Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for

Strategic emission color tuning of highly fluorescent imidazole-based excited-state intramolecular proton transfer molecules

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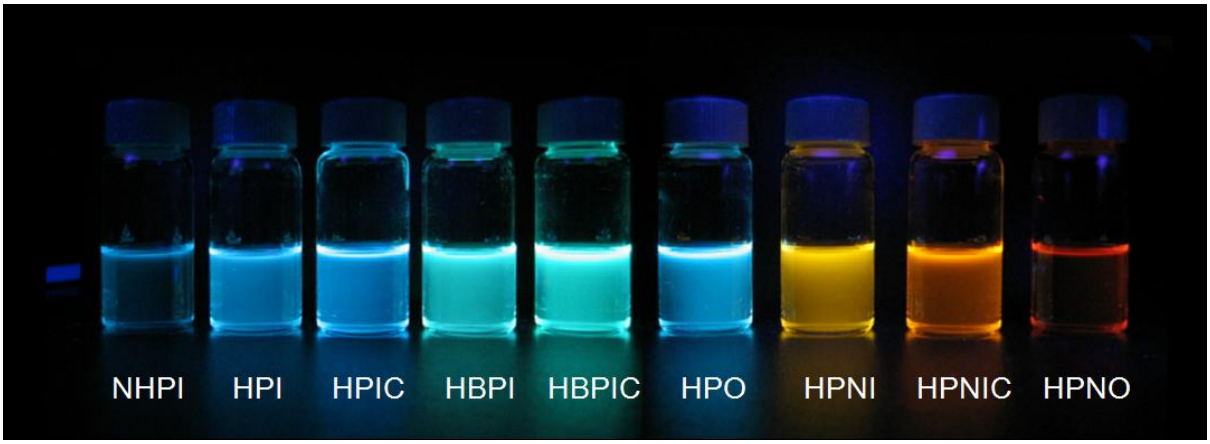


Figure S1. Photograph of the nine synthesized molecules in solution state (10μM in $CHCl_3$).

Photographs were taken under 365-nm hand-held UV lamp at room temperature.

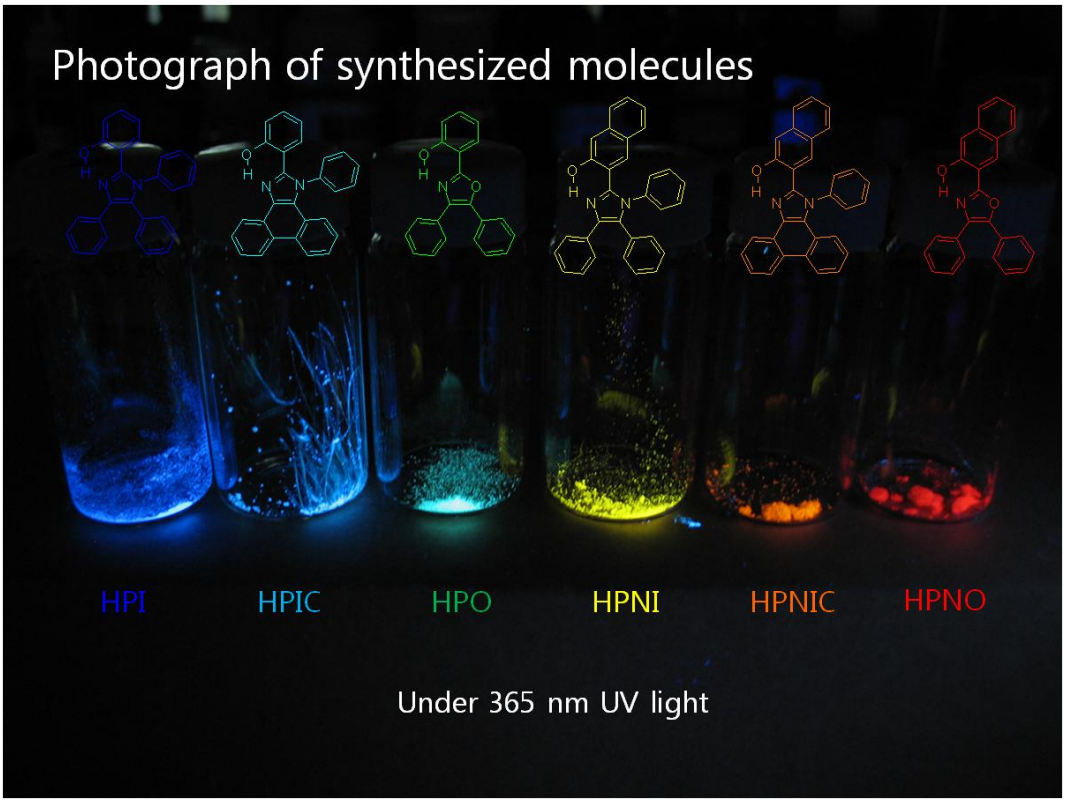


Figure S2. Photograph of the synthesized molecule in solid state (powder). Photographs were taken under 365-nm hand-held UV lamp at room temperature.

