

Supporting Information for:

Fluorescent Hyperbranched Conjugated Polymer Nanoparticles for Cyanide Ion Sensing

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Synthesis

4: A mixture of 2-tributylstannylthiophene (3.74 g, 10 mmol), di(4-bromophenyl)-4-methylaniline (16.68 g, 40 mmol), and Pd(PPh₃)₄ (173 mg, 0.15 mmol) are placed in an inert atmosphere. Then, 100 mL distilled toluene are added to the mixture. The temperature was set at 90 °C overnight. After cooling down, the mixture was washed with water for 3 times and dried with anhydrous Na₂SO₄. The organic phase was evaporated with reduced pressure. The product is purified by column chromatography on silica gel with petroleum ether as eluent, affording about **4** as white foam. Yield: 74% ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.50~7.44 (d, 2H), 7.24~7.20 (m, 2H), 7.12~7.07 (d, 2H), 7.07~6.99 (m, 5H), 6.98~6.92 (d, 2H), 2.36~2.30 (s, 3H).

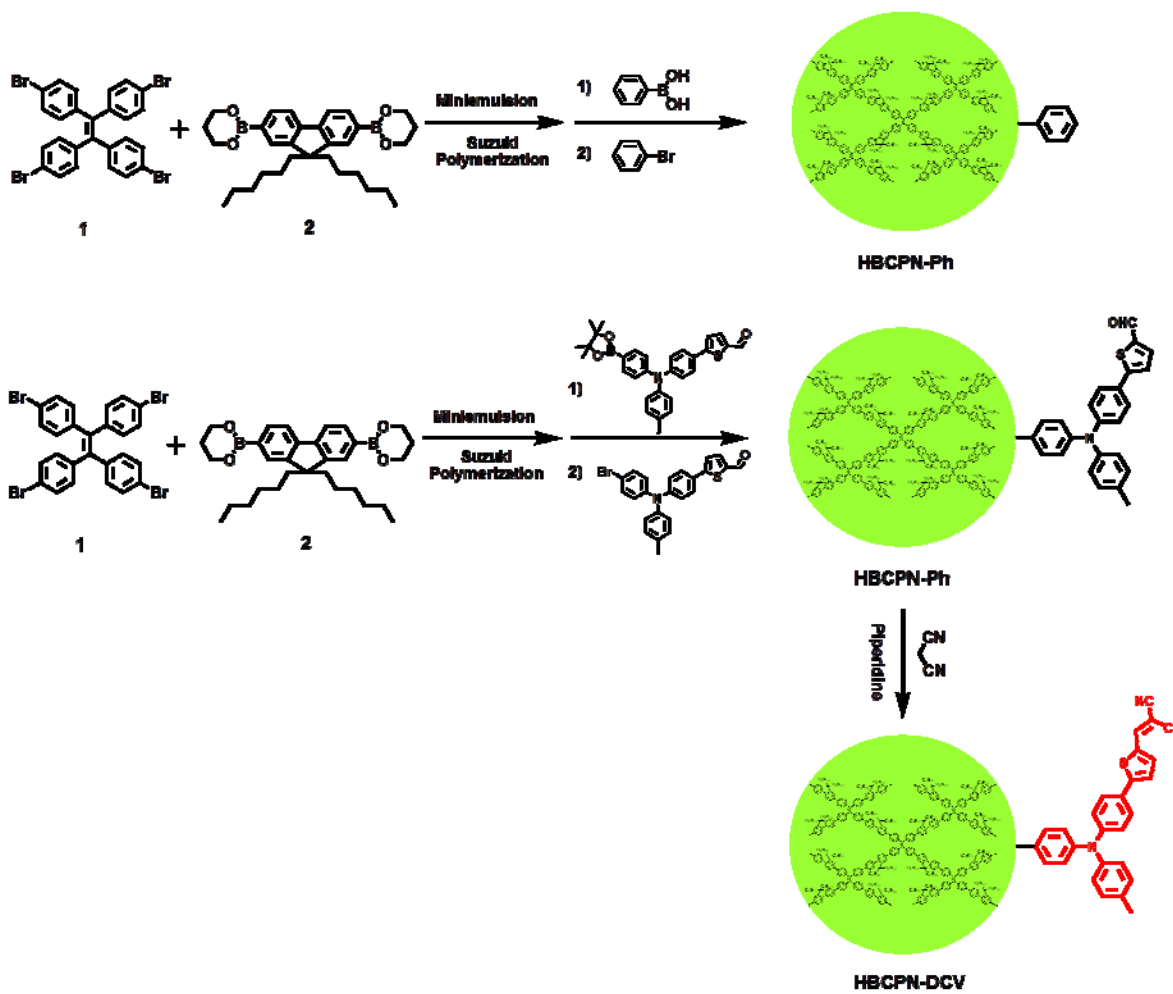
5: Under an inert atmosphere, POCl₃ (1.2 mL, 12 mmol) was added to a solution of compound **4** (3.0 g, 7.4 mmol) in 60 mL 1, 2-dichloroethane. Then, anhydrous DMF (1.2 mL, 15 mmol) was added to the solution. The mixture was kept refluxing for 20 hours. After cooling to room temperature, the mixture was poured to the sodium acetate aqueous slowly. The mixture was extracted with CH₂Cl₂ for 3 times, and the organic phase was washed with water for 3 times. After dried with anhydrous Na₂SO₄, the solvent was evaporated under reduced pressure. The product was purified by column chromatography on silica gel with petroleum ester/ethyl acetate (10:1) as eluent, affording **5** as yellow solid (2.29 g, 5.1 mmol). Yield: 69% ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 9.87~9.84 (s, 1H), 7.72~7.69 (d, 2H), 7.53~7.47 (d, 2H), 7.38~7.33 (d, 2H), 7.31~7.29 (d, 2H), 7.15~7.10 (d, 2H), 7.05~6.96 (m, 6H), 2.36~2.32 (s, 3H).

