Electronic Supplementary Information for

A Br substituted phenanthroimidazole derivative with aggregation induced emission from intermolecular halogen-hydrogen interactions

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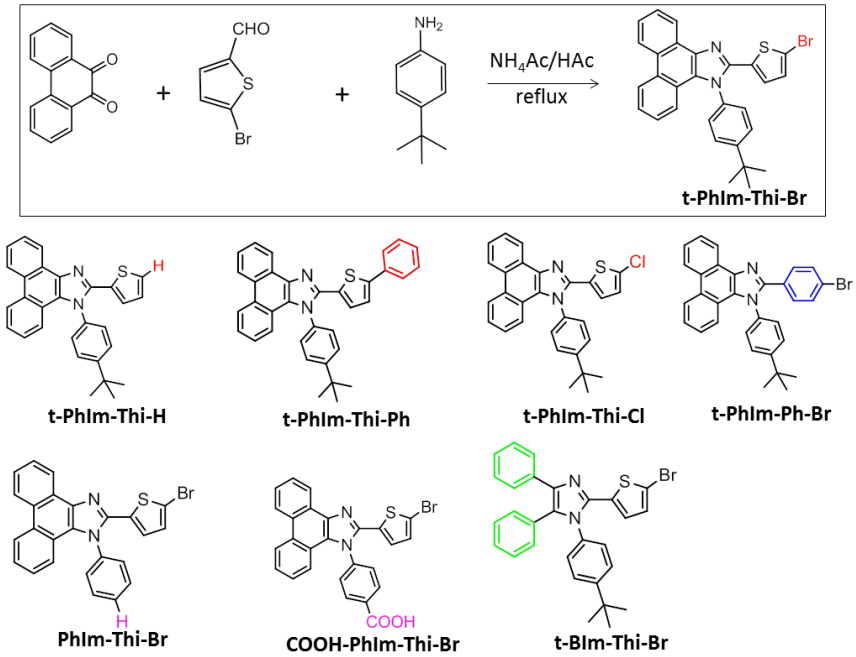


Scheme S1 Synthetic route of *t*-PhIm-Thi-Br and chemical structures of other similar synthesized molecules.

Synthetic procedure of 2-(5-bromothiophen-2-yl)-1-(4-(tert-butyl)phenyl)-1H-phenanthro-[9,10-d]imidazole (*t*-PhIm-Thi-Br)

The product was prepared by refluxing 9,10-phenanthrenequinone (4.16 g, 20 mmol), 5-bromothiophene-2-carbaldehyde (2.45 mL, 20 mmol), 4-*tert*-butylbenzenamine (4.8 mL) and ammonium acetate (18.87 g) in glacial acetic acid (100 mL) for 24 hours under an argon

atmosphere. After cooling to room temperature, the mixture was poured into a methanol solution under stirring. The separated solid was filtered off, washed with methanol and dried to give a pale yellow solid. The solid was purified by column chromatography (petroleum ether: CH_2Cl_2, 3:1) on silica gel. The product was finally obtained after it was stirred in refluxing ethanol, subsequently filtered and dried in vacuum. Yield: (80 %). Mp (213.2 ºC). ^{1}H NMR (400 MHz, DMSO) δ1.40 (d, *J* = 52.0 Hz, 9H), 6.51 (d, *J* = 4.0 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 4.0 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.56 (t, *J* = 7.1 Hz, 1H), 7.64 – 7.88 (m, 6H), 8.62 (d, *J* = 6.8 Hz, 1H), 8.90 (dd, *J* = 19.2, 8.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ32.26 (s), 36.00 (s), 121.41 (s), 124.89 (s), 124.36 – 122.08 (m), 125.88 (s), 126.62 (s), 127.21 (s), 127.48 (s), 128.52 (t, *J* = 33.4 Hz), 129.23 (d, *J* = 16.0 Hz), 130.07 (s), 131.10 (s), 135.81 (s), 145.74 (s), 155.33 (s). MS (ESI^+): m/z 512.5 (MH^+), Calc. 511.48. Anal. Found: C, 68.45; H, 4.535; N, 5.45; S, 6.45%. Calc. For $C_{29}H_{23}BrN_2S$: C, 68.10; H, 4.53; N, 5.48; S, 6.27%.

