Supporting Information

Thin Film Fabricated from Solution-Dispersible Porous Hyperbranched Conjugated Polymer Nanoparticles without Surfactants

Xiaofu Wu, Haibo Li, Yuxiang Xu, Bowei Xu, Hui Tong and Lixiang Wang**

Measurement and Characterization. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-300 with $CDCl_3$ as solvents. The ^{13}C $\{^{1}H\}$ 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 5000 scans were recorded with 5 s recycle delay for each sample. All ^{13}C CP MAS chemical shifts are referenced to resonances of adamantine ($C_{10}H_{16}$) standard (δ_{CH2}=38.5). Molecularmass spectra of compounds and were recorded on a LDI-1700 MALDI-TOF mass spectroscope. 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. Elemental analysis was performed on Bio-Rad elemental analysis system. Ionic chromatography was performed on a Dionex ISC-1000 system. 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. AFM characterization was performed on a SPA300HV with a SPI3800N controller (Seiko Instruments, Inc., Japan) in tapping mode. 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. The pore size distribution for all samples was calculated by using NLDFT methods. 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.

Fabrication of spin-coating film. The FTPA-HBCPN film was fabricated by spin-coating its solution (4 mg mL^{-1}) in THF with a rate of 1000 rpm on glass substrates at room temperature.

Detection process.

A 10 × 10 mm quartz cuvette was used for spectra, and emission was collected at 90° relative to the excitation beam.

The solutions of FTPA-HBCPN and FTPA-LP were diluted to a concentration of 1 mg L^{-1} in THF. Fluorescence quenching experiment of solution was carried out by sequentially adding small aliquots of nitroaromatics stock solutions in THF to 3.00 mL of the testing solution.

All fluorescence detection experiments of the spin-coated film were carried out by inserting the polymer film into sealed cuvettes containing different analytes at room temperature to ensure a constant vapor pressure.[1] A small quantity of the analytes was placed beneath some cotton wool inside a sealed quartz cuvette and left overnight to allow the analyte vapor to reach equilibrium (fully saturated). The cotton wool will also prevent direct contact of the film with the analytes. The fluorescence spectra of the film were measured immediately after immersing inside the cuvette.

The fluorescence of the film after exposure to explosives can be recovered. After exposing to NB vapor, the film was simply blew with an air blower for 5 minutes to remove the absorbed NB, and the

fluorescence could be recovered. After exposing to less volatile TNT and DNT, the film was washed with excess methanol followed by drying with the air blower.

Materials. 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 tris(4-bromophenyl)amine were synthesized as previously described.[2]

Synthesis of N-(4-methylphenyl) diphenylamine. 4-methy-1-bromobenzene (17.1g, 100 mmol) , N, N-diphenylamine (20.3 g, 120 mmol), sodium t-butanolate (14.4 g, 150 mmol), tri-tert-butyl phosphine (20.2 mg, 0.1 mmol) and $Pd(OAc)_2$ (5.6 mg, 0.025mmol) were dissovled in degassed dimethylbenzene (150 mL) under argon atmosphere. The solution was stirred at 120 °C overnight. The reaction mixture was diluted by dichloromethane and washed with water. Upon removal of the solvent, the residue was purified by column chromatography on silica gel with petrol ether as the eluent. The product was obtained as white solid (25 g, 96%). ^{1}H NMR ($CDCl_3$): δ (ppm): 7.21 (m, 4H), 7.06 (m, 4H,), 6.98 (m, 4 H), 2.31 (s, 4H). ^{3}C NMR ($CDCl_3$): δ (ppm): 148.0, 145.2, 132.7, 129.9, 129.1, 124.9, 123.6, 122.2, 20.8. FT-IR (cm^{-1}): 3021, 2915, 1596, 1509, 1489, 1325, 1273, 1173, 1076, 1026, 899, 818, 755, 698, 620, 573, 505. m/z [MALDI-TOF]: 259.1 $[M+H]^+$.

Synthesis of N,N-bis(4-bromophenyl)-4-methylbenzenamine. To a solution of N-(4-methylphenyl) diphenylamine (12.9g, 50 mmol) in chloroform (200 mL), bromine (16.4 g, 100.3 mmol) in chloroform (20 mL) was added slowly at 0°C. Then, the solution was stirred at room temperature overnight. The reaction mixture was washed with $NaHSO_3$ aqueous solution and water. Upon removal of the solvent, the residue was purified by recrystallization from hexane to afford product as white solid (20.0g, 95%). ^{1}H NMR ($CDCl_3$): δ (ppm): 7.31 (d, 4H, J= 8.9 Hz), 7.08 (d, 2H, J= 8.2 Hz), 6.96 (d, 2 H, J= 8.2 Hz), 6.90 (d, 4H, J= 8.9), 2.32 (s, 4H). ^{13}C NMR ($CDCl_3$): δ (ppm): FT-IR (cm^{-1}): 3027, 2915, 1577, 1509, 1484, 1313, 1288, 1267, 1174, 1072, 1007, 819, 702, 577, 506. m/z [MALDI-TOF]: 415.0 $[M+H]^+$.

Synthesis of 2,7-dibromo-9,9-dimethylfluorene. To a solution of 2, 7-dibromofluorene (16.2 g, 50 mmol) in dimethylsulfoxide (100 mL) under argon atmosphere, KOH (11.2 g, 200 mmol) and KI (0.83g,

5mmol) was added. The solution was stirred at room temperature for 30 min, and then CH_3I was added and stirred overnight. The reaction mixture was poured into water (200 mL) and filtered. The solid was washed with water and dried under vacuum. The solid purified by recrystallization from mixed solvent of methanol and dichloromethane, and dried under high vacuum to afford product as white solid (14.8 g, 84%). ^{1}H NMR ($CDCl_3$): δ (ppm): 7.58 (m, 4H), 7.50 (dd,2H, J= 8.1 Hz, J=1.6 Hz), 1.51 (S, 6 H). ^{13}C NMR ($CDCl_3$): δ (ppm): 156.9, 154.2, 147.4, 144.6, 135.8, 130.9, 126.6, 123.5, 122.8, 120.3, 118.4, 47.6, 26.6. FT-IR (cm^{-1}): 2962, 2921, 1598, 1576, 1448, 1400, 1260, 1128, 1084, 1060, 1003, 866, 817, 794, 730, 667. m/z [MALDI-TOF]: 350.9 $[M+H]^+$.

Synthesis of 2,7-Bis(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane)-9,9-dimethylfluorene. 2,7-dibromo-9,9-dimethylfluorene (10 g, 29 mmol) , bis(pinacolato)diboron (17.7 g, 69.6 mmol), Pd(dppf)Cl_2 (0.211 g, 0.29 mmol) and KOAc (8.5 g, 87 mmol) were dissovled in degassed DMF (100 mL) under argon atmosphere. The reaction mixture was stirred at 90°C for 24h. Dichloromethane were added and the solution was washed with water. Upon removal of the solvent, the residue was purified by column chromatography on silica gel with dichloromethane–petrol ether as the eluent. The product was obtained as white solid (7.4 g, 51%). ^{1}H NMR ($CDCl_3$): δ (ppm): 7.88 (s, 2H), 7.81 (d, 2H, J= 6.8 Hz), 7.75(d, 2H, J= 6.8 Hz), 1.51 (S, 6 H), 1.37 (s, 24). ^{13}C NMR ($CDCl_3$): δ (ppm): 153.6, 142.0, 134.1, 129.2, 120.0, 84.1, 47.1, 27.4, 25.3. FT-IR (cm^{-1}): 2973, 2931, 1609, 1574, 1474, 1419, 1349, 1314, 1259, 1141, 1097, 1078, 962, 878, 850, 828, 748, 689. m/z [MALDI-TOF]: 447.3 $[M+H]^+$.

