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Light Blue Rigid Excited-State Intramolecular Proton Transfer Organic Semiconductor Laser Chromophores

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Material Synthesis

Experimental: General

All NMR spectra were recorded using Bruker Ascend 500 MHz spectrometers in CDCl₃. All chemical shifts (δ) were reported in parts per million (ppm) and referenced to the residual solvent peak at δ 7.26 ppm and 77 ppm for ¹H and ¹³C NMR, respectively. Multiplicities were reported as singlet (s), doublet (d), triplet (t), multiplet (m), doublet of doublets (dd) and doublet of triplets (dt); br = broad, Ph-H = phenyl H, PI-H = phenanthroimidazolyl H, POI-H = phenanthridinolimidazolyl H and Ts-H = Tosyl H. All coupling constants (*J*) were quoted in Hertz (Hz) and rounded to the nearest 0.5 Hz. Melting point (m.p.) was measured in a glass capillary on a BÜCHI Melting Point B-545 or SRS DigiMelt MPA161 and were uncorrected. Infrared spectra were recorded on a Perkin Elmer Spectrum 1000 FT-IR spectrometer with ATR attachment as solid state. Mass spectrometry was performed on either an Applied Biosystems Voyager MALDI-TOF MS using a 2,5-dihydroxy benzoic acid (TA) matrix or a BRUKER MicrOTof-Q for the accurate mass in ESI mode. Absorption spectra were recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer in 10 × 10 mm quartz cuvettes and λ_{abs} values are quoted in nm with shoulders denoted as "sh".

2-(1*H*-Phenanthro[9,10-d]imidazol-2-yl)phenol (4)



A mixture of salicylaldehyde (0.9 mL, 8.48 mmol), 9,10-phenanthrenequinone (1.77 g, 8.48 mmol), ammonium acetate (1.96 g, 25.5 mmol), and iodine (117 mg, 0.46 mmol) in ethanol (42 mL) was deoxygenated under vacuum and

backfilled with $Ar_{(g)}$. This was repeated three times. The mixture was heated at reflux for 3 h. The solution was allowed to cool to room temperature (r.t.) and diluted with a saturated aqueous solution of sodium thiosulfate pentahydrate (60 mL). The solid product was filtered off and washed thoroughly with water (250 mL). The crude product was purified by column chromatography over silica using acetone/light petroleum (1:3) as eluent to give 4 as an off-white solid (1.25, 48%); ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.90 (d, *J* = 8.0 Hz, 2H, PI-H), 8.55 (br s, 2H, PI-H), 8.26 (dd, *J* = 8.0, 5.0 Hz, 1H, Ph-H), 7.79 (t, *J* = 8.0 Hz, 2H, PI-H), 7.73–7.65 (m, 2H, PI-H), 7.44–7.36 (m, 1H, Ph-H), 7.12–7.06 (m, 2H, Ph-H), which is identical to reported literature; ¹ HRMS (ESI/QTOF) m/z: [M+H]⁺ Calcd for C₂₁H₁₅N₂O 311.1184; Found 311.1182.

2-(1H-Phenanthro[9,10-d]imidazol-2-yl)phenyl 4-methylbenzenesulfonate (5)



A mixture of 4 (3.35 g, 10.8 mmol) and triethylamine (2.8 mL, 54.0 mmol) in dichloromethane (76 mL) was deoxygenated using vacuum and backfilled with $Ar_{(g)}$. This was repeated three times. The mixture was cooled to 0–2 °C in an ice-water bath. A solution of tosyl chloride (2.68 g, 14.1 mmol) in

dichloromethane (203 mL) was added dropwise to the cold reaction mixture. The mixture was further degassed using vacuum and backfilled with Ar(g). This was repeated three times. The suspension was allowed to warm to room temperature and stirred at room temperature under Ar_(g) for 3 days. Water (250 mL) was added to the mixture. The aqueous and organic phases were separated. The aqueous layer was extracted with dichloromethane (4 \times 250 mL). All organic extracts were combined, dried over anhydrous sodium sulphate and filtered. The filtrate was collected, and the solvent removed in vacuo. The crude was purified by column chromatography over silica using ethyl acetate/dichloromethane/light petroleum = (0:2:1) to (1:100:0) as eluents to give 5 as a fluffy white solid (3.28 g, 65%); Mp 198.3-199.3 °C (decomposition); IR v_{max}(solid)/cm⁻¹: 1360 (S=O), 3594 (N-H); ¹H NMR (500 MHz, DMSO*d*₆) δ 8.90 (d, *J* = 8.5 Hz, 1H, PI-H), 8.86 (d, *J* = 8.0 Hz, 1H, PI-H), 8.46 (d, *J* = 8.0 Hz, 1H, PI-H), 8.38 (d, J = 8.0 Hz, 1H, PI-H), 7.94 (dd, J = 7.5, 1.5 Hz, 1H, Ph-H), 7.79–7.70 (m, 2H, PI-H), 7.71–7.61 (m, 3H, PI-H, PhI-H), 7.61–7.55 (m, 1H, Ph-H), 7.50 (d, J = 8.0 Hz, 1H, Ph-H), 7.24 (1/2AA'XX', 2H, Ts-H), 6.63 (1/2AA'XX', 2H, Ts-H), 1.71 (s, 3H, CH₃); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 146.09, 144.86, 144.63, 136.82, 131.43, 131.20, 130.69, 129.23, 127.89, 127.72, 127.56, 127.45, 127.15, 127.08, 127.02, 126.99, 125.40, 125.17, 125.13, 124.41, 124.00, 123.68, 122.42, 122.06, 121.90, 20.53; HRMS (ESI/Q-TOF) m/z: [M + H]⁺ Calcd for C₂₈H₂₁N₂O₃S 465.1267; Found 465.1252; C₂₈H₂₀N₂O₃S requires: C, 72.4; H, 4.3; N, 6.0; S, 6.9 found: C, 72.0; H, 4.4; N, 6.0; S, 7.0.

2-(1-Methyl-1H-phenanthro[9,10-d]imidazol-2-yl)phenyl 4-methylbenzenesulfonate (6)



A solution of 5 (2.82 g, 6.07 mmol) in tetrahydrofuran (72 mL) was degassed using vacuum and backfilled with $Ar_{(g)}$. This was repeated three times. Sodium hydride (60% in mineral oil, 316 mg, 7.90 mmol) was added to the reaction solution and stirred under $Ar_{(g)}$ for 1 h. Iodomethane (0.38 mL, 6.10 mmol)

was added dropwise and the solution was stirred at room temperature for 18 h. Brine (72 mL) was added. The organic and aqueous phases were separated, and the aqueous phase was extracted with dichloromethane (4×72 mL). All organic phases were combined, dried over

anhydrous sodium sulfate and filtered. The filtrate was collected, and the solvent removed *in vacuo* to reveal a yellow gum. The crude was purified by column chromatography over silica using dichloromethane/light petroleum (1:6) as eluent to give **6** as a fluffy white solid (2.00 g, 69%); M_p 152.4–153.9 °C; IR v_{max} (solid)/cm⁻¹: 1367 (S=O); ¹H NMR (500 MHz, DMSO- d_6) δ 8.99 (dd, J = 8.0, 1.5 Hz, 1H, PI-H), 8.88 (d, J = 8.0 Hz, 1H, PI-H), 8.46 (ddd, J = 8.0, 4.0, 1.0 Hz, 2H, PI-H), 7.78–7.69 (m, 5H, PI-H, Ph-H), 7.67 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H, PI-H), 7.60 (td, J = 7.5, 1.0 Hz, 1H, Ph-H), 7.54 (dd, J = 8.0, 1.0 Hz, 1H, Ph-H), 7.18 (1/2AA'XX', 2H, Ts-H), 6.50 (1/2AA'XX', 2H, Ts-H), 3.89 (s, 3H, *N*-CH₃), 1.58 (s, 3H, Ts-CH₃); ¹³C NMR (126 MHz, DMSO- d_6) δ 147.06, 146.89, 144.73, 136.79, 132.87, 131.59, 131.56, 129.21, 128.28, 127.87, 127.46, 127.24, 127.08, 126.81, 126.69, 126.67, 125.46, 125.18, 124.40, 124.29, 124.12, 123.55, 123.06, 121.89, 121.26, 35.44, 20.37; HRMS (ESI/Q-TOF) m/z: [M + H]⁺ Calcd for C₂₉H₂₃N₂O₃S 479.1424; Found 479.1408; C₂₉H₂₂N₂O₃S requires: C, 72.8; H, 4.6; N, 5.9; S, 6.7 found: C, 72.4; H, 4.8; N, 5.9; S, 6.6.

