Supporting information for

Intramolecular charge-transfer emission from conjugated polymer nanoparticles: terminal group effect on electronic and optical properties

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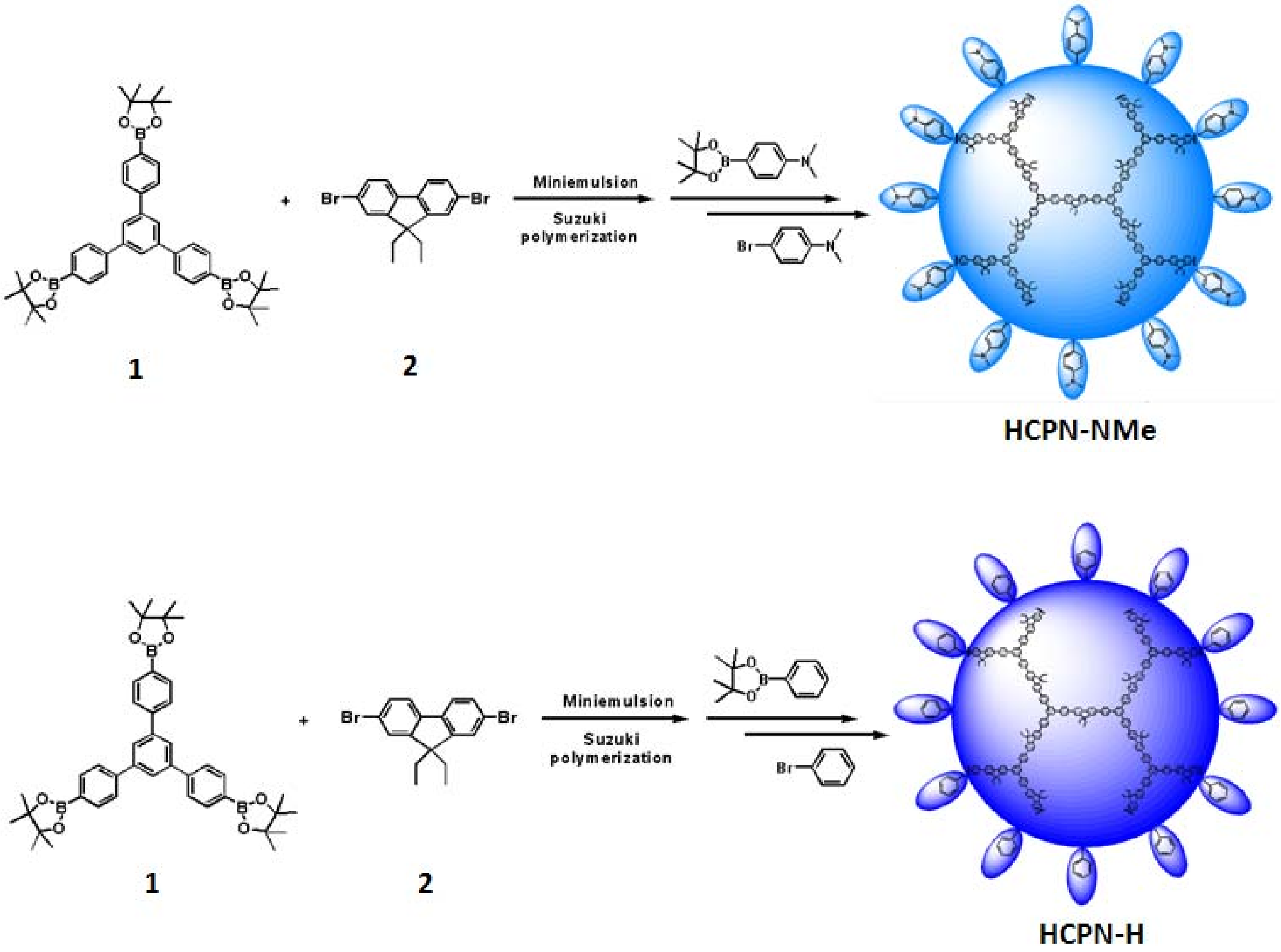
Materials. All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to standard procedures. Monomer 9,9-diethyl-2,7-dibromofluorene **(2)**,[1] 1,3,5-tris-(-p-bromophenyl)-benzene,[2] 2-(4-(N,N-dimethylamino)-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane,[3] and 1,1'-biphenyl-4-yl-boronic acid[4] were synthesized as previously described.

Synthesis of 1,3,5-tris-{4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane)phenyl}-benzene (1). To a vigorously stirred solution of 1,3,5-tris(p-bromophenyl) benzene (5.43 g, 10 mmol) in dry THF (250 mL), butyllithium solution in hexanes (2.5 mol/L, 13.2 mL, 33 mmol) was added slowly at –78 °C. After stirring for 1 h at –78 °C, trimethyl borate (4 mL, 36 mmol) was added slowly. The solution was stirred for 1 h at –78 °C then warmed to room temperature and stirred for 12 h. The reaction was quenched by adding 2M HCl a.q. (200 mL). The resulting mixture was extracted with ether and washed by water. Upon removal of the solvent, the residue was dried under vacuum and then dissolved in toluene (150 mL). Pinacol (4.3 g, 36 mmol) was added to the solution and the reaction mixture was stirred at 90°C overnight. Upon removal of the solvent, the crude product was purified by recrystallization from mixed solvent of ethanol and trichloromethane, and dried under high vacuum to afford product as white solid (5.4 g, 73%). ^{1}H NMR ($CDCl_3$): δ (ppm): 7.92 (d, 6H, J=8.1Hz), 7.50 (S, 3H), 7.70 (d, 6 H, J=8.1Hz), 1.37(s, 36). m/z [MALDI-TOF]: 684.4 $[M]^+$.

