Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Modulating the Spectroscopy and Dynamics of a Proton-Transfer Dye by Functionalizing with Phenyl Groups

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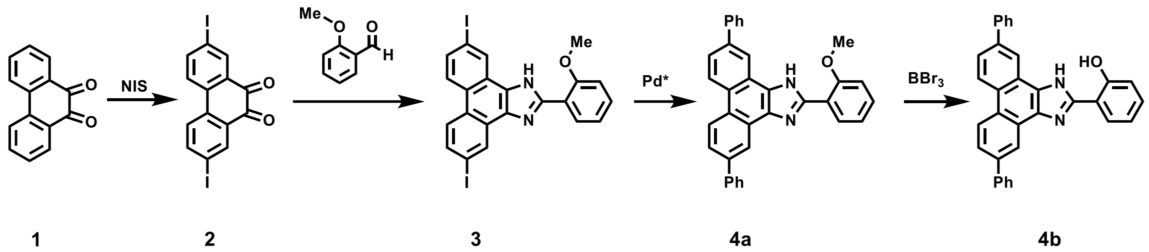
Synthesis and characterization of the different molecules (DP-MPPI and DP-HPPI)



Scheme S1. Representation of the steps followed for the synthesis of the different molecules: DP-MPPI (4a) and DP-HPPI (4b).

Synthesis of 5,10-diiodo-2-(2-methoxyphenyl)-1H-phenantro[9,10-d]imidazole (3)

A mixture of 2,7-diiodophenanthrene-9,10-dione (2) (1.74 mmol, 800 mg, 1 eq.), 2-methoxybenzaldehyde (6.09 mmol, 829 mg, 3.5 eq.) and ammonium acetate (13.04 mmol, 1005 mg, 7.5 eq.) in acetic acid (20 mL) was refluxed under argon for four hours. The reaction was monitored by TLC using chloroform as eluent. Water (~ 20 mL) was added to induce the precipitation of the final product. The crude was filtered, washed with water several times and dried by suction. The solid obtained was recrystallized from toluene and dry in vacuum to give a solid (65%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.84 (s, 1H), 9.17 (d, J = 1.8 Hz, 1H), 8.90 (d, J = 1.9 Hz, 1H), 8.60 (t, J = 8.8, 7.4 Hz, 2H), 8.24 (dd, J = 7.7, 1.8 Hz, 1H), 7.90 (dd, J = 8.7, 1.9 Hz, 2H), 7.52 (ddd, J = 8.2, 7.3, 1.8 Hz, 1H), 7.28 (dd, J = 8.4, 1.0 Hz, 1H), 7.16 (td, J = 7.5, 1.0 Hz, 1H), 4.05 (s, 3H).

FT-IR (KBr) ν (cm^{-1}) = 3426 (m), 3307 (m), 3068 (m), 2935 (m), 2836 (m), 1698 (w), 1598 (w), 1471 (w), 1452 (w), 1238 (w), 1021 (w), 983 (m), 798 (w), 739 (m), 713 (w).

MS (EI): *m/z* = 576 (100) M$^+$.

Synthesis of 2-(2-methoxyphenyl)-5,10-diphenyl-1H-phenantro[9,10-d]imidazole, DP-MPPI (4a)

A suspension of 5,10-diiodo-2-(2-methoxyphenyl)-1*H*-phenantro[9,10-*d*]imidazole **(3)** (0.26 mmol, 150 mg, 1 eq)), phenylboronic acid (0.57 mmol, 70 mg, 2.2 eq)), triphenylphosphine (0.065 mmol, 17 mg, 0.25 eq.)) and sodium hydrogencarbonate (0.57 mmol, 48 mg, 2.2 eq.)) in *N*,*N'*-dimethylformamide (3.4 mL) and water (0.6 mL) were degassed by argon bubbling. Then, diacetoxypalladium (7.81 μmol, 1.7 mg, 3%) was added. The reaction was performed by microwave and the conditions were 75 W, 150 PSI, and 190 ºC for five minutes. The reaction was monitored by TLC using heptane/ethyl acetate (4:1) as eluent. After that, CH_2Cl_2 was added, and the mixture was filtered through a column of Celite®. The obtained solution was washed with water several times, a saturated solution of NaCl, and dried over Na_2SO_4. After removing the solvent by rotary evaporation, a brown powder was obtained. The solid was washed with pentane, recrystallized from toluene, and dried in vacuum to give compound **4a** as a brown solid (70%).