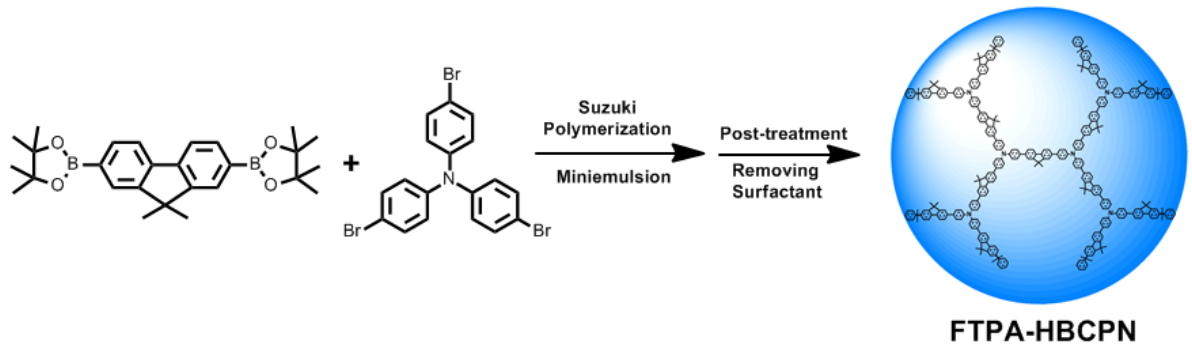
Synthesis of FTPA-HBCPN by miniemulsion Suzuki polymerization. 2,7-Bis(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane)-9,9-dimethylfluorene (267 mg, 0.6 mmol), tris(4-bromophenyl)amine (193 mg , 0.4 mmol) and Pd(PPh_3)$_4$ (2.8mg) were dissolved in degassed toluene (10 mL). Under argon atmosphere, the mixture solution was added to a solution of cetyltrimethylammonium bromide (CTAB) (4.36g, 12 mmol) in degassed deionized water (135 mL). The mixture was stirred and then ultrasonicated in an ultrasonic bath at 50°C for 20 min. A solution of 2 M aqueous K_2CO_3 (5 mL) was added under this condition. After ultrasonicating for 10 min. The reaction emulsion was stirred in oil bath at 80°C for 40 h under argon

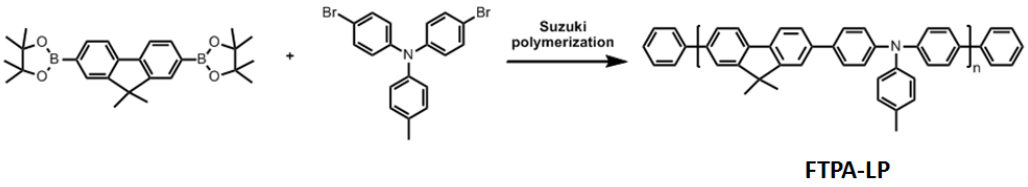
atmosphere. The phenylboronic acid and bromobenzene as end-capped agents was added in turn. The resulting mixture poured into saturated NaCl aqueous solution, and dichloromethane was added. The organic layer was separated, and the most of solvents were removed. The residue was precipitated in methanol. 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 130 °C under vacuum for 24 h, to afford the product with a yield of 80% (169 mg). ^{13}C CP-MAS NMR: δ (ppm): 154.4, 146.6, 138.2, 127.3, 120.4, 46.7, 27.1. FTIR (KBr): ν= 3030, 2956, 2922, 2857, 1599, 1511, 1485, 1462, 1316, 1285, 1184, 1072, 1012, 890, 813, 738, 535 cm^{-1}.

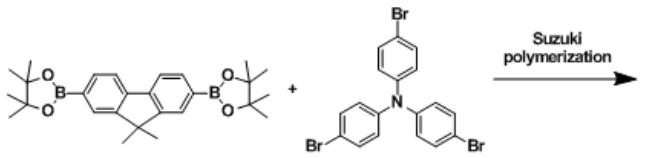
Synthesis of FTPA-CP by conventional Suzuki polymerization. A mixture of 2,7-Bis(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane)-9,9-dimethylfluorene (334 mg,0.75 mmol), tris(4-bromophenyl) amine (241mg , 0.5 mmol) and $Pd(PPh_3)_4$ (3.4 mg) were degassed for 30 min. Then a solution of 2 M aqueous K_2CO_3 (3 mL) and toluene (10 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 dichloromethane, extracted by Soxhlet with methanol, acetone, and dichloromethane for 1 day, respectively, and dried at 130 °C under vacuum for 24 h to afford the product with a yield of 83% (218 mg). ^{13}C CP/MAS NMR: δ (ppm): 154.4, 146.3, 138.3, 127.3, 120.5, 46.7, 27.7. FTIR: (cm^{-1}): 3028, 2958, 2916, 2846, 1602, 1511, 1462, 1315, 1252, 1182, 1113, 1012, 889, 806, 736, 533.

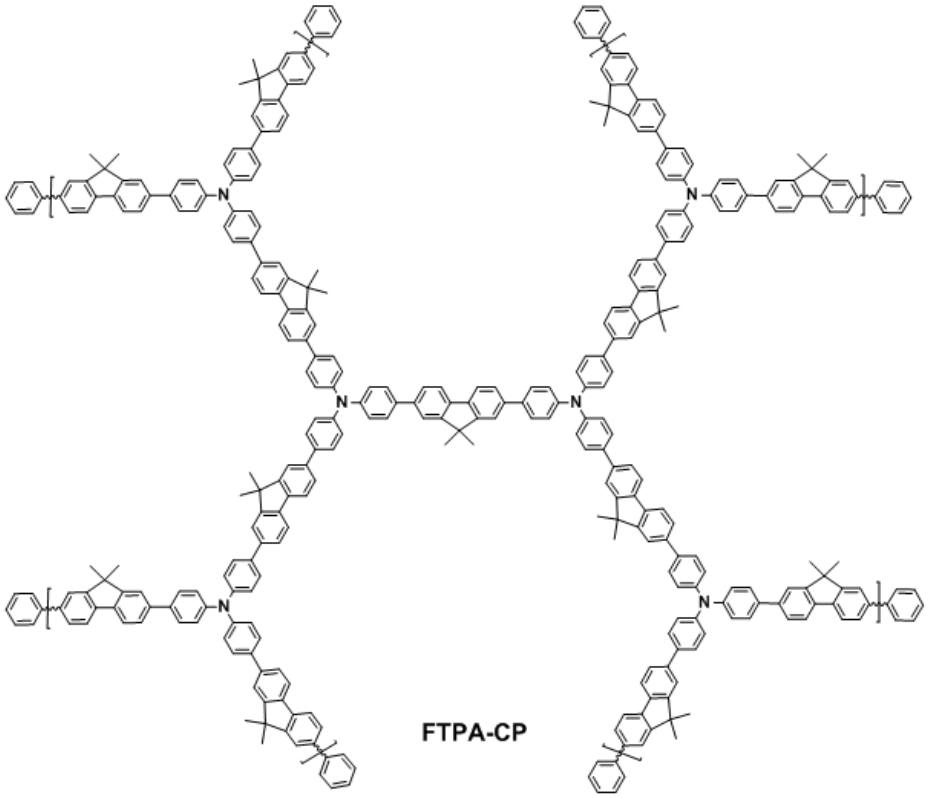
Synthesis of FTPA-LP. A mixture of 2,7-Bis(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane)-9,9-dimethylfluorene (223 mg, 0.5 mmol), N,N-bis(4-bromophenyl)-4-methylbenzenamine (207mg , 0.5 mmol) and $Pd(PPh_3)_4$ (2.3 mg) were degassed for 30 min. Then a solution of 2 M aqueous K_2CO_3 (2 mL) and toluene (6 mL) was added and the reaction mixture was degassed and stirred at 85 °C for 40 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 most of solvent was removed, and the residue was precipitated in methanol. The resulting polymers were obtained after drying in vacuum with a yield of 75% (168 mg). ^{1}H NMR ($CDCl_3$): δ (ppm): 7.77 (d, 2H, J= 7.6 Hz), 7.58 (m, 8H), 7.23 (d, 4H, J= 8.6 Hz), 7.13 (s, 4H), 2.36 (s, 3 H), 1.58 (s, 6H). ^{13}C NMR ($CDCl_3$): δ (ppm): 153.5, 146.0, 143.9, 138.7, 136.7, 134.4, 132.1, 131.0, 129.1, 126.7, 124.2, 122.7, 119.8, 119.2, 46.0, 26.4, 19.9. FTIR: (cm^{-1}): 3028, 2957, 2922, 2858, 1602, 1510, 1465, 1320, 1294, 1263, 1185, 1108, 1012, 890, 813, 745, 586, 520.