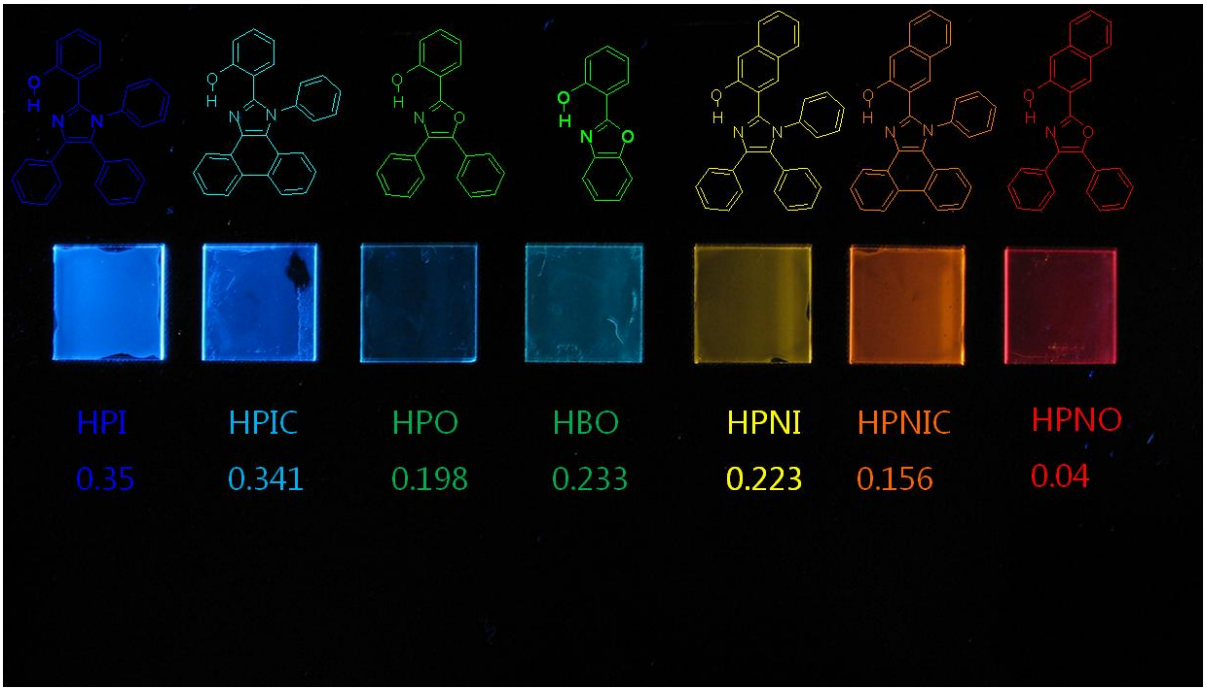


Figure S3. Photograph of the synthesized molecule in thin film state (in PMMA polymer matrix, 5 wt.% compare to PMMA). Photographs were taken under 365-nm hand-held UV lamp at room temperature.

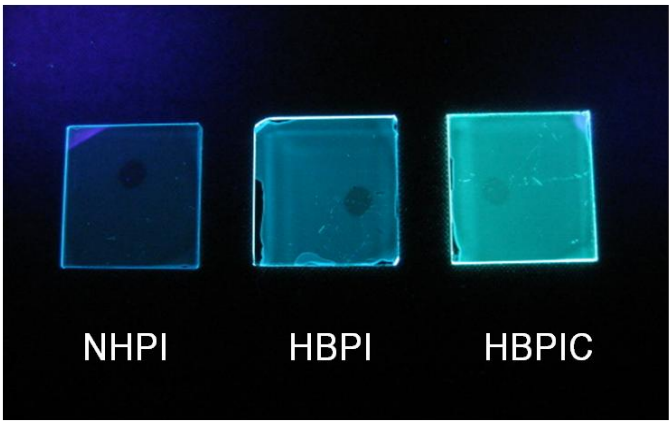


Figure S4. Photograph of the synthesized molecule in thin film state (in PMMA polymer matrix, 5 wt.% compare to PMMA). Photographs were taken under 365-nm hand-held UV lamp at room temperature.

Table S1. Photophysical properties of nine emission tuned HPI derivatives in film state

	Abs. λ_{max}	**E_g(eV)**	**Ems. λ_{max}**	**Stokes' Shift**	**PLQY**	**Lifetime (τ_{avg})**	***k_r***	***k_{nr}***
HPI	319 nm	3.55	461 nm	9656.0	0.35	3.48	1.0×10^8 /s	1.9×10^8 /s
HPIC	364 nm	3.32	470 nm	6195.9	0.341	2.63	1.3×10^8 /s	2.5×10^8 /s
NHPI	335 nm	3.31	370 nm 480 nm	9017.4	0.158	1.50 (@410 nm) 2.63 (@470 nm)		
HBPI	342 nm	3.43	481 nm	8449.7	0.433	4.53	1.4×10^8 /s	1.0×10^8 /s
HBPIC	368 nm	3.25	492 nm	6848.7	0.564	4.16	9.5×10^7 /s	3.9×10^8 /s
HPO	332 nm	3.42	477 nm	9156.1	0.198	2.08	9.6×10^7 /s	1.3×10^8 /s
HPNI	332 nm	3.13	566 nm	12452.6	0.223	4.97	4.5×10^7 /s	1.6×10^8 /s
HPNIC	364 nm	3.08	588 nm	10465.7	0.156	2.81	5.6×10^7 /s	3.0×10^8 /s
HPNO	342 nm	3.11	621 nm	13136.7	0.04	0.96	4.2×10^7 /s	1.0×10^9 /s

