# Supporting information for

# Water-dispersible hyperbranched conjugated polymer nanoparticles with sulfonate terminal groups for amplified fluorescence sensing of trace TNT in aqueous solution

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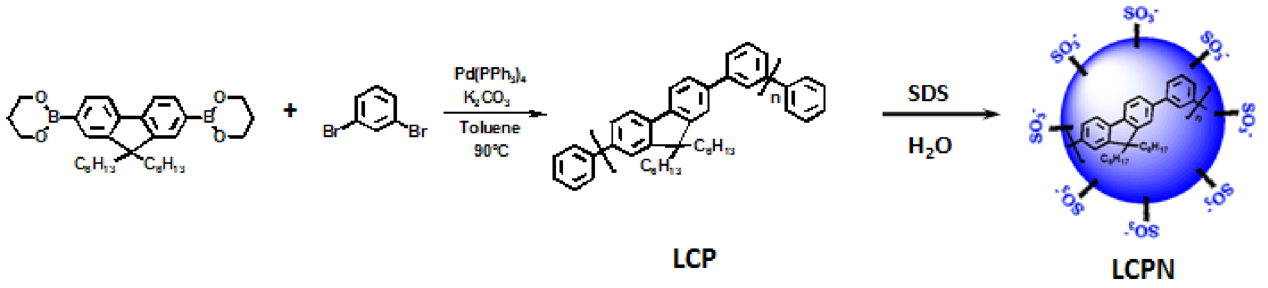



**Scheme S1.** The preparation of LCP and LCPN.

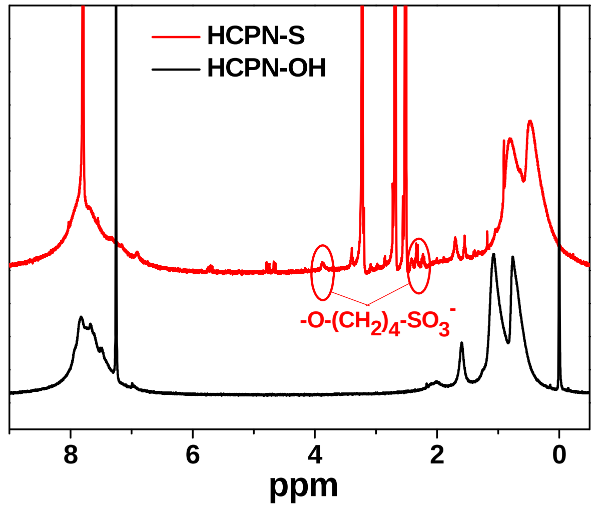



**Figure S1** $^1$H NMR spectra of HCPN-OH in $CDCl_3$ and HCPN-S in DMF-$d_7$.

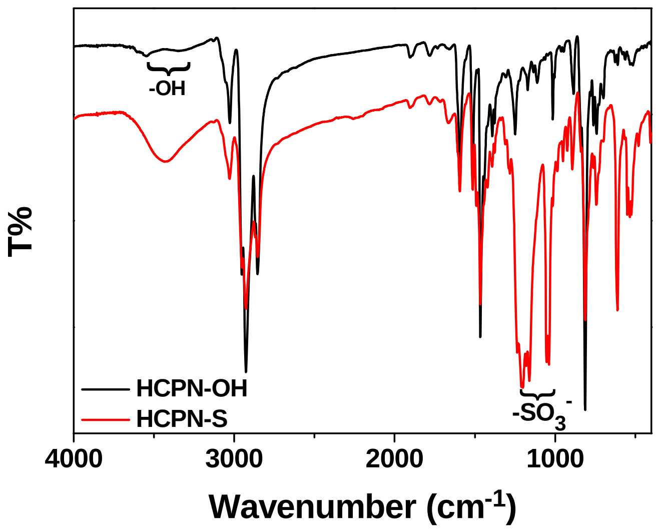



**Figure S2** FT-IR spectra of HCPN-OH and HCPN-S.

**Table S1.** Elemental analysis of HCPN-OH and HCPN-S

| | | C (%) | H(%) | N (%) | S (%) |
|---|---|---|---|---|---|
| HCPN-OH | Theoretical[a] | 91.28 | 7.78 | 0 | 0 |
| | experimental | 89.28 | 7.89 | 0 | 0 |
| HCPN-S | Theoretical[a] | 86.09 | 7.44 | 0 | 1.74 |
| | experimental | 84.91 | 7.72 | 0 | 0.94 |

[a] The theoretical value are based on three fluorene units and two triphenylbenzene units and one terminal units.[1]