Scheme S1. The preparation of FTPA-HBCPN, FTPA-LP, FTPA-CP.

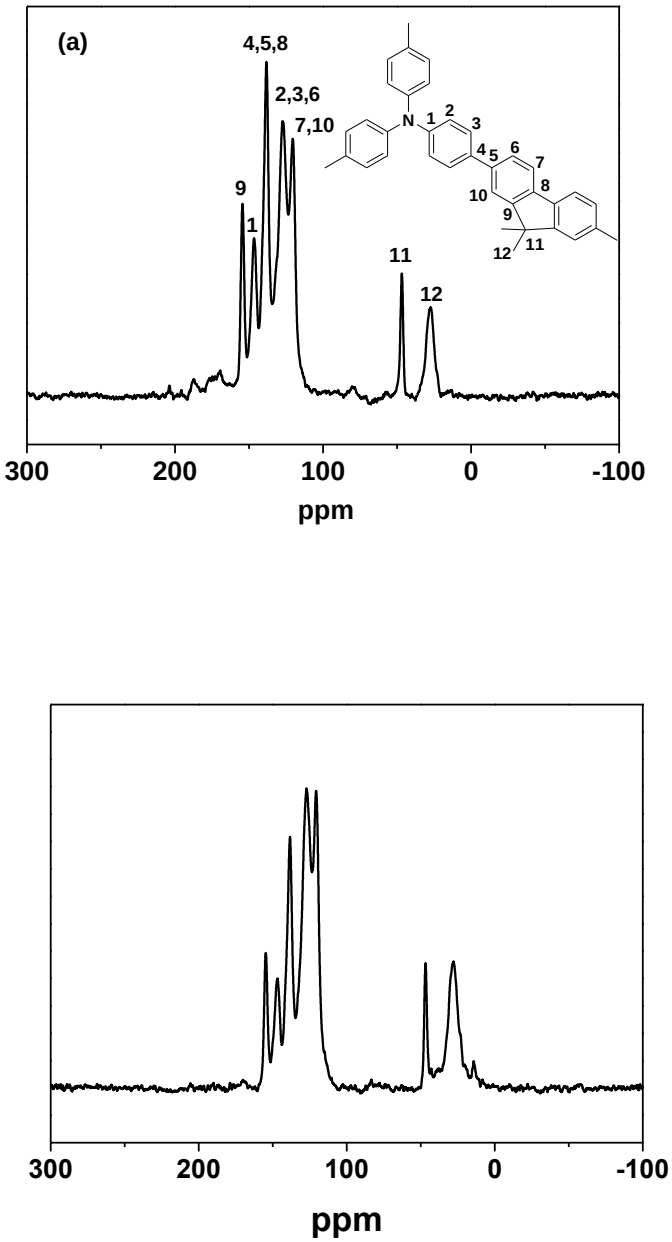


Figure S1. Solid-state ^{13}C CP/MAS NMR spectra of FTPA-HBCPN (a) and FTPA-CP.

In the solid-state ^{13}C CP/MAS NMR spectra of FTPA-HBCPN, there was no chemical shift peak around 32.0 ppm of the methylene carbons of CTAB,[3] which indicated that CTAB was removed completely from the resulting nanoparticles.

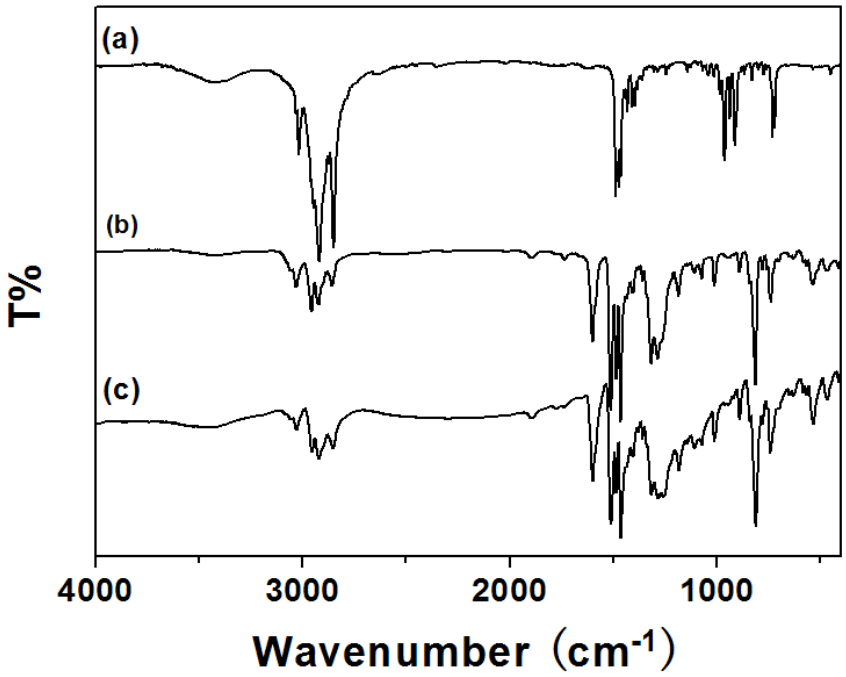


Figure S2. FT-IR spectra of CTAB (a), FTPA-HBCPN (b) and FTPA-CP (c).

In FT-IR spectra of CTAB, FTPA-HBCPN and FTPA-CP, it is clear that the IR spectra of FTPA-HBCPN and FTPA-CP are very similar. Especially, the characteristic peaks of the quatemary ammonium salt (–$N(CH_3)_3^+$) at 961 and 912 cm^{-1} of CTAB cannot be observed in the IR spectra of both FTPA-HBCPN and FTPA-CP, indicating the complete removal of CTAB from the resulting FTPA-HBCPN.

The amount of the Br^- anion was further determined by the ion exchanged chromatography. No signal of Br^- anion could be detected, also indicating that the surfactant CTAB can be removed completely.

Table S1. Elemental analysis of FTPA-HBCPN, FTPA-CP and FTPA-LP.