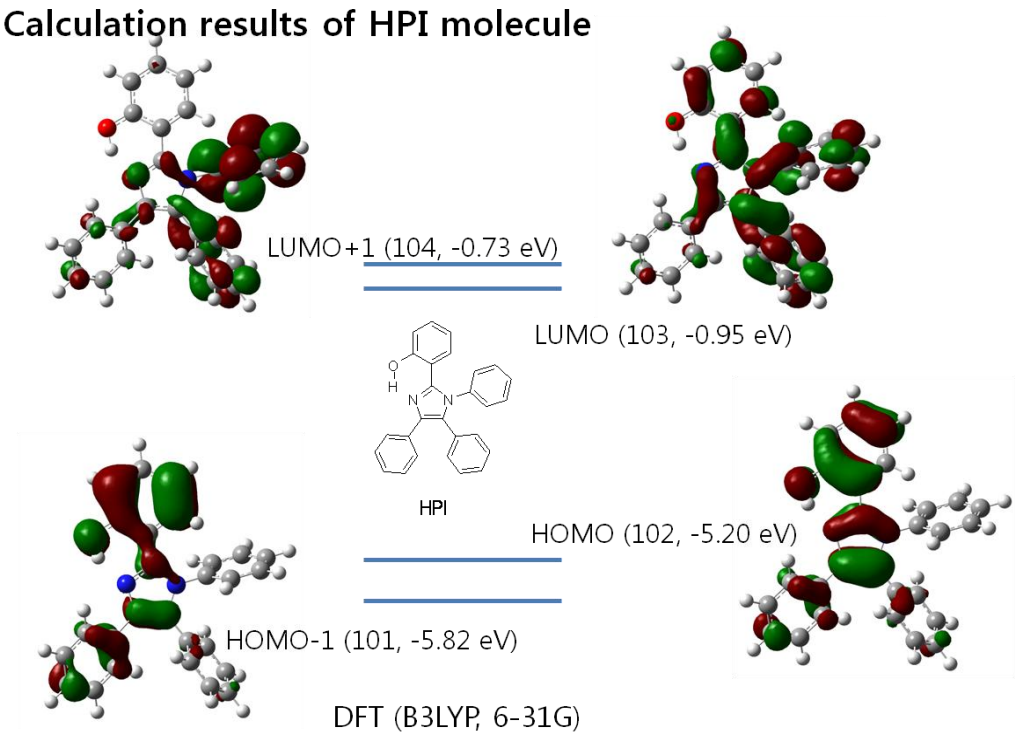


Figure S5. Calculation results for HPI molecule.

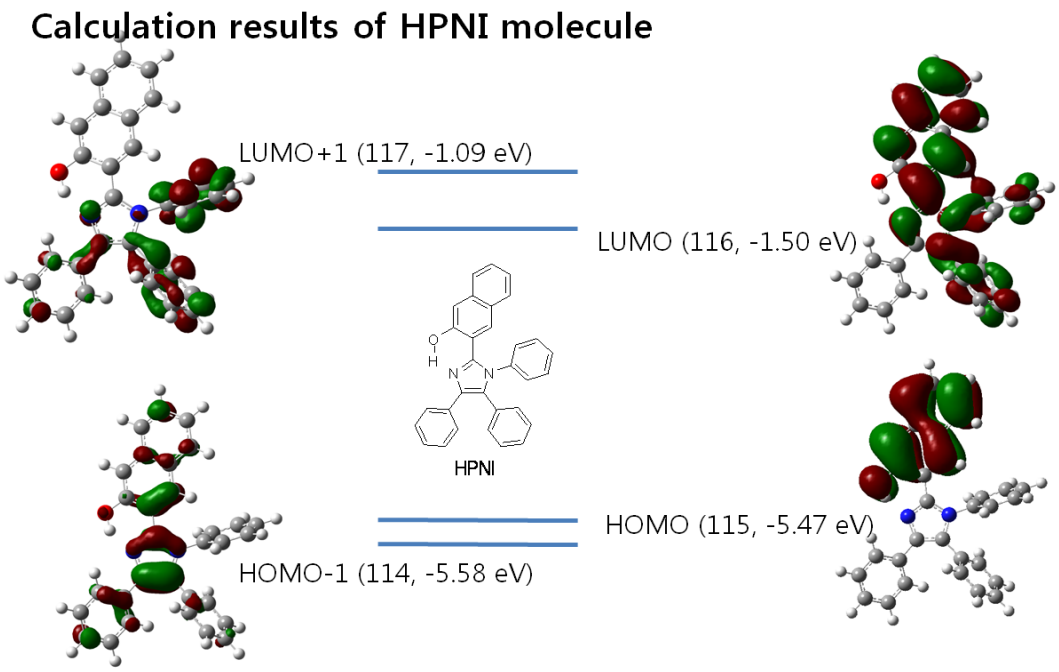


Figure S6. Calculation results for HPNI molecule.

