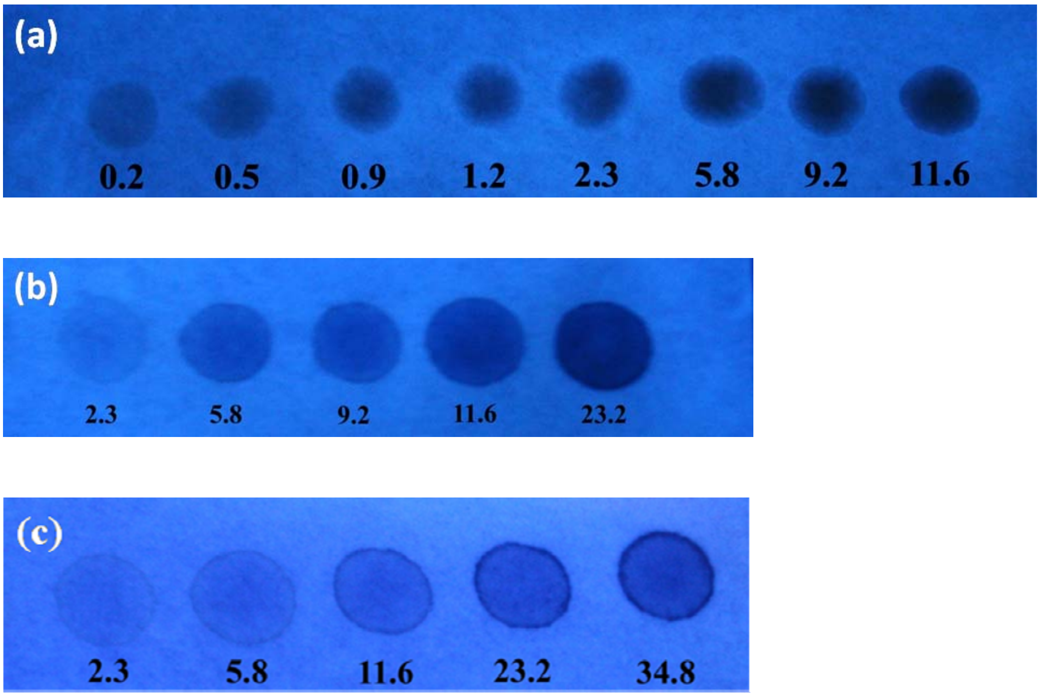
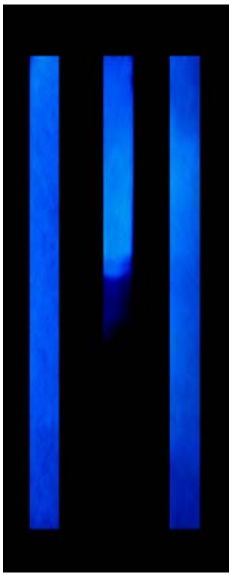


Fig. S13 The image of reversible fluorescent sensing of PHCPN-coated indicating paper to TNT. (Left: fluorescence of blank PHCPN-coated indicating paper under the UV lamp; middle: fluorescence quenching of PHCPN-coated indicating paper by immerging into 1 mM TNT in methanol solution; right: fluorescence restore of PHCPN-coated indicating papers by simply blowing treatment with an air blower.



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