^{1}H NMR (300 MHz, DMSO-d$_6$) δ 12.95 (s, 1H), 9.08 (d, J = 2.0 Hz, 1H), 8.96 (dd, J = 8.9, 5.7 Hz, 2H), 8.84 (d, J = 2.1 Hz, 1H), 8.25 (dd, J = 7.7, 1.8 Hz, 1H), 8.06 – 7.86 (m, 6H), 7.66 – 7.40 (m, 7H), 7.30 (d, J = 8.4 Hz, 1H), 7.18 (td, J = 7.5, 1.0 Hz, 1H), 4.05 (s, 3H).

FT-IR (KBr) ν (cm^{-1}) = 3435 (m), 3027 (m), 2837 (m), 1617 (m), 1599 (m), 1470 (w), 1237 (m), 1022 (m), 758 (w).

MS (EI): *m/z* = 476 (100) M$^+$, 458 (47).

2-(5,10-diphenyl-1H-phenantro[9,10-d]imidazole-2-yl)phenol, DP-HPPI (4b)

A dispersion of 2-(2-methoxyphenyl)-5,10-diphenyl-1*H*-phenantro[9,10-*d*]imidazole **(4a)** (0.21 mmol, 100 mg, 1 eq.)) in dry dichloromethane (15 mL) was cooled to -78 ºC. A solution of 1M boron tribromide in dichloromethane (0.92 mmol, 920 µL, 4.4 eq.)) was added dropwise. After two hours, the mixture was stirred at room temperature overnight. The crude product was added on ice-water, neutralized with a saturated solution of $NaHCO_3$ and then it was acidified with a saturated solution of NH_4Cl. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and a saturated solution of NaCl, and dried over Na_2SO_4. After removing the solvent by rotary evaporation, the crude solid was recrystallized from toluene (500 mL/g) and dried in vacuum to give compound **4b** as a yellow solid (60%).

^{1}H NMR (300 MHz, DMSO-d_6) δ 13.75 (s, 1H), 13.08 (s, 1H), 8.95 (t, *J* = 6.0 Hz, 4H), 8.70 (s, 1H), 8.24 (dd, *J* = 8.1, 1.2 Hz, 1H), 8.12 – 7.80 (m, 4H), 7.59 (q, *J* = 7.9 Hz, 4H), 7.49 (t, *J* = 6.8 Hz, 2H), 7.41 (td, *J* = 7.9, 1.3 Hz, 2H), 7.11 (dt, *J* = 7.0, 3.0 Hz, 2H).

FT-IR (KBr) ν (cm^{-1}) = 3433 (m), 3056 (m), 3027 (m), 1620 (m), 1599 (m), 1484 (m), 758 (w).

MS (EI): *m/z* = 462 (100) M$^+$, 231 (14), 135 (14).