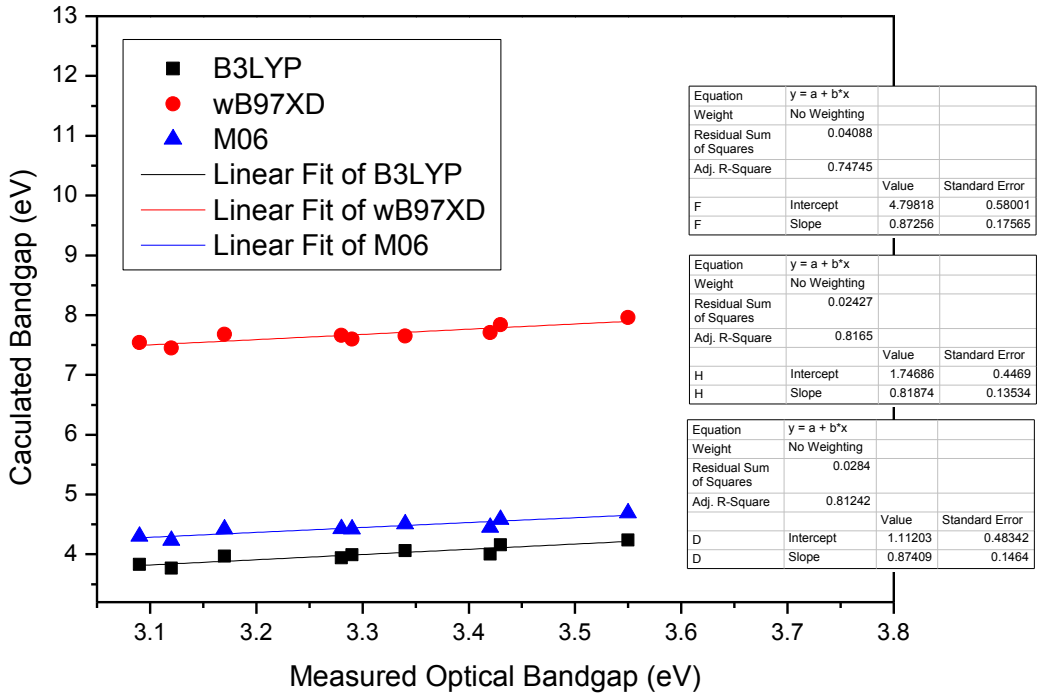


Figure S7. Calculation results for ground state E form of nine molecules using M06, wB97XD, and B3LYP functionals with 6-31G** basis set. Each line shows the linear fit for the three different parameters.