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

HO N

6 (100 mg, 0.21 mmol) was suspended in methanol (5 mL). The suspension was degassed with vacuum and backfilled with $Ar_{(g)}$. This was repeated three times. 2 M NaOH_(aq) (1.2 mL) was added to the suspension and the mixture

was degassed and backfilled an additional three times, heated to reflux and stirred for 5 h. The reaction mixture was allowed to cool to room temperature and the methanol was removed *in vacuo*. Water (10 mL) was added and the pH was adjusted to 8 with 1 M HCl_(aq). The aqueous phase was extracted with dichloromethane (3 × 20 mL) and then ethyl acetate (3 × 20 mL). All organic phases were combined, dried over anhydrous sodium sulfate and filtered. The filtrate was collected, and the solvent removed *in vacuo* to reveal a white powder. The crude was recrystallised from dichloromethane/ethyl acetate/methanol to reveal **1** as a white crystalline solid (51 mg, 75%); M_p 226.4–227.2 °C; T_d 318 °C; UV-vis (CH₂Cl₂) λ_{max} (log ε) 254 (sh, 4.54), 263 (4.70), 329 (4.27), 346 (4.11), 363 nm (4.07); IR ν_{max} (ATR, solid)/cm⁻¹: 3028 (w, OH); ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.46 (s, 1H, OH), 8.97 (d, *J* = 8.0 Hz, 1H, PI-H), 8.86 (d, *J* = 8.5 Hz, 1H, PI-H), 8.61 (d, *J* = 8.0 Hz, 1H, PI-H), 7.43 (td, *J* = 8.5, 1.5 Hz, 1H, PI-H), 7.09 (d, *J* = 7.5 Hz, 1H, Ph-H), 7.03 (td, *J* = 7.5, 1.0 Hz, 1H, Ph-H), 4.14 (s, 3H, *N*-CH₃); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 156.03, 150.50, 136.27, 131.71, 131.24, 128.07, 127.35, 127.26, 127.09, 126.76, 126.57, 125.32, 124.99, 124.41, 123.61, 123.14, 121.75,

121.20, 119.26, 117.11, 116.06, 35.55; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for C₂₂H₁₇N₂O 325.1335; Found 325.1328; C₂₂H₁₆N₂O requires: C, 81.5; H, 5.0; N, 8.6; found: C, 81.1; H, 4.9; N, 8.6.

2-(1-(4-butylphenyl)-1*H*-phenanthro[9,10-d]imidazol-2-yl)phenol (2)

HO

A mixture of salicylaldehyde (0.36 mL, 3.39 mmol), 9,10phenanthrenequinone (708 mg, 3.40 mmol) ammonium acetate (394 mg, 5.12 mmol), 4-*n*-butylaniline (0.80 mL, 5.07 mmol) iodine (54 mg, 0.21 mmol) and

ethanol (17 mL) was degassed via vacuum and backfilled with Ar(g). This was repeated three times. The mixture was heated to reflux under Ar(g) for 67 h. The reaction was allowed to cool to room temperature and ethanol was removed. A saturated aqueous solution of sodium metabisulfite (10 mL), brine (10 mL) and ethyl acetate (20 mL) were added. The aqueous and organic phases were separated, and the aqueous phase was extracted with ethyl acetate (5×20 mL). All organic extracts were combined, dried over anhydrous sodium sulfate and filtered. The filtrate was collected, and the solvent was removed in vacuo to give a viscous brown oil. The crude was purified by MPLC using dichloromethane/light petroleum (0:1 to 1:3) as eluent to give 2 as a white powder (540 mg, 36%); M_p 133.2–133.8 °C; T_d 342 °C; UVvis (CH₂Cl₂) λ_{max} (log ε) 254 (sh, 4.69), 264 (4.85), 333 (4.85), 346 (4.38), 364 nm (4.41); IR *v*_{max}(ATR, solid)/cm⁻¹: 3064 (OH); ¹H NMR (500 MHz, DMSO-*d*₆) δ 12.10 (s, 1H, OH), 8.94 (d, *J* = 8.5 Hz, 1H, PI-H), 8.89 (d, *J* = 8.5 Hz, 1H, PI-H), 8.60 (dd, *J* = 8.0, 1.0 Hz, 1H, PI-H), 7.84–7.75 (m, 1H, PI-H), 7.71 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H, PI-H), 7.61 (1/2AA'XX', 2H, Ph-H), 7.57 (ddd, *J* = 8.5, 7.0, 1.0 Hz, 1H, PI-H), 7.51 (AA'XX', 2H, Ph-H), 7.31 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H, PI-H), 7.23 (ddd, J = 9.0, 7.5, 1.5 Hz, 1H, Ph-H), 7.05 (dd, J = 8.5, 1.0 Hz, 1H, PI-H), 6.99 (dd, J = 8.0, 1.5 Hz, 1H, Ph-H), 6.96 (dd, J = 8.0, 1.0 Hz, 1H, Ph-H), 6.67– 6.59 (m, 1H, Ph-H), 2.78 (t, J = 7.5 Hz, 2H, CH₂), 1.69 (p, J = 7.5 Hz, 2H, CH₂), 1.36 (h, J =7.5 Hz, 2H, CH₂), 0.96 (t, J = 7.5 Hz, 3H, CH₃); ¹³C NMR (126 MHz, DMSO- d_6) δ 157.55, 148.91, 144.77, 135.66, 134.51, 130.91, 130.24, 128.58, 128.50, 128.33, 127.72, 127.67, 126.87, 126.66, 125.96, 125.78, 125.42, 124.53, 123.77, 122.23, 121.80, 120.29, 118.14, 116.79, 114.90, 34.41, 32.79, 21.49, 13.82; HRMS (ESI/Q-TOF) m/z: [M + H]⁺ Calcd for C₃₁H₂₇N₂O 443.2118; Found 443.2116; C₃₁H₂₆N₂O requires: C, 84.1; H, 5.9; N, 6.3; found: C, 84.1; H, 5.9; N, 6.3.