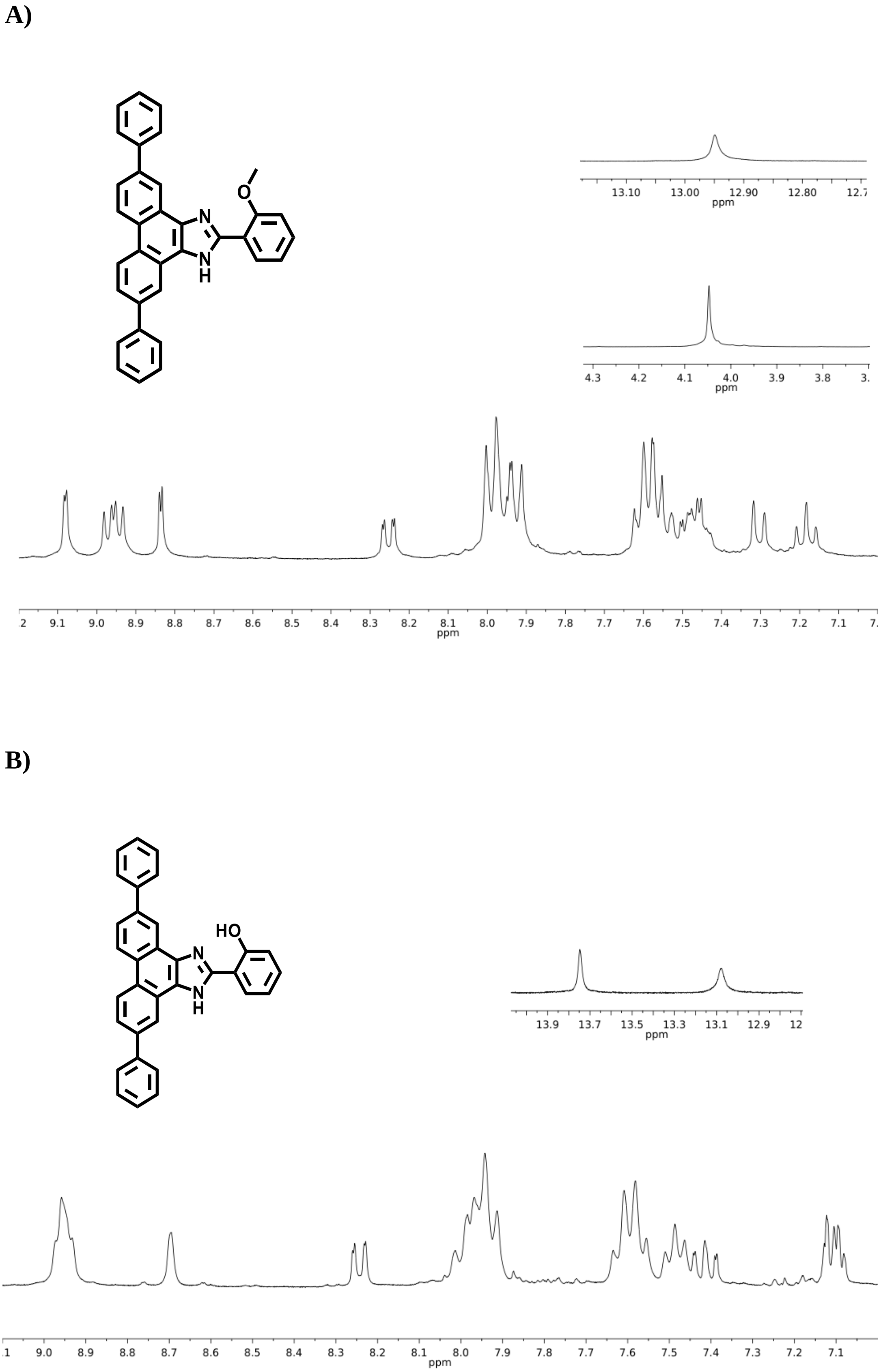


Figure S1. ^{1}H NMR spectra of A) DP-MPPI and B) DP-HPPI in DMSO-d_6.