6: Under an inert atmosphere, 30 mL of distilled DMF were added to the mixture of

compound **5** (1.12 g, 2.5 mmol), bis(pinacolato)diboron (0.76 g, 3.0 mmol), KOAc (0.74 g, 7.5 mmol) and Pd(dppf)Cl₂ (41 mg, 0.05mmol). Then the reacting system was heated to 90 °C and kept stirring for 12 hours. After cooling, 100 mL of water were added to dissolve the salts. The hetero mixture was extracted by CH₂Cl₂ for 3 times and washed with water for 3 times. Then, the organic solution is concentrated with reduced pressure. The product was purified by column chromatography on silica gel with petroleum ester/ethanyl acetate (8:1) as eluent, affording **6** as yellow foam (1.20 g, 2.4 mmol). Yield: 96% ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 9.87~9.84 (s, 1H), 7.74~7.66 (m, 3H), 7.54~7.46 (d, 2H), 7.32~7.28 (d, 1H), 7.15~7.10 (d, 2H), 7.10~7.00 (m, 5H), 2.36~2.32 (s, 3H), 1.37~1.31 (s, 12H).

7: Under an inert atmosphere, 30 mL of toluene and 8 mL of 2M K₂CO₃ were added to the mixture of compound **5** (1.12 g, 2.5 mmol), 9,9-dihexylfluorene-2-boronic acid bis(1,3-propanediol) ester (1.25 g, 3.0 mmol) and Pd(PPh₃)₄ (58 mg, 0.05mmol). Then the reacting system was heated to 90 °C and kept stirring for 12 hours. After cooling, 100 mL of water were added to dissolve the salts. The hetero mixture was extracted by CH₂Cl₂ for 3 times and washed with water for 3 times. Then, the organic solution is concentrated with reduced pressure. The product was purified by column chromatography on silica gel with petroleum ester/ethanyl acetate (10:1) as eluent, affording **7** as yellow foam (1.61 g, 2.4 mmol). Yield: 91% ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 9.87~9.84 (s, 1H), 7.78~7.68 (m, 3H), 7.60~7.50 (m, 6H), 7.38~7.28 (m, 4H), 7.24~7.18 (m, 2H), 7.18~7.06 (m, 6H), 7.05~6.96 (m, 6H), 2.36~2.32 (s, 3H), 2.04~1.95 (t, 4H), 1.13~0.96 (m, 12H), 0.79~0.71 (t, 6H), 0.70~0.60 (m, 4H).

Scheme S1: Preparation of HBCPN-DCV and HBCPN-Ph.



Scheme S2: Synthesis route of M-DCV and end-capping reagents 5 and 6.

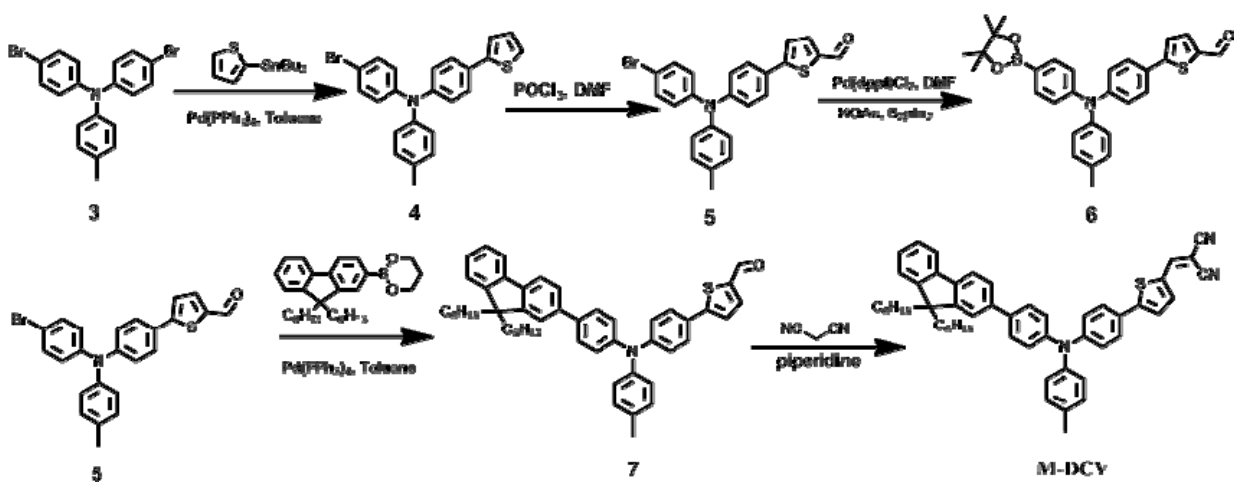


Table S1: Element Analysis results of HBCPN-CHO, HBCPN-DCV and HBCPN-Ph.