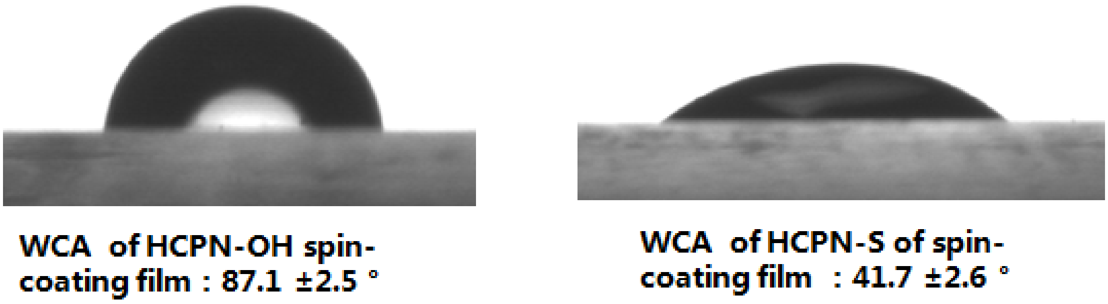



**Figure S3** Water contact angle (WCA) images of HCPN-OH and HCPN-S in their spin-coating films

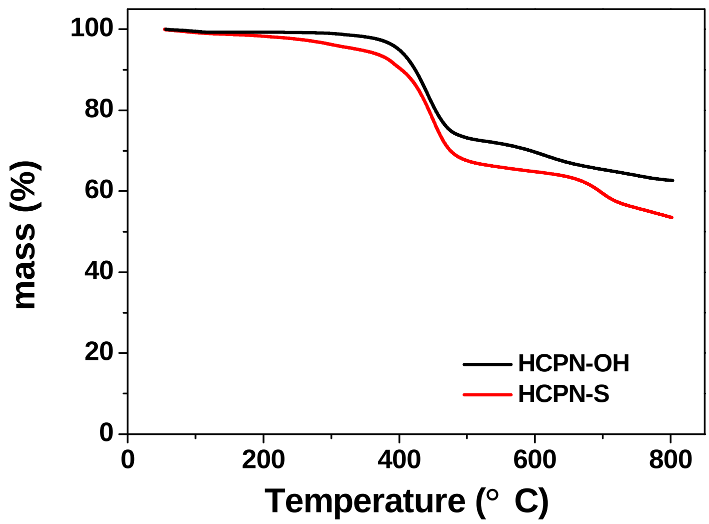



**Figure S4** TGA curve recorded under N2 for HCPN-OH and HCPN-S.

Both HCPN-S and HCPN-OH are thermally stable in nitrogen atmosphere up to 340 °C.