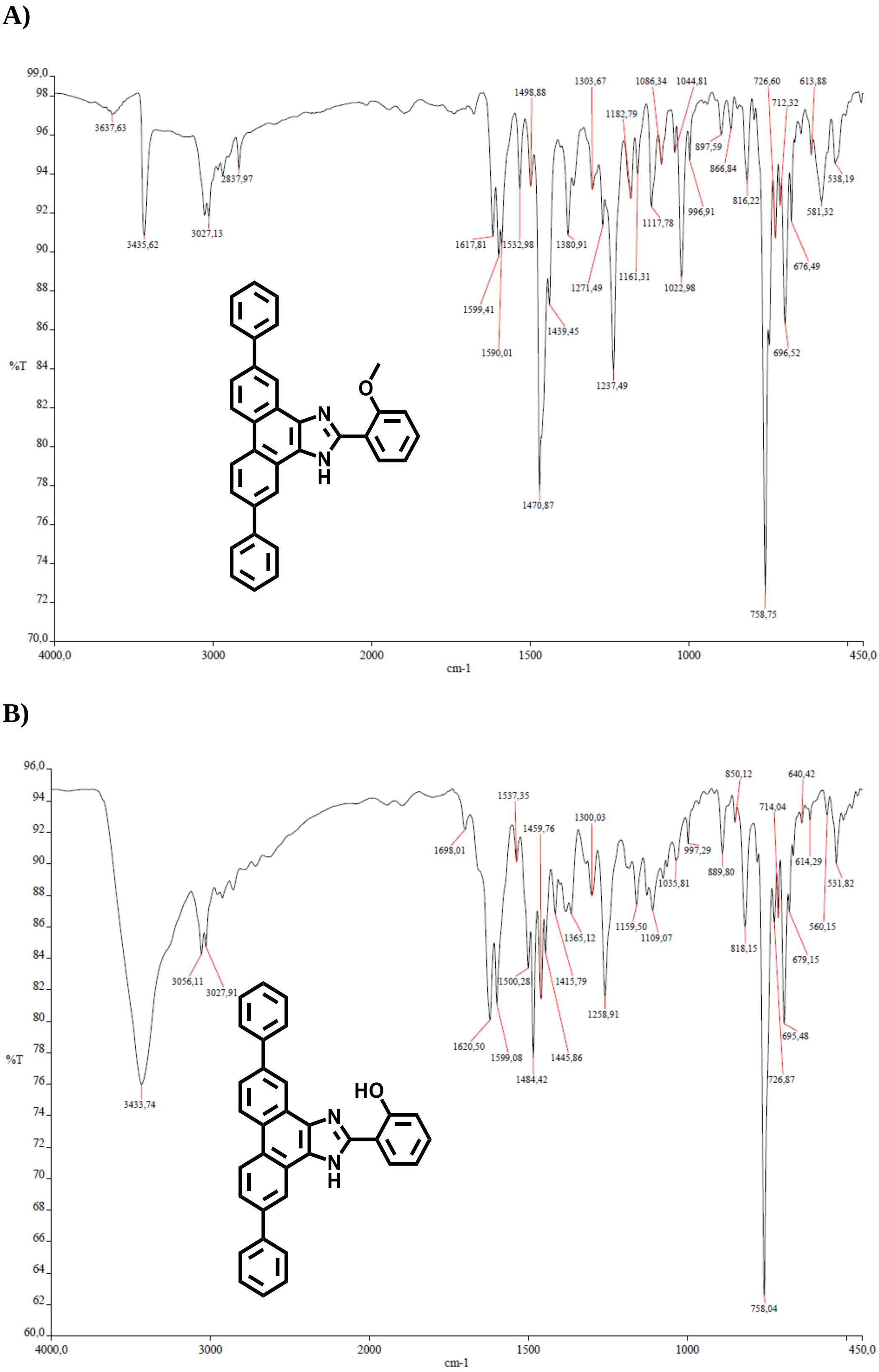


Figure S2. FTIR-spectra of A) DP-MPPI and B) DP-HPPI in potassium bromide (KBr).