	HBCPN-CHO	HBCPN-DCV	HBCPN-Ph
C	87.73%	87.17%	87.36%
H	7.89%	7.84%	7.84%
N	0.23	0.65	0

Table S2: Absorption peak, emission peak and fluorescent quantum yield of HBCPN-CHO, HBCPN-DCV, HBCPN-Ph and M-DCV.

	λ_{abs} (nm)	λ_{em} (nm) ^a	Φ_{PL} (%) ^c
HBCPN-CHO	357	531	22.1
HBCPN-DCV	360	640	1.8
HBCPN-Ph	359	528	20.4
M-DCV	500	660 ^b	1.5
HBCPN-DCV + CN ⁻ ^d	362	538	7.0

All the absorption and emission spectra are measured in THF.

^a Excited at 360 nm; ^b Excited at 500 nm; ^c Using quinine sulfate or Rhodamine B as the standard references; ^d Measured half an hour after adding 20 μM cyanides to HBCPN-DCV in THF.

Figure S1. (A) ^1H NMR and (B) FT-IR spectra of HBCPN-CHO, HBCPN-DCV and HBCPN-Ph.

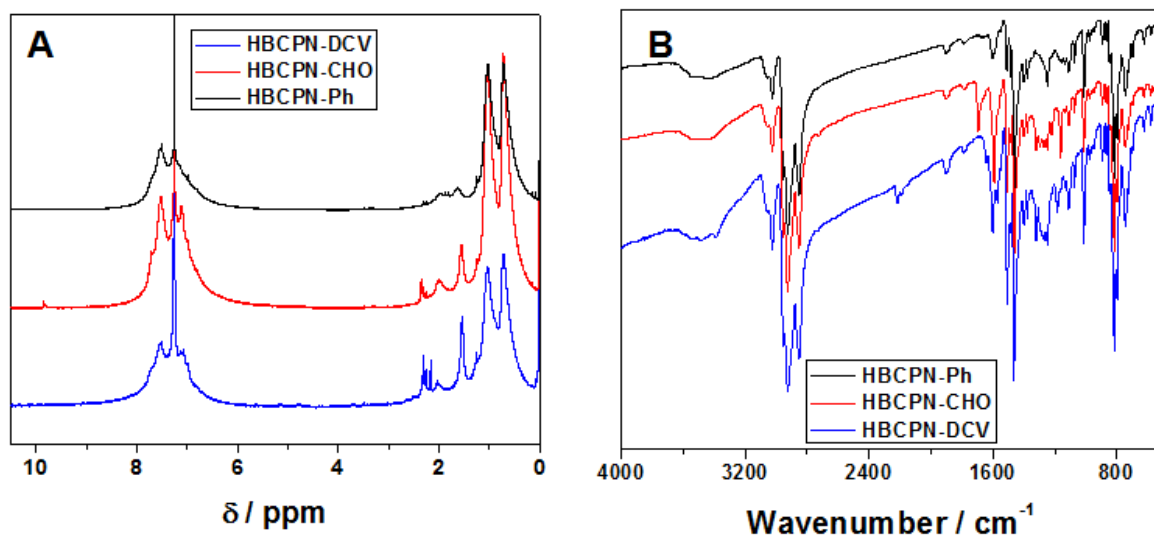


Figure S2. TGA curves of HBCPN-CHO, HBCPN-DCV and HBCPN-Ph recorded under N_2 .