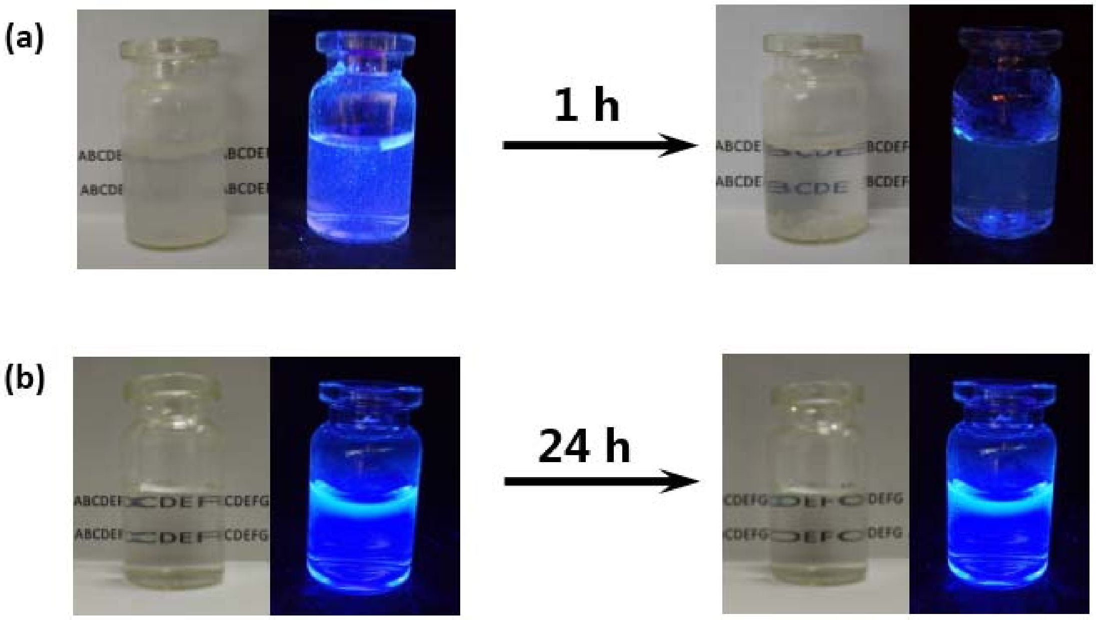



**Figure S5.** The images of HCPN-OH (a) and HCPN-S (b) in water under sunlight and a UV lamp (concentrations: 0.05 g/L)

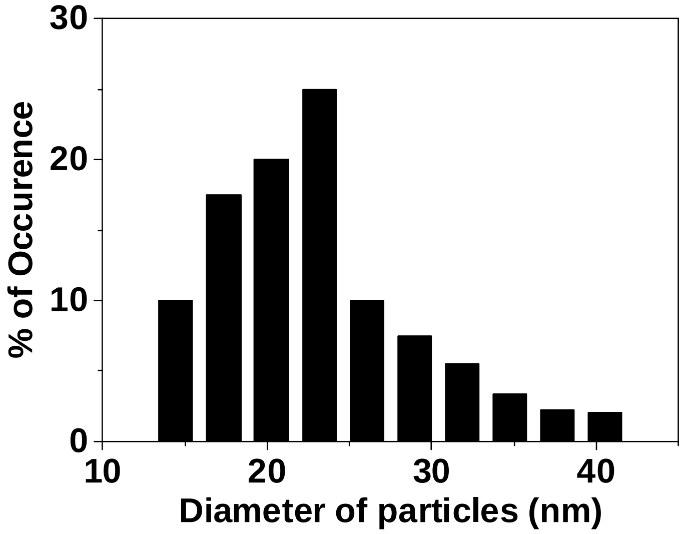
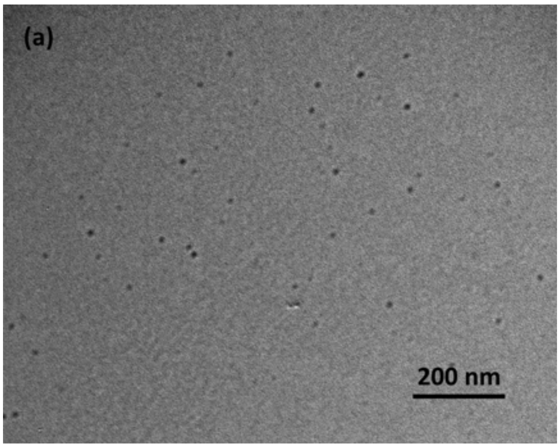



**Figure S6** Size distribution histogram using TEM images of HCPN-OH.



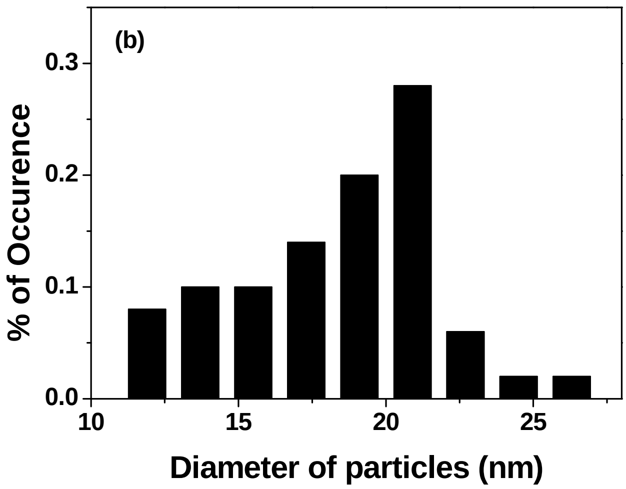




**Figure S7** (a) TEM image by drop-casting aqueous LCPN dispersion onto a copper grid. (b) Size distribution histogram using TEM images of LCPN.

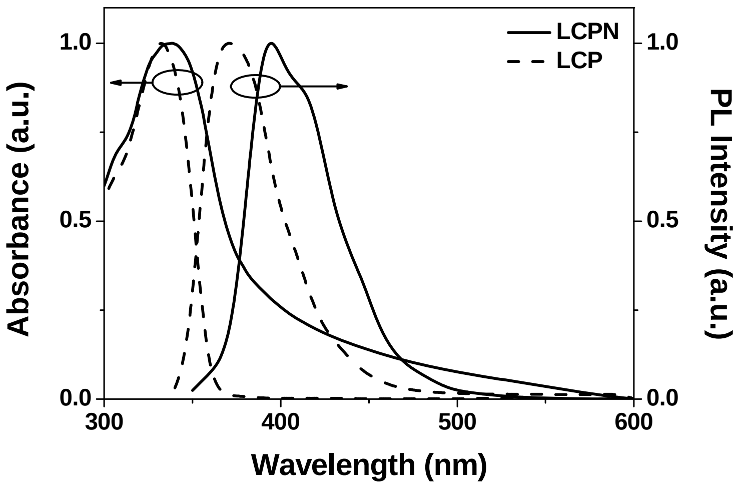



**Figure S8** Absorption and emission spectra of aqueous LCPN dispersion and LCP in THF solution.

**Table S2** Optical properties of HCPN-OH in THF, HCPN-S in water, LCP in THF and LCPN in water.

| Samples | UV ($\lambda_{max}$ [nm]) | PL ($\lambda_{max}$ [nm]) | $\Phi_{PL}$ |
|---|---|---|---|
| **HCPN-OH** | 345 | 396 | 0.38 |
| **HCPN-S** | 340 | 419 | 0.23 |
| **LCP** | 332 | 370 | 0.49 |
| **LCPN** | 340 | 394 | 0.32 |

