Supporting Information for

Imidazole-Based Excited-State Intramolecular Proton-Transfer (ESIPT) Materials: Observation of Thermally Activated Delayed Fluorescence (TDF)

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Synthesis of Hydroxy-Substituted Tetraphenyl Imidazole (HPI), 2-(1,4,5-Triphenyl-1H-imidazol-2-yl)-phenol. 5.0 g of benzil (23.8 mmol) and 2.55 mL of salicylaldehyde (23.8 mmol) were dissolved in 120 mL of glacial acetic acid at room temperature. 3.25 mL (35.7 mmol) of aniline was added dropwise in this solution and 9.17 g of ammonium acetate (119 mmol) was added subsequently. The mixture was heated at 110 °C for 12 h. After termination of reaction, the dark solution was poured into copious amount of water. Recrystallization from ethyl acetate solution afforded 6.50 g of white HPI powder with 72% overall yield. HPI, m.p. 254 ^{o}C, ^{1}H NMR (300 MHz, $CDCl_3$) δ[ppm] 6.46 (t, 1H), 6.54 (d, 1H), 7.08 (d, 1H), 7.12-7.41 (m, 14H), 7.55 (d, 2H), 13.48 (s, 1H), ^{13}C NMR (300 MHz, $CDCl_3$) δ[ppm] 113.19, 117.88, 118.08, 126.22, 127.11, 127.21, 128.48, 128.67, 128.87, 129.38, 129.79, 130.03, 130.11, 130.66, 131.53, 133.30, 135.37, 137.34, 145.13, 158.66. Anal. Calcd for $C_{27}H_{20}N_2O$: C, 83.48; H, 5.19; N, 7.21. Found: C, 83.37; H, 5.19; N, 7.19. MS (EI) (calcd for $C_{27}H_{20}N_2O$, 388.16; found, 388)

Synthesis of Acetyloxyethyl-Substituted HPI (HPI-Ac), Acetic Acid 2-{4-[2-(2-Hydroxy-phenyl)-4,5-diphenyl-imidazol-1-yl]-phenyl}-ethyl Ester. 5.0 g of benzil (23.8 mmol) and 2.55 mL of salicylaldehyde (23.8 mmol) were dissolved in 120 mL of glacial acetic acid at room temperature. 4.89 g of 2-(4-Amino-phenyl)-ethanol (35.7 mmol) and 9.17 g of ammonium acetate (119 mmol) were added subsequently. The mixture was heated at 110 °C for 12 h. After termination of reaction, the dark solution was poured into copious amount of water. Recrystallization from ethyl acetate solution afforded 7.9 g of

white HPI-Ac powder with 70% overall yield. HPI-Ac, m.p. 164 °C, 1H NMR (300 MHz, $CDCl_3$) δ[ppm] 2.00 (s, 3H), 2.95 (t, 2H), 4.28 (t, 2H), 6.46 (t, 1H), 6.54 (d, 1H), 7.05-7.28 (m, 14H), 7.51-7.55 (m, 2H), 13.46 (s, 1H), ^{13}C NMR (300 MHz, $CDCl_3$) δ[ppm] 21.05, 34.91, 64.41, 113.20, 117.89, 118.07, 126.20, 127.11, 127.21, 128.48, 130.04, 130.12, 130.29, 131.53, 133.29, 135.80, 139.38, 145.15, 158.66, 171.01. Anal. Calcd for $C_{31}H_{26}N_2O_3$: C, 78.46; H, 5.52; N, 5.90. Found: C, 78.24; H, 5.53; N, 5.87. MS (EI) (calcd for $C_{31}H_{26}N_2O_3$, 474.19; found, 474)

Synthesis of nonproton-transfer molecule (MeOPI-Ac), Acetic acid 2-{4-[2-(2-methoxy-phenyl)-4,5-diphenyl-imidazol-1-yl]-phenyl}-ethyl ester. 1.94 g of 2-methoxy-benzaldehyde (14.3 mmol) and 3 g of benzyl (14.3 mmol) were dissolved in in 100 mL of glacial acetic acid at room temperature. 2.94 g of 2-(4-Amino-phenyl)-ethanol (21.4 mmol) and 5.50 g of ammonium acetate (71.4 mmol) were added subsequently. The mixture was heated at 110 °C for 12 h. After termination of reaction, the dark solution was poured into copious amount of water. Recrystallization from ethyl acetate solution afforded 4.3 g of white MeOPI-Ac powder with 65% overall yield. ^{1}H NMR (300 MHz, $CDCl_3$), δ[ppm] 1.98 (s, 3H), 2.89 (t, 2H), 4.23 (t, 2H), 6.97 (d, 2H), 7.07-7.13 (m, 4H), 7.17-1.27 (m, 11H), 7.42 (m, 2H), 7.58 (m, 2H). ^{13}C NMR (300 MHz, $CDCl_3$), δ [ppm] 21.01, 34.68, 54.74, 64.60, 11066, 120.60, 120.80, 126.55, 127.50, 127.91, 128.19, 128.51, 128.69, 129.70, 130.87, 131.07, 131.20, 132.64, 134.80, 135.99, 137.07, 138.29, 145.67, 157.07, 170.95.