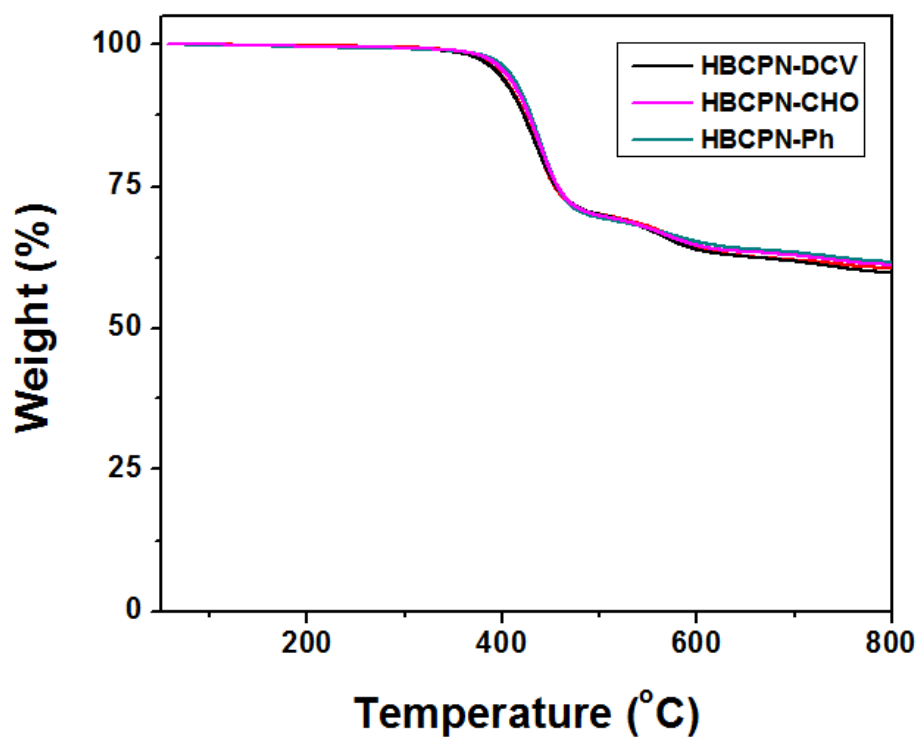


Figure S3. SEM image of HBCPN-DCV in solid state.

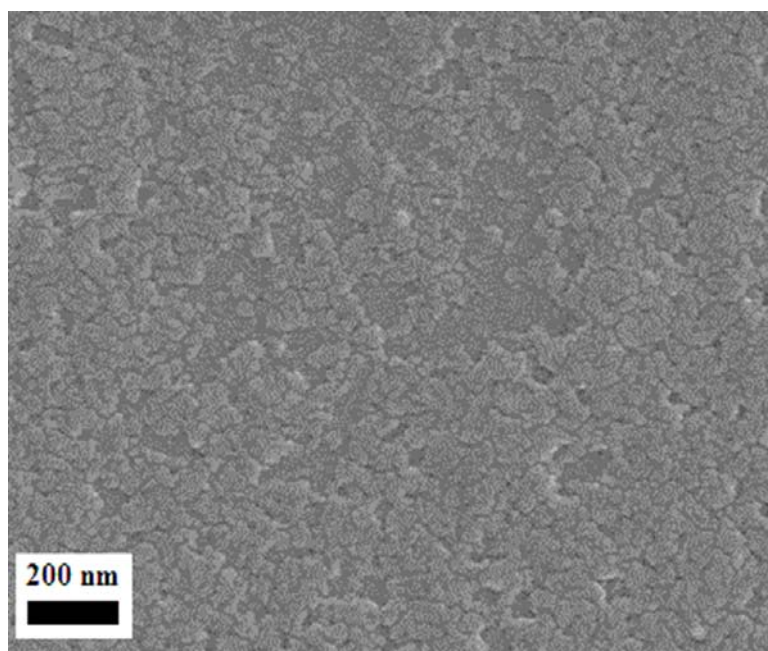


Figure S4. The hydrodynamic diameter of HBCPN-Ph measured by dynamic light scattering.

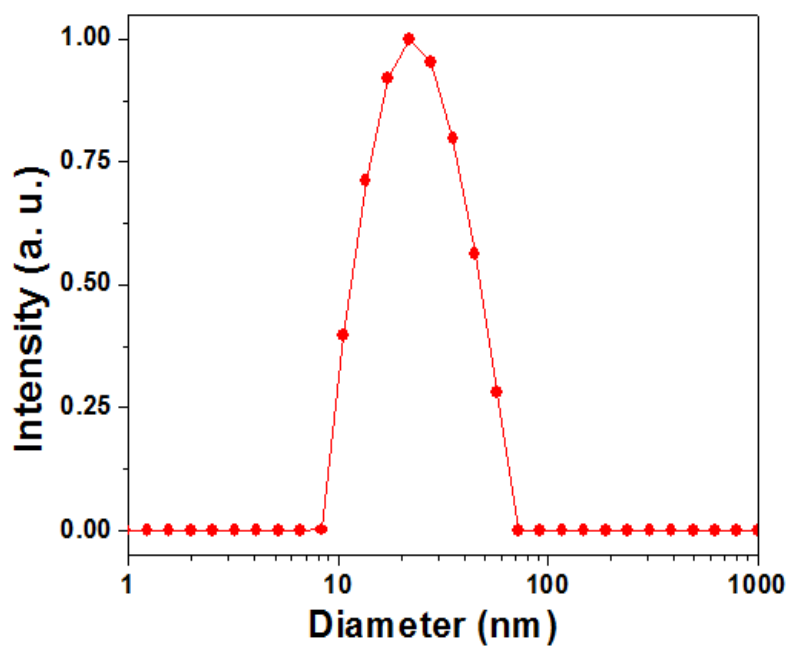


Figure S5. The absorption spectral changes of M-DCV with various concentrations of cyanide in THF.