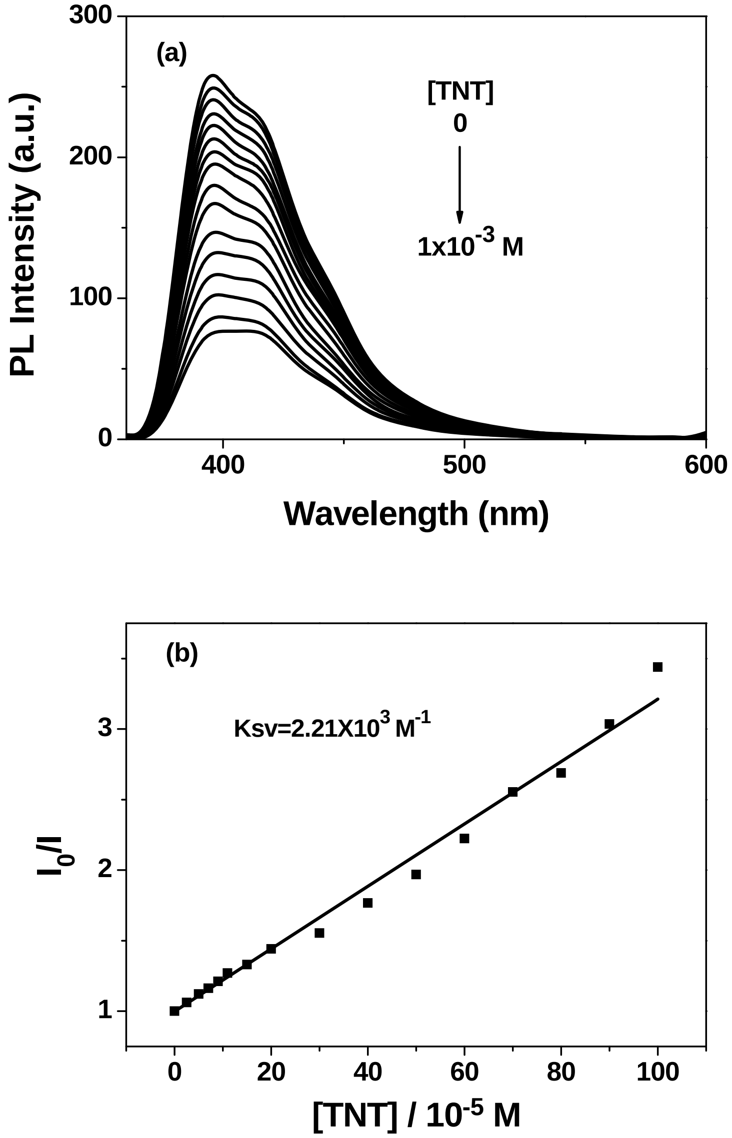



**Figure S9** (a) Fluorescence response profiles of HCPN-OH in THF upon addition of TNT. The excitation wavelength was 345 nm. (b) Stern–Volmer plots for the fluorescence quenching of HCPN-OH at 398 nm by TNT.

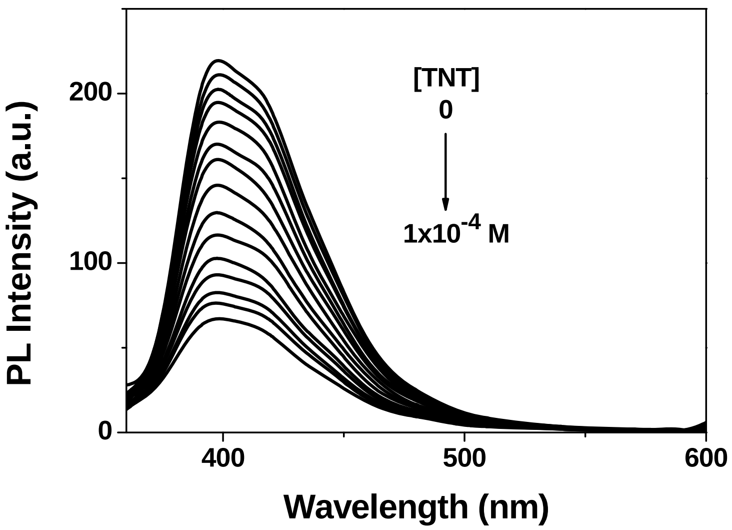



**Figure S10** Fluorescence response profiles of aqueous LCPN dispersion upon addition of TNT. The excitation wavelength was 340 nm.