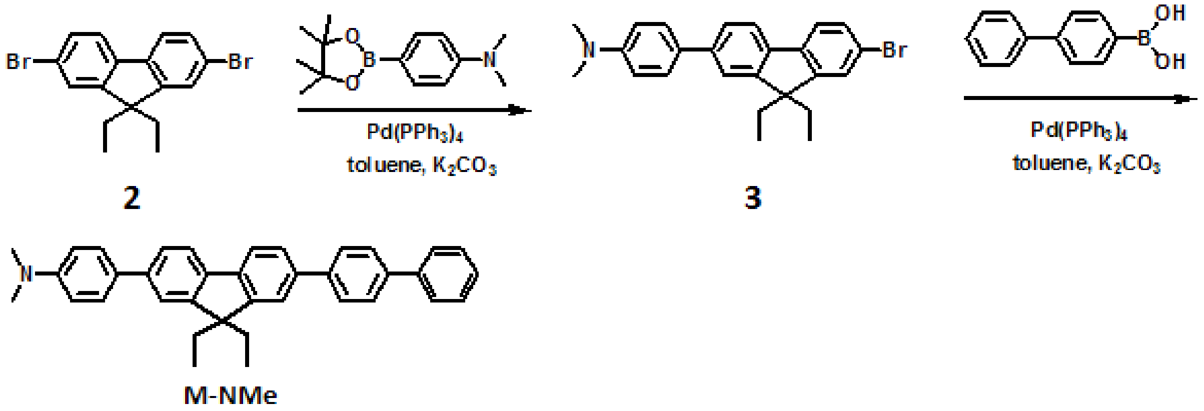
Synthesis of HCPN-H. 1,3,5-tris-{4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane)phenyl}-benzene (164 mg, 0.24 mmol), 9,9-diethyl-2,7-dibromofluorene (136.8 mg, 0.36 mmol) and $Pd(PPh_3)_4$ (2.8mg) were dissolved in degassed toluene (6 mL). Under argon atmosphere, the mixture solution was added to a solution of cetyltrimethylammonium bromide (CTAB) (5.82g, 16 mmol) in degassed deionized water (90 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 (3.0 mL) was added under this condition. After ultrasonicating for 10 min, the reaction emulsion was stirred in oil bath at 80°C for 24 h under argon atmosphere. The end-capped agents 4,4,5,5-tetramethyl-2-phenyl-[1,3,2]-dioxaborolane were added and stirring for 4 h. Then bromobenzene were added and stirring for 4 h. 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 80 °C under vacuum for 24 h to afford the final nanoparticles (136 mg).

Synthesis of intermediate 3. A mixture of 9,9-diethyl-2,7-dibromofluorene **(2)** (6.1 g, 16.2 mmol), 2-(4-(N,N-dimethylamino)-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (2 g , 8.1 mmol) and $Pd(PPh_3)_4$ (180 mg) were degassed for 30 min. Then a solution of 2 M aqueous K_2CO_3 (15 mL) and toluene (30 mL) was added and the reaction mixture was degassed and stirred at 85 °C for 24 h under argon atmosphere. 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 purified by column chromatography on silica gel with dichloromethane–petrol ether as the eluent. The product was obtained as yellow solid (1.4 g, 42%). ^1H NMR ($CDCl_3$): δ: 7.66(d, 1H, J=7.9), 7.58-7.52(m, 4H), 7.45(m,3H), 6.84(br, 2H), 3.01(s, 6H), 2.03 (m, 4H), 0.36(t, 6H, J=7.3Hz). m/z [MALDI-TOF]: 419.1$[M]^+$.

Synthesis of M-NMe. A mixture of intermediate 3 (420 mg, 1 mmol), 1,1'-biphenyl-4-yl-boronic acid (1.5 g , 4 mmol) and $Pd(PPh_3)_4$ (46 mg) were degassed for 30 min. Then a solution of 2 M aqueous K_2CO_3 (10 mL) and toluene (25 mL) was added and the reaction mixture was degassed and stirred at 85 °C for 24 h under argon atmosphere. 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 purified by column chromatography on silica gel with dichloromethane–petrol ether as the eluent. The product was obtained as yellow solid (100 mg, 40%). ^{1}H NMR ($CDCl_3$): δ: 7.78(m, 4H), 7.71-7.59(m,8H), 7.55(dd,1H, J=7.8Hz, J=1.6Hz), 7.52 (s, 1H), 7.47(t, 2H, J=7.4Hz), 7.36(t , 1H, J=7.4Hz), 6.88(br, 2H), 3.02(s, 6H), 2.10 (m, 4H), 0.42(t, 6H, J=7.3Hz). m/z [MALDI-TOF]: 493.3$[M]^+$.



Scheme S1. The preparation of HCPN-NMe and HCPN-H.