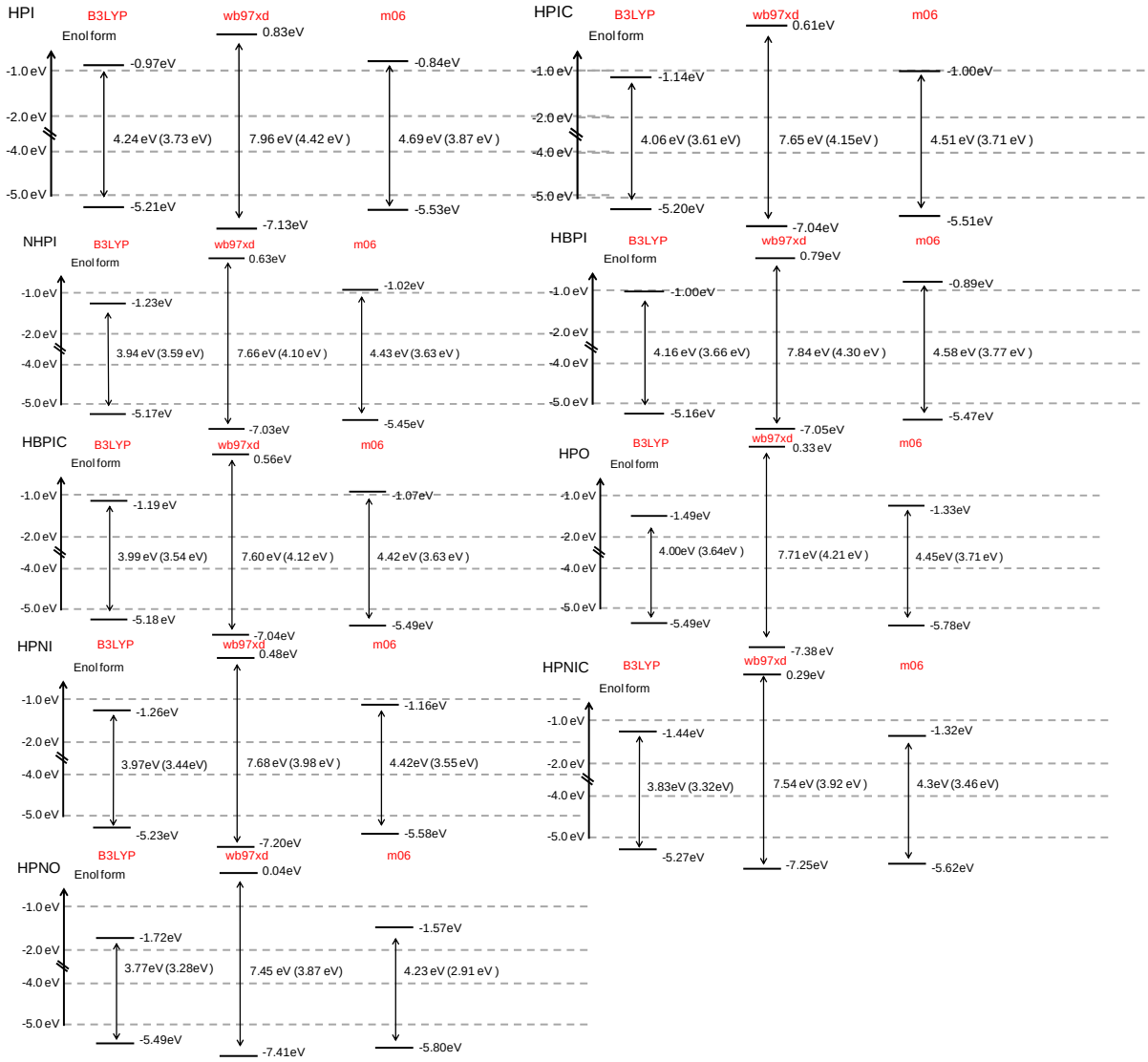


Figure S8. Calculation results for ground state E form of nine molecules using M06, wB97XD, and B3LYP functionals with 6-31G** basis set.

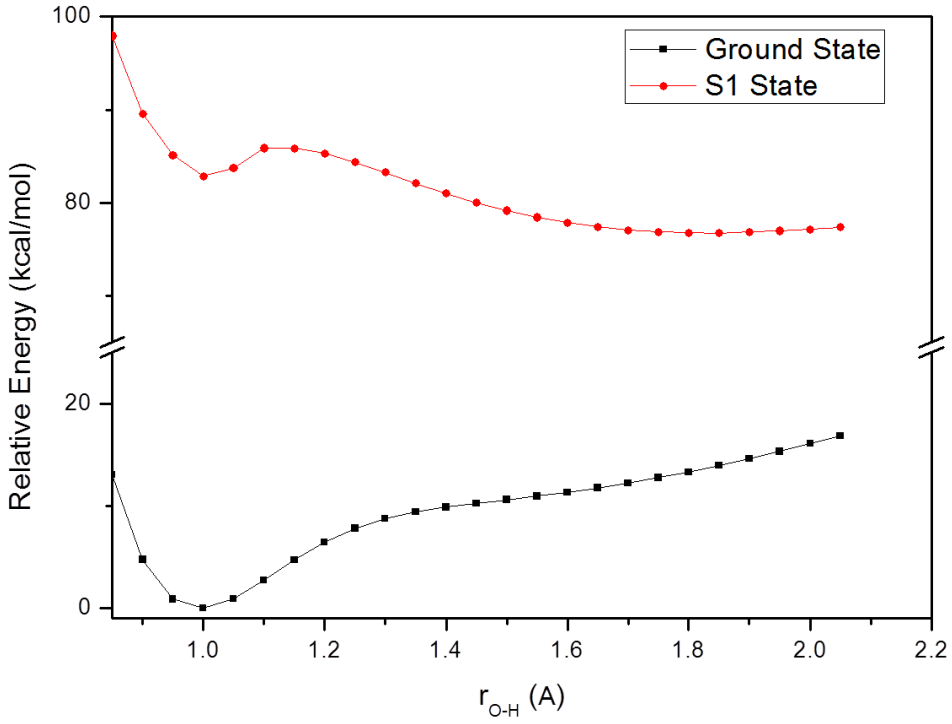


Figure S9. GISPT and Frank-Condon ESIPT curves of HPI obtained from DFT and TD-DFT with B3LYP/6-31G(d,p).

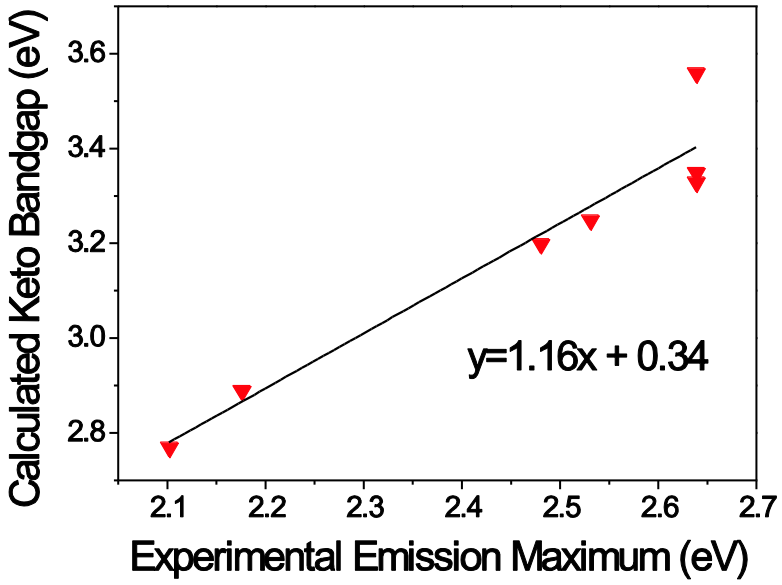


Figure S10. The plot of measured emission maximum (eV) vs. calculated transition energy of keto form.