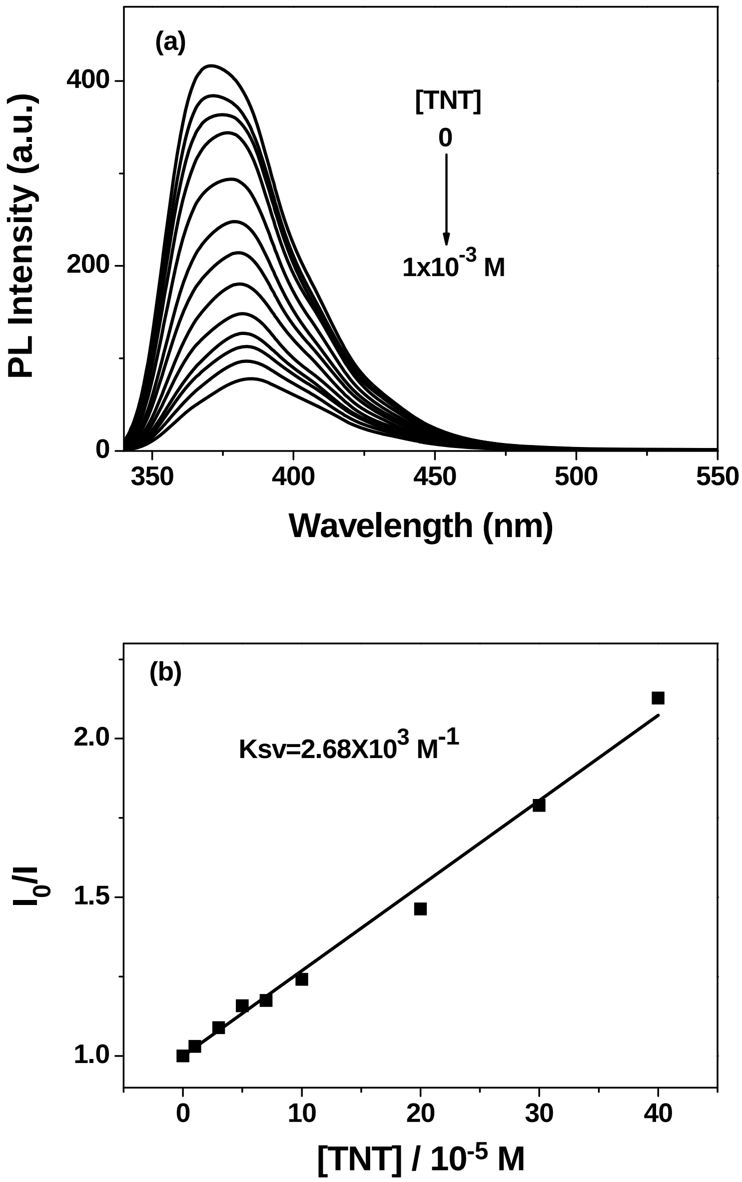



**Figure S11** (a) Fluorescence response profiles of LCP in THF solution upon addition of TNT. The excitation wavelength was 330 nm. (b) Stern–Volmer plots for the fluorescence quenching of LCP at 370 nm by TNT.

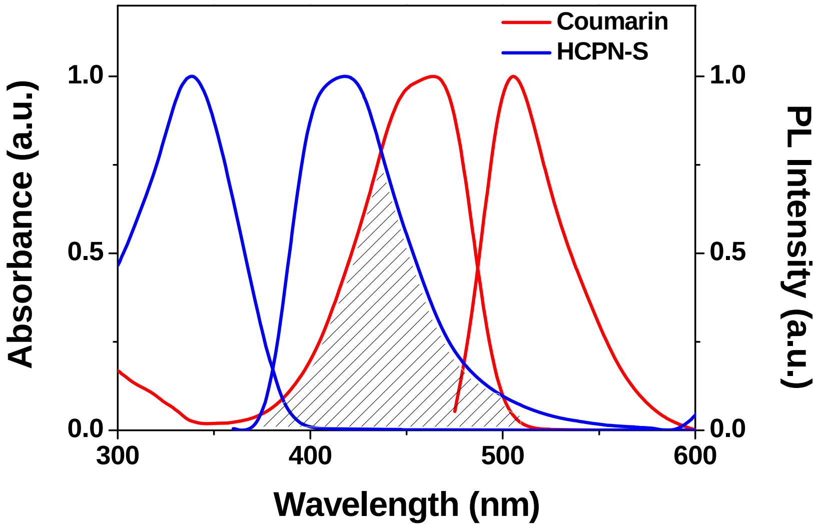



**Figure S12** Absorption and emission spectra of aqueous HCPN-S dispersion (blue) and coumarin-6 in DMF solution (red). The shadow represents that overlap between the emission spectrum of HCPN-S and absorption spectrum of coumarin-6.