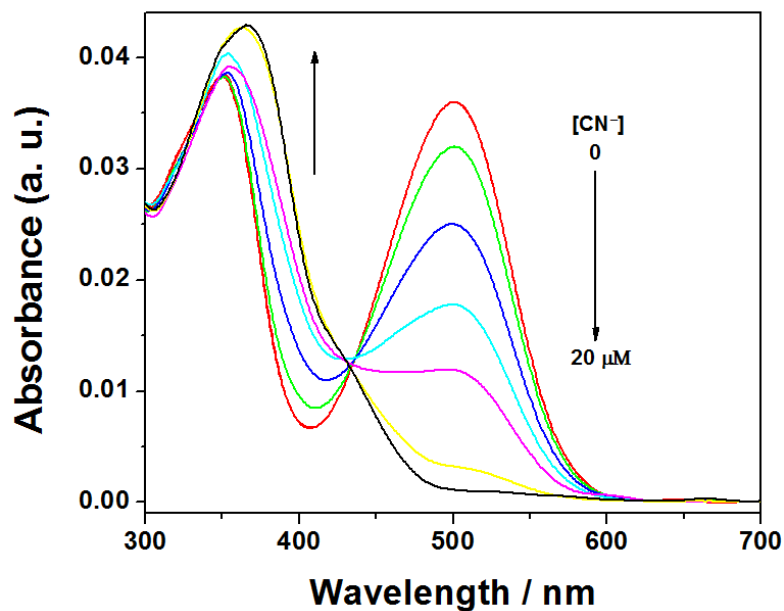


Figure S6. (A) Fluorescence spectral changes of M-DCV with various concentrations of cyanides in THF. (B) Titration profile of M-DCV based on its emission quenching at 660 nm.

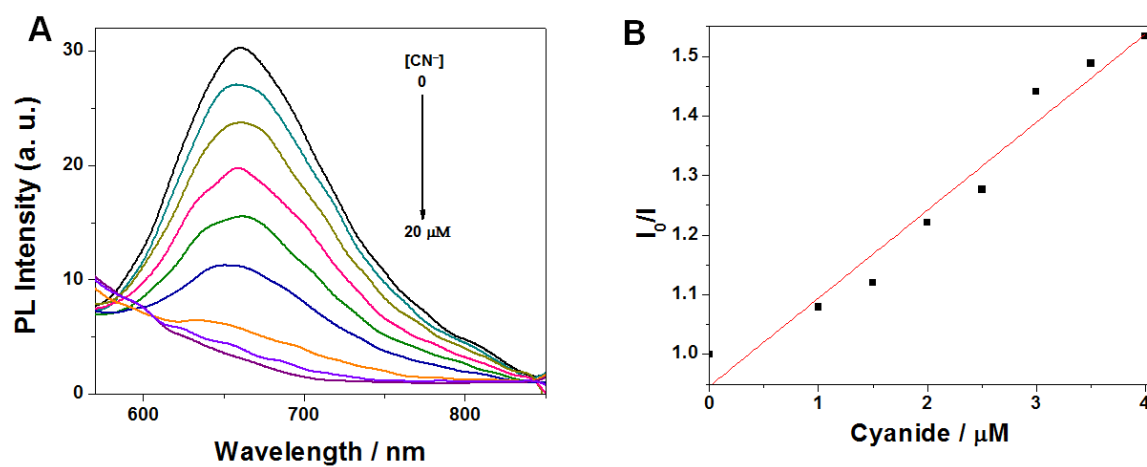


Figure S7. (A) Fluorescence spectral changes of M-DCV with various concentrations of cyanides in H₂O/THF = 1:99 solution. (B) Titration profile of M-DCV in H₂O/THF = 1:99 solution based on the emission quenching at 660 nm.

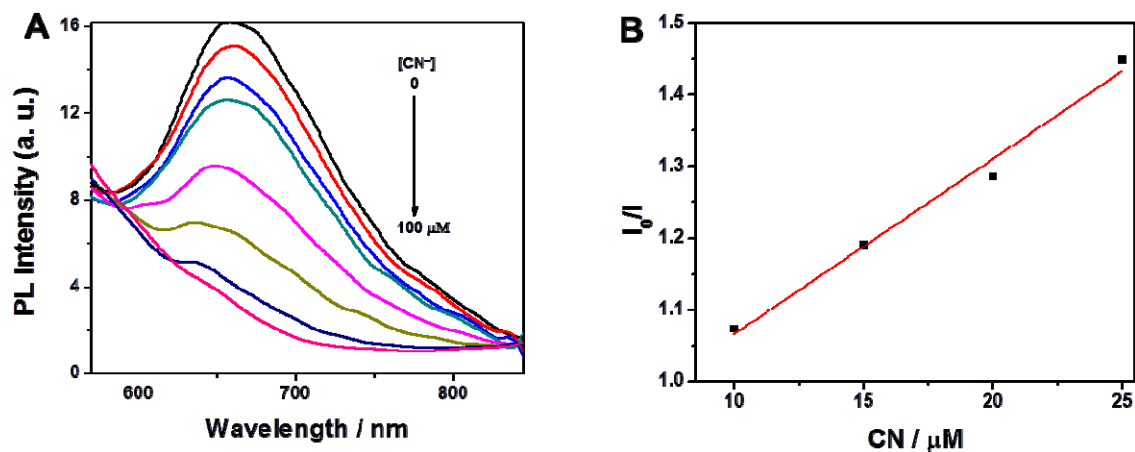


Figure S8. Job's plot curve of model compound M-DCV with CN⁻ in THF. The total concentration of M-DCV and CN⁻ anion is 1 μM.