Scheme S2. The preparation of model compounds M-NMe

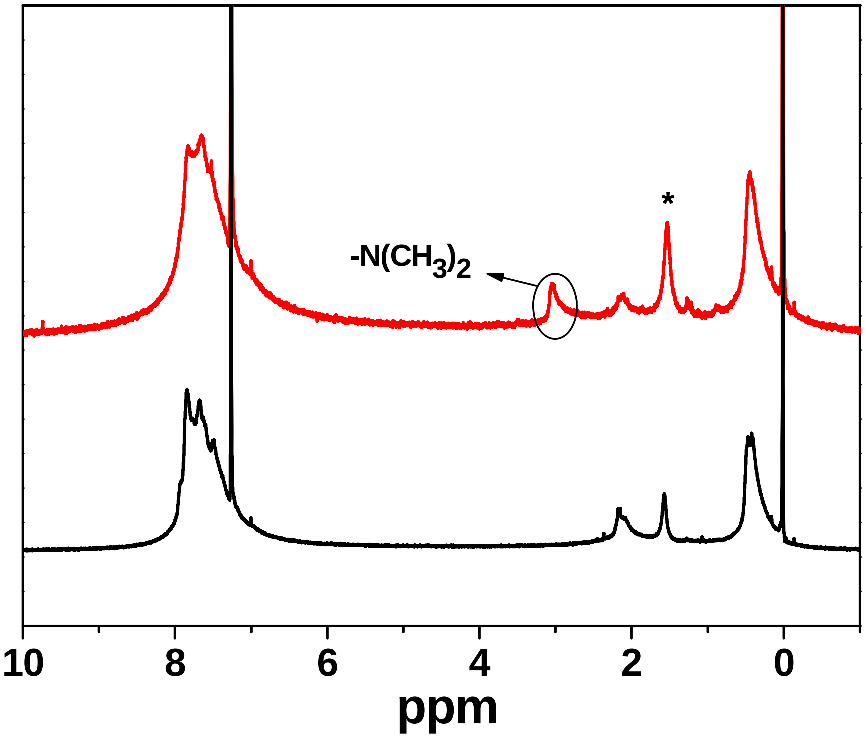


Figure S1 ^{1}H NMR spectra of HCPN-NMe (red line) and HCPN-H (black line) in $CDCl_3$. (The peaks marked by asterisks (*) are attributed to proton of H_2O.)

Table S1. Elemental analysis of HCPN-NMe and HCPN-H.

		C (%)	H(%)	N (%)	C/H
HCPN-NMe	Theoretical[a]	92.60	6.39	1.01	14.49
	experimental	91.84	6.34	0.36	14.48
HCPN-H	Theoretical[b]	93.78	6.22	0	15.07
	experimental	91.27	6.09	0	14.98

[a] The theoretical value of HCPN-NMe are based on three fluorene units and two triphenylbenzene units and one N,N-dimethylaniline units; b The theoretical value of HCPN-H are based on three fluorene units and two triphenylbenzene units and one benzene units.

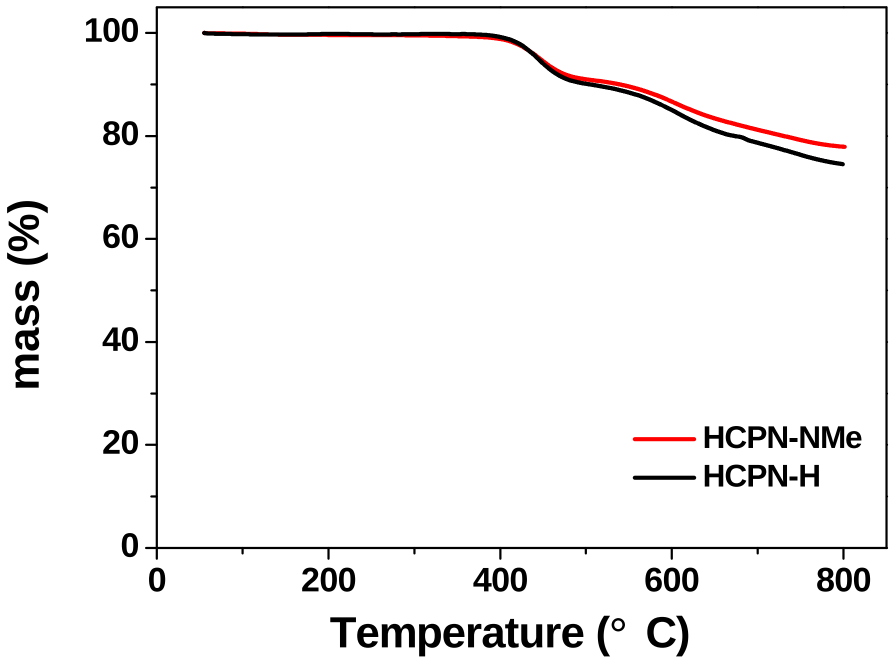


Figure S2 TGA curve recorded under N_2 for HCPN-NMe and HCPN-H.

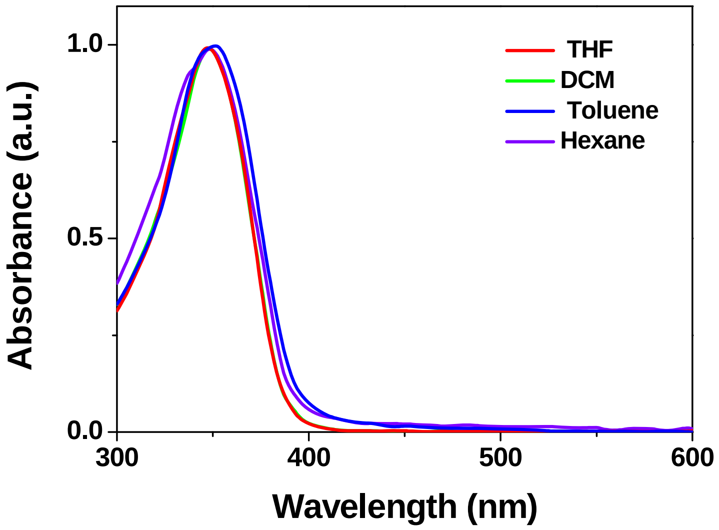


Figure S3 Normalized absorption spectra of HCPN-NMe in different solvents. (THF= tetrahydrofuran, DCM= dichloromethane, TOL=toluene, HEX=hexane.)