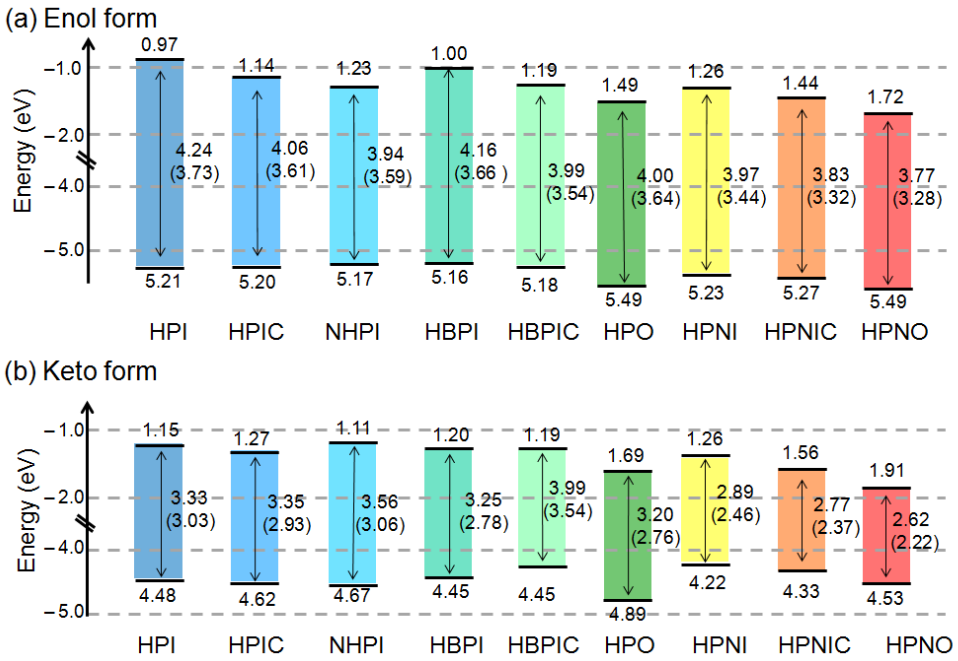


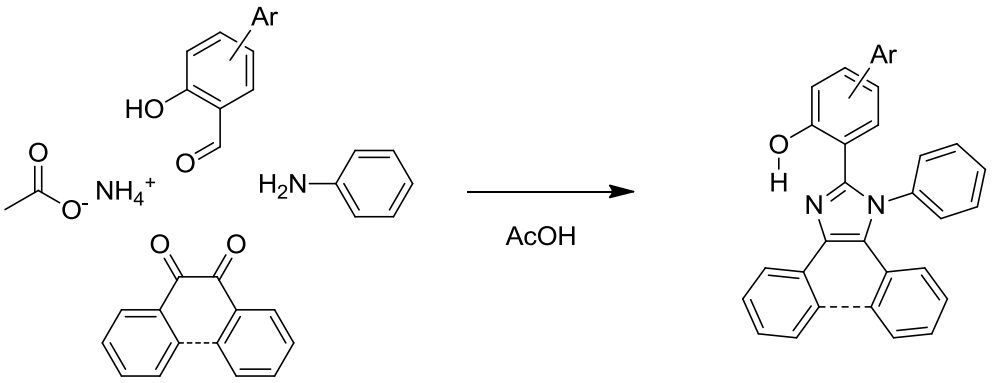
Figure S11. Calculated energy levels of HPI derivatives in (a) enol and (b) keto form (DFT, B3LYP/6-31G**). Figures in parenthesis refer to $S_0 \rightarrow S_1$ transition energy (TD-DFT).

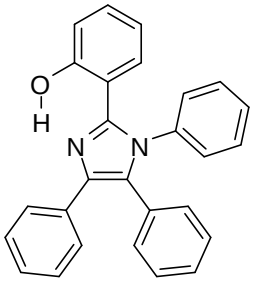
Synthesis

Materials

Benzil, 4,4'-oxydianiline, 2-naphthol, *tert*-buthyllithium (*t*-BuLi) solution (1.7 M in pentane), 4-((2-hydroxyethyl)(methyl)amino)benzaldehyde, 2-(2,6-dimethyl-4H-pyran-4-ylidene)malononitrile, dicyclohexylcarbodiimide, dimethylaminopyridine, phenanthrene-9,10-dione, and ammonium acetate were purchased from Aldrich. Salicylaldehyde was purchased from Lancaster. Glacial acetic acid was obtained from J. T. Baker. All reagents were used as received.

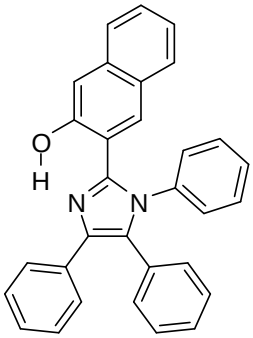
General procedure and scheme for the synthesis of imidazole compounds





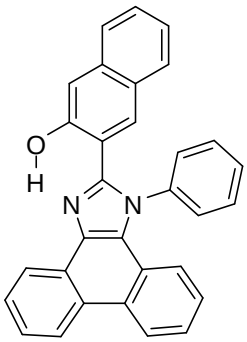
HPI **Synthesis of Hydroxy-Substituted Tetraphenyl Imidazole (HPI),**

A 5.0 g amount 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. A 3.25 mL amount of aniline (35.7 mmol) was added dropwise to 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 the termination of reaction, the dark solution was poured into a copious amount of water. Recrystallization from an ethyl acetate solution afforded 6.50 g of white HPI powder with a 72% overall yield. HPI, mp 254 °C; ^{1}H NMR (300 MHz, CDCl3) 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); MS (EI) calcd for C27H20N2O 388.16, found 388. Anal. Calcd for C27H20N2O: C, 83.48; H, 5.19; N,7.21. Found: C, 83.37; H, 5.19; N, 7.19.

