## **Supporting Information**

## Dimensionally Controlled Water-Dispersible Amplifying Fluorescent Polymer Nanoparticles for Selective Detection of Charge-Neutral Analytes

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## 1. Synthesis

#### **<u>1-1. Synthesis of Norbornene Derivatives</u>**



Both monomers were prepared through previously reported procedures.<sup>1,2</sup>

#### *N*-cyclohexyl-*exo*-norbornene-5,6-dicarboximide (M1)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) : δ 6.27 (s, 2H), 3.91-3.96 (m, 1H), 3.25 (s, 2H), 2.60 (s, 2H), 2.10-2.18 (m, 2H), 1.20-1.83 (m, 10H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) : δ 178.22, 137.88, 51.60, 47.43, 45.42, 42.58, 28.78, 25.85, 25.07

#### exo-*N*-PEG-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (M2)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.51 (s, 2 H), 5.26 (s, 2 H), 3.59-3.70 (m, 34 H), 3.54-3.56 (m, 2 H), 3.38 (s, 3 H), 2.85 (s, 2 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 176.15, 136.60, 80.94, 71.99, 70.63, 70.13, 67.16, 59.09, 47.53, 38.22

#### **1-2.** Synthesis of [2,2]paracyclophane-1,9-diene (PCPDE)



Scheme S1. Synthetic routes to [2,2]paracyclooctaphane-1,9-diene.

#### Synthesis of 1,4-bis(thiolatomethyl)benzene (1)

A suspension of 1,4-bis(bromomethyl)benzene (9.0 g, 34.1 mmol) and thiourea (6.2 g, 96.6 mmol) was dissolved in acetone (100 mL) and stirred under reflux for 5 hours. The solution was cooled and removed most of solvent. The resulting bis(isothiouronium) salt was collected and heated under reflux with a deoxygenated solution of KOH (7.64 g, 136 mmol) in water (210 mL) under a nitrogen atmosphere for 5 hours. Sulfuric acid was added under a nitrogen atmosphere with ice bath. The reaction mixture was extracted into DCM, the combined organic layers were washed with water, dry with anhydrous MgSO<sub>4</sub>, filtered and evaporated. The crude product was precipitate from hot methanol and gave compound 1 as white solids in a yield of 97%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.28 (s, 4H), 3.73 (d, J = 7.8 Hz, 4H), 1.75 (t, J = 7.8 Hz, 2H). ). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  140.29, 128.48, 28.73. HRMS (EI, [M]<sup>+</sup>): calculated for [C<sub>8</sub>H<sub>10</sub>S<sub>2</sub>]<sup>+</sup>: *m/z* 170.0218, found *m/z* 170.0214.

#### Synthesis of 2,11-dithia[3,3]-paracyclophane (2)

A deoxygenated mixture of 1,4-bis(bromomethyl)benzene (7.6 g, 28.8 mmol) and 1,4-bis(thiolatomethyl)benzene (4.9 g, 28.8 mmol) in toluene (480 mL) was added dropwise to a solution of KOH (4.0 g, 71.3 mmol) in ethanol (720 mL) under a nitrogen atmosphere for a period at least 72 hours. After a further 2 hours, the solvent was evaporated and the residue was extracted with HCl and DCM. The organic layers were combined, washed by water, dried with anhydrous MgSO<sub>4</sub>, filtered and evaporated. The residue were purified by column chromatography with using DCM:hexane (2:8) as the eluent. The cyclic compound was obtained as white solids in a yield of 63%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  6.86 (s, 8H), 3.81(s, 8H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  135.65, 129.71, 38.45. HRMS (EI, [M]<sup>+</sup>): calculated for [C<sub>16</sub>H<sub>16</sub>S<sub>2</sub>]<sup>+</sup>: *m/z* 272.0688, found *m/z* 272.0687.