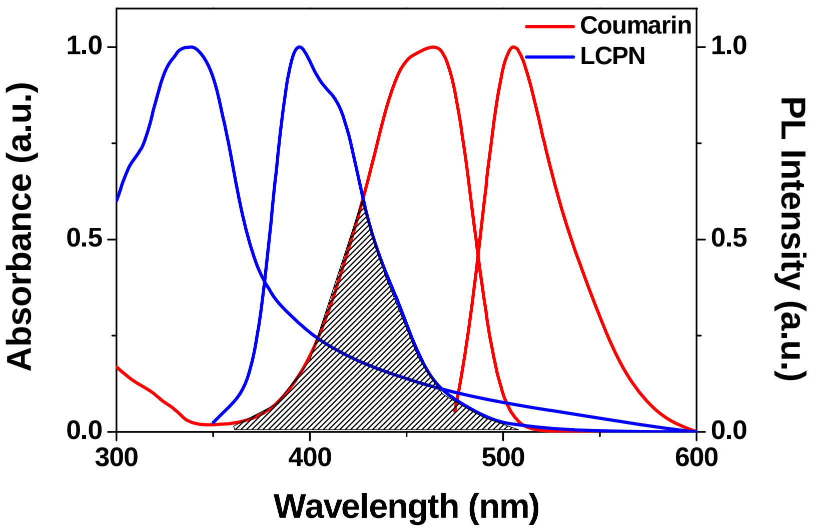



**Figure S13** Absorption and emission spectra of aqueous LCPN dispersion (blue) and coumarin-6 in DMF solution (red). The shadow represents that overlap between the emission spectrum of LCPN and absorption spectrum of coumarin-6.

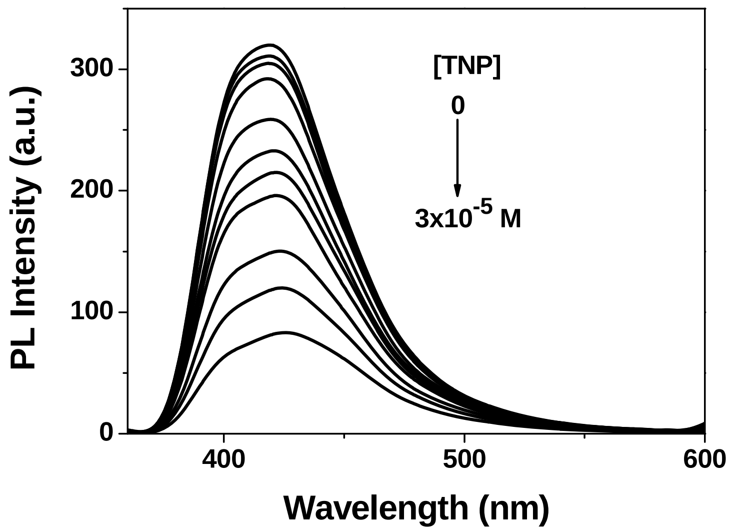



**Figure S14** Fluorescence response profiles of aqueous HCPN-S dispersion upon addition of TNP. The excitation wavelength was 340 nm.

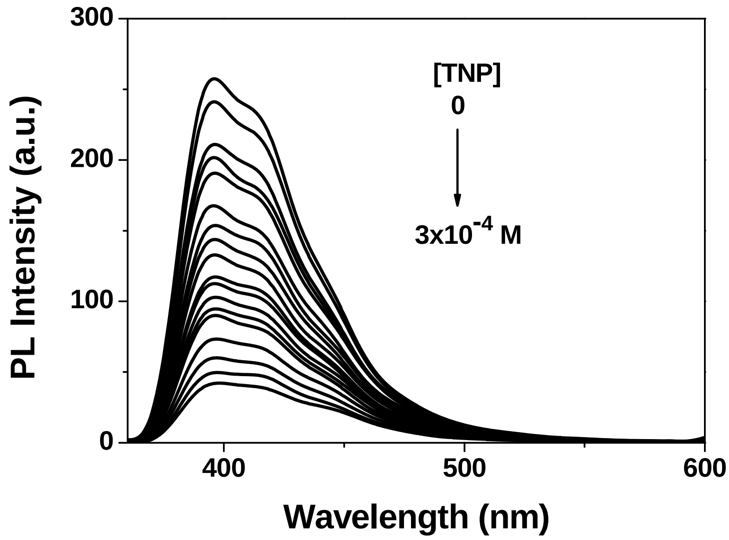



**Figure S15** Fluorescence response profiles of HCPN-OH in THF upon addition of TNP. The excitation wavelength was 345 nm.