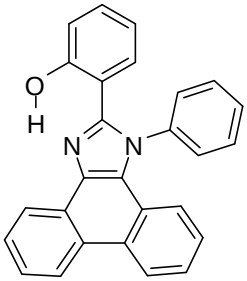


HPNI **Synthesis of 3-(1,4,5-triphenyl-1H-imidazol-2-yl)naphthalen-2-ol (HPNI)** 1.61g (yield 63%) of the title compound was obtained by the same procedure for HPI, using 1.0 g of 3-hydroxy-2-naphthaldehyde (5.81 mmol). ^{1}H NMR (300 MHz, DMSO) δ [ppm] 7.17-7.25 (m,3H), 7.27-7.30 (m, 3H), 7.31-7.32 (m, 6H), 7.35-7.37 (m, 6H), 7.49 (d, 3H), 7.65 (d, 1H), 12.04 (s, 1H) ^{13}C NMR (75 MHz, DMSO) δ [ppm] 110.09, 117.27, 123.36, 125.66, 126.23, 126.43, 126.93, 127.15, 127.82, 128.26, 128.45, 128.59, 128.74, 129.07, 129.30, 129.73, 131.03, 131.22, 133.38, 134.29, 135.22, 136.59, 144.19, 154.24. MS

(EI) (calcd for $C_{31}H_{22}N_2O$, 438.17; found 438). Analysis (calcd, found for $C_{31}H_{22}N_2O$): C (84.91, 85.12), H (5.06, 5.12), N (6.39, 6.48), O (3.65, 3.69). T_m (DSC) 279 °C.

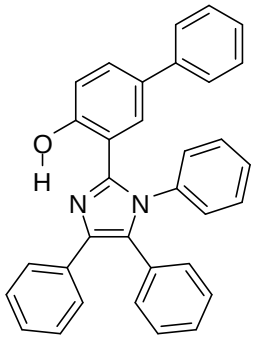


HPNIC **Synthesis of 3-(1-phenyl-1H-phenanthro[9,10-d]imidazol-2-yl)naphthalen-2-ol (HPNIC)** 1.55g (yield 61%) of the title compound was obtained by the same procedure for HPI, using 1.0 g of 3-hydroxy-2-naphthaldehyde (5.81 mmol) and 1.21 g (6.42 mmol) of phenanthrene-9,10-dione. ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] 6.97 (s, 1H), 7.14-7.20 (m, 4H), 7.28 (d, 1H), 7.36 (m, 1H), 7.44 (s, 1H), 7.54 (t, 1H), 7.62-7.72 (m, 4H), 7.75-7.87 (m, 4H), 8.70-8.79 (m, 3H), 13.50 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm] 111.85, 115.54, 121.27, 122.80, 122.86, 123.36, 123.46, 124.46, 125.72, 126.03, 126.08, 126.42, 126.82, 126.92, 127.59, 127.62, 127.81, 128.63, 128.75, 129.42, 129.92, 130.90, 131.22, 135.04, 135.17, 139.42, 148.10, 155.89. MS (EI) (calcd for $C_{31}H_{20}N_2O$, 436.16; found 436). Analysis (calcd, found for $C_{31}H_{20}N_2O$): C (85.30, 85.51), H (4.62, 4.75), N (6.42, 6.58), O (3.67, 3.70).



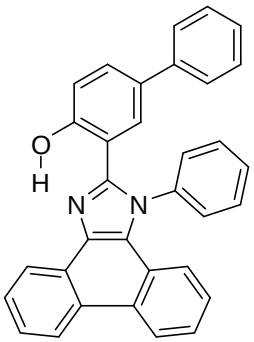
HPIC **HPIC (2-(1-phenyl-1H-phenanthro[9,10-d]imidazol-2-yl)phenol)**

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.04 (d, 1H, J = 8.2 Hz), 7.13 (d, 1H, J = 8.0 Hz), 7.18-7.27 (m, 2H), 7.51 (t, 1H, J = 7.4 Hz), 7.61-7.77 (m, 7H), 8.68-8.77 (m, 3H), 13.83 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 113.3, 118.3, 121.1, 122.8, 123.4, 124.4, 125.5, 126.0, 126.3, 126.7, 127.3, 127.7, 128.7, 129.3 129.7, 130.8, 130.9, 131.1, 134.7, 139.3, 148.7, 159.4. HRMS (EI, positive): Calcd for $C_{27}H_{18}N_2O$ (M), 386.1419; found 386.1419. Anal. calcd for calcd for $C_{27}H_{18}N_2O$: C, 83.92; H, 4.69; N, 7.25; O, 4.14. found: C, 83.06; H, 4.69; N, 7.08; O, 5.02.