Optical properties of DP-MPPI and DP-HPPI

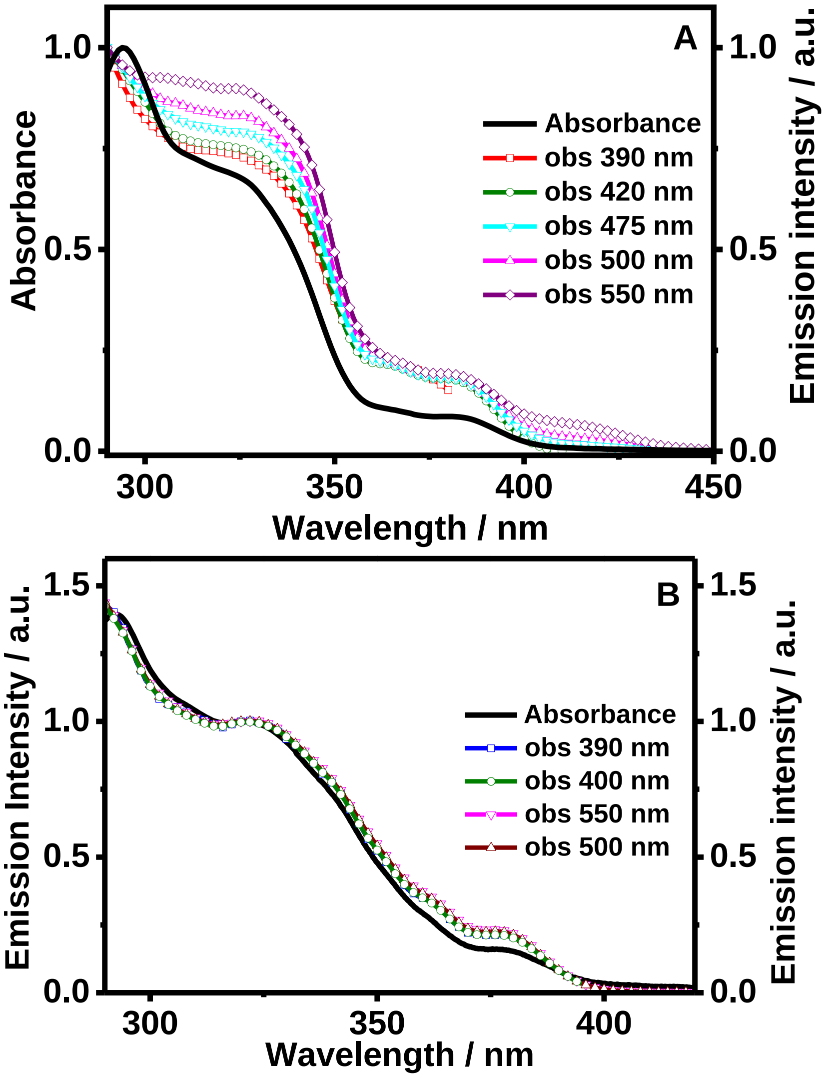


Figure S3. Absorption and excitation spectra of A) DP-MPPI and B) DP-HPPI in DCM solutions. For the excitation spectra, the observation wavelengths are indicated in the graph.