3-Bromo-2-(1-(4-butylphenyl)-1H-phenanthro[9,10-d]imidazol-2-yl)phenol (8)



A mixture of 2-bromo-hydroxybenzaldehyde (2.11 g, 19.9 mmol), 9,10phenanthrenequinone (4.14 g, 19.9 mmol), ammonium acetate (2.3 g, 29.8 mmol), 4-*n*-butylaniline (4.71 mL, 29.8 mmol) and iodine (254 mg, 1.00 mmol) in EtOH (102 mL) was deoxygenated with vacuum and backfilled with

Ar_(g) three times. The mixture was heated at reflux under Ar_(g) for 20 h. The reaction mixture was allowed to cool to r.t. and the EtOH was removed. A saturated aqueous sodium metabisulfite solution (100 mL) and EtOAc (100 mL) were added to the mixture. The aqueous and organic phases were separated, and the aqueous phase was extracted with EtOAc (5×100 mL). All organic phases were combined, dried over anhydrous sodium sulfate and filtered. The filtrate was collected, and the solvent removed in vacuo. The crude was purified by column chromatography over silica using EtOAc/DCM (1:9) as eluent. Recrystallisation from DCM/EtOAc/MeOH (1:2:3) was performed to give 8 as an off-white solid (2.11 g, 20%); M_p 278.9–280.5 °C; IR v_{max}(ATR, solid)/cm⁻¹ 3054 (OH); ¹H NMR (500 MHz, DMSO-d₆) 10.33 (s, 1H, OH), 8.94 (d, J = 8.5 Hz, 1H, PI-H), 8.88 (d, J = 8.5 Hz, 1H, PI-H), 8.59 (dd, J = 8.0, 1.5 Hz, 1H, PI-H), 7.76 (ddd, J = 8.5, 7.0, 1.0 Hz, 1H, PI-H), 7.68 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H, PI-H), 7.56 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H, PI-H), 7.44–7.49 (m, 2H, Ph-H), 7.35–7.39 (m, 2H, Ph-H), 7.31–7.34 (m, 1H, PI-H), 7.16 (t, J = 8.5 Hz, 1H, Ph-H), 7.05–7.09 (m, 2H, Ph-H, PI-H), 6.86 (dd, *J* = 8.5, 1.0 Hz, 1H, Ph-H), 2.68 (t, *J* = 7.5 Hz, 2H, CH₂), 1.61 (p, *J* = 7.5 Hz, 2H, CH₂), 1.32 (sxt, J = 7.5 Hz, 2H, CH₂), 0.91 (t, J = 7.5 Hz, 3H, CH₃); ¹³C NMR (126 MHz, DMSO) δ 13.79, 21.67, 32.67, 34.37, 114.59, 119.76, 120.17, 121.99, 122.18, 122.39, 123.67, 124.48, 124.88, 125.19, 125.57, 126.58, 126.63, 126.86, 127.21, 127.24, 127.42, 127.47, 128.28, 129.35, 129.39, 132.23, 134.74, 136.66, 144.11, 148.16, 158.24. HRMS (ESI/Q-TOF) m/z: [M+H]⁺ Found: 521.1229/523.1206; Calc. for C₃₁H₂₇BrN₂O₃: 521.1223/523.1203; Found: C, 71.2; H, 4.9; N, 5.3 Calc. for C₃₁H₂₆BrN₂O₃: C, 71.4; H, 4.8; N, 5.4%.

3-n-Butylphenanthro[9',10':4,5]imidazo[1,2-f]phenanthridin-8-ol (3)



8 (2.00 g, 3.84 mmol), $Pd_2(dba)_3$ (353 mg, 0.39 mmol) and tricyclohexylphosphine tetrafluoroborate (426 mg, 1.16 mmol) were added to degassed toluene (130 mL). After addition, the solution was degassed using vacuum and backfilled with $Ar_{(g)}$. This was repeated three times. Caesium

carbonate (3.75 g, 11.5 mmol) in water (22 mL) was added under protection of $Ar_{(g)}$. The solution was degassed and backfilled with $Ar_{(g)}$ an additional three times. The reaction mixture was heated to reflux and stirred for 18 h. The aqueous and organic phases were separated. The

aqueous phase extracted with toluene (5 \times 50 mL). All organic phases were combined, dried over anhydrous sodium sulfate and filtered. The filtrate was collected, and the solvent removed in vacuo. The crude was purified by recrystallisation from dichloromethane/light petroleum to give **3** as a white solid (763 mg, 45%); M_p 177.3–178.9 °C; T_d 381 °C; UV-vis (CH₂Cl₂) λ_{max} $(\log \varepsilon)$ 284 (4.77), 299 (sh, 4.60), 312 (sh, 4.31), 375 nm (4.25);); IR $v_{max}(ATR, solid)/cm^{-1}$: 3062 (OH); ¹H NMR (500 MHz, DMSO- d_6 , 333 K) δ 12.39 (s, 1H, OH), 8.96 (d, J = 7.5 Hz, 1H, PI-H), 8.91 (d, J = 8.0 Hz, 1H, PI-H), 8.69 (d, J = 7.5 Hz, 1H, PI-H), 8.49–8.44 (m, 2H, PI-H, POI-H), 8.27 (d, J = 8.5 Hz, 1H, POI-H), 8.15 (d, J = 8.0 Hz, 1H, POI-H), 7.82 (t, J = 7.5 Hz, 1H, PI-H), 7.77 (t, J = 7.5 Hz, 1H, PI-H), 7.74–7.65 (m, 3H, PI-H, POI-H), 7.53 (d, J = 8.0 Hz, 1H, POI-H), 7.24 (d, J = 8.0 Hz, 1H, POI-H), 2.84 (t, J = 7.5 Hz, 2H, CH₂), 1.75 (p, J = 8.0 Hz, 2H, CH₂), 1.44 (h, J = 7.5 Hz, 2H, CH₂), 0.98 (t, J = 7.5 Hz, 3H, CH₃); ¹³C NMR (126 MHz, DMSO-d₆, 333 K) & 156.19, 146.69, 140.32, 137.77, 131.29, 130.33, 130.08, 129.00, 128.21, 127.83, 127.49, 126.70, 125.76, 125.52, 124.98, 124.64, 124.57, 123.38, 122.74, 122.53, 122.44, 122.28, 122.17, 118.75, 114.47, 113.16, 108.56, 34.26, 32.70, 21.59, 13.43; HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for C₃₁H₂₅N₂O 441.1961; Found 441.1964; C₃₁H₂₄N₂O requires: C, 84.5; H, 5.5; N, 6.4; found: C, 84.5; H, 5.5; N, 6.4.



Scheme S1 Attempt to form 3 directly from 2 using a palladium catalysed oxidative coupling.²



Fig. S1 TGA of 1, 2, and 3 at 10 $^{\circ}$ C/min under N_{2(g)}.



Fig. S2 DSC of 1, 2, and 3, showing the first (dashed lines) and the second (solid lines) heating cycles with a scan rate of 100 °C/min under $N_2(g)$, and the corresponding expansion of the glass transition temperatures for 1, 2, and 3 (the 2nd heating cycle).



Fig. S3 Solution CV (solid lines) and DPV (dashed lines) of the oxidation of 1, 2, and 3 at a concentration of 1 mM in DCM against the ferrocenium/ferrocene couple (Fc+/Fc).. Working electrode = platinum; reference electrode = Ag/Ag^+ ; counter electrode = platinum; electrolyte = 0.1 M tetra-*n*-butylammonium perchlorate; scan rate = 200 mV/s. Only one cycle (*i.e.*, the 2^{nd} cycle) is shown for each compound.

HPI	E1/2(ox) ^a (eV)	IP (eV)		EA (eV)	Eg ^{opt d} (eV)
		\mathbf{CV}^{b}	PESA	Calculated ^c	
1	0.61	-5.41	-5.79	-2.08	3.33
2	0.71	-5.51	-5.76	-2.18	3.33
3	0.72	-5.52	-5.67	-2.30	3.22

^a Estimated from DPV; ^b calculated from $E_{1/2(ox)}$ by referencing to IP of ferrocene;^{3,4 c} calculated by addition of the optical gap (E_g^{opt}) to the IP as determined from CV; ^d determined from the λ_{onset} of their respective solution absorption spectra (Fig. S5).



Fig. S4 Results of PESA (photoelectron spectroscopy in air) for neat films of 1, 2, and 3.



Fig. S5 Solution absorption spectra of 1, 2, and 3 (in toluene), showing their molar extinction coefficients.