		C (%)	H(%)	N (%)	C/H*
FTPA-HBCPN	theoretical	90.58	6.22	3.20	14.56
	experimental	88.32	6.36	3.33	13.84
FTPA-CP	theoretical	90.58	6.22	3.20	14.56
	experimental	86.50	6.47	3.12	13.37
FTPA-LP	theoretical	90.83	6.05	3.12	14.93
	experimental	89.39	6.18	3.06	14.46

*It was already observed by Cooper et al. that elemental analysis gives most times wrong results (too low carbon to hydrogen ratio and too low carbon content) for microporous conjugated polymers.[4]

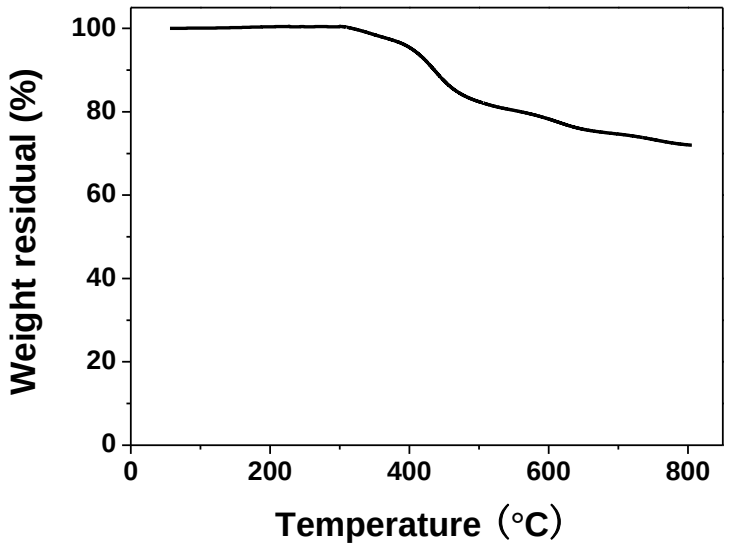


Figure S3. TGA curve recorded under N_2 for FTPA-HBCPN.

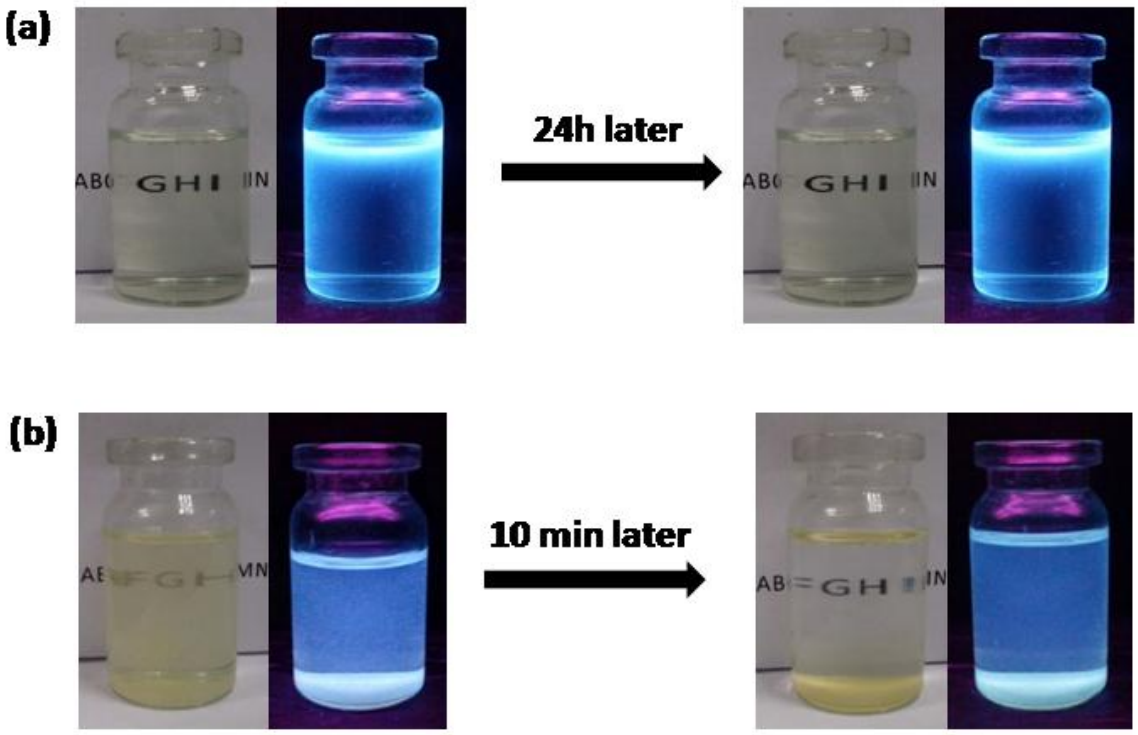


Figure S4. The images of FTPA-HBCPN (a) and FTPA-CP (b) in THF with the concentration of 4 mg/mL under sunlight and a UV lamp.

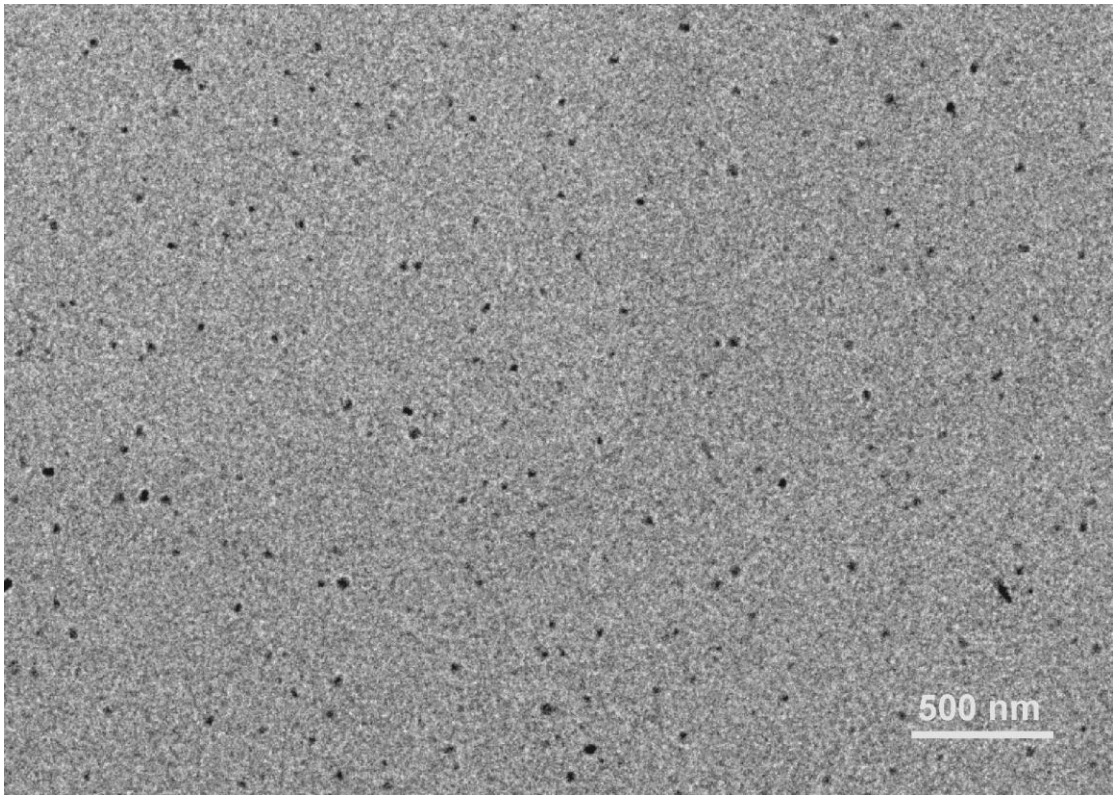


Figure S5. TEM image obtained by drop-casting a THF solution of FTPA-HBCPN onto a copper grid.