1-(4-(tert-butyl)phenyl)-2-(thiophen-2-yl)-1H-phenanthro[9,10-d]imidazole (*t*-PhIm-Thi-H)

Mp (227.5 ºC). ^{1}H NMR (400 MHz, CD_2Cl_2) δ1.54 (s, 9H), 6.99 (s, 1H), 7.17 – 7.25 (m, 1H), 7.28 – 7.35 (m, 1H), 7.39 (d, J = 4.9 Hz, 1H), 7.51 – 7.61 (m, 3H), 7.66 – 7.87 (m, 5H), 8.78 (dd, J = 18.9, 8.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ32.30 (s), 36.03 (s), 121.44 (s), 123.81 (d, *J* = 14.2 Hz), 124.91 (s), 125.91 (s), 126.64 (s), 127.70 (d, *J* = 68.5 Hz), 128.33 – 128.43 (m), 128.43–129.77 (m), 130.09 (s), 131.13 (s), 135.84 (s), 145.76 (s), 155.37 (s). MS (ESI^+): m/z 433.21 (MH^+), Calc. 432.58. Anal. Found: C, 80.21; H, 5.68; N, 6.34; S, 7.46%; Calc. For $C_{29}H_{24}N_2S$: C, 80.52; H, 5.59; N, 6.48; S, 7.41%.

1-(4-(tert-butyl)phenyl)-2-(5-phenylthiophen-2-yl)-1H-phenanthro[9,10-d]imidazole (*t*-PhIm-Thi-Ph)

Mp (280 ºC). ^{1}H NMR (400 MHz, CD_3Cl): 1.54 (s, 9H), 6.69 (d, *J* = 4.0 Hz, 1H), 7.16 (d, *J* = 4.0 Hz, 1H), 7.25 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.28-7.37 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.49-7.85 (m, 9H), 8.74 (d, *J* = 8.3 Hz, 1H), 8.77-8.85(m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ31.53 (s), 35.22 (s), 120.67 (s), 123.01 (d), 123.99 (dd), 124.88 (s), 125.65 (s), 126.26 (d), 126.66 (s), 127.12 (d), 127.64 (d), 128.01 (d), 128.33 (d), 128.67 (d), 129.20 (s), 131.24 (s), 132.53 (s), 132.87 (s), 133.57 (s), 135.62 (s), 137.62 (s), 145.78 (s), 146.00 (s), 154.25 (s). MS (ESI^+): m/z 509.5 (MH^+),

Calc. 508.2. Anal. Found: C, 82.61; H, 5.56; N, 5.54. Calc. for $C_{35}H_{28}N_2S$: C, 82.64; H, 5.55; N, 5.51%.

1-(4-(tert-butyl)phenyl)-2-(5-chlorothiophen-2-yl)-1H-phenanthro[9,10-d]imidazole (*t*-PhIm-Thi-Cl)

Mp (220 ºC). ^{1}H NMR (400 MHz, DMSO) δ1.46 (s, 9H), 6.50 (d, *J* = 4.1 Hz, 1H), 7.06 (t, *J* = 5.5 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.1 Hz, 1H), 7.86 – 7.62 (m, 6H), 8.62 (d, *J* = 6.7 Hz, 1H), 8.90 (dd, *J* = 19.0, 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ32.22 (s), 35.93 (s), 121.33 (s), 123.70 (d, *J* = 20.0 Hz), 124.81 (s), 125.75 (s), 126.47 (s), 126.82 – 128.11 (m), 127.98 (s), 128.32 (s), 129.17 (d, *J* = 18.9 Hz), 129.96 (s), 132.53 (s), 132.82 (s), 135.88 (s), 138.04 (s), 145.71 (s), 155.15 (s). MS (ESI^+): m/z 468.36 (MH^+), Calc. 467.02. Anal. Found: C, 74.71; H, 4.93; N, 5.79. Calc. for $C_{29}H_{23}ClN_2S$: C, 74.58; H, 4.96; N, 6.00%.