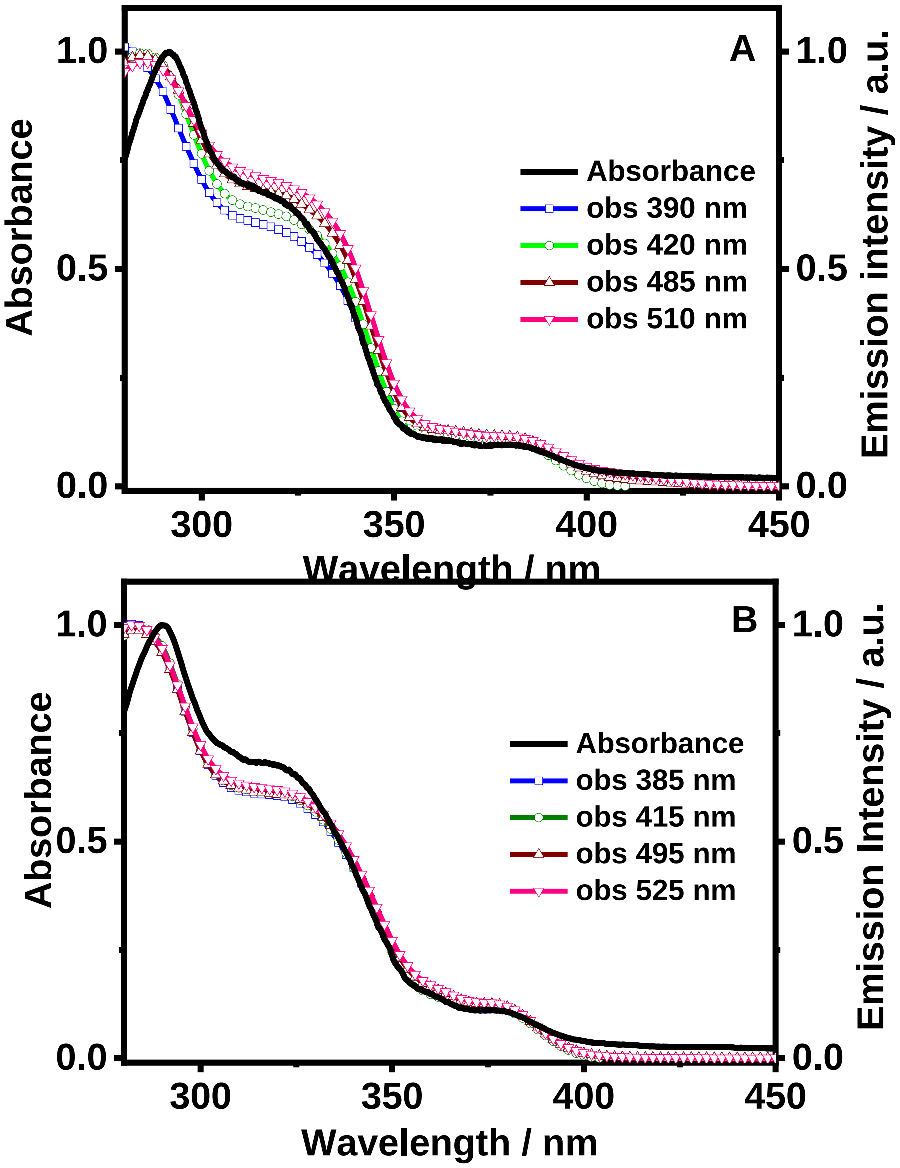


Figure S4. Absorption and excitation spectra of A) DP-MPPI and B) DP-HPPI in ACN solutions. For the excitation spectra, the observation wavelengths are indicated in the graph.

Classical Birks Model

$$I_f(ECT) = A_{11}e^{-t/\tau_1} + A_{12}e^{-t/\tau_2} \tag{1}$$

$$I_f(K) = A_{21}e^{-t/\tau_1} + A_{22}e^{-t/\tau_2} \tag{2}$$

$$A = A_{12}/A_{11} \tag{3}$$

Where τ_1 and τ_2 are the time constants of the slow and fast component, respectively, A_{11}, A_{12} and A_{21}, A_{22} are the amplitudes in the blue (1) and red (2) parts of the emission spectrum (Table 2). The selected wavelengths were (1) 410 and (2) 600 nm. The existence of reversible reaction is reflected by $A_{22}/A_{21} \approx -1$. Using the values τ_1 and τ_2 together with the amplitudes ratio A (eq. 3) and the lifetime of non-planar ECT, which we can suppose that is 2.1 ns, according to that observed for DP-MPPI in the same solvent, the rate constants k_{DPT} (direct proton transfer reaction, ECT*→K*) and k_{RPT} (reverse proton transfer reaction, ECT*← K*) together with the K lifetime, τ(K), were calculated applying the following equations:

$$K_{DPT} = (1/\tau_1 + A/\tau_2)/(1+A) - 1/\tau(ECT) \tag{4}$$

$$K_{RPT} = \left[(1/\tau_1 + A/\tau_2)^2 - \left(2K_{DPT} + \frac{2}{\tau(ECT)} - \frac{1}{\tau_1} - \frac{1}{\tau_2}\right)^2\right]/4K_{DPT} \tag{5}$$

$$\frac{1}{\tau(K)} = 1/\tau_1\left(1 + K_{RPT}\frac{\tau(ECT)-\tau_1}{1+K_{RPT}\tau(ECT)-\tau(ECT)/\tau_1}\right) \tag{6}$$