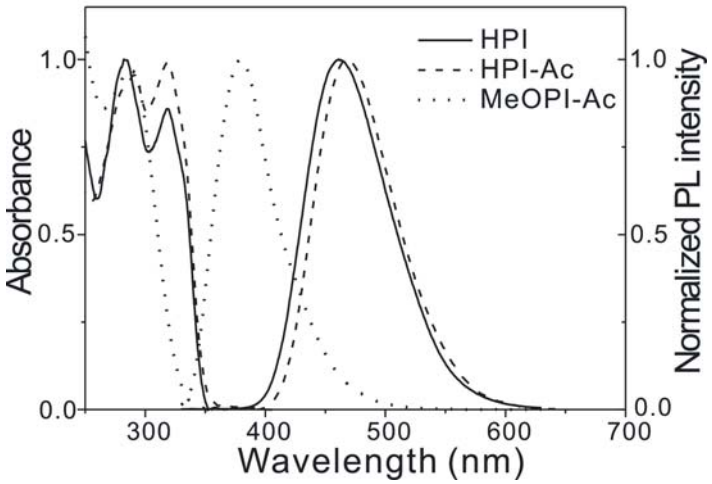

Figure S-1. Absorption and emission spectra of HPI (solid), HPI-Ac (dashed), and MeOPI-Ac (dotted line) at room temperature (excited at 320 nm).

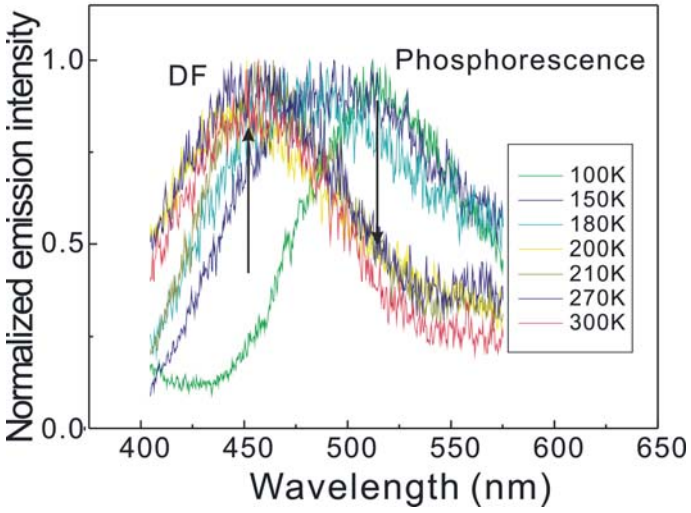

Figure S-2. Temperature dependence of the phosphorescence and DF spectra of HPI-Ac (excited at 315 nm) from 100 to 300 K (collected at 25 μs after the photoexcitation with the gate time of 2.5 μs).

Figure S-3. Photograph showing the fluorescence of HPI-Ac solution after degassing by Argon gas purging. The cuvette was specially designed for efficient gas purging.

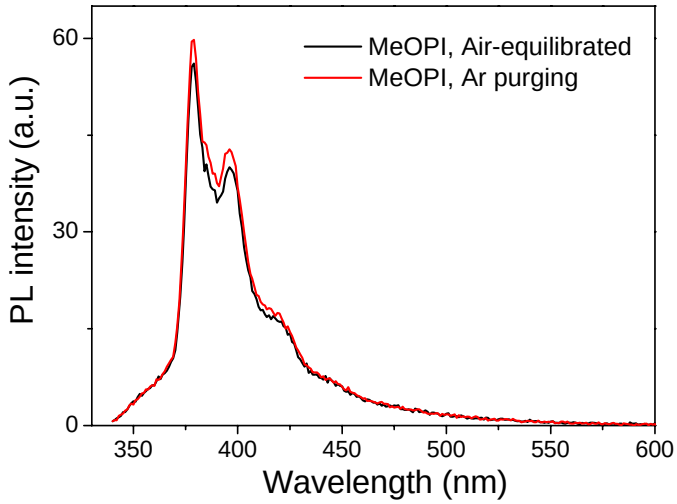

Figure S-4. Emission spectra of MeOPI-Ac (excited at 320 nm) in $CHCl_3$ (1×10^{-5} M) at room temperature.

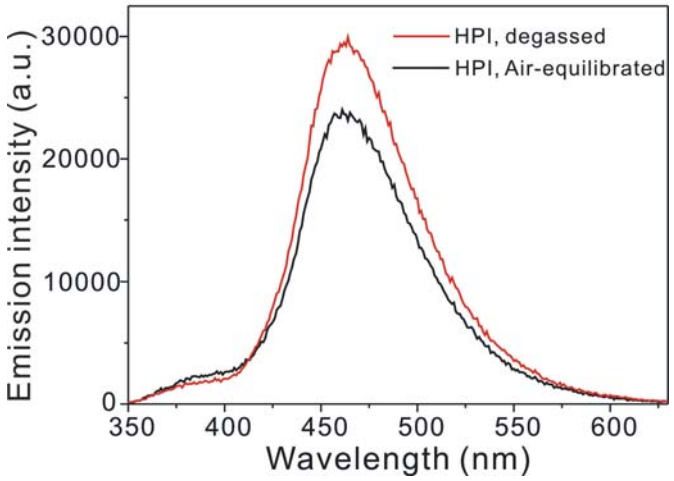

Figure S-5. Emission spectra of HPI (excited at 320 nm) in $CHCl_3$ (1×10^{-5} M) at room temperature.