2-(4-bromophenyl)-1-(4-(tert-butyl)phenyl)-1H-phenanthro[9,10-d]imidazole (*t*-PhIm-Ph-Br)

Mp (243 ºC). ^{1}H NMR (400 MHz, CD_3Cl): 1.47 (s, 9H), 7.16-7.83 (m, 13H), 8.76 (dd, *J* = 15.2, 8.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ31.99 (s), 35.58 (s), 121.41 (s), 123.29 (s), 123.65 (d, *J* = 13.9 Hz), 124.63 (s), 125.54 (s), 126.24 (s), 126.88 (s), 127.74 (d, *J* = 13.6 Hz), 128.94 (s), 129.95 (d, *J* = 19.9 Hz), 131.26 (s), 131.89 (s), 136.24 (s), 137.90 (s), 150.21 (s), 153.94 (s). MS (ESI^+): m/z 505.5 (MH^+), Calc. 504.12. Anal. Found: C, 73.92; H, 4.93; N, 5.45%. Calc. for $C_{31}H_{25}BrN_2$: C, 73.66; H, 4.99; N, 5.54%.

2-(5-bromothiophen-2-yl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (PhIm-Thi-Br)

Mp (220.5 ºC). ^{1}H NMR (400 MHz, CD_2Cl_2) δ6.96 (s, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.27-7.36 (m, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.64-7.89 (m, 8H), 8.78 (dd, *J* = 19.8, 8.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ115.97 (s), 121.57 (s), 123.25 – 124.67 (m), 125.15 (s), 126.13 (s), 126.85 (s), 127.61 (d, *J* = 23.7 Hz), 127.76 (s), 128.66 (dd, *J* = 93.2, 26.9 Hz), 130.21 (s), 130.75 – 131.23 (m), 131.65 (t, *J* = 19.4 Hz), 135.52 (s), 138.96 (s), 145.80 (s). MS (ESI^+): m/z 456.31 (MH^+), Calc. 455.37. Anal. Found: C, 66.35; H, 3.24; N, 6.06%; Calc. for $C_{25}H_{15}BrN_2S$: C, 65.94; H, 3.32; N, 6.15%.

4-(2-(5-bromothiophen-2-yl)-1H-phenanthro[9,10-d]imidazol-1-yl)benzoic acid (COOH-PhIm-thi-Br)

Mp (N.D). ^{1}H NMR (400 MHz, DMSO) δ6.42 (d, *J* = 4.0 Hz, 2H), 7.04 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 4.1 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.70 (dd, *J* = 11.2, 4.3 Hz, 1H), 7.79 (t, *J* = 7.1 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 8.32 (d, *J* = 8.4 Hz, 2H), 8.57 – 8.69 (m, 1H), 8.91 (dd, *J* = 19.8, 8.3 Hz, 2H), 13.47 – 13.79 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ118.49 (s), 127.56 (s), 128.10 (s), 130.28 (d, *J* = 18.5 Hz), 131.87 (d, *J* = 12.1 Hz), 141.77 (s), 142.75 (s), 149.15 (s), 156.13 (s), 167.56 (d, *J* = 14.1 Hz). MS (ESI^{+}): m/z 500.12 (MH^{+}), Calc. 499.38. Anal. Found: C, 62.99; H, 3.26; N, 5.31%; Calc. For $C_{26}H_{15}BrN_2O_2S$: C, 62.53; H, 3.03; N, 5.61%.

2-(5-bromothiophen-2-yl)-1-(4-(tert-butyl)phenyl)-4,5-diphenyl-1H-imidazole (*t*-BIm-Thi-Br)

Mp (212.2 ºC). ^{1}H NMR (400 MHz, DMSO) δ1.26 (d, *J* = 11.6 Hz, 9H), 6.22 (d, *J* = 4.0 Hz, 1H), 7.05 (d, *J* = 4.0 Hz, 1H), 7.16 – 7.21 (m, 1H), 7.21 – 7.33 (m, 7H), 7.33 – 7.39 (m, 2H), 7.45 (ddd, *J* = 10.6, 7.6, 4.5 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ32.02 (s), 35.53 (s), 114.16 (s), 126.88 (d, *J* = 34.4 Hz), 127.46 (s), 128.03 (s), 128.63 – 129.59 (m), 130.79 (s), 131.64 (s), 132.04 (s), 134.16 (s), 134.82 (s), 135.68 (s), 139.06 (s), 142.08 (s), 153.51 (s). MS (ESI^{+}): m/z 514.71 (MH^{+}), Calc. 513.49. Anal. Found: C, 67.97; H, 4.99; N, 5.33%; Calc. for $C_{25}H_{15}BrN_2S$:C, 67.83; H, 4.91; N, 5.46%.