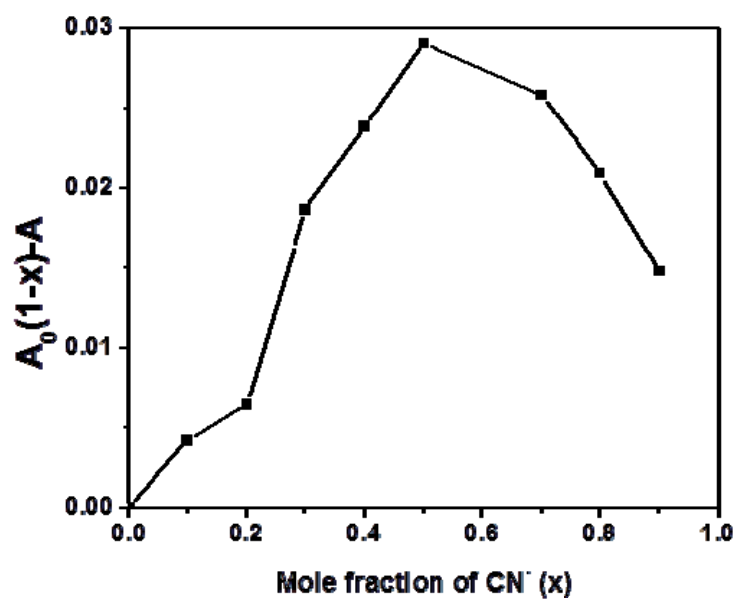
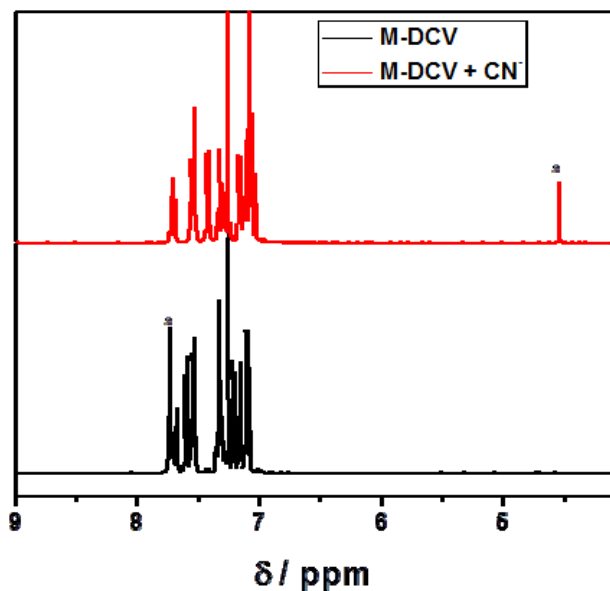


Figure S9. ^1H NMR spectra of M-DCV and M-DCV treated with 2 equiv of cyanides in CDCl_3 .



As shown in Figure S10, the vinylic proton shown at 7.74 ppm completely disappears upon the addition of 2 equiv. of cyanide anion, while a new signal arises at 4.51 ppm, which support the cyanide anion is added to the vinyl group in M-DCV.¹ The MALDI-TOF mass spectrometry of negative ion mode shows the appearance of its cyanide adduct (Calculated for $[\text{M-CN}]^-$: 775.38, Found: $[\text{M-CN-H}]^-$ =774.4, $[\text{M-CN}]^-$ =775.4).

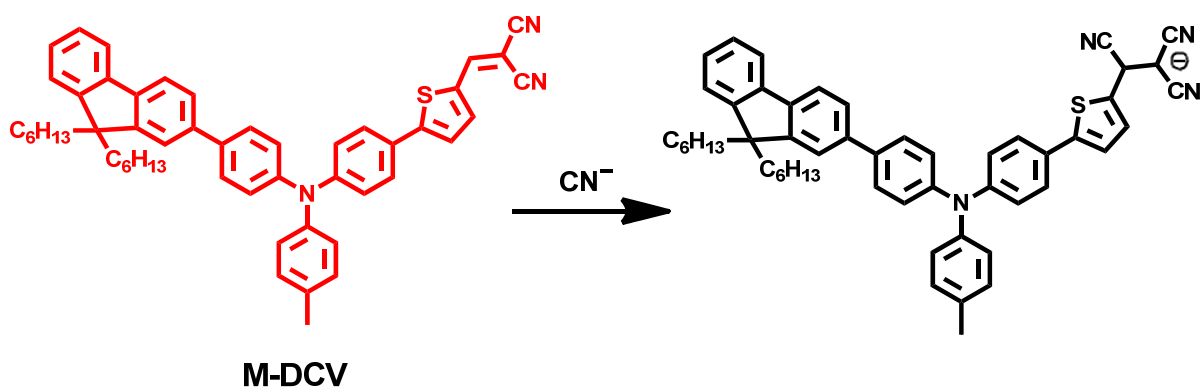


Figure S10. Fluorescence spectral changes of HBCPN-DCV in the THF–H₂O (99:1 v/v) dispersion in the presence of 100 μM anions in their tertbutylammonium water solution.