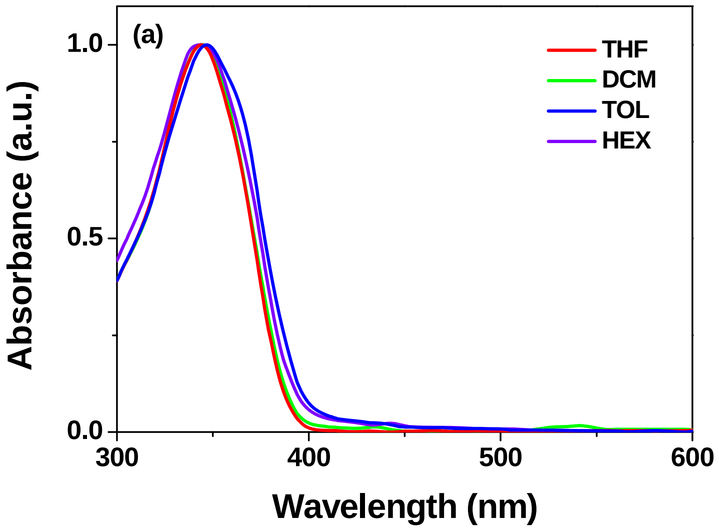


Figure S4 Normalized absorption spectra of HCPN-H in different solvents. (THF= tetrahydrofuran, DCM= dichloromethane, TOL=toluene, HEX=hexane.)

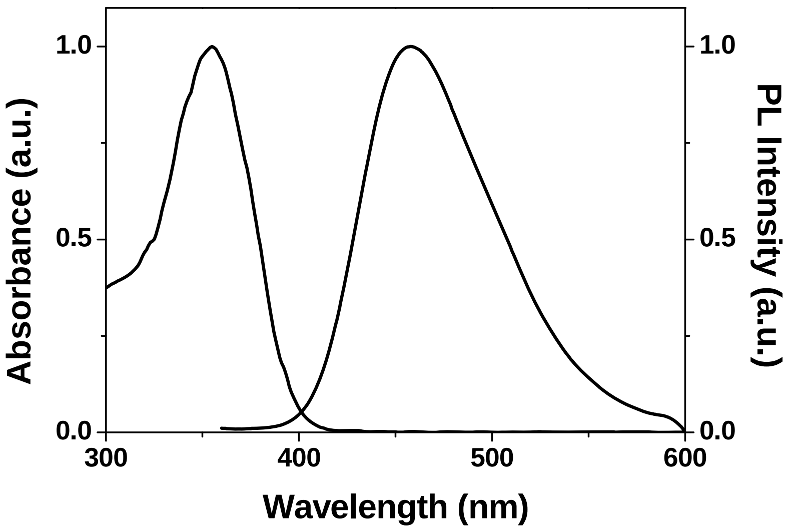


Figure S5 Absorption and emission spectra of M-NMe in THF.