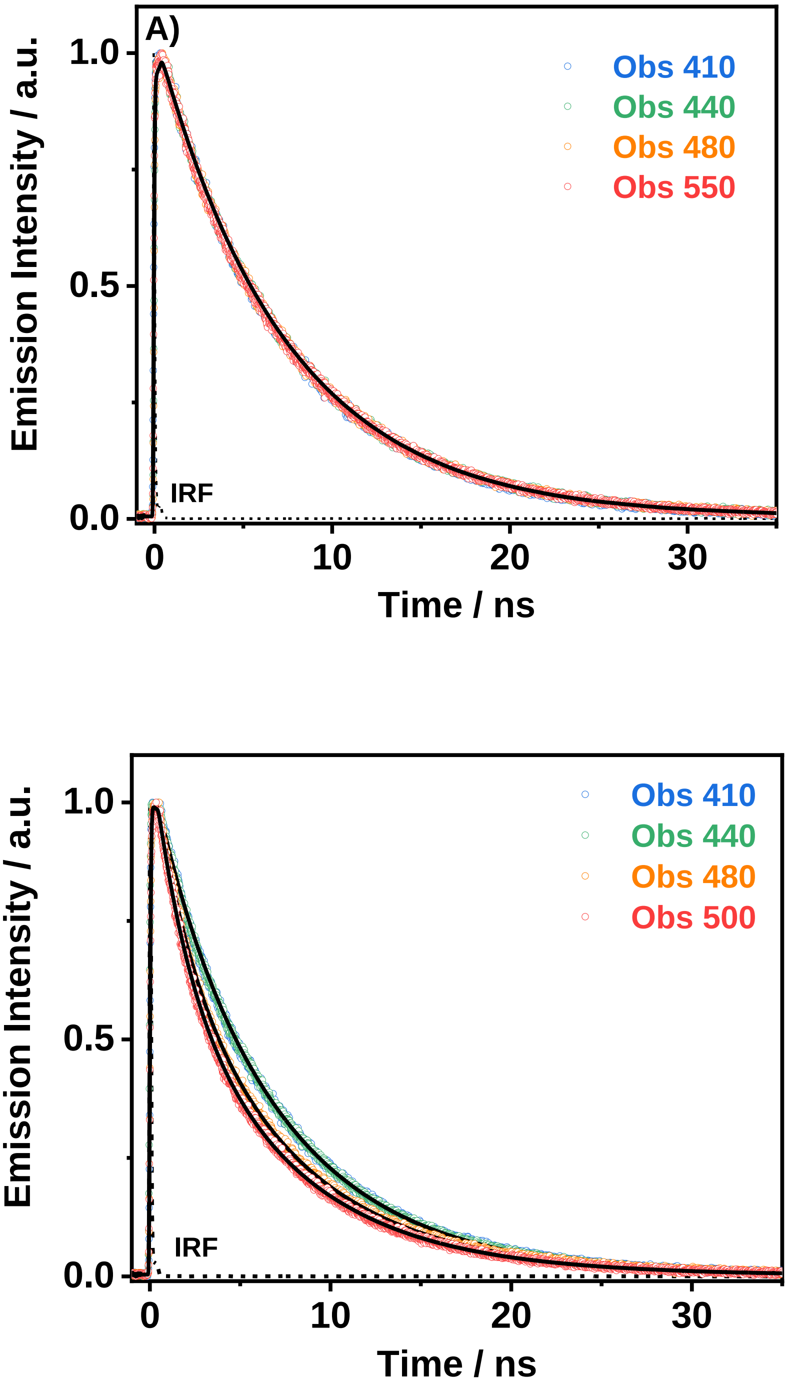


Figure S5. Magic-angle ps-emission decays of A) DP-MPPI and B) DP-HPPI in ACN solutions upon excitation at 371 nm. The observation wavelengths are indicated in the graph. The solid lines are from the best fit using multiexponential global function and the IRF is the instrumental response function.