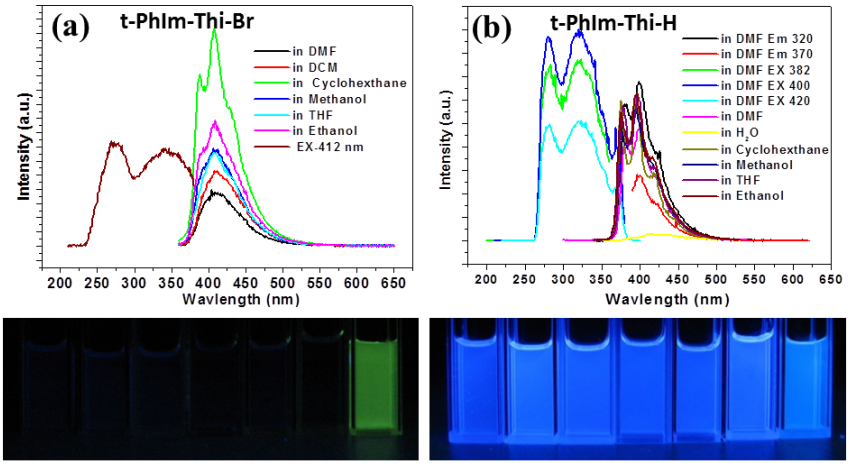


Fig. S1 Emission and excitation spectra of *t*-PhIm-Thi-Br (a) and *t*-PhIm-Thi-H (b) in different solvents. Lower set: Emission images of *t*-PhIm-Thi-Br and *t*-PhIm-Thi-H in different solvents. Left to right: Cyclohexthane, Dichloromethane (DCM) ,THF, Methaol, Ethanol, DMF, H_2O.

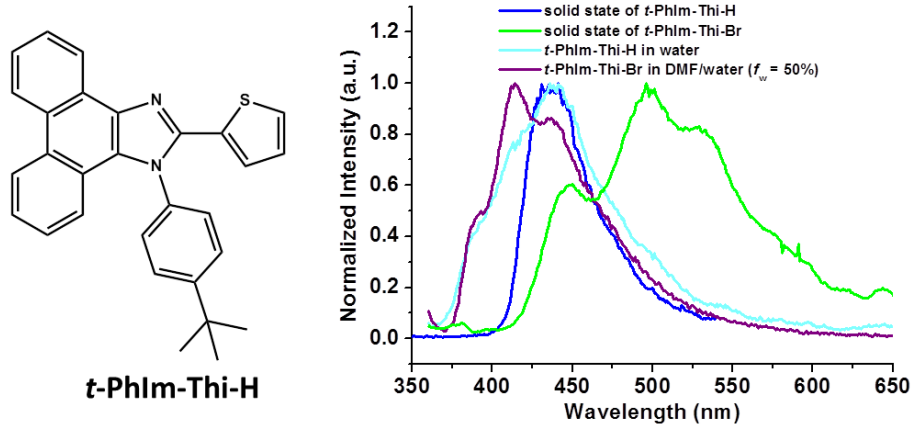


Fig. S2 Structure (left) and emission spectra (right) of *t*-PhIm-Thi-H (in solid state and aggregation state in pure water) and *t*-PhIm-Thi-Br (in DMF solution with 50% water content).