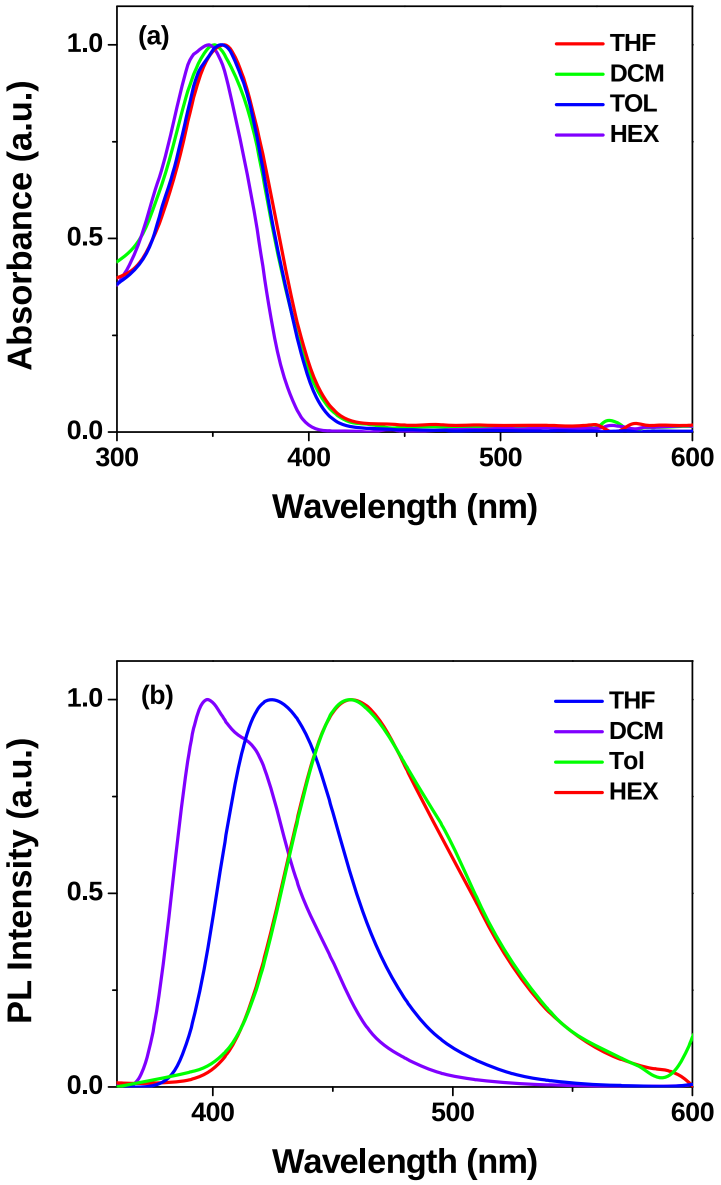


Figure S6 Normalized absorption (a) and emission (b) spectra of M-NMe in different solvents. (THF= tetrahydrofuran, DCM= dichloromethane, TOL=toluene, HEX=hexane.)

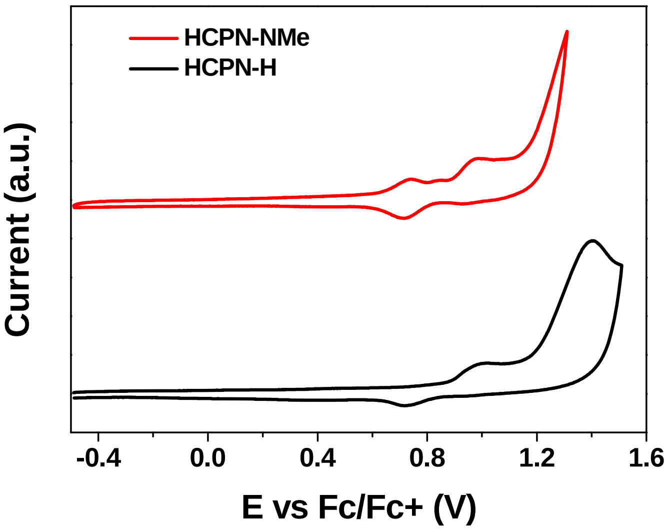


Figure S7 Cyclic voltammograms of HCPN-NMe and HCPN-H measured in CH_2Cl_2 at a scan rate of 100 mV s^{-1}.

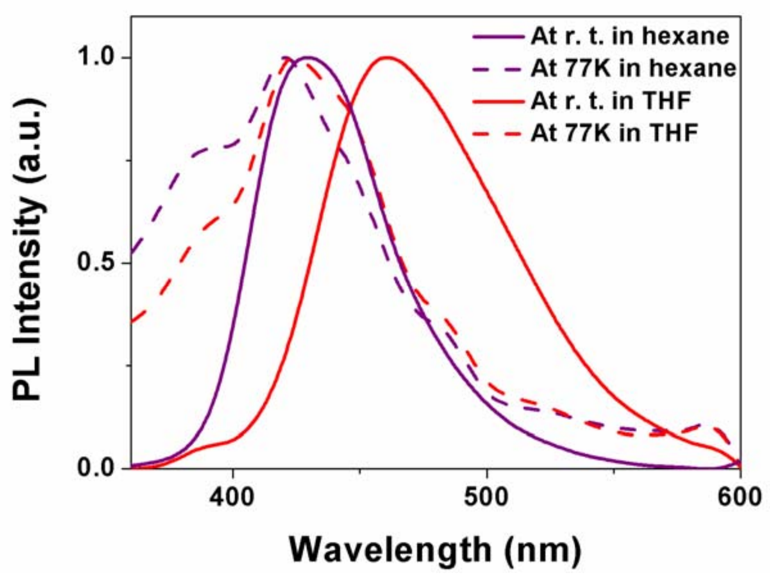


Figure S8 Normalized emission spectra of HCPN-NMe in THF and hexane at room temperature and 77K.

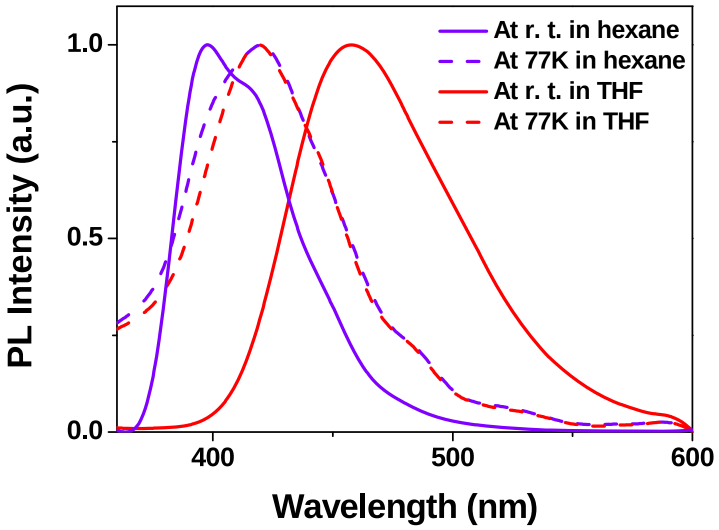


Figure S9 Normalized emission spectra of M-NMe in THF and hexane at room temperature and 77K.