Fig. S6 TCSPC of 1, 2, and 3 in solution (toluene), blend (6wt% in CBP) and neat films.

Quantitative Description of Local Excitation and Charge Transfer

To understand the local excitation and charge transfer quantitatively, several metrics to describe the process have been considered as indicated in **Table S2.** Recently, Guido *et al.* proposed a new index, called Δr , which has been developed as a new tool to explore the charge-transfer capabilities of the photoexcited molecules.⁵ The Δr index is based on the charged centroids of the orbitals involved in the transition. It measures the average hole-electron distance upon excitation. Based on their study, they proposed a threshold value which could help in characterising a transition as being a local excitation, charge transfer or Rydberg excitation. A Δr index with a value less than 2.0 Å indicates the transition is due to the local excitation modes and values greater than 2.0 Å correspond to a charge transfer or Rydberg excitation. Another metric which could be used is the distance between centroid and hole electron, *D*. The *D* metric measures the charge transfer length. The larger the *D* value, the longer the length of the charge transfer.

Molecule	Δr index (Å)	D (Å)
1	0.931	0.264
2'	0.822	0.205
3'	2.033	0.685

Table S2 Excited state metrics calculated at ω B97x-D/6-31+G(d,p) level of theory in toluene.

The result from this study indicates that **1** and **2'** shows local excitation character with Δr index value less than 2.0 Å and a very small *D* value for both. Contrarily for **3'**, the analysis indicates a borderline Δr index of 2.033 Å; the value is rather large in comparison to **1** and **2'**. The *D* value for **3'** is approximately three times that of **1** and **2'**. This large difference of Δr index and *D* of **3'** indicates that upon excitation the transition has both local excitation and charge transfer character.

<u>Performance of Different Quantum Mechanical Methods for Computing ESIPT</u> <u>Properties</u>

The benchmarking studies were carried out with seven different functionals that represent different rung of "Jacob's ladder" approximations, which included several hybrid functionals, where the amount of Hartree–Fock (HF) exchange is constant over all space (Method A–E), and range-separated hybrid functionals, where the amount of HF exchange increases as the interelectronic distance increases (Methods F and G). The ground-state (S₀) and excited-state (S₁) geometries of both the enol and keto forms of **1** were optimised using all seven methods. Four metrics were used to assess the performance of each functional: (i) the computed geometries at the S₀ and S₁ states, (ii) how well the simulated maximum absorption wavelength agreed with the experimental, (iii) the match between the calculated and experimental emission wavelengths, and (iv) the Stokes shift.

Method	Functional	% HF
А	BP86 ⁶	0
В	B3LYP ⁷	20
С	PBE0 ⁸	25
D	M06-2X ⁹	54
Е	M06-HF ⁹	100
F	CAM-B3LYP ¹⁰	19–65
G	$\omega B97 X-D^{11}$	22-100

(i) The computed geometries at the S₀ and S₁ states

While the accuracy in excitation or emission energies is one of the key criteria for benchmarking TD-DFT methods, other properties like S_0 and S_1 geometries are important as the absorption and emission wavelengths are computed based on the geometries at S_0 and S_1 state, respectively. **Fig. S7** shows the computed geometries of enol and keto form of **1** with different methods at the S_0 and S_1 states.



Fig. S7 Optimised geometries of 1 at the ground and excited state computed with different theoretical methods. The calculations were performed using 6-31+G(d,p) basis set in PCM toluene. The dihedral angle between the phenol and phenanthroimidazole rings (NCCC) for each optimised structure is included in red.

The dihedral angle between the phenol and phenanthroimidazole rings (NCCC) was determined to be the main indicator of the geometric criteria as the O–H–N core needs to be in

plane. Therefore, it is expected that the S_1 state geometry of enol and keto tautomer of the HPI system favours the planar conformation in between the phenol and phenanthroimidazole groups so that a feasible proton transfer can occur between two groups.¹²

First, it was determined that the computed S_0 ground state geometries of the enol tautomers are very similar for the different functionals. The dihedral angle between the phenol and phenanthroimidazole rings (N=C-C=C) computed to be in between -19° and -27°. The computed geometries of the enol tautomer at the S₁ excited state with the different functionals are all similar, with dihedral angles of -13 to -14°, which is as expected to be more planar than the ground state geometry. Interestingly, all attempts to locate the enol form at the S₁ excited state using BP86 functional failed; attempted optimisations led to spontaneous convergence to the keto tautomer. That explain why there is no enol structure shown for the S₁ excited state for BP86 functional in **Fig. S7**.

It was found that the predicted S_1 excited state geometry of the keto tautomer of **1** was different for different functionals. For BP86, B3LYP and PBE0, the dihedral angles were computed to be -29°, -113° and -114°, respectively. Meanwhile the M06-2X, CAM-B3LYP and ω B97X-D functionals gave relatively similar excited state geometries for the keto tautomer with dihedral angles of -26 to -28°. The difference in excited state geometries for functionals with a % HF exchange below 25 illustrates the "twisting problem" in low HF exchange hybrid functionals with small %HF exchange tending to overfavour twisted forms.¹³

To further understand the influence of different functionals on the prediction of the global minimum geometry of the keto tautomer; a torsional potential energy scan of **1** using PBE0 and ω B97X-D functionals was performed as illustrated in **Fig. S8**. For these calculations the structures were partially optimised while varying the dihedral angle between the phenol and phenanthroimidazole rings (N–C=C–C) from -180 to 0° for both functional. The results indicated that the global and local minima for PBE0 and ω B97X-D are switched. For PBE0, the global minimum is when the CC central bond lies at -120° and there is a second, local minimum which lies at -28°. In contrast for ω B97X-D, the local and global minimum is when the CC central bond lies at -120° and effect in low HF exchange functionals.



Fig. S8 (a) Torsional potential energy surface for the central CC bond of the keto forms of ω B97X-D (pink) and PBE0 (blue) at the S₁ excited state. Relative energies are calculated with respect to the minimum-energy conformation (corresponding to dihedral angles of -28° and -120° for ω B97X-D and PBE0, respectively). (b) Computed emission wavelength and oscillator strength of **1** keto using PBE0. The calculations were performed using the 6-31+G(d,p) basis set in PCM toluene.

To understand the effect of different geometries on the predicted emission wavelength, both of the local and global minimum structures of PBE0 then were fully optimised and the photophysical properties were calculated using PBE0 functional as indicated in **Fig. S8b**. First, the results showed that at -28°, the calculated keto emission wavelength is within 31 nm of the experimental measured wavelength. Meanwhile at -120°, the predicted emission wavelength falls within the infrared wavelength which deviates from the experimental measured wavelength. This explanation agrees with the computed oscillator strength value at -120° was calculated to be zero, suggesting that there is no emission occurs from the twisted structure. Second, if experimentally the emission were to occur from the structure with a dihedral of -120°, the emission process might lead to a "dark state" where the emission process will have a high non-radiative rate. This will result in a very low or zero PLQY. However, experimentally the PLQY of **1** was determined to be rather high (46%), so it is expected that the molecule will undergo emission from the geometry at -28° instead.

(ii), (iii) and (iv) The calculated absorption and emission wavelengths and the Stokes shifts.

Table S3 Absorption wavelengths (λ_{abs}), and oscillator strengths (f_{abs}) for the S₀ \rightarrow S₁ transition, and emission wavelength for enol and keto tautomer of **1** in toluene computed with different theoretical methods with the 6-31+G(d,p) basis set. The Stokes shift (SS) was calculated from the absorption and emission wavelength of enol and keto species, respectively. Values in parentheses represent the deviation from experimental.

