Electronic Supplementary Information (ESI†)

Experimental and Theoretical Insights into the Electronic Density Influence on Proton-Transfer Reactions

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