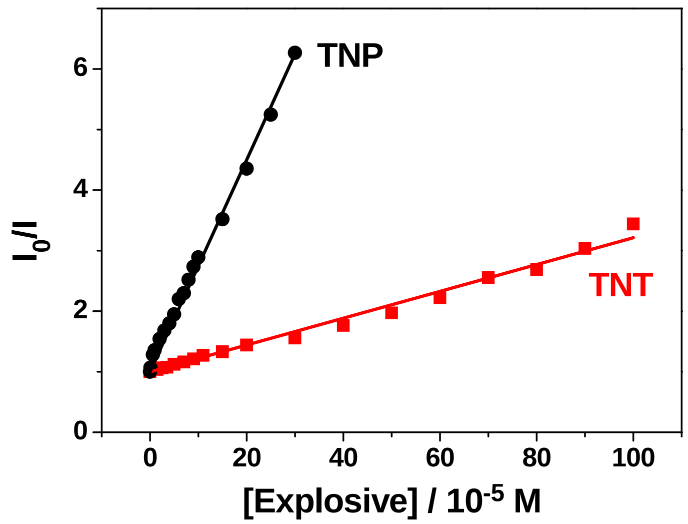



**Figure S16** Stern–Volmer plots for the fluorescence quenching of HCPN-OH at 398 nm by TNT and TNP.

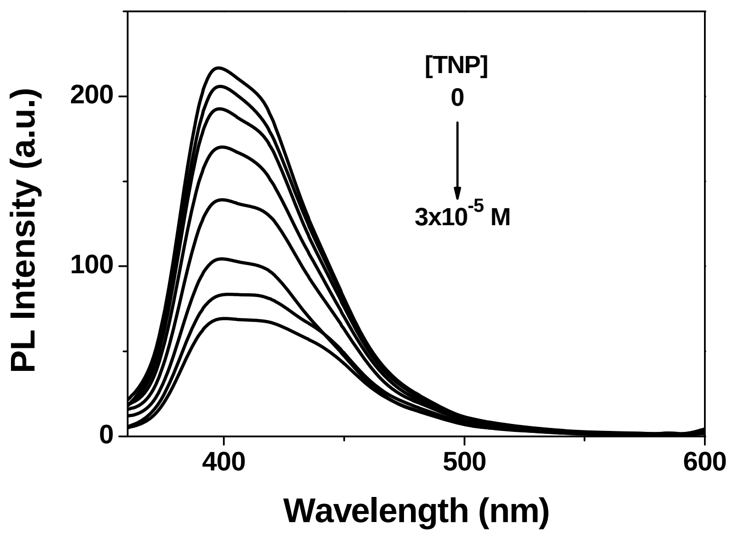



**Figure S17** Fluorescence response profiles of aqueous LCPN dispersion upon addition of TNP. The excitation wavelength was 340 nm.