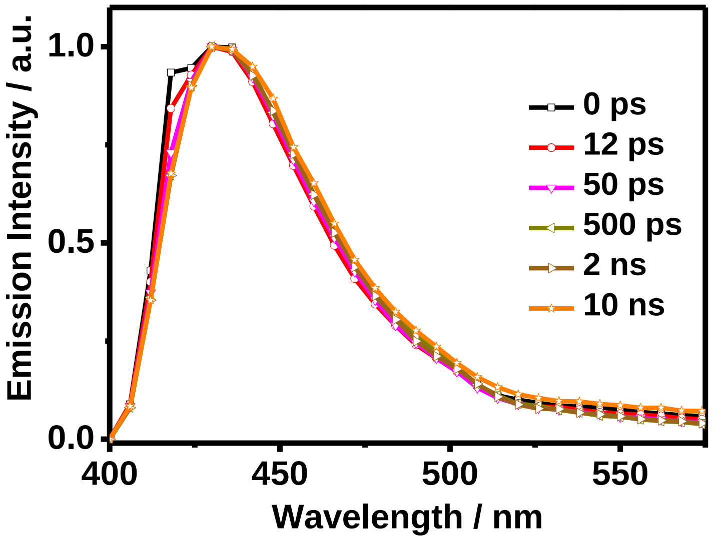


Figure S6. Normalized time-resolved emission-spectra (TRES) of DP-HPPI in ACN upon excitation at 371 nm and gating at the indicated delay times.

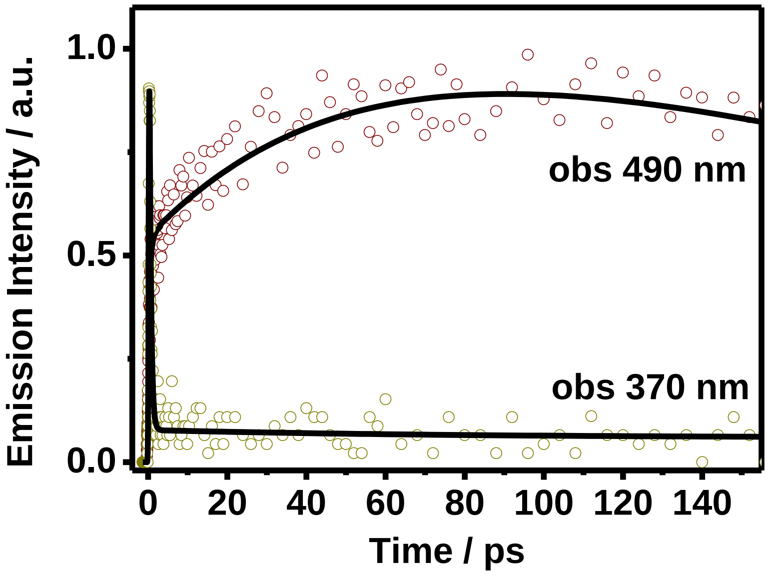


Figure S7. Representative fs-emission transients of DP-HPPI in DCM solutions upon excitation at 320 nm and probing at the wavelengths indicated in the graph. The solid lines are from the best fit using multiexponential function**.**

Table S1. Values of time constants (τi) and normalized (to 100) pre-exponential factors (ai) obtained from the fit of the ps-ns decays of DP-MPPI and DP-HPPI in ACN solutions upon excitation at 370 nm and observation as indicated.

Sample	**λ_{Obs} / nm**	**τ_1 / ns** (±0.2)	**a_1**	**τ_2 / ns** (±0.2)	**a_2**
DP-MPPI	410	-	-	7	100
	440		-		100
	480		-		100
	550		-		100
DP-HPPI	410	2	5	6.9	95
	440		9		91
	480		25		75
	500		39		61