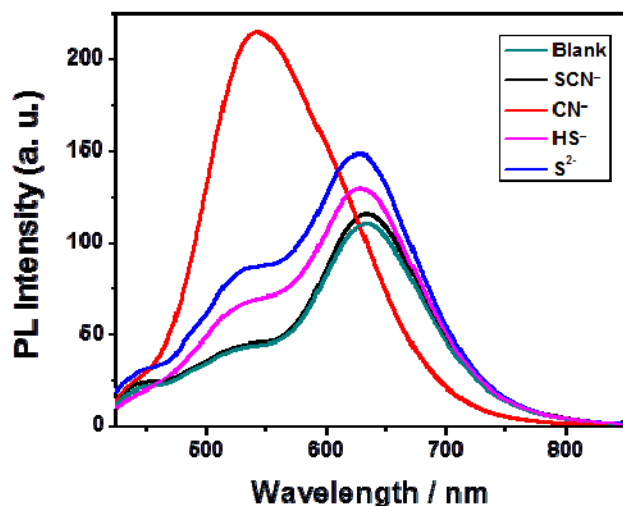


Figure S11. (A) Ratiometric fluorescence response profiles of HBCPN-DCV in the THF–H₂O (99:1 v/v) dispersion in the presence of 100 μM anions. (B) The spectral change of the HBCPN-DCV dispersion before and after adding 100 μM cyanide, fluoride or both in THF–H₂O (99:1 v/v).

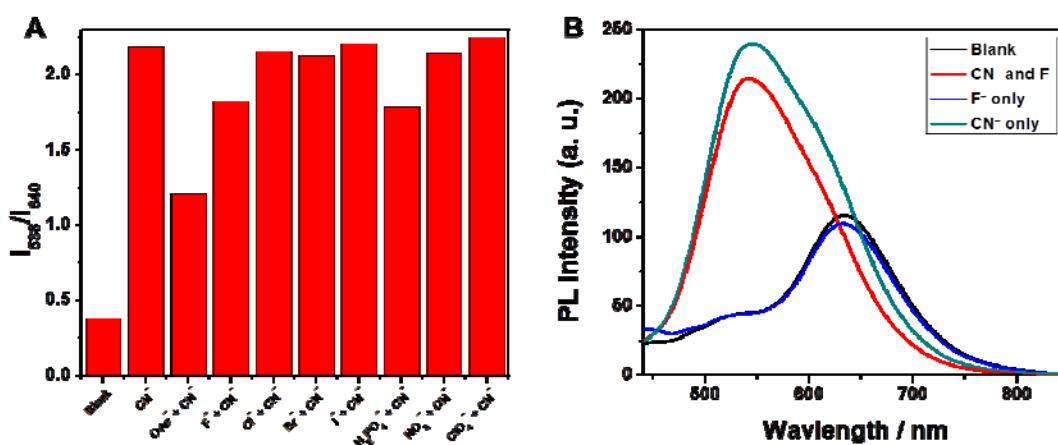


Figure S12. (A) Hydrodynamic diameters of larger HBCPN-DCV particles (average particle size: 50 nm). (B) TEM image of larger HBCPN-DCV particles by drop-casting the THF dispersion of HBCPN-DCV onto a copper grid.