#### Synthesis of bis(sulfide) compounds (3)

Isoamyl nitrite (11.3 mL, 84.2 mmol) was added dropwise into a solution of anthranilic acid (10.0 g, 20.63 mmol) and 2,11-dithia[3,3]-paracyclophane (5.6 g, 20.6 mmol) in dichloroethane (630 mL) under reflux and a nitrogen atmosphere for at least 30 minutes. The reaction mixture was boiled under reflux for another 30 minutes. After the reaction mixture was concentrated under reduced pressure, the residue was purified by column chromatography using a solvent system of DCM and hexane (1:9). Collection of the main fraction gave the oil in a yield of 35%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.47-7.42 (m, 4H), 7.17-7.24 (m, 4H), 7.12-7.17 (m, 2H), 6.96-7.07 (m, 2H), 6.41-6.81 (m, 6H), 4.37-4.81 (m, 2H), 3.75-3.83 (m, 2H), 2.67-2.90 (m, 2H). HRMS (EI, [M]<sup>+</sup>): calculated for [C<sub>28</sub>H<sub>24</sub>S<sub>2</sub>]<sup>+</sup>: *m/z* 424.1314, found *m/z* 424.1311.

#### Synthesis of bis(sulfoxide) compounds (4)

Hydrogen peroxide (1.3 mL) was added dropwise to the solution of compound **3** (3.1 g, 7.22 mmol) in toluene (175 mL) and acetic acid (56 mL) at 0°C under a nitrogen atmosphere over a period of 20 minutes. The mixture was allowed to warm up to room temperature and stirred for additional 18 hours. The resulting solution was then extracted successively with brine and DCM, dried with MgSO<sub>4</sub> and concentrated to give pale yellow oil in an overall yield of 99%. The compounds contain a large number of stereoisomers and were used as starting materials for the next step without purification. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.67-7.86 (m, 4H), 7.42-7.58 (m, 6H), 6.83-7.28 (m, 4H), 6.12-6.63 (m, 4H), 3.94-4.20 (m, 2H), 3.5-3.61 (m, 1H), 3.38-3.50 (m, 1H), 3.15-3.36 (m, 2H). HRMS (FD, [MH]<sup>+</sup>): calculated for [C<sub>28</sub>H<sub>25</sub>O<sub>2</sub>S<sub>2</sub>]<sup>+</sup>: *m/z* 457.1291, found *m/z* 

457.1281.

#### Synthesis of [2,2]paracyclooctaphane-1,9-diene (PCPDE)

A solution of compound 4 in *N*,*N*-dimethylformamide was refluxed under a nitrogen stream for 20 hours. The solution was cooled to room temperature and extracted successively with dilute aqueous HCl and DCM, dried with anhydrous MgSO<sub>4</sub>, filtered and concentrate. The crude compound was then chromatographed over silica gel using DCM:hexane (1:9) for elution and gave compound **5** as white solids in a yield of 35%.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  7.20 (s, 4H), 6.50 (s, 8H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  137.98, 137.20, 130.80. HRMS (EI, [M]<sup>+</sup>): calculated for [C<sub>16</sub>H<sub>12</sub>]<sup>+</sup>: *m/z* 204.0934, found *m/z* 204.0927.

#### **<u>1-3. Polymer Synthesis</u>**

#### General procedure for the one-shot INCP

Both comonomers (62.8 µmol for **M1** or **M2** and 6.28-37.7 µmol for PCPDE) were weighed into a 2 mL sized screw-cap vial with a septum and purged with argon. Anhydrous and degassed THF was added (43-360 µL) to the vial. THF solution of the third-generation Grubbs catalyst (1.26 µmol) was added (20 µL) to the monomer solution at once under vigorous stirring. The mixture was stirred for 4-12 h at the room temperature. The reaction was quenched by excess ethyl vinyl ether. The crude mixture was precipitated into methanol(**P1-P3**) or cold ether at -78 °C(**P4-P5**), and the obtained powder or sticky gel was dried *in vacuo*.

#### General procedure for conventional blockcopolymerisation via sequential monomer addition.

M1 or M2 (62.8 µmol) were weighed in a 2-mL sized screw-cap vial with septum and purged with argon. Anhydrous and degassed THF was added (23-300 µL) to the vial. The THF solution of the third-generation Grubbs catalyst (1.26 µmol) was added (0.03 mL) to the monomer solution at once under vigorous stirring. After 20 minutes, the THF solution of PCPDE (6.28-37.7 µmol) was added (20-60 µL), and the mixture was stirred for 4-12h at the room temperature. The reaction was quenched by excess ethyl vinyl ether. The crude mixture was precipitated into methanol(PS1-PS3) or cold ether at -78 °C(PS4-PS5), and the obtained powder or sticky gel was dried *in vacuo*.