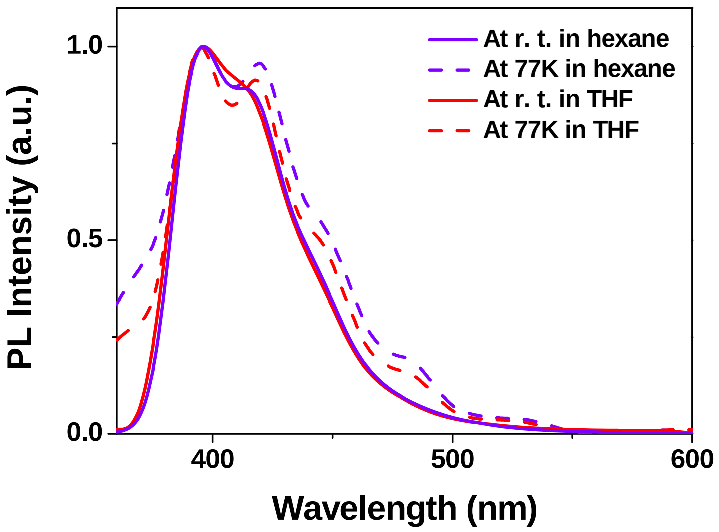
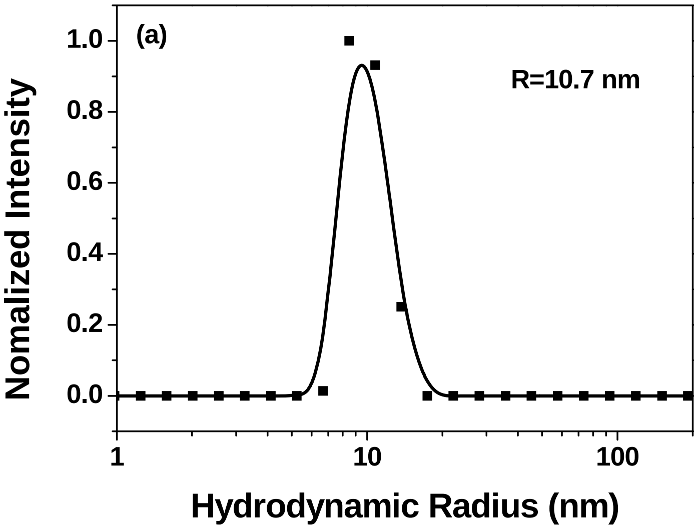


Figure S10 Normalized emission spectra of HCPN-H in THF and hexane at room temperature and 77K.



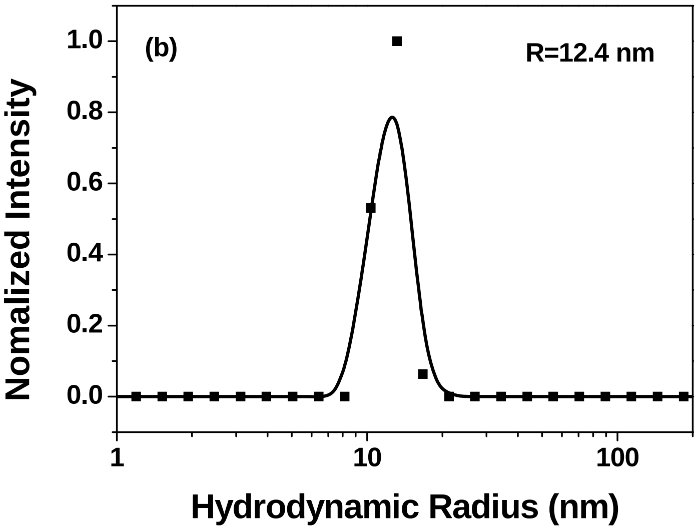


Figure S11 Hydrodynamic radii distribution of HCPN-NMe in THF containing 1% H_2O (a) and in THF containing 10% H_2O (b) measured by dynamic light scattering (DLS).

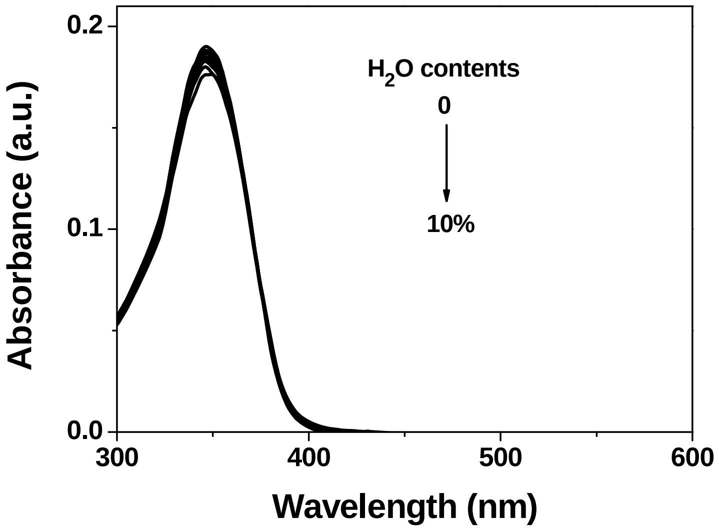


Figure S12 Absorption spectral changes of HCPN-NMe with the increasing contents of H_2O in THF.