Functional	Method	$\lambda_{ m abs}$	$f_{\rm abs}$	λ_{em} enol	$\lambda_{\rm em}$ keto	SS
		(nm)		(nm)	(nm)	(nm)
BP86	А	418 (+53)	0.21	_	995 (+508)	577 (+455)
B3LYP	В	345 (-20)	0.54	393 (+2)	1858 (+1371)	1513 (+1391)
PBE0	С	333 (-32)	0.56	377 (-14)	1429 (+942)	1096 (+974)
M06-2X	D	304 (-61)	0.55	359 (-32)	420 (-67)	116 (-6)
M06-HF	Е	274 (-91)	0.58	334 (-57)	394 (-93)	120 (-2)
CAM-B3LYP	F	304 (-61)	0.62	363 (-28)	414 (-73)	110 (-12)
ωB97X-D	G	300 (-65)	0.55	358 (-33)	413 (-74)	113 (-9)
Experimental	_	365	—	391	487	122

The following conclusions are drawn from the results in Table S3;

- For absorption wavelength, BP86 overestimates the predicted absorption wavelength by 53 nm. All six other functionals underestimate the calculated absorption wavelength, with errors of 20–91nm. For the hybrid functionals (Methods A –E), increasing HF exchange leads to a blue-shift of the absorption wavelength. The M06-2X, CAM-B3LYP and ωB97X-D functionals give almost identical excitation wavelengths and energies, with differences of 61, 61 and 65 nm, respectively, compared to experiment. The B3LYP functional provides the closest approximation to the experiment, with an error of 20 nm relative to experiment.
- Furthermore, the effect of functional in predicting the HOMO and LUMO energies is as important as the prediction of absorption wavelength. Figure S9 shows the calculated HOMO and LUMO energies of the ground state optimised geometry of 1 with different functionals. There is a clear correlation in the increase of HOMO–LUMO gap with increasing %HF exchange. This explains the trends in the predicted absorption wavelength observed above, where the wavelength blue-shift from 418 nm (BP86) to 274 nm (M06-HF).



Fig. S9 HOMO and LUMO energy of 1 enol at ground state in toluene computed with different theoretical methods with the 6-31+G(d,p) basis set.

- Emission wavelength of enol: For all functionals except M06-HF, the predicted emission wavelength of enol is close to the experimental value, with an error of ± 30 nm.
- Emission wavelength of keto: The small %HF exchange hybrid functionals BP86, B3LYP and PBE0 overestimated the emission wavelength by >500 nm. The main reasons attributed for the overestimation of B3LYP and PBE0 functionals is due to the twisted excited geometry of keto. On the other hand, the M06-2X, CAM-B3LYP and ωB97X-D functionals gave similar emission wavelengths, which were blue-shifted relative to experiment by ≈70 nm.
- Stokes shift: Due to the overestimation in the prediction of the emission wavelength by BP86, B3LYP and PBE0 functionals, the Stokes shift is computed to be overestimated compared to experiment. The M06-2X, CAM-B3LYP and ω B97X-D functionals gave a good prediction in Stokes shift with errors of less than 15 nm in comparison to the experiment.
- The ωB97X-D/6-31+G(d,p) method was selected here as the method of choice for predicting the photophysical properties of HPI dyes due to its ability to capture the charge transfer more accurately and represent a reasonable balance of cost vs accuracy in investigating ESIPT systems.

DFT and TD-DFT Computed Geometries and Energies

Cartesian coordinates of structures optimized with ω B97XD/6-31+G(d,p) are listed below, together with the following energies. All calculations were performed in PCM implicit toluene.

- E: ω B97XD/6-31+G(d,p) electronic potential energy
- H: ω B97XD/6-31+G(d,p) enthalpy at 298.15 K
- G: ω B97XD/6-31+G(d,p) Gibbs free energy at 298.15 K and 1 mol/L

All energies are reported in Hartree.

1-Enol (S₀)

С	1.80628300	-1.40242200	0.02678800
С	0.53334300	-0.73041700	-0.00707700
С	0.42304100	0.63871300	-0.12214500
С	2.84406200	0.89563700	-0.02437500
С	2.96284100	-0.56902800	0.04166000
Ν	-0.89362400	1.00813200	-0.18556200
С	-1.58806400	-0.11571300	-0.10127400
С	-3.05427700	-0.12943300	-0.12584900
С	-3.79635700	-1.21182000	-0.62245100
С	-3.75088500	1.01546300	0.32729700
С	-5.18377800	-1.20584800	-0.60715800
Н	-3.27630300	-2.06170100	-1.05176900
С	-5.14875600	1.00684900	0.36268900
С	-5.85711800	-0.09523000	-0.09333600
Н	-5.73532700	-2.05306600	-0.99967100
Н	-5.65743200	1.88957100	0.73505700
Н	-6.94224700	-0.08011400	-0.06867800
0	-3.12235700	2.13357000	0.73537700
Н	-2.17385800	2.06224100	0.48197300
Ν	-0.76981800	-1.21002400	0.03346300
С	-1.18168300	-2.52918600	0.49424100
Н	-1.18880900	-3.25700500	-0.32125400
Н	-0.50049300	-2.86086500	1.27851400
Н	-2.18077700	-2.46039800	0.92157800
С	4.22333000	-1.19896500	0.08703500
H	5.12530500	-0.59945800	0.10478100
С	4.35596000	-2.57363300	0.09589700
H	5.34415100	-3.02063300	0.12912600
С	3.21596000	-3.38429000	0.04039100
H	3.31189000	-4.46500200	0.01799100
С	1.96392800	-2.80459000	0.00333200
H	1.09697400	-3.44786800	-0.06871600
С	3.96700000	1.75083200	-0.00000100
H	4.96620400	1.34247300	0.09246700
С	3.83070900	3.12288300	-0.09013100
H	4.71516800	3.75157300	-0.06745200
С	1.57008300	1.50050300	-0.13716500
С	1.44074100	2.89791100	-0.23462400
Н	0.44710600	3.32440400	-0.32584800
С	2.55929700	3.70475700	-0.21211600
H	2.45744800	4.78270800	-0.28619900
U imaginary fre	quencies		
E = -1032.47485	6		
H = -1032.12540	1		

G = -1032.187718

1-Enol (S₁)

С	1.77454900	-1.39953700	-0.02645200
С	0.52810400	-0.74976000	0.04980700
С	0.40041100	0.66981300	0.00854800
С	2.84134700	0.89182300	-0.02200800
С	2.95563400	-0.57166600	-0.03753800
Ν	-0.87638000	1.03312700	0.03266800
С	-1.61306800	-0.12688500	0.08343000
С	-3.00849300	-0.15574700	-0.05063700
С	-3.75644400	-1.34902400	-0.31610800
С	-3.76359500	1.08329900	0.05097100
С	-5.13185900	-1.32582600	-0.40864700
Н	-3.22751500	-2.28037800	-0.47888100
С	-5.15257300	1.07153900	-0.03864500
С	-5.84181200	-0.12002500	-0.25443300
Н	-5.67007400	-2.24542200	-0.61556800
Н	-5.67548200	2.01724700	0.05698500
Н	-6.92485600	-0.11283400	-0.32062400
0	-3.15577800	2.25433300	0.25535500
Н	-2.17220400	2.11484200	0.20369200
Ν	-0.75482500	-1.25506100	0.14292700
С	-1.08034900	-2.44900100	0.92365700
Н	-1.26118400	-3.31733800	0.28461800
Н	-0.25585900	-2.66845000	1.60599100
Н	-1.97320300	-2.25307800	1.51885700
С	4.19810100	-1.21934600	-0.08907200
Н	5.11231500	-0.63735200	-0.08695600
С	4.30955500	-2.60030800	-0.15951700
Н	5.29207800	-3.05883000	-0.20032800
С	3.15371700	-3.40096000	-0.20324900
Н	3.23928200	-4.47875900	-0.29563500
С	1.91238200	-2.81298400	-0.13831400
Н	1.02610100	-3.43374500	-0.19731500
С	3.96454200	1.74103800	-0.01994600
Н	4.96537600	1.32638500	-0.01203900
С	3.83115800	3.12124700	-0.02707300
Н	4.72245400	3.74078100	-0.02572100
С	1.56543700	1.51529600	-0.02487100
С	1.44036900	2.91202800	-0.03418200
Н	0.44583800	3.34625000	-0.03850200
С	2.56533200	3.71846500	-0.03674100
Н	2.46692900	4.79868400	-0.04444600
0 imaginary fre	quencies	-	
E = -1032.33715	4		
H = -1031.99185	1		