#### Poly(NBCyH)-*b*-poly(PCPDE) one-shot copolymers (P1-P3)

Yield: 82-93% (see Table 1). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.08-7.39 (m), 6.30-6.57 (m) 5.73 (s, 1H), 5.47-5.50 (d, 1H), 3.85 (s, 1H), 2.66-3.18 (m, 4H), 2.08 (s, 3H), 1.80 (s, 2H), 1.52-1.63 (m, 4H), 1.20-1.29 (m, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  178.6, 133.8, 132.0, 52.9, 52.6, 51.5, 50.9, 46.6, 46.1, 42.4, 41.0, 28.9, 26.0, 25.2 (all the PNBCyH-*b*-P(PCPDE) one-shot copolymers have identical <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra).

#### Poly(NBCyH)-b-poly(PCPDE) conventional copolymers (PS1-PS3)

Yield: 84-95% (see Supplementary Table 1). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.08-7.39 (m), 6.31-6.60 (m), 5.72 (s, 1H), 5.45-5.50 (d, 1H), 3.85 (s, 1H), 2.66-3.17 (m, 4H), 2.07 (s, 3H), 1.79 (s, 2H), 1.55-1.62(m, 4H), 1.20-1.28 (m, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  178.6, 133.8, 132.0, 52.9, 52.5, 51.5, 50.8, 46.6, 46.1, 42.4, 41.0, 28.9, 26.0, 25.2 (all the PNBCyH-*b*-P(PCPDE)

conventional copolymers have identical <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra).

#### Poly(ONBmPEG)-*b*-poly(PCPDE) one-shot copolymers (P4-P5)

Yield: 70-86% (see Table 1). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.28-7.37 (m), 7.06-7.13 (m), 6.71-6.77 (m), 6.53-6.59 (m), 6.36 (m), 6.08s (s, 1H), 5.77-5.80 (m, 1H), 4.92-5.01 (m, 1H), 4.45 (s, 1H), 3.33-3.67 (m, 41H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  175.6, 131.9, 131.0, 81.0, 72.0, 70.7, 70.0, 66.9, 59.1, 53.6, 53.4, 52.5, 38.1 (all the PONBmPEG-*b*-P(PCPDE) one-shot copolymers have identical <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra).

#### Poly(ONBmPEG)-b-poly(PCPDE) conventional copolymers (PS4-PS5)

Yield: 72-85% (see Supplementary Table 1). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.27-7.70 (m), 7.01-7.14 (m), 6.74-6.84 (m), 6.53-6.59 (m) 6.08 (s, 1H), 5.77-5.80 (m, 1H), 4.92-5.01 (m, 1H), 4.44 (s, 1H), 3.33-3.62 (m, 41H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  175.6, 131.8, 131.1, 81.0, 72.0, 70.6, 70.0, 66.9, 59.1, 53.5, 53.4, 52.5, 38.1 (all the PONBmPEG-*b*-P(PCPDE) conventional copolymers have identical <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra).





The <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of *N*-cyclohexyl-*exo*-norbornene-5,6-dicarboximide (**M1**)



The <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of *N*-cyclohexyl-*exo*-norbornene-5,6-dicarboximide (**M1**)



The <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of exo-*N*-PEG-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (M2)



The <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of exo-*N*-PEG-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (**M2**)





The <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum of 2,11-dithia[3,3]-paracyclophane (2).





The <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of [2,2]paracyclooctaphane-1,9-diene (PCPDE).



The <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) spectrum of PNBCyH-*b*-PPV conventional copolymer (**PS1-PS3**)



The <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) spectrum of PONBmPEG-*b*-PPV one-shot copolymer (P4-P5)



The <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) spectrum of PONBmPEG-*b*-PPV conventional copolymer **(PS4-PS5)** 

## 2. Experimental Details

## 2-1. In Situ <sup>1</sup>H NMR Analysis

157  $\mu$ mol of **M1** and 62.8  $\mu$ mol of PCPDE and hexamethyldisilane (~3 mg, an internal standard) were added into NMR tube and purged with argon. Anhydrous and degassed deuterated THF was added (550  $\mu$ L) to the NMR tube and stabilized at 0 °C in NMR instrument. Then, the initial ratio of all compounds was measured by <sup>1</sup>H NMR analysis. After that, the solution of the third-generation Grubbs catalyst (3.14  $\mu$ mol, 70  $\mu$ L, 0 °C) was added and the conversion of the two monomers was monitored by every 25 seconds. The measurement was done by Avance-500 (500 MHz for <sup>1</sup>H, Bruker, Germany) in the National center for Inter-University Research Facilities (NCIRF) at SNU.