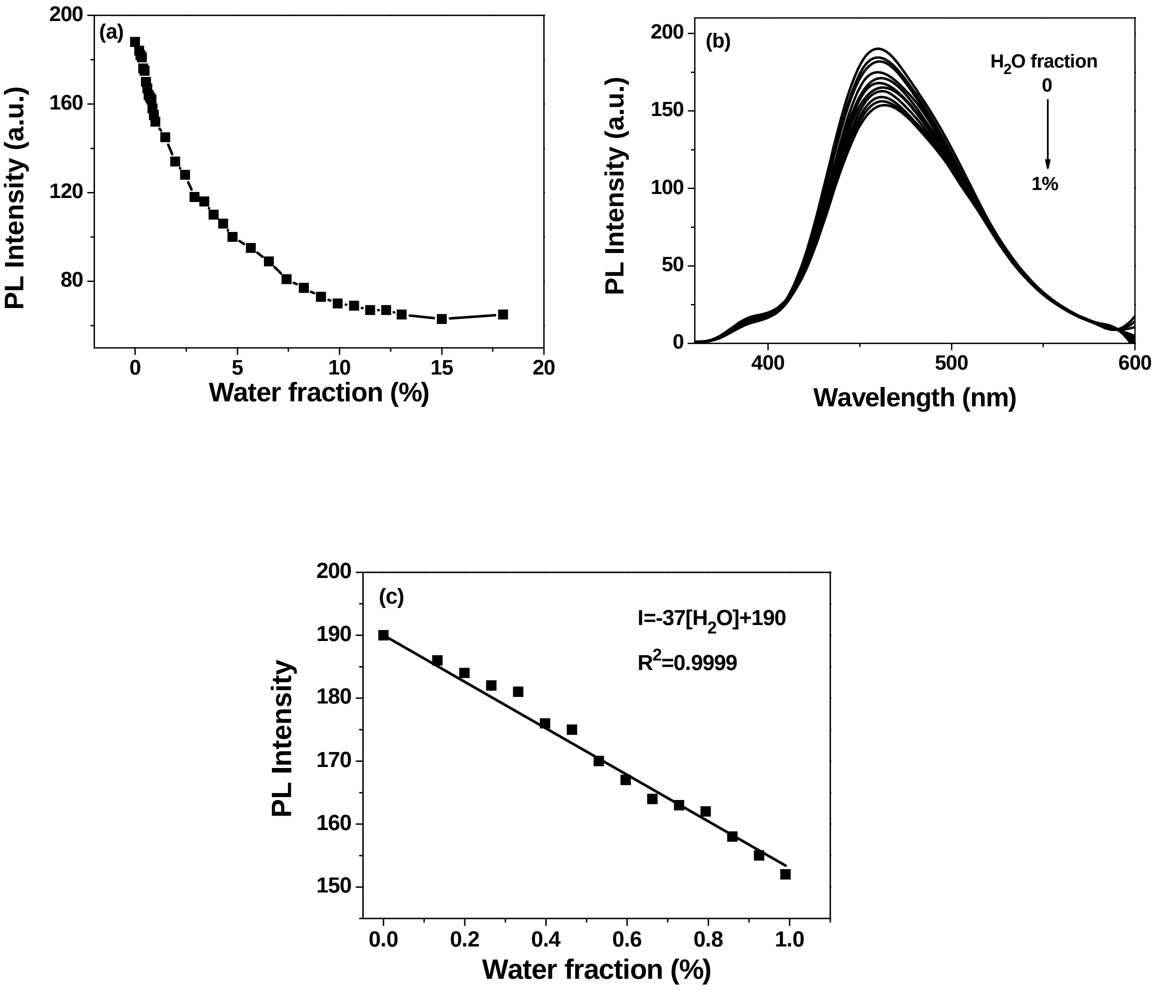
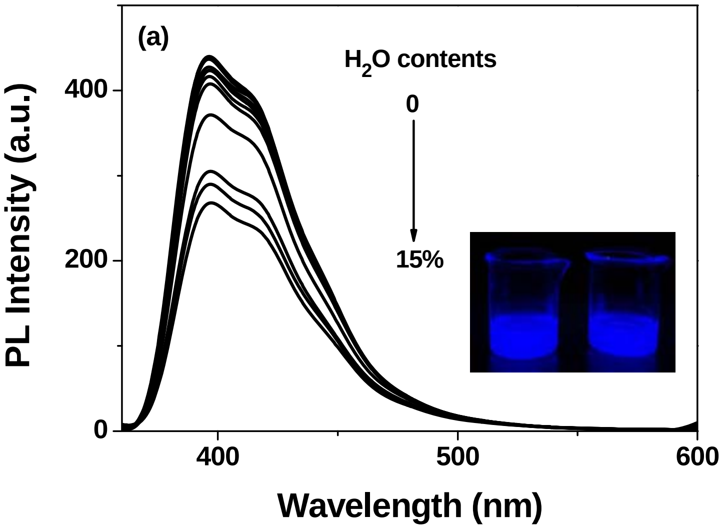


Figure S13 (a) The fluorescent intensity of HCPN-NMe as a function of H_2O content in the THF solution. (b) Fluorescence spectral changes of HCPN- NMe in the region of the low water contents (0-1.0%). (c) The calibration curve of PL intensity in the region of the low water contents (0-1.0%).

The detection limit of H_2O content for HCPN-NMe was determined by the equation: detection limit = $3\sigma/m$.[5,6] The value of σ was the standard deviation of blank sample, which was calculated to be 1.6 by measuring the fluorescent intensities of blank samples. The value of m is the absolute value of the slope of the calibration curve of PL intensity in the region of the low water content (0-1.0%), which was calculated to be 37 by fitting experimental data in figure S13c. According to the equation, the detection limit can be calculated to be 0.13 (v/v)%.