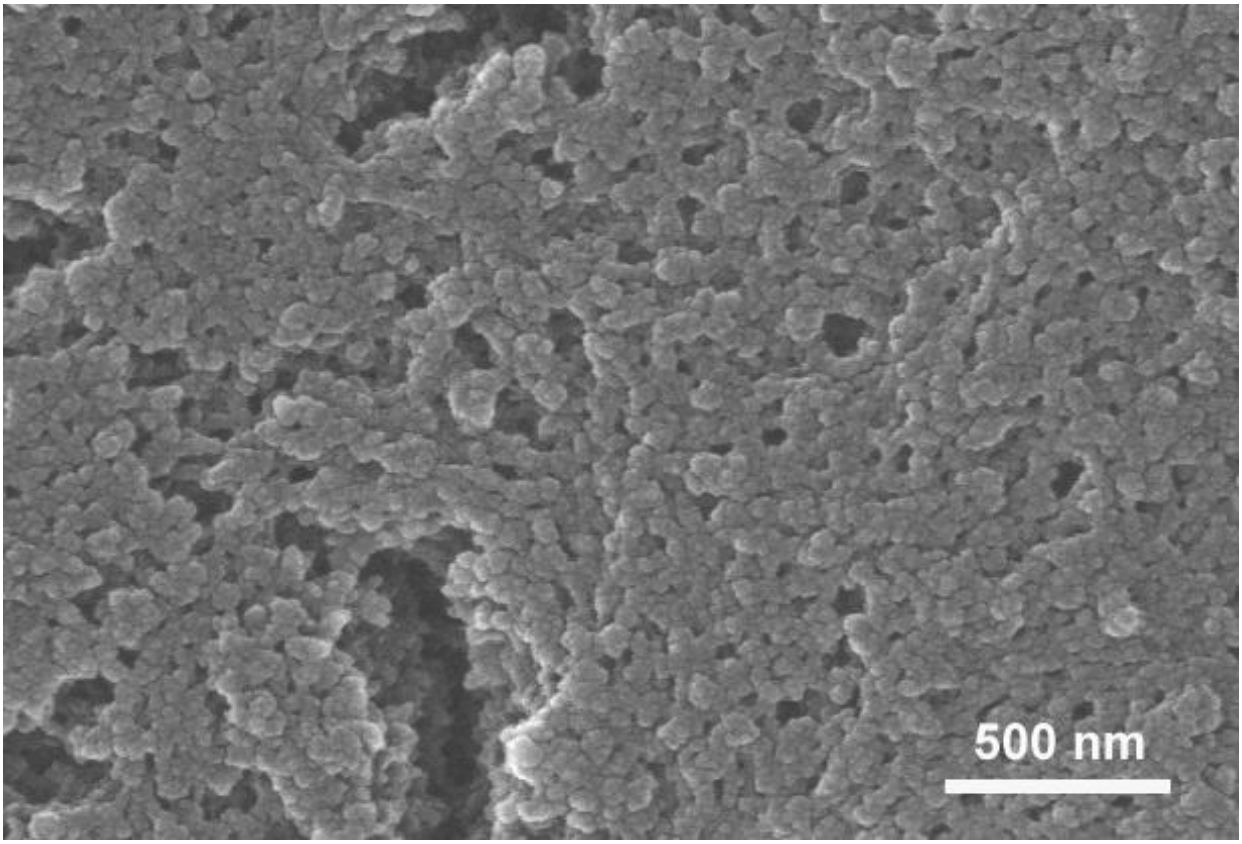


Figure S6. SEM image of FTPA-HBCPN in solid states.

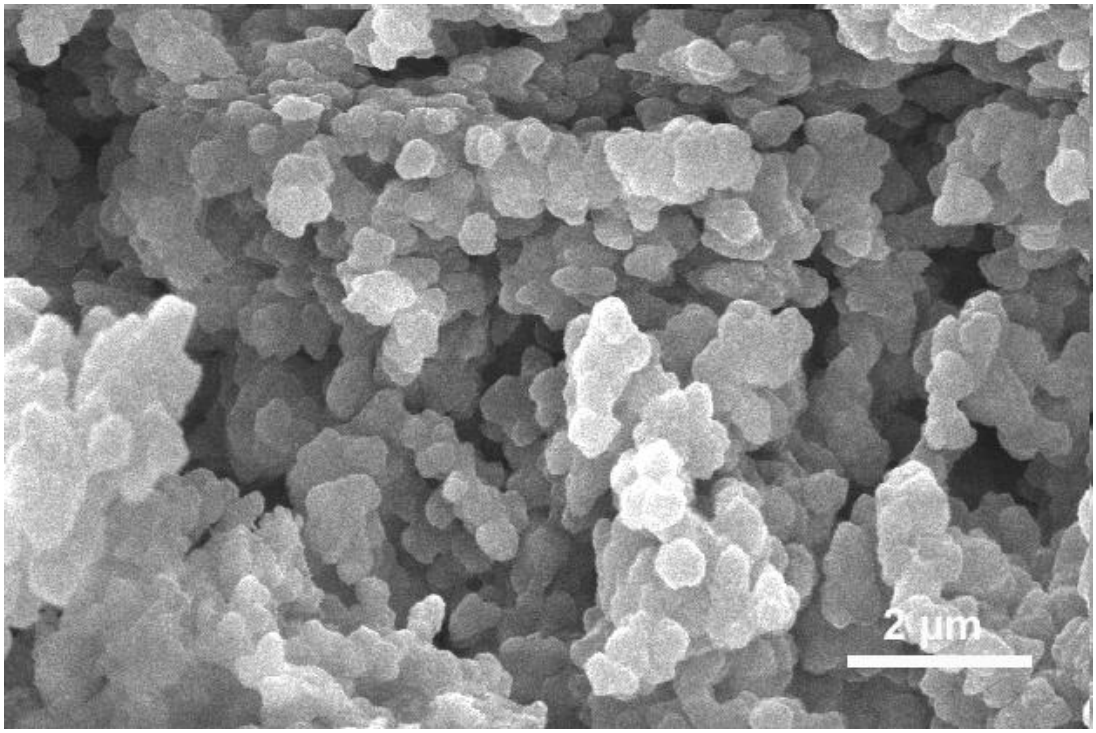


Figure S7. SEM image of solid powder of FTPA-CP.

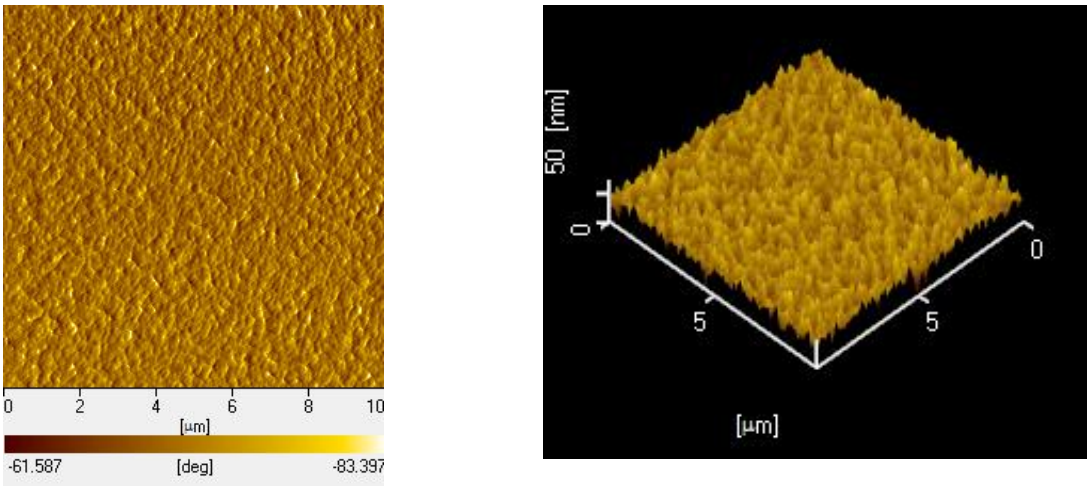


Figure S8. AFM phase and three-dimensional topography image of spin-casted thin film (10 µm×10µm) from the FTPA-HBCPN THF solution.