## 2-2. Atomic Force Microscopy

Multimode 8 and Nanoscope V controller (Veeco Instrument) were used for AFM imaging. All images were obtained on tapping mode using noncontact mode tip from Nanoworld (Pointprobe tip, NCHR type) with spring constant of 42 N m<sup>-1</sup> and tip radius of  $\leq$ 8 nm. The samples were prepared by spin-coating one drop of the polymer solution (0.1 mg/mL, 3000 rpm for 30 sec using CHCl<sub>3</sub> solution, 1000 rpm for 30 sec using aqueous solution). Mica substrate was used for a CHCl<sub>3</sub> solution and the glass substrate was used for the aqueous solution.

#### 2-3. Transmission Electron Microscopy

TEM imaging were performed by JEM-2100 operated at 120 kV and SC 1000 CCD camera (Gatan Inc.). The samples for dry-TEM imaging were prepared by drop casting one drop (~ 10  $\mu$ L) of sample solution (0.1 mg/mL) on the carbon-coated copper grid.

## 3. Supporting Tables and Figures



**Figure S1.** Full scale conversion vs time plot for one-shot ROMP of **M1** and PCPDE with feed ratio [**M1**]:[PCPDE]=50:20 at 0.1 M based on the concentration of PCPDE



**Figure S2.** Comparison between the steric hindrance near the reactive olefin of NB and PCPDE monomers.

(a) P5 and PS5, tt, <sup>1</sup>H NMR, 500 MHz, *d*<sub>6</sub>-DMSO (b) P5



Figure S3. (a) Overlays of <sup>1</sup>H NMR spectrum (500 MHz,  $d_6$ -DMSO) of aromatic and olefinic regions of PONBmPEG-b-PPV block copolymers synthesized by one-shot ROMP (P5) and the conventional sequential addition of monomers (PS5). Additional peaks of P5 indicated that a few PCPDEs were reacted during the propagation of PONBmPEG 1st block. Integrated spectrum of P5 (b) and PS5 (c) showed 21.41 larger value of the integration of PPV from P5, which means average 1.8 equivalents of PCPDE was reacted.



Figure S4. AFM and TEM images and their height and width profiles of P1 (a, d), P2 (b, e) and P3 (c, f). Height and width of nanostructures increased with increasing DP of PPV.



Figure S5. (a) AFM topography, (b) height profile, and (c) 3D projection image of P2, indicating undulated nanocaterpillar structure.



**Figure S6.** Analysis of samples taken during one-shot ROMP of PNBCyH-*b*-PPV with a monomer ratio of 50:30 ([NBCyH]:[PCPDE]). (a) PCPDE conversion plot. The conversions and average DP of PPV were measured by <sup>1</sup>NMR. UV/Vis absorbance (b), DLS profiles (c), and AFM and TEM images of samples taken at 3 min (d, g), 10 min (e, h) and 60 min (f, i) after initiation. The measured samples were prepared by taking aliquots during the polymerization at different times and then the samples were diluted in THF without any quenching or precipitation processes.



Figure S7. DLS profiles of P4-P5 in chloroform under concentration of 0.1 mg/ml.



Figure S8. AFM and TEM images of P4 (a, b) and P5 (c, d) in chloroform.



**Figure S9.** Cryo TEM images of **P5** in chloroform (a) and water (b). Inset images for higher magnification. Higher electron density of a chloroform solvent caused brighter PONBmPEG shell part in the solution, different with the image of aqueous solution. The experiments were performed with a thin film of solution (5  $\mu$ L, 0.1 mg/mL) transferred to a lacey supported grid. The thin solution films were prepared under solvent vapor saturated condition (chloroform or water) within a custom-built environmental chamber in order to prevent evaporation of solvent from sample solution. The excess liquid was blotted with filter paper for 2-4 seconds, and the thin solution films were rapidly vitrified by plunging them into liquid ethane (-170 °C) using Gatan Cryoplunge<sup>TM</sup>3 system. The grid was transferred on a Gatan 626 cryoholder, using a cryo-transfer device. After that they were transferred to a JEM-2100. Direct imaging was carried out at a temperature of approximately -175 °C and with a 120 kV accelerating voltage.