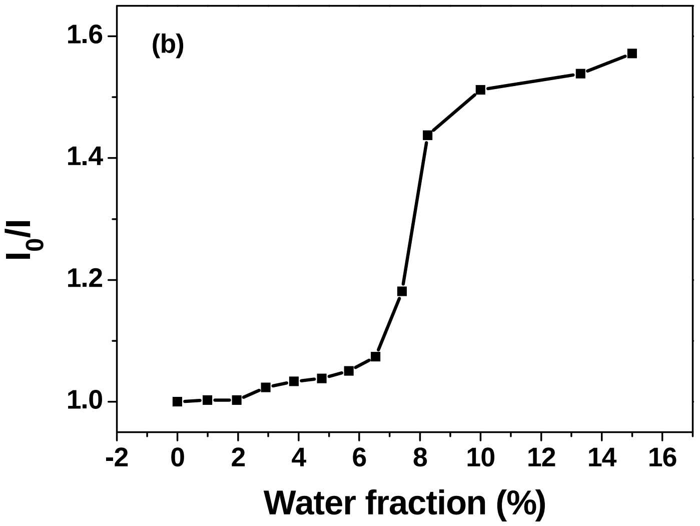


Figure S14 (a) Fluorescence spectral changes of HCPN-H with the increasing contents of H_2O in THF. Inset: the images of HCPN-H in THF under UV lamp before (left) and after (right) adding 5% H_2O. (b) The curve of I_0/I against varying H_2O contents.

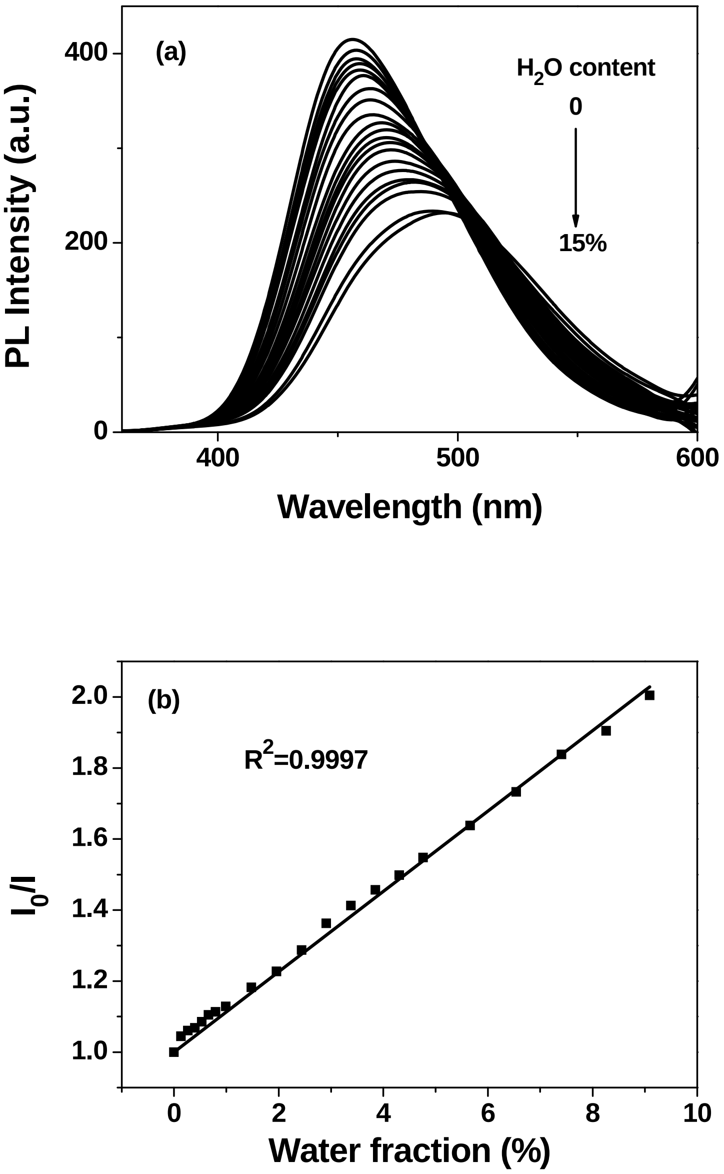


Figure S15 (a) Fluorescence spectral changes of M-NMe with the increasing contents of H_2O in THF. (b) The Stern-Volmer quenching plot of M-Me by varying H_2O contents.

1 X. Feng, F. Lv, L. Liu, Q. Yang, S. Wang, G. C. Bazan, *Adv. Mater.*, **2012**, *24*, 5428.

2 S. Kotha, D. Kashinath, K. Lahiri, R. B. Sunoj, *Eur. J. Org. Chem.*, **2004**, 4003.

3 C. Sooambar, V. Troiani, C. Bruno, M.Marcaccio, F. Paolucci, A.Listorti, A. Belbakra, N. Armaroli, A. Magistrato, R. D. Zorzi, S. Geremiaf, D. Bonifazi, *Org. Biomol. Chem.*, **2009**, *7*, 2402.

4 T. J. Dingemans, N. S. Murthy, E. T. Samulski, *J. Phys. Chem. B*, **2001**, *105*, 8845.

5. C.-G. Niu, A.-L. Guan, G.-M. Zeng, Y.-G. Liu and Z.-W. Li, *Anal. Chim. Acta* **2006**, *577*, 264.

6. S. Ishihara, J. Labuta, T. ikorský, J. V. Burda, N. Okamoto, H. Abe, K. Ariga and J. P. Hill, *Chem. Commun.* 2012, **48,** 3933.