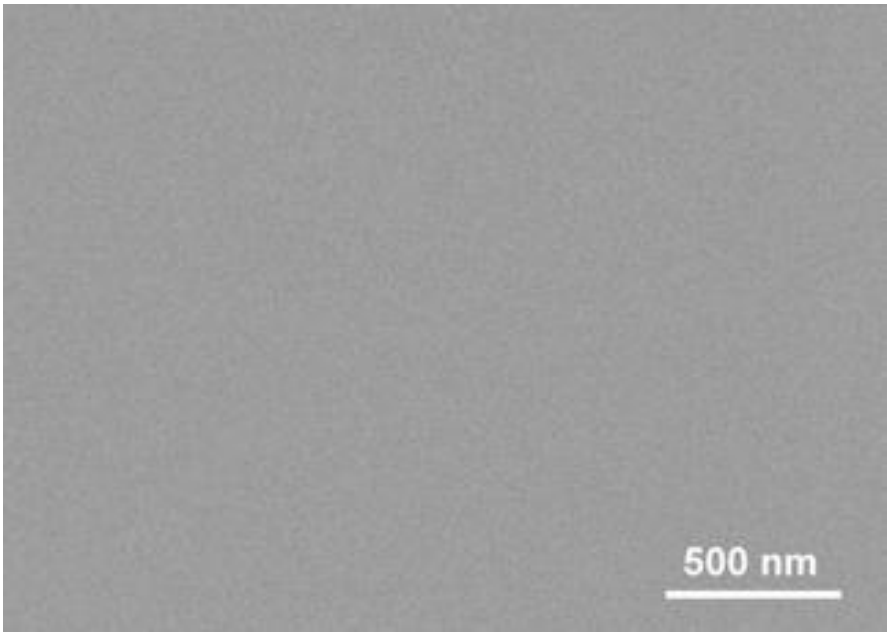


Figure S9. SEM images of thin films spun-cast from THF solutions of FTPA-LP onto glass surface.

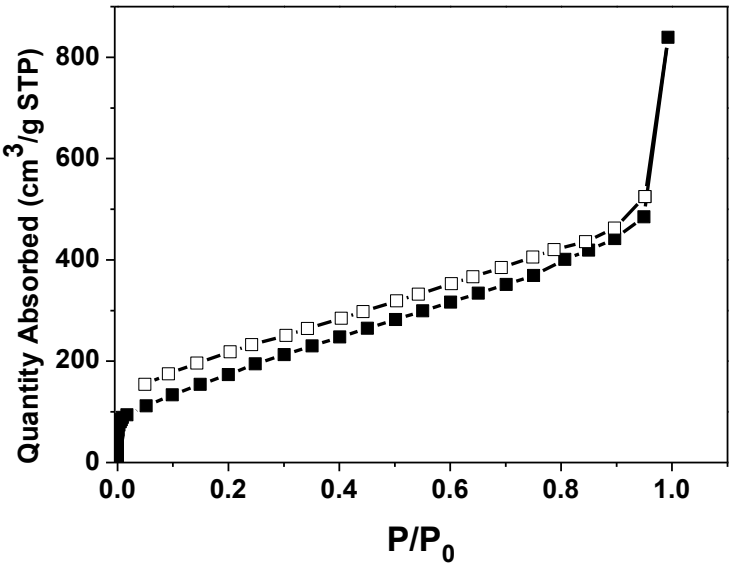


Figure S10. Nitrogen sorption isotherms for FTPA-HBCPN. Full symbols: adsorption, open symbols: desorption.

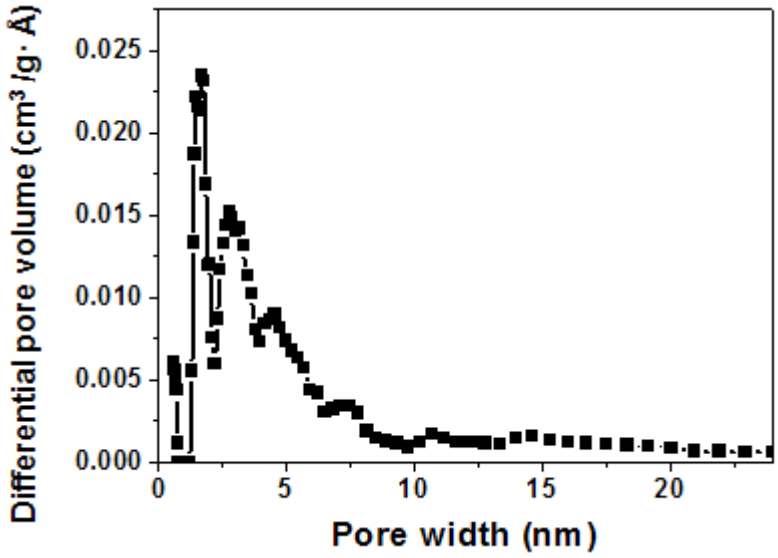


Figure S11. Pore size distributions for FTPA-CP calculated using NLDFT method (slit pore models, differential pore volume vs. pore width).

Table S2. Surface areas and pore volumes of FTPA-HBCPN, FTPA-CP and FTPA-LP.

	S_{BET} (m^2/g) [a]	$S_{Langmuir}$ (m^2/g) [b]	V_{micro} (cm^3/g) [c]	V_{total} (cm^3/g) [d]
FTPA-HBCPN	225	390	0.07	0.24
FTPA-CP	693	1161	0.24	0.62
FTPA-LP	0	0	-	-

a) Surface areas calculated from the N_2 adsorption isotherms using BET method; b) Surface areas calculated from the N_2 adsorption isotherms using Langmiur method 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 0.8. [5]

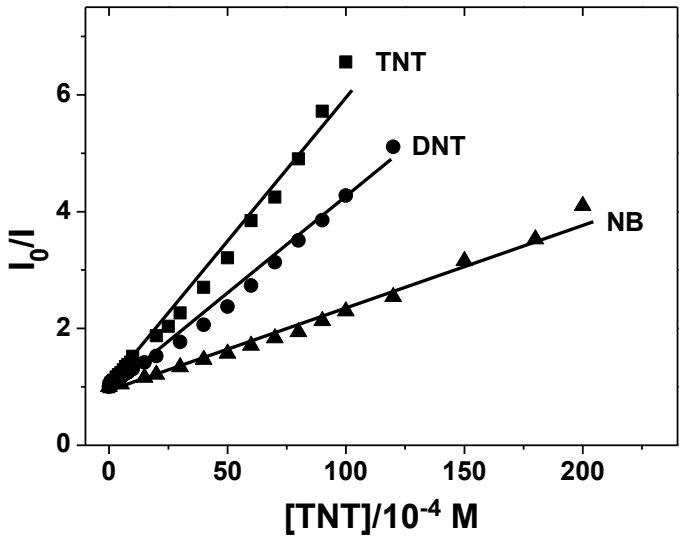


Figure S12. The Stern–Volmer plot of FTPA-HBCPN in THF solution against different nitroaromatics.