G = -1032.055411

1-Keto (S₁)

С	1.78796400	-1.39136400	0.00323100
С	0.52689400	-0.71400600	0.03877700
С	0.44580100	0.66311500	-0.04122100
С	2.86531100	0.88059300	-0.03254700
С	2.96328300	-0.58002800	-0.00610200
Ν	-0.87318500	1.00284600	-0.06322000
С	-1.64684000	-0.12717300	0.07963900
С	-3.06174600	-0.14730300	-0.06635800
С	-3.78265300	-1.26527200	-0.50710400
С	-3.80483400	1.10083900	0.23491800
С	-5.18697100	-1.24055400	-0.57215900
Н	-3.25895300	-2.16478300	-0.81261900
С	-5.22239500	1.08067000	0.10238100
С	-5.90560100	-0.07708300	-0.26860500
Н	-5.71516500	-2.13809500	-0.87867200
Н	-5.75018500	1.99878700	0.34000800
Н	-6.98887500	-0.07672800	-0.33001100
0	-3.17220600	2.13191800	0.61586500
Ν	-0.77127900	-1.21260300	0.11515200
С	-1.12828800	-2.46226600	0.78217700
Н	-1.21029500	-3.28987500	0.07290900
Н	-0.37596800	-2.69975400	1.53737200
Н	-2.08638500	-2.33095700	1.28469300
С	4.21132700	-1.23670100	-0.02336800
Н	5.12649400	-0.65707200	-0.02335200
С	4.31323900	-2.61286500	-0.05620100
Н	5.29186200	-3.08117400	-0.07162600
С	3.15292900	-3.40108500	-0.09241900
Н	3.22736100	-4.48207100	-0.15050900
С	1.91432200	-2.79856400	-0.06507700
Н	1.02899900	-3.41856400	-0.12081900
С	3.99968900	1.72066300	-0.03076600
Н	4.99442400	1.29422300	0.01319200
С	3.88222200	3.09568400	-0.08200500
Н	4.77680100	3.70994400	-0.07853500
С	1.59477000	1.51027000	-0.08199100
С	1.48575500	2.91454600	-0.13948800
Н	0.50505200	3.37829300	-0.18273900
С	2.61654000	3.70192900	-0.14043200
Н	2.52911200	4.78237400	-0.18426600
Н	-1.32970600	1.90413800	0.08285000
0 imagin	ary frequencies		
E = -103	2.339838		
H = -103	1.993794		

G = -1032.057649

2'-Enol (S₀)

C	-1.67986200	1.43733800	0.01043800
C	-0.83860800	0.23393900	-0.03730600
C	-1.39020400	-1.01300000	-0.07751000
C	-3.08990700	1 22506100	-0.02387000
N	-0.39165400	-1 9/9/5100	-0 11304400
IN C	0.75221600	-1 28190500	-0 12124700
C	2 04883900	_1 97678900	-0 11617600
C	3 27294800	-1 35971700	-0 42823400
C	2 06710000	-3 35830800	0.42025400
C	4 47280000	-2 05292000	-0 38223300
ч	3 29152600	-0 31949600	-0 72226400
C	3 28561400	-4 04526200	0.72220400
C	4 47697200	-3 40123800	-0 01919600
С Н	5 39778500	-1 54437500	-0 63130600
н	3 26148900	-5 09638300	0.53793800
Н	5 41064200	-3.95333500	0.02572600
0	0 95758900	-4.06711600	0.47892200
Н	0 17429500	-3.48691600	0.30156400
N	0 52135400	0 07590700	-0.09062700
C	-3.92336200	2.36074500	0.08261700
H	-4.99962300	2.23995200	0.08902500
C	-3.41279000	3.64216800	0.14250700
H	-4.08756000	4.49068300	0.19128700
С	-2.02696500	3.83977000	0.14625600
H	-1.61587600	4.84262700	0.20170200
С	-1.17709400	2.75442600	0.08267900
Н	-0.10970800	2.92633700	0.09294800
С	-5.04871900	-0.37385800	-0.02351700
Н	-5.75017500	0.45120900	0.00486800
С	-5.55711400	-1.65821200	-0.05769300
Н	-6.63198200	-1.80887300	-0.05510500
С	-2.80396000	-1.25776000	-0.06627900
С	-3.32941500	-2.56218500	-0.10076100
Н	-2.64263300	-3.40160900	-0.13440200
С	-4.69389400	-2.76413800	-0.09588600
Н	-5.09760000	-3.77114400	-0.12309000
С	1.50046600	1.11642600	-0.03949600
С	2.07186600	1.46302100	1.17867900
С	1.85938200	1.78148400	-1.20828400
С	3.01811800	2.48273700	1.22236100
Н	1.77577000	0.93629400	2.07982200
С	2.80273700	2.80066200	-1.15071100
Н	1.39570200	1.50081500	-2.14847100
С	3.39941300	3.16477200	0.06267800
Н	3.46439700	2.75343500	2.17484300
Н	3.07982500	3.32246300	-2.06221600
С	4.44556500	4.24857400	0.10953400
Н	4.22776500	5.04131000	-0.61106200
Н	4.51024100	4.69633500	1.10424300
H	5.43186800	3.84045000	-0.13632900
0 imaginary fre	equencies		
E = -1263.46994 H = -1263 03513	48 30		
II - IZ03.0331.			

G = -1263.111004

2'-Enol (S₁)

С	-1.80840900	1.23060000	-0.05677700
C	-0 74479700	0 29851100	-0.08210000
C	-0 96871000	-1 10803000	-0 03406700
C	-3 39000600	-0 7/936800	-0 01214700
C	-3 15216500	0.74550000	-0 02/53200
N	0 17921200	1 77466700	0.02435200
N C	1 10501000	-1.77400700	-0.012/3200
C	1.19501000	-0.85526400	-0.06101300
C	2.55064500	-1.22760300	-0.08607700
С	3.65671800	-0.32999400	-0.27242400
С	2.89268900	-2.64182700	0.07467400
С	4.95957000	-0.78046600	-0.27626900
H	3.47353200	0.72293100	-0.42597700
С	4.22195700	-3.05868600	0.06711300
С	5.25808200	-2.14472100	-0.10102000
Н	5.76453800	-0.06715100	-0.42291200
Н	4.41588100	-4.11822200	0.19621900
Н	6.28822200	-2.48555600	-0.10320700
0	1.95839500	-3.57563300	0.24571100
Н	1.06062400	-3.13795000	0.18125100
Ν	0.62781000	0.44515200	-0.12515000
С	-4.21659400	1.60959900	0.00151100
Н	-5.23722000	1.24671100	0.02623100
С	-4.01852000	2.98021300	0.00153200
н	-4 87310600	3 64850500	0 02300000
C	-2 71115200	3 49937500	-0 02199300
ч	-2 54781900	4 57212100	-0.01563800
II C	_1 63393500	2 64593500	-0.05023500
U U	-0 63769400	2.04595500	-0.05023500
п		1 21251700	-0.00370900
	-4.00240100	-1.31331700	0.00330700
H Q	-5.55945500	-0.67769400	-0.00024300
C 	-4.8/558600	-2.68542800	0.022/9600
H	-5.88/44800	-3.0/840100	0.03381300
C	-2.29/94000	-1.65612900	-0.01035600
С	-2.50303100	-3.04375200	0.00990300
H	-1.63848100	-3.69966700	0.00835600
С	-3.78470100	-3.56462000	0.02723200
H	-3.94241900	-4.63766800	0.04177600
С	1.33736400	1.67684500	-0.00386700
С	1.76428900	2.10141700	1.25144400
С	1.59342300	2.43509700	-1.14425300
С	2.46098500	3.30180700	1.36426700
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С	2.28552400	3.63626700	-1.02367300
Н	1.25120500	2.07723800	-2.10960500
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Н	2.48936400	4.23148200	-1.90753800
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0 imaginarv fre	equencies		
E = -1224.02107	1		