**Table S1.** Synthesis of PNB-*b*-PPV by conventional sequential addition of the monomers using **M1**, **M2** and PCPDE



Polymer 1	NIDa	[PCPDE]	time	conv. <sup>b</sup>	Yield	$D_{\rm h}{}^{\rm c}$
	IND		(h)	(%)	(%)	(nm)
PS1	M1	10	4	>99	84	80
PS2	M1	20	8	>99	90	150
PS3	M1	30	12	>99	95	290
PS4	M2	5	4	>99	72	80
PS5	M2	15	12	>99	85	200

<sup>a</sup>Use 50 equivalent. <sup>b</sup>Measured by <sup>1</sup>H NMR. <sup>c</sup>Measured by DLS. (in chloroform for **PS1-PS3** and in water for **PS4-PS5** under concentration of 0.1 mg/ml)



Figure S10. DLS profiles of PS1-PS3 in chloroform (a), PS4-PS5 in water (b), and PS4-PS5 in chloroform (c) under concentration of 0.1 mg/ml.

**Table S2.** Average hydrodynamic diameter  $(D_h)$  and polydispersity index (PDI) values of different block copolymers in chloroform and water. <sup>a</sup>

polymer	Solvent	$D_{\rm h}({\rm nm})$	PDI	polymer	Solvent	$D_{\rm h}({\rm nm})$	PDI
P1	CF	80	0.146	PS1	CF	80	0.214
P2	CF	155	0.176	PS2	CF	150	0.203
P3	CF	220	0.267	PS3	CF	290	0.281
	CF	7.5/40	0.701 <sup>b</sup>	PS4	CF	10.8/55	0.581 <sup>b</sup>
P4	Water	70	0.164		Water	80	0.189
Р5	CF	140	0.271	PS5	CF	40/195	0.334 <sup>b</sup>
	water	135	0.306		water	200	0.306

<sup>a</sup>all measurement was done by intensity distribution with the solutions under concentration of 0.1 mg/ml. <sup>b</sup>broad dispersities were originated from bimodal distribution of samples.



Figure S11. AFM and TEM images of PS1 (a, d) and PS2 (b, e), and PS3 (c, f) in chloroform.



Figure S12. AFM and TEM images of PS4 in water (a, e) and chloroform (b, f), and PS5 in water (c, g) and chloroform (d, h).



Figure S13. Film XRD spectra of P1-P3 (a) and PS1-PS3 (b) compared with the spectrum of PNBCyH homopolymer, and the spectra of P4-P5 (c) and PS4-PS5 (d) compared with the spectrum of PONBmPEG homopolymer. All samples were prepared by drop casting of polymer solutions (10 mg/ml, chloroform) on SiO<sub>2</sub> wafer.



**Figure S14.** The FTIR spectra of **P2** and PNBCyH homopolymer indicating both *cis* (CH=CH at 880 cm<sup>-1</sup>) and *trans* (CH=CH at 970 cm<sup>-1</sup>) vinylene in PPV backbone.



Figure S15. The absorbance spectrum of (a) P1-P3 in chloroform and (b) P4-P5 in chloroform and aqueous solution. The emission spectrum of (c) P1-P3 in chloroform and (b) P4 and P5 in chloroform and aqueous solution. (Concentration of all polymer solution = 0.05 mg/ml) The emission of P1 at the region of shorter wavelength and smaller  $2^{nd}$  peak indicates weaker aggregation due to shorter PPV. The additional peak at 473 nm of P4 in chloroform stands for single-chromophore emission.



**Figure S16.** Cyclic voltammograms of (a) ferrocene standard (1 mM in acetonitrile) and (b-d) **P1-P3** (polymer film on the glassy carbon working electrode prepared by drop casting of the polymer solution with the concentration of 5 mg/ml). Ag/Ag+ (0.1M AgNO<sub>3</sub> in acetonitrile) reference electrode and platinum wire counter electrode were used at a scan rate of 100 mV/s.