The emission intensity of FTPA-HBCPN solution decreased with the increasing concentrations of those nitroaromatics (Figure S12). According to the Stern-Volmer plot, the quenching constant (Ksv), was calculated to be 4.98 $\times 10^2$ M^{-1} for TNT, while decreased to 3.17 $\times 10^2$ M^{-1} and 1.39$\times 10^2$ M^{-1} for DNT and NB, respectively. The limits of detection for TNT, DNT and NB were 5 $\times 10^{-5}$ M, 2 $\times 10^{-4}$ M and 5$\times 10^{-4}$M, respectively. Thus, their quenching ability is TNT>DNT>NB, which is in good agreement with the trend in reduction potentials of these nitroaromatics.

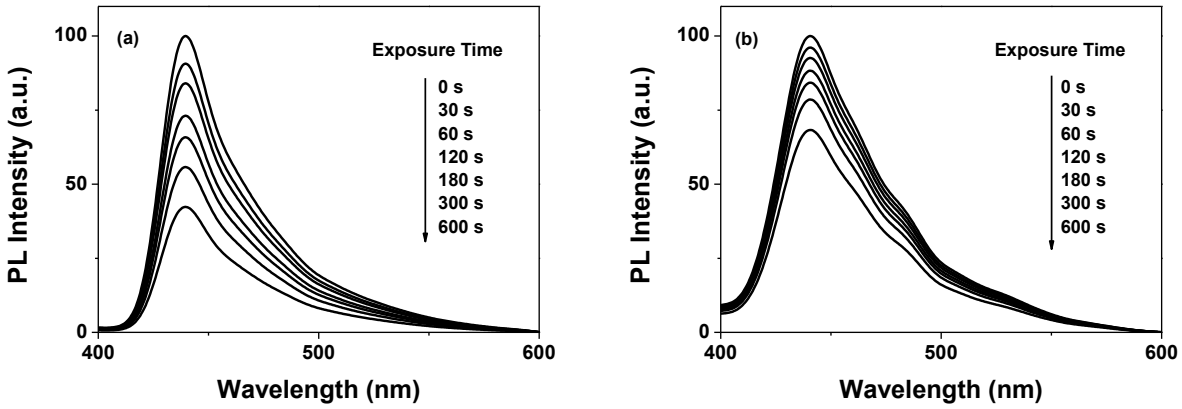


Figure S13. Fluorescence spectra of FTPA-HBCPN (a) and FTPA-LP (b) films upon exposure to TNT vapor.

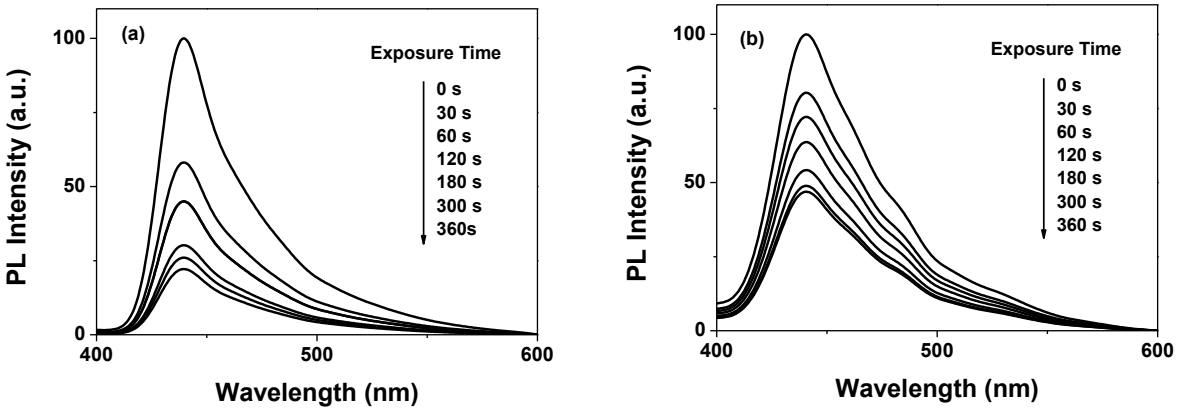


Figure S14. Fluorescence spectra of FTPA-HBCPN (a) and FTPA-LP (b) films upon exposure to DNT vapor.

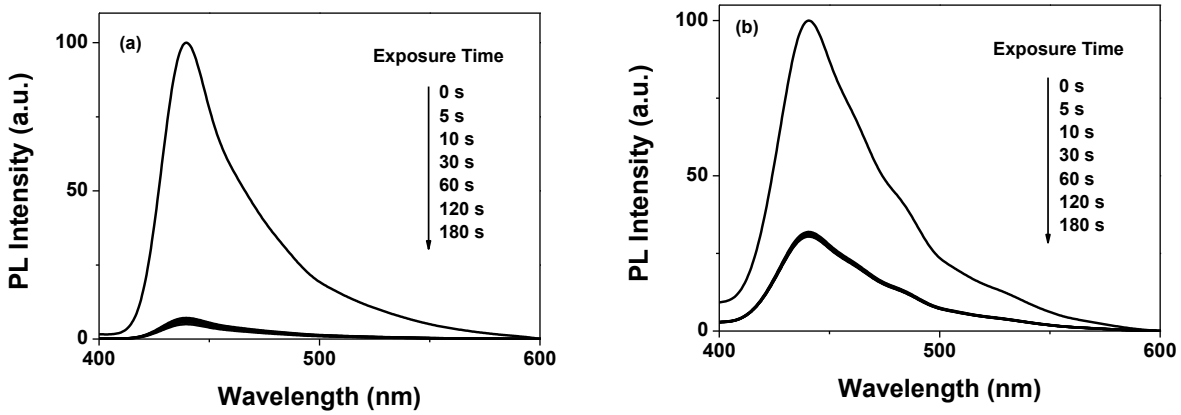


Figure S15. Fluorescence spectra of FTPA-HBCPN (a) and FTPA-LP (b) films upon exposure to NB vapor.

Table S3 The quenching efficiencies of FTPA-HBCPN and FTPA-LP upon exposure to TNT vapor.

Time (s)		0	30	60	120	180	300	600
$(I_0-I)/I_0$*	**FTPA-HBCPN**	0	0.09	0.16	0.27	0.34	0.44	0.60
	FTPA-LP	0	0.04	0.07	0.11	0.16	0.21	0.31

*I_0 is the original fluorescence intensity in absence of TNT vapor, I is the fluorescence intensity at a certain time after exposure to the saturate TNT vapor, and $(I_0-I)/I_0$ is the fluorescence quenching efficiency. [6]

Table S4 The quenching efficiencies of FTPA-HBCPN and FTPA-LP upon exposure to DNT vapor.

Time (s)		0	30	60	120	180	240	300
$(I_0-I)/I_0$*	**FTPA-HBCPN**	0	0.42	0.54	0.65	0.69	0.72	0.74
	FTPA-LP	0	0.19	0.26	0.36	0.41	0.44	0.45

*I_0 is the original fluorescence intensity in absence of DNT vapor, I is the fluorescence intensity at a certain time after exposure to the saturate DNT vapor, and $(I_0-I)/I_0$ is the fluorescence quenching efficiency. [7]

Table S5 The quenching efficiencies of FTPA-HBCPN and FTPA-LP upon exposure to NB vapor.