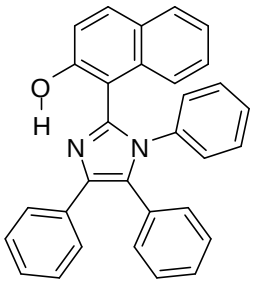
HBPI **HBPI (3-(1,4,5-triphenyl-1H-imidazol-2-yl)biphenyl-4-ol)**

1.4g (yield 60%) of the title compound was obtained by the same procedure for HPI, using 1.0 g of 2-hydroxy-5-phenylbenzaldehyde (5.04 mmol). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.87 (d, 1H, J = 2.1 Hz), 6.97-7.00 (m, 2H), 7.12-7.31 (m, 14H), 7.41-7.50 (m, 4H), 7.55-7.58 (m, 2H), 13.48 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 113.2, 118.2, 125.0, 126.2, 126.5, 127.1, 127.3, 128.5, 128.5, 128.6, 128.7, 129.0, 129.3, 130.0, 130.1, 130.6, 130.7, 131.6, 133.3, 135.5, 137.7, 140.5, 145.1, 158.2. HRMS (EI, positive): Calcd for $C_{33}H_{24}N_2O$ (M), 464.1889; found 464.1889. Anal. calcd for $C_{33}H_{24}N_2O$: C, 85.32; H, 5.21; N, 6.03; O, 3.44. found: C, 85.42; H, 5.25; N, 6.07; O, 3.45.



HBPIC **HBPIC (3-(1-phenyl-1H-phenanthro[9,10-d]imidazol-2-yl)biphenyl-4-ol)**

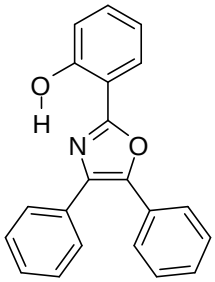
0.17g (yield 15%) of the title compound was obtained by the same procedure for HPI, using 0.5 g of 2-hydroxy-5-phenylbenzaldehyde (2.52 mmol) and 0.53 g (2.52 mmol) of phenanthrene-9,10-dione. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.04 (d, 2H, J = 6.9 Hz), 7.11-7.31 (m, 7H), 7.48-7.56 (m, 2H), 7.67-7.85 (m, 7H), 8.71-8.80 (m, 3H), 13.86 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 113.4, 118.6, 121.1, 122.8, 123.4, 124.4, 125.1, 125.5, 126.0, 126.3, 126.3, 126.7, 126.8, 127.3, 127.7, 128.7, 129.3, 129.4, 129.7, 130.7, 130.8, 131.3, 134.7, 139.6, 140.4, 148.5, 159.0. HRMS (EI, positive): Calcd for $C_{33}H_{22}N_2O$ (M), 462.1732; found 462.1729. Anal. calcd for $C_{33}H_{22}N_2O$: C, 85.69; H, 4.79; N, 6.06; O, 3.46. found: C, 85.81; H, 4.81; N, 6.05; O, 3.31.



NHPI **N-HPI (1-(1,4,5-triphenyl-1H-imidazol-2-yl)naphthalen-2-ol)**

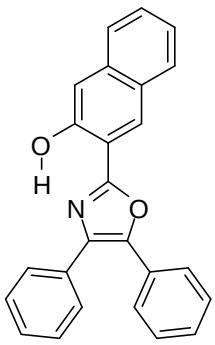
1.6g (yield 31%) of the title compound was obtained by the same procedure for HPI, using 2.0 g of 2-hydroxy-1-naphthaldehyde (11.62 mmol). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.69 (d, 1H, J = 8.9 Hz), 6.84-6.98 (m, 7H), 7.12-7.33 (m, 8H), 7.40-7.45 (m, 2H), 7.53-7.59 (m, 3H),

11.15 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 119.7, 123.1, 124.5, 126.3, 127.2, 127.4, 127.5, 127.8, 127.9, 128.4, 128.5, 128.6, 130.4, 131.4, 134.1, 136.4, 144.2, 155.3. HRMS (EI, positive): Calcd for $C_{31}H_{22}N_2O$ (M), 438.1732; found 438.1729. Anal. calcd for $C_{31}H_{22}N_2O$: C, 84.91; H, 5.06; N, 6.39; O, 3.65. found: C, 84.95; H, 4.99; N, 6.38; O, 3.66.



HPO **HPO (2-(4,5-diphenyloxazol-2-yl)phenol)**

^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.96 (t, 1H, J = 7.5 Hz), 7.08 (d, 1H, J = 8.3 Hz), 7.43-7.31 (m, 7H), 7.68 (t, 4H, J = 6.8 Hz), 7.91 (d, 1H, J= 7.8 Hz), 11.24 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 111.1, 117.4, 119.6, 126.2, 127.0, 128.1, 128.6, 128.8, 128.9, 129.0, 129.2, 131.6, 132.6, 134.8, 144.6, 157.7, 160.1. HRMS (EI, positive): calcd for $C_{21}H_{15}NO_2$ (M), 313.1103; found 313.1103. Anal. calcd for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.82; N, 4.47; O, 10.21. found: C, 80.33; H, 4.83; N, 4.53; O, 10.31.



HPNO

HPNO (3-(4,5-diphenyloxazol-2-yl)naphthalen-2-ol)

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.24-7.84 (m, 15H), 8.44 (s, 1H), 11.12 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 111.7, 113.2, 124.1, 126.7, 127.0, 127.1, 127.7, 128.1, 128.1, 128.5, 128.6, 128.9, 129.1, 129.4, 131.5, 135.1, 136.3, 145.2, 153.8, 159.8. HRMS (EI, positive): Calcd for $C_{25}H_{17}NO_2$ (M), 363.1259; found 363.1260. Anal. calcd for $C_{25}H_{17}NO_2$: C, 82.63; H, 4.72; N, 3.85; O, 8.81. found: C, 82.87; H, 4.63; N, 3.97; O, 8.80.