Polymer	Optical $E_{\rm g}$ (eV) <sup>a</sup>	HOMO (eV) <sup>b</sup>	LUMO (eV) <sup>c</sup>
P1	2.7	-5.6	-2.9
P2	2.6	-5.6	-3.0
<b>P</b> 3	2.6	-5.6	-3.0

**Table S3.** Optical  $E_g$ , HOMO, and LUMO level calculated from the UV/vis spectra and CV spectra.

<sup>a</sup>calculated from the onset point of the UV/vis spectra (Supplementary Figure 12). <sup>b</sup>HOMO = -4.8- (E<sub>ox,onset</sub>-Fc<sup>1/2</sup>) (Figure S16). <sup>c</sup>LUMO = HOMO + optical E<sub>g</sub>

Table S4. Quantum efficiency (QE) of P1-P5

Polymer	Solvent	External QE (%)	Internal QE (%)
P1	chloroform	5.1	8.8
P2	chloroform	9.6	14.2
P3	chloroform	8.4	11.2
P4	chloroform	12.2	17.8
	water	1.6	2.4
P5	chloroform	10.4	17.5
	water	2.5	3.3

The above values were obtained by absolute QE measurement using integrating hemisphere technique (QE-1200, Otsuka Electronics) at the transmittance values between 0.2-0.6 at the  $\lambda_{max}$ .

#### **Stern-Volmer Plots**



Figure S17. Stern-Volmer plot for the fluorescence titration of P4 with DNT.  $K_{SV}$  is  $3.3 \times 10^3$  M<sup>-1</sup>.



Figure S18. Stern-Volmer plot for the fluorescence titration of P4 with TNT.  $K_{SV}$  is  $1.5 \times 10^4$  M<sup>-1</sup>.



Figure S19. Stern-Volmer plot for the fluorescence titration of P5 with DNT.  $K_{SV}$  is  $7.2 \times 10^4$  M<sup>-1</sup>.



Figure S20. Stern-Volmer plot for the fluorescence titration of P5 with DNT.  $K_{SV}$  is  $3.9 \times 10^5$  M<sup>-1</sup>.

**Table S5**. Stern-Volmer quenching constants of various fluorescent probes, representative of their own material class, toward TNT and paraquat in water.

Probe	Structure/Notes	Analyte	Quenching Constant (Ksv, M <sup>-1</sup> )	Ref <sup>a</sup>
PPV	SO <sub>3</sub> - SO <sub>3</sub> - CH <sub>3</sub> n	TNT	1.02 × 10 <sup>4</sup>	41
PPV	$SO_3^-$ $OCH_3^-$ + Cationic Surfactant	TNT	9.13 × 10 <sup>4</sup>	41
PPV	SO <sub>3</sub> -	Paraquat	1.7 × 107	37
Oligosilole Nanoparticle	Ph $PhPh$ $PhSi$ $h$	TNT	4,500	42
Metal-Organic Framework	$Zr_6O_4(OH)_4(TCPP)_3$ (TCPP = tetrakis(4-carboxyphenyl)porphyrin)	TNT	$3.5 \times 10^{4}$	46
Pentacenequinone Derivative Nanoaggregates	o contractions of the second s	TNT	4,300	44
PPE Thin Film	$ \begin{array}{c} OC_{16}H_{33} \\ \hline \\ C_{16}H_{33}O \end{array} \\ n \end{array} $	TNT	7,750	43
Pyrene- Containing PPE Thin Film	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	TNT	$3.65 \times 10^{4}$	43
Pyrene- Polyethersulfone Composite Nanofiber	N/A	TNT	1.80 × 10 <sup>5</sup>	45

<sup>a</sup>The references are numbered from the main paper

#### **Time-Resolved Photoluminescence**



Figure S21. Time-resolved photoluminescence decay profiles of P4 in water in the presence of various amounts of DNT.

### **Paraquat Quenching Studies**



Figure S22. Photoluminescence spectra of aqueous P5 in presence of various amounts of paraquat dichloride.



Figure S23. Photoluminescence spectra of P5 in 1 mM aqueous paraquat upon treatment with increasing amounts of TNT.

#### 4. References

- 1. Contreras, A. P. *et al.* Synthesis and Gas Transport Properties of New High Glass Transition Temperature Ring-Opened Polynorbornenes. *Macromolecules* **35**, 4677-4684 (2002).
- 2. Menk, F. *et al.* Synthesis of Functional Block Copolymers Carrying One Poly(pphenylenevinylene) and One Nonconjugated Block in a Facile One-Pot Procedure. *Macromolecules* **49**, 2085-2095 (2016).