Time (s)		0	5	10	30	60	120	180
$(I_0-I)/I_0$*	**FTPA-HBCPN**	0	0.92	0.93	0.94	0.94	0.95	0.95
	FTPA-LP	0	0.66	0.68	0.68	0.69	0.69	0.69

*I_0 is the original fluorescence intensity in absence of NB vapor, I is the fluorescence intensity at a certain time after exposure to the saturate NB vapor, and $(I_0-I)/I_0$ is the fluorescence quenching efficiency. [6]

The vapor pressures of nitroaromatics are 2.41×10^{-1} mmHg, 1.44×10^{-4} mmHg and 8.02×10^{-6} mmHg for NB, DNT and TNT at 25 °C, respectively. Thus, the vapor concentrations of NB, DNT and TNT at 25 °C are ca.300 ppm, ca.100 ppb and ca.10 ppb, respectively.[7] Thus, the faster and greater quenching response of the FTPA-HBCPN film to NB vapor could be attributed to the much higher vapor pressure of NB.[8]

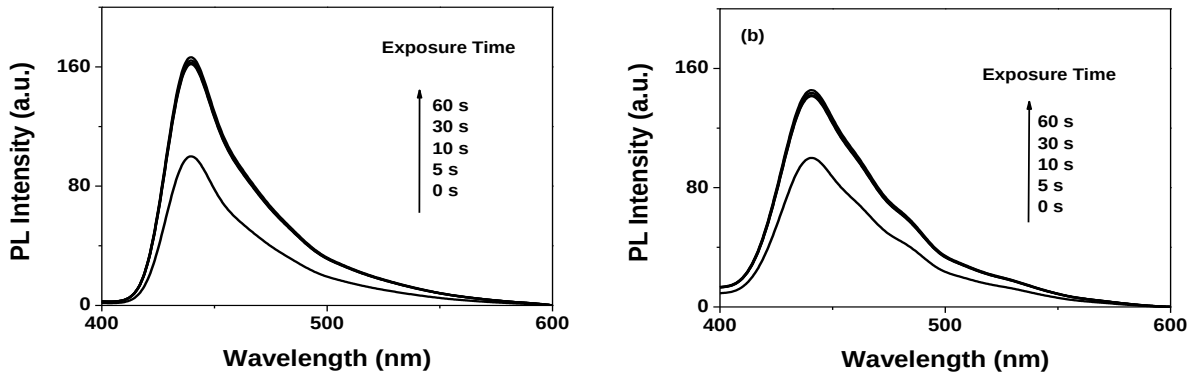


Figure S16. Fluorescence spectra of FTPA-HBCPN (a) and FTPA-LP (b) film upon exposure to toluene vapor.

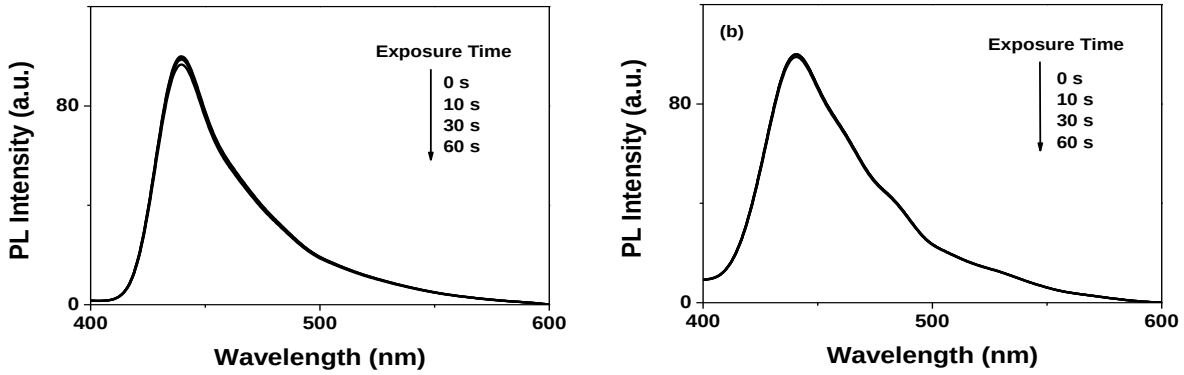


Figure S17. Fluorescence spectral changes of FTPA-HBCPN (a) and FTPA-LP (b) upon exposure to EtOH vapor.

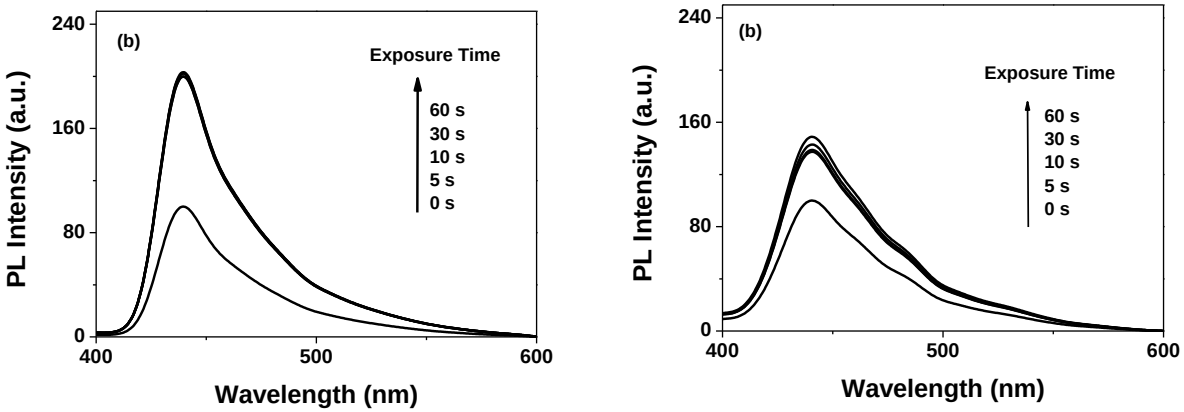


Figure S18. Fluorescence spectra of FTPA-HBCPN (a) and FTPA-LP (b) upon exposure to THF vapor.

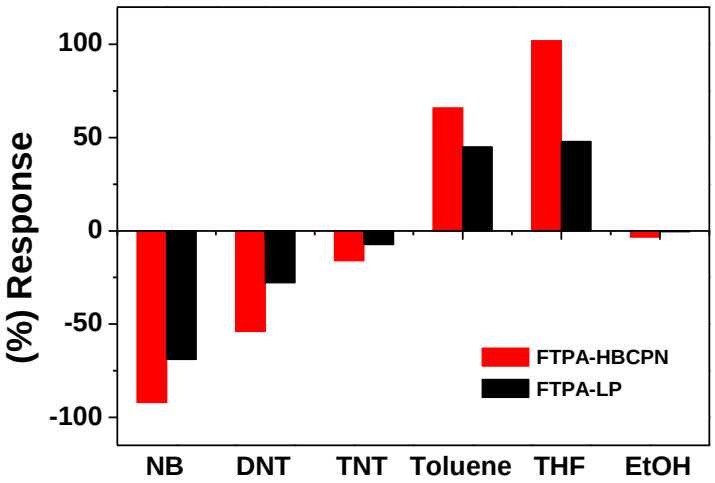


Figure S19. Changes in fluorescence emission intensity of spin-coated films upon exposure to the vapors of varied analytes at 60 s. A negative response indicates a quenching response in fluorescence intensity. A positive response indicates an enhancement response in fluorescence intensity.

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