H = -1223.619475

G = -1223.692664

2'-Keto (S1)

С	-1.71855000	1.41442700	-0.06027300
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С	-1.41593100	-1.02361300	-0.07571300
С	-3.68486200	-0.16156200	-0.02499400
С	-3.13072600	1.19325000	-0.02555300
Ν	-0.39128400	-1.92118600	-0.11071200
С	0.81520800	-1.25778500	-0.10265300
С	2.07753200	-1.91276700	-0.15409300
C	3,27167600	-1.32910800	-0.60805400
C	2.12312500	-3.33708300	0.28216500
C	4 47841800	-2 04786100	-0 61305600
е н	3 28061400	-0 30805900	-0.96643200
C	3 36659700	-4 02570700	0.20488800
C	4 53370700	-3 389/1700	-0 21395400
U U	5 38062500	-1 54604700	-0.04000700
П Ц	3 37089400	-5 05836300	0.53015700
п	5.37000400	-3.03830300	0.33913700
	1 07060000	-3.92020700	-0.23101700
U	1.07989000	-3.89837300	0.13703300
N	0.30364000	0.10295800	-0.1/815000
C	-3.9/1/2200	2.32434100	0.02599900
H	-5.04676300	2.19531000	0.04968000
C	-3.4/100600	3.609/1900	0.05551500
Н	-4.15152400	4.45391900	0.09643700
C	-2.08444700	3.81///900	0.04222400
Н	-1.68099500	4.82450600	0.07884000
С	-1.22716100	2.74053800	-0.01347000
H	-0.16205100	2.92196700	-0.01416900
С	-5.07231700	-0.42117800	-0.00001500
H	-5.78165000	0.39731800	0.00996500
С	-5.56720000	-1.71040300	0.01157100
Н	-6.64015700	-1.87178200	0.03039600
С	-2.81836300	-1.28331900	-0.04045500
С	-3.33276400	-2.59617600	-0.02949300
Н	-2.65264700	-3.44211600	-0.04847800
С	-4.69343700	-2.81040500	-0.00255000
Н	-5.08668100	-3.82149100	0.00464700
С	1.47933700	1.13781900	-0.04403600
С	2.10683900	1.34047900	1.17925000
С	1.82154800	1.91198300	-1.15136200
С	3.07859200	2.33129600	1.29442400
Н	1.84050300	0.71874200	2.02796500
С	2.78561400	2.90325300	-1.02116700
Н	1.33035200	1.73159400	-2.10217100
С	3.43036100	3.12886000	0.20237100
Н	3.57036400	2.48387300	2.25074800
Н	3.04992800	3.50665500	-1.88517000
С	4.46933800	4.21342600	0.32810600
Н	4.00585200	5.20341800	0.26306500
Н	4.99660200	4.15146800	1.28289700
Н	5.20858100	4.14424200	-0.47538800
H	-0.36930300	-2.90641000	0.16980800
0 imaginary fre	auencies	2.30011000	
E = -1263.33385	76		
H = -1262.90226	52		

G = -1262.980140

3'-Enol (S₀)

С	1.77071800	1.40029800	0.35554500
С	0.91716800	0.28159700	0.03910300
С	1.42823500	-0.99271100	-0.11378800
С	3.70392500	-0.11976100	-0.18292900
С	3.17092000	1.19720900	0.19341700
Ν	0.42702800	-1.93047100	-0.12729500
С	-0.69183500	-1.23772600	-0.01786100
С	-2.01681200	-1.77296400	0.14611900
С	-3.10407000	-0.88208100	0.25698200
С	-2.20313900	-3.16788300	0.28248300
С	-4.37169900	-1.40266500	0.54130300
С	-3.47719400	-3.66001200	0.54824000
С	-4.54323000	-2.77459100	0.68460800
Н	-5.22811400	-0.74965600	0.65580000
Н	-3.61304100	-4.73003200	0.65880100
Н	-5.53089200	-3.16656200	0.90609700
0	-1.18167100	-4.03535400	0.17880800
Н	-0.34630700	-3.53457500	0.03020300
N	-0.47144700	0.11835200	0.03417500
C	4.03029800	2,27367500	0.49484200
H	5.10062600	2.15838100	0.37361500
C	3.55438600	3.47425800	0.98389600
Н	4 24707900	4,27777800	1,21184700
C	2 18432700	3,63119300	1,22866900
н	1 80749100	4.54757500	1.67130900
C	1 31121700	2.60699400	0.92435100
н	0 26046000	2 72345400	1 15870400
C	5 07591400	-0 34759100	-0 42025400
н	5 77982700	0 47592800	-0 39699800
C	5 55806900	-1 61350100	-0 69407100
е н	6 61885700	-1 75510600	-0 87485400
C	2 83603000	-1 23388700	-0 26110700
C	3 33678500	-2 52097400	-0 52673100
н	2 64106500	-3 35220500	-0 57510700
C	4 68660200	-2 71260900	-0 73890400
н	5 07106400	-3 70537800	-0 94930700
C	-1 53922200	1 01211600	-0 20146900
C	-1 31502500	2 29231900	-0 71683500
C	-2 85385000	0 54293200	-0 01920800
C	-2 37674600	3 15217400	-0 93029500
е н	-0.31212400	2 60270000	-0 97906400
C	-3 90465500	1 44980600	-0 23839400
C	-3 69400500	2 75403000	-0 66203100
ч	-2 18313800	4 14240100	-1 33274700
п ц	-4 92666900	1 11145000	-0 10713100
C	- <u>4</u> 8/128000	3 70013300	-0 86760700
ч	-5 80350000 -5 80350000	3 19/02500	
тт П	_/ Q2610200	A AQ217000	
ц ц	4.03010200 -1 77300300	4.4921/000 1.20215500	_1 8/10//00
11 O imaginary fro	auencies	7.2024000	1.04194400
E = -1262 27720	9		
H = -1261 86/80	2		
	<u>ب</u>		

G = -1261.937928

3'-Enol (S₁)