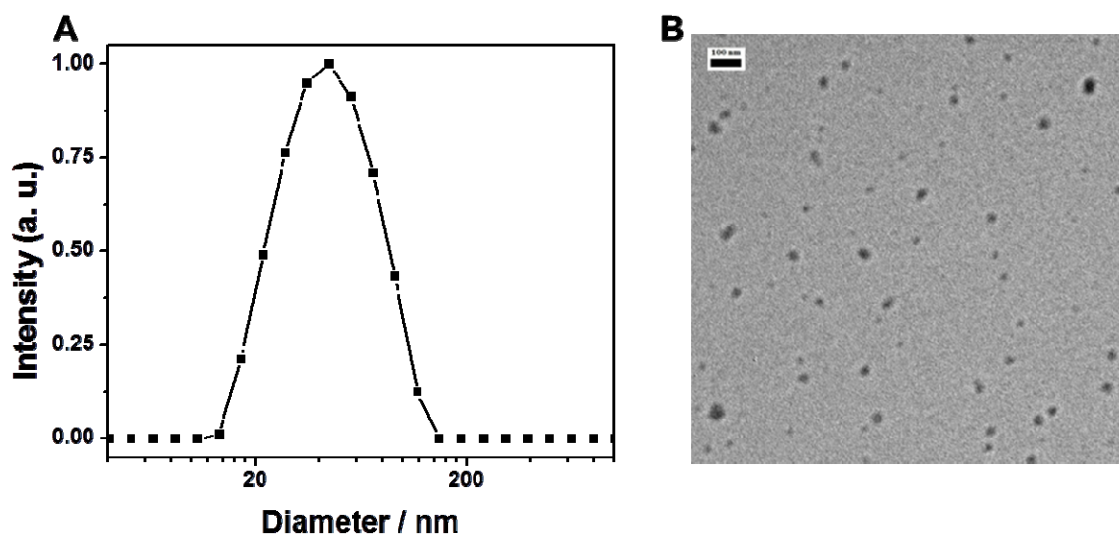


Figure S13. (A) Emission responses of larger HBCPN-DCV particles (average particle size: 50 nm) in presence of different concentrations of cyanide anion in THF. (B) Titration profiles based on the fluorescence intensity ratio I_{538}/I_{632} .

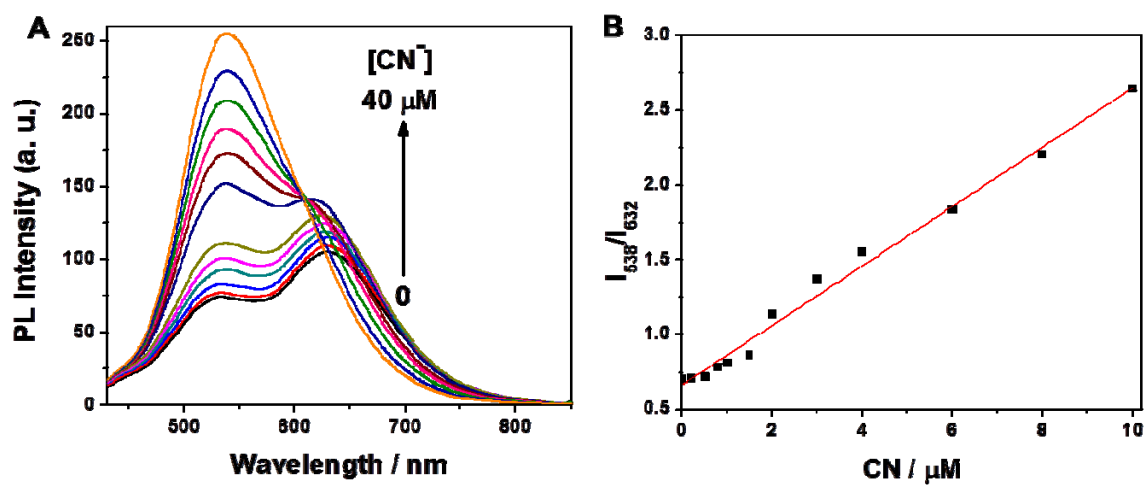
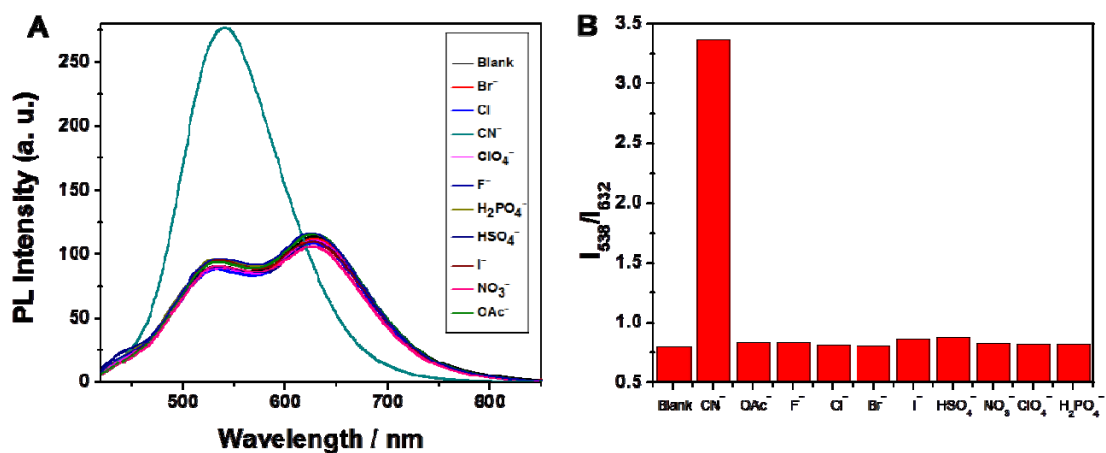


Figure S14. (A) Fluorescence spectral changes of larger HBCPN-DCV particles (average particle size: 50 nm) in the THF–H₂O (99:1 v/v) dispersion in the presence of 100 μM anions in their tertbutylammonium water solution. (B) Ratiometric fluorescence response profiles in the THF–H₂O (99:1 v/v) dispersion in the presence of 100 μM anions.



Reference:

- (a) Z. Liu, X. Wang, Z. Yang and W. He, *J. Org. Chem.*, 2011, **76**, 10286-10290; (b) C.-H. Lee, H.-J. Yoon, J.-S. Shim and W.-D. Jang, *Chem. Eur. J.*, 2012, **18**, 4513-4516.