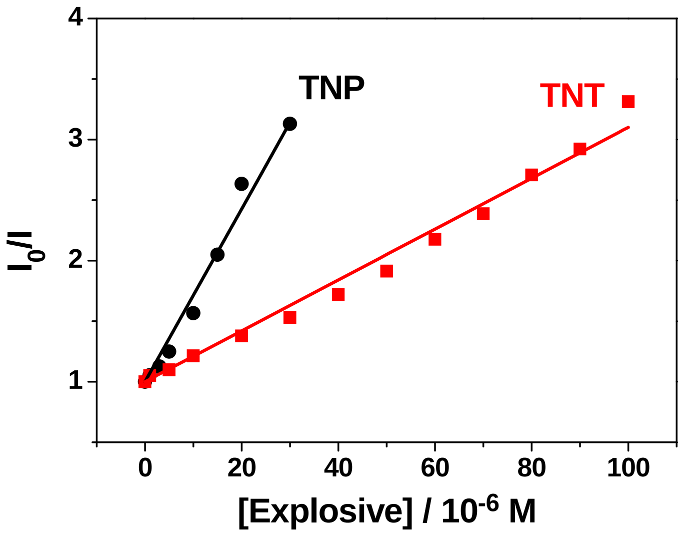



**Figure S18** Stern–Volmer plots for the fluorescence quenching of LCPN at 394 nm by TNT and TNP.

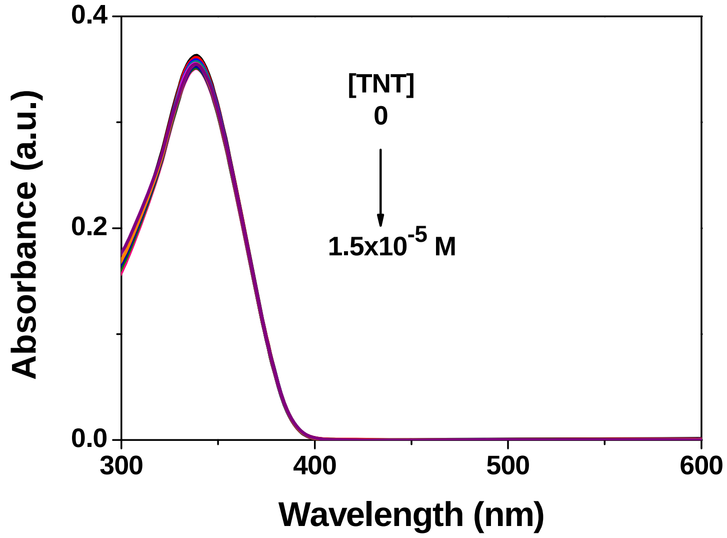



**Figure S19** Absorption spectra of aqueous HCPN-S dispersion upon addition of TNT.

The hardly changed absorption spectra of HCPN-S upon addition of TNT indicated that fluorescence resonance energy transfer (FRET) and the inner filter effect should not be considered as the major factors in the fluorescence quenching of HCPN-S by TNT. Considering our previous results,[2-4] the quenching could be explained by photoinduced electron transfer (PET) between HCPN-S and TNT.

**Table S3** A comparative study of recently reported conjugated polymer or conjugated polymer nanoparticles for sensing of TNT with our results.

| Publication | Material used | Stern-Volmer Constant ($M^{-1}$) | Detection Limit | Medium |
|---|---|---|---|---|
| Current Manuscript | ***Hyperbranched conjugated polymer nanoparticles*** | ***1.21×10⁶*** | ***3.7 nM (0.8 ppb)*** | ***water*** |
| *J. Am. Chem. Soc.* **2003**, 125, 3821–3830 | Poly(tetraphenylsilole) | $3.99\times10^{3}$ | - | Toluene |
| *J. Phys. Chem. C* **2008**, 112, 881–884. | Pentiptycene-based conjugated polymer | 730 | - | chloroform |
| *Chem. Commun*., **2005**, 5465–5467 | Colloidal oligo(tetraphenyl)silole nanoparticles | $4.5\times10^{3}$ | 20 ppb | THF/H2O |
| *Chem. Mater.* **2007,** *19*, 6459–6470 | Poly(tetraphenylsilolevinylene) | $1.05\times10^{4}$ | - | Toluene |
| *Sens. Actuators, B* **2010,** 145, 438–443 | Conjugated polymer-grafted silica nanoparticles | $3.11\times10^{3}$ | 1 µM | DMSO |
| *Macromolecules* **2011**, 44, 4759–4766 | Poly(pyrene-co-phenyleneethynylene)s film | $3.65\times10^{4}$ | - | Aqueous medium |
| *Macromolecules* **2011**, 44, 5089–5092 | Conjugated polymer (TPE-BT-Fl ) Film | $1.2\times10^{5}$ | 23 ppb | Aqueous solutions |
| *J. Mater. Chem.*, **2012,** 22, 3075–3081 | Conjugated Poly(aryleneethynylenesiloles) | $1.11\times10^{3}$ | 1 ppm | Dichloromethane |
| *Anal. Chim. Acta*, **2012**, 744, 82– 91 | benzothiophene based conjugated polymer | 1789 | 0.1 mM | chloroform |
| *Chem. Commun*., **2012,** 48, 4633–4635 | PPV@MSN-$NH_2$ | $7.42\times10^{4}$ | 0.6 µM | Ethanol |
| *J. Polym. Sci., Part A: Polym. Chem.*, **2013**, 51, 4150–4155 | Conjugated polymer (PFBT) nanoparticles | $1.2\times10^{4}$ | 29 µM | Acetonitrile (3.13%) in water |
| *Polymer*, **2014,** 55, 2792-2798 | t-Butyl pyrene containing poly(arylene ethynylene)s film | $1.45\times10^{5}$ | - | Aqueous medium. |
| *J. Polym. Sci., Part A: Polym. Chem.*, **2014**, 52, 1487–1492 | Conjugated polymers | 980 | - | THF |
| *Polym. Chem.*, **2014**, 5, 4521–4525 | Hyperbranched conjugated polymer nanoparticles | $1.38\times10^{3}$ | 10 µM | THF |
| *Dyes and Pigments* ***2016***, 125, 367-374. | GO-PPV@MSN hybrid material | $2.37\times10^{5}$ | 0.13 µM | water |
| *Polym. Chem.*, **2016**, 7, 310-318 | Benzo[5]helicene-based conjugated polymers | 331 | - | chloroform |
| *ACS Appl. Mater. Interfaces* **2016,** *8*, 24901−24908 | NMPPY−SDBS | 59526 | 100 nM | water |

**References**

[1] X. Wu, H. Li, Y. Xu, H. Tong, L. Wang, *Polym. Chem.* **2015**, *6*, 2305.

[2] H. Li, X. Wu, B. Xu, H. Tong, L. Wang, *RSC Adv.* **2013**, *3*, 8645.

[3] X. Wu, H. Li, B. Xu, H. Tong and L. Wang, *Polym. Chem.* **2014**, *5*, 4521.

[4] X. Wu, H. Li, Y. Xu, B. Xu, H. Tong and L. Wang, *Nanoscale* **2014**, *6*, 2375.