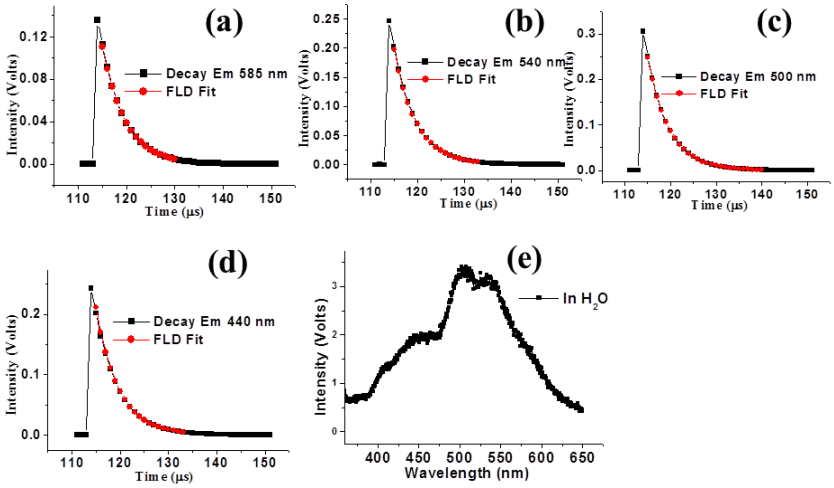


Fig. S3 Emission life-time of *t*-PhIm-Thi-Br mornitored at: 585 nm, 540 nm, 500 nm, 440 nm of the nano-aggregate state in H_2O (a)~(d). Time-resolved emssion spectrum of *t*-PhIm-Thi-Br in H_2O with concentration of 10 μM, delay time: 5 μs (e). The emission-life time and time-resolved emission was performed on optical spectrometer excited by N_2 laser (PTI: QM-TM, USA) using single shot method.

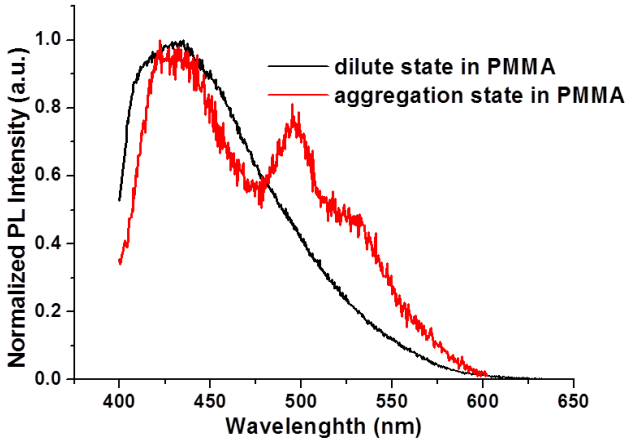


Fig. S4 Emission spectrum of *t*-PhIm-Thi-Br embedded in glassy polymer of PMMA with different concentration: dilute state (5 mg / 400 mg), aggregation state (10 mg / 50 mg).

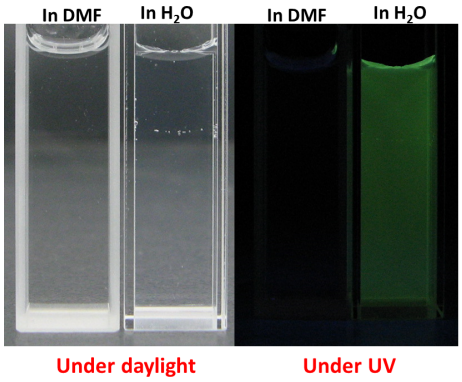


Fig. S5 Pictures of *t*-PhIm-Thi-Br in DMF and H_2O under daylight and UV, respectively.

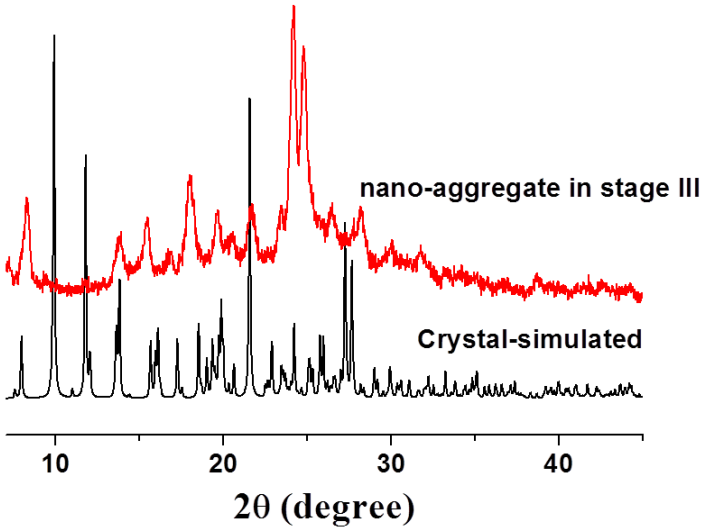


Fig. S6 XRD patterns of crystal-simulated and nano-aggregate in stage III. The nano-aggregate was collected by centrifugation.