С	1.72629500	1.37730800	0.42209700
С	0.89914300	0.28871100	0.07343900
С	1.43464200	-1.02479700	-0.13762400
С	3.70067800	-0.08967000	-0.16254400
С	3.14767100	1.20409000	0.26429500
N	0.48144100	-1.94777400	-0.16216800
С	-0.69569500	-1.26329500	-0.00648400
С	-1.96179700	-1.77734100	0.18293000
С	-3.07433000	-0.86385400	0.31758200
С	-2.18215600	-3.20132500	0.30166100
С	-4.31964400	-1.39521100	0.65215000
С	-3.44073600	-3.67599700	0.61085500
С	-4.49844800	-2.77038600	0.80395600
Н	-5.17218400	-0.74093500	0.79659400
Н	-3.58723000	-4.74485800	0.71854500
Н	-5.47847100	-3.15291700	1.07021100
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Н	-0.33469000	-3.56650700	-0.02365300
Ν	-0.47344300	0.12477100	0.06357300
С	3.97224900	2.28774100	0.58876800
Н	5.04668600	2.20370500	0.47560400
С	3.46250900	3.47764700	1.09272200
Н	4.13834700	4.29038700	1.33739800
С	2.08444700	3.60972400	1.32792000
Н	1.69107400	4.51554800	1.77749000
С	1.23198600	2.57861500	1.00523800
Н	0.17491600	2.66807200	1.22414400
С	5.07245300	-0.28650300	-0.40394600
Н	5.76707000	0.54136400	-0.32729900
С	5.57495500	-1.53231300	-0.74889200
Н	6.63948200	-1.64455200	-0.92837700
С	2.85276600	-1.21663100	-0.30891100
С	3.36937000	-2.47457100	-0.65006900
Н	2.68408900	-3.30987200	-0.75055900
С	4.72640400	-2.63867300	-0.86759600
Н	5.12558500	-3.61093400	-1.13574600
С	-1.53168100	1.01442800	-0.24367700
С	-1.30513200	2.27025000	-0.79147800
С	-2.84998100	0.53835900	-0.03742000
С	-2.37846400	3.13165900	-1.03270900
Н	-0.29808400	2.58450800	-1.03644000
С	-3.89971200	1.42938400	-0.30369500
С	-3.68549500	2.73007600	-0.76812100
Н	-2.18344600	4.11874600	-1.44115100
Н	-4.92328800	1.09123000	-0.17789500
С	-4.85198200	3.65863500	-0.99241800
Н	-5.68511000	3.13847300	-1.47451200
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Н	-4.56947700	4.50602600	-1.62237800
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E = -1262.142161			
H = -1261.733681			

G = -1261.808364

3'-Keto (S1)

C	1 75712200	1 35256700	0 39151900
C	0 91913300	0 23634600	0.05455300
C	1 46055900	-1 02093900	-0 13247000
C	3 71655400	-0 11966300	-0 15555800
C	3 16389900	1 17758100	0.133330000
N	0 44005700	1 02207100	0.23941000
N C	0.44095700	-1.95207100	-0.16213400
C	-0.75006900	-1.28056800	-0.01511600
C	-2.03290600	-1./6914200	0.18495300
C	-3.095/3900	-0.84486500	0.30141100
С	-2.26994400	-3.22282700	0.28114900
С	-4.38881400	-1.34670300	0.62718500
С	-3.59536900	-3.64528400	0.57847400
С	-4.62471100	-2.71314100	0.76810700
H	-5.20978600	-0.65636900	0.78425100
Н	-3.77086500	-4.71102700	0.68106700
Н	-5.62081900	-3.05559100	1.02809100
0	-1.30161900	-4.01444300	0.10700100
Ν	-0.47259100	0.08349400	0.04094700
С	3,99982100	2.26648300	0.56211100
H	5 07339700	2 17485600	0.44962000
C	3 49445000	3 45099600	1 05944200
е н	4 16853700	4 26518400	1 30419600
C C	2 11669000	3 59111700	1 20051000
	1 71006600	1 10710000	1 72226200
п	1.71900000	4.40/40900	1.73330200
C II	1.20308000	2.54720000	1 17710000
H	0.20777000	2.64336700	1.1//10900
C	5.09403500	-0.32655700	-0.38003600
Н	5.78681200	0.50395800	-0.31914000
С	5.59627000	-1.57593700	-0.68712900
H	6.66124900	-1.69818300	-0.85558400
С	2.86387200	-1.24612500	-0.27954500
С	3.38742500	-2.51873500	-0.58395800
H	2.72051600	-3.37017400	-0.67696400
С	4.74072500	-2.68527500	-0.78376300
Н	5.14018500	-3.66492900	-1.02343200
С	-1.51039300	0.99215600	-0.25139000
С	-1.26124800	2.24610100	-0.80366600
С	-2.84261800	0.55218700	-0.03271200
С	-2.31234100	3.13302200	-1.02264700
Н	-0.25254700	2,53078200	-1.07444600
C	-3 87195500	1 47886400	-0.26561900
C	-3 62821800	2 77259200	-0 72861300
С Н	-2 09857200	4 11240000	-1 44058500
и и	-4 00107200	1 17204700	_0 11/00700
11 C	-4.JUIJ/200	1.1/294/00 2 7/102000	-U.11409/UU
	-4./0010900	J. /4192000	-0.92131/00
H	-5.64/56300	3.24204900	-1.33356200
H 	-5.05959300	4.19128500	0.03391400
Н	-4.48636900	4.55313000	-1.59842800
Н	0.45371100	-2.94619300	-0.16786000
0 imaginary free	quencies		
E = -1262.14518	5		
11 10/1 70/16			

 $\begin{array}{rcl} H &=& -1261.736159 \\ G &=& -1261.811083 \end{array}$



Fig. S10 Line narrowing and input-output curve of Rhodamine 6G in 10⁻² M propylene glycol solution.



Fig. S11 Solution (toluene) spectral narrowing and input-output-FWHM for 1, 2, and 3.



Fig. S12 Neat-film spectral narrowing and input-output-FWHM for 1 and 2, while neat films of 3 did not show ASE.



Fig. S13 Photostability of the HPI 1–3 (6 wt% in CBP), pumped at a constant pump intensity about twice the threshold ($2 \times E_{th}$) with the evolution of emission intensity from ASE peak plotted as a function of pump pulses.

Characterisation Data



Fig. S14 ¹H NMR (500 MHz, DMSO-*d*₆) of **4**.



Fig. S15 COSY (500 MHz, DMSO-*d*₆) of 4.



Fig. S16 Theoretical (top) and measured (bottom) HRESI mass spectrum of 4 $[M+H]^+$.



Fig. S18 ¹³C NMR (126 MHz, DMSO-*d*₆) of **5**.



Fig. S19 COSY (500 MHz, DMSO-*d*₆) of 5.



Fig. S20 Theoretical (top) and measured (bottom) HRESI mass spectrum of 5 [M+H]⁺.



Fig. S22 ¹³C NMR (126 MHz, DMSO-*d*₆) of **6**.



Fig. S23 COSY (500 MHz, DMSO-*d*₆) of 6.



Fig. S24 Theoretical (top) and measured (bottom) HRESI mass spectrum of 6 [M+H]⁺.



Fig. S25 ¹H NMR (500 MHz, DMSO-*d*₆) of **1**.



Fig. S26 ¹³C NMR (126 MHz, DMSO-*d*₆) of 1.



Fig. S27 COSY (500 MHz, DMSO-*d*₆) of 1.



Fig. S28 Theoretical (top) and measured (bottom) HRESI mass spectrum of 1 [M+H]⁺.





Fig. S30 ¹³C NMR (126 MHz, DMSO-*d*₆) of **2**.



Fig. S31 COSY (500 MHz, DMSO-*d*₆) of 2.



Fig. S32 Theoretical (top) and measured (bottom) HRESI mass spectrum of 2 $[M+H]^+$.



Fig. S34 13 C NMR of 8 in DMSO- d_6



Fig. S35 COSY of 8 in DMSO-d₆



Fig. S36 Theoretical (top) and measured (bottom) HRESI mass spectrum of 8 [M+H]⁺.



Fig. S38 ¹H NMR (500 MHz, DMSO- d_6) of **3** collected at 25°C (blue) and 60°C (black) to allow increased concentration in solution. Normalised to DMSO- d_6 peak.



Fig. S39 ¹³C NMR (126 MHz, DMSO-*d*₆, 333 K) of **3**.



Fig. S40 COSY (500 MHz, DMSO-*d*₆, 333 K) of 3.



Fig. S41 Theoretical (top) and measured (bottom) HRESI mass spectrum of 3 [M+H]⁺.

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