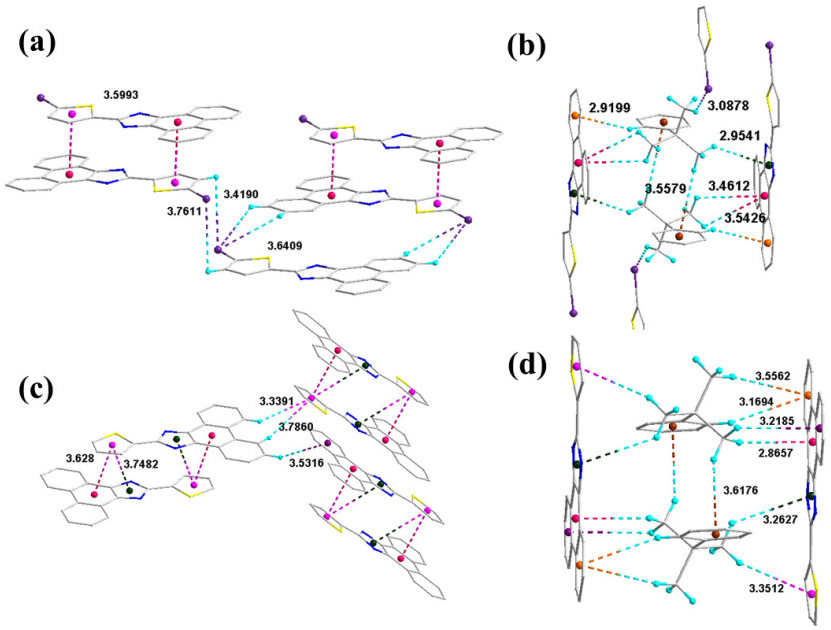


Fig. S7 Interaction analysis of *t*-PhIm-Thi-Br (a) (b) and *t*-PhIm-Thi-H (c) (d), dot lines for weak interactions.

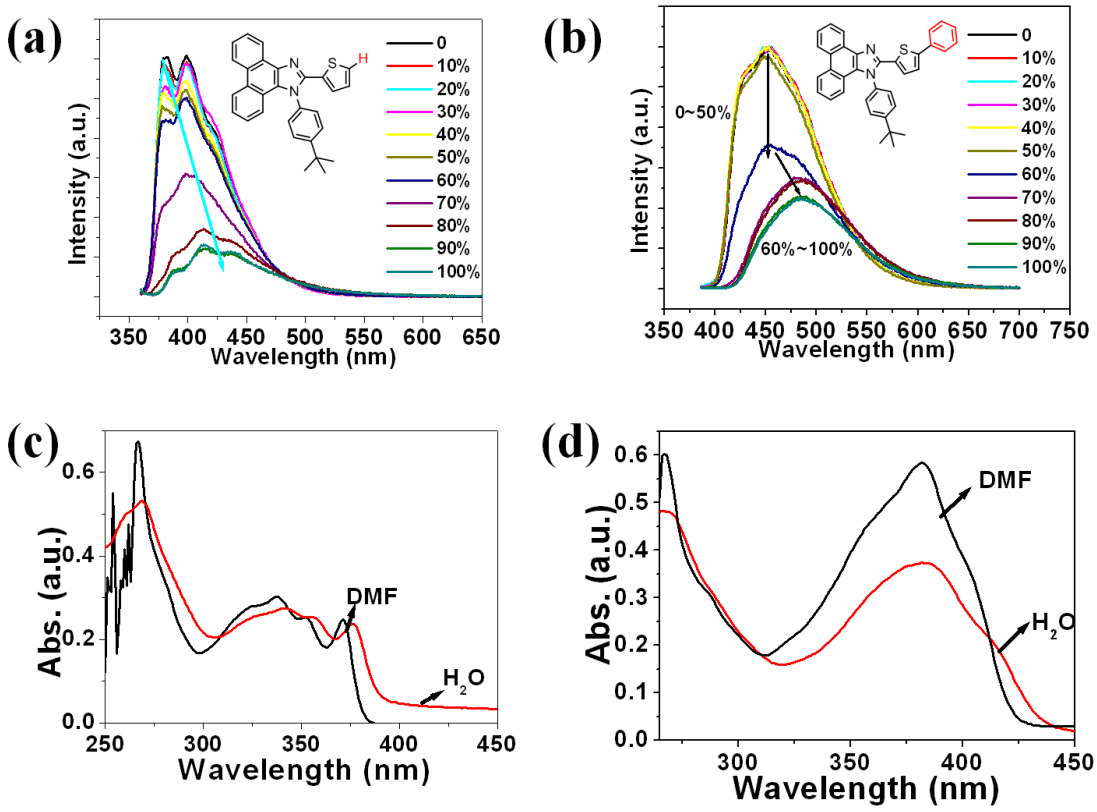


Fig. S8 Emission spectra of *t*-PhIm-Thi-H (a) and *t*-PhIm-Thi-Ph (b) in DMF solutions with different water contents (0 ~ 100%); UV-Vis absorption spectra of *t*-PhIm-Thi-H (c) and *t*-PhIm-Thi-Ph (d) in DMF and H_2O, respectively.

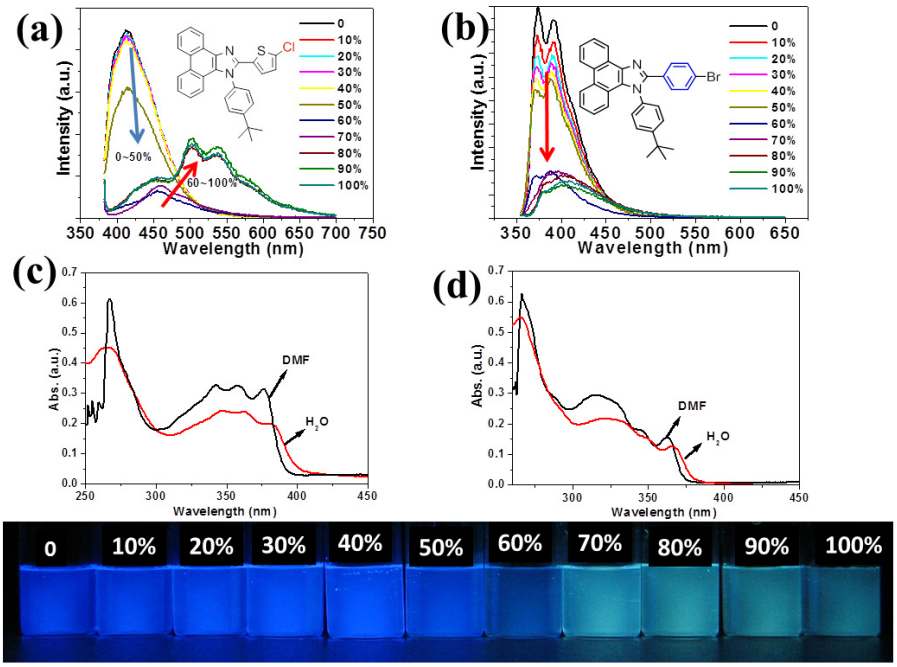


Fig. S9 Emission spectra of *t*-PhIm-Thi-Cl (a) and *t*-PhIm-Ph-Br (b) in DMF with different water contents (0 ~ 100%); UV-Vis absorption spectra of *t*-PhIm-Thi-Cl (c) and *t*-PhIm-Ph-Br (d) in DMF and H_2O, respectively, Emission photos of *t*-PhIm-Thi-Cl in DMF solutions with different water contents (0 ~ 100%).

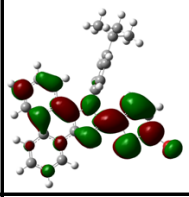
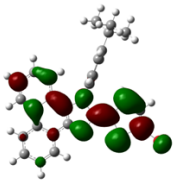
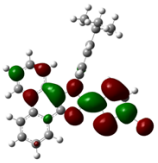
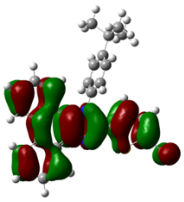
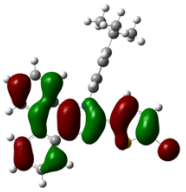
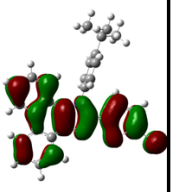
	S_0 state		S_1 state	T_1 state
LUMO		HSOMO		
HOMO		LSOMO		

Fig. S10 HOMO and LUMO frontier molecular orbitals of *t*-PhIm-Thi-Br, noting that both HOMO and LUMO localize at Br atom in excited and ground states.

Computational Method

Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculation was carried out with the Gaussian 09 A. 02 software package[S1]. All the calculations

were performed using the B3LYP[S2, S3] functional with 6-31g** basis set [S4]. The calculations of molecular orbitals are based on the geometries of S_0 state optimized by DFT and the geometries of S_1 state as well as T_1 state optimized by TD-DFT.

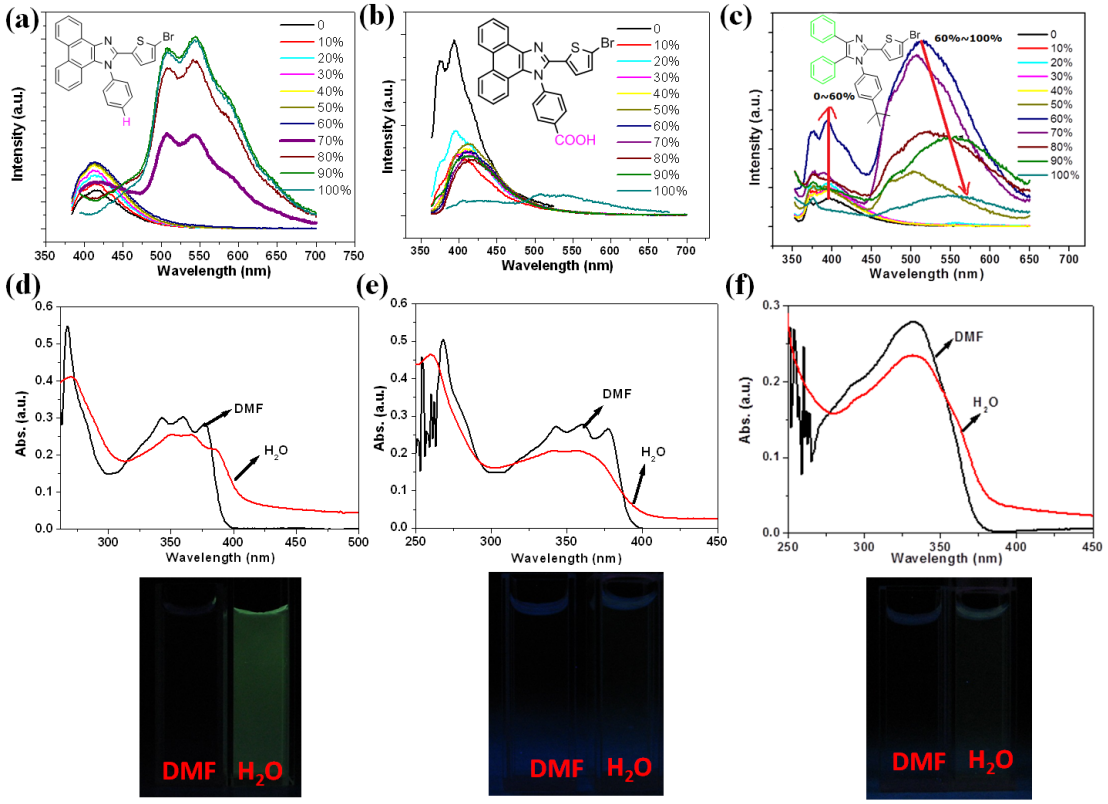


Fig. S11 Emission spectra of PhIm-Thi-Br (a) COOH-PhIm-Thi-Br (b) and *t*-BIm-Thi-Br (c) in DMF with different water contents (0 ~ 100%); UV-Vis absorption spectra and of PhIm-Thi-Br (d) COOH-PhIm-Thi-Br (e) and *t*-BIm-Thi-Br (f) in DMF and H_2O, respectively; below: emission photos taken under a 365 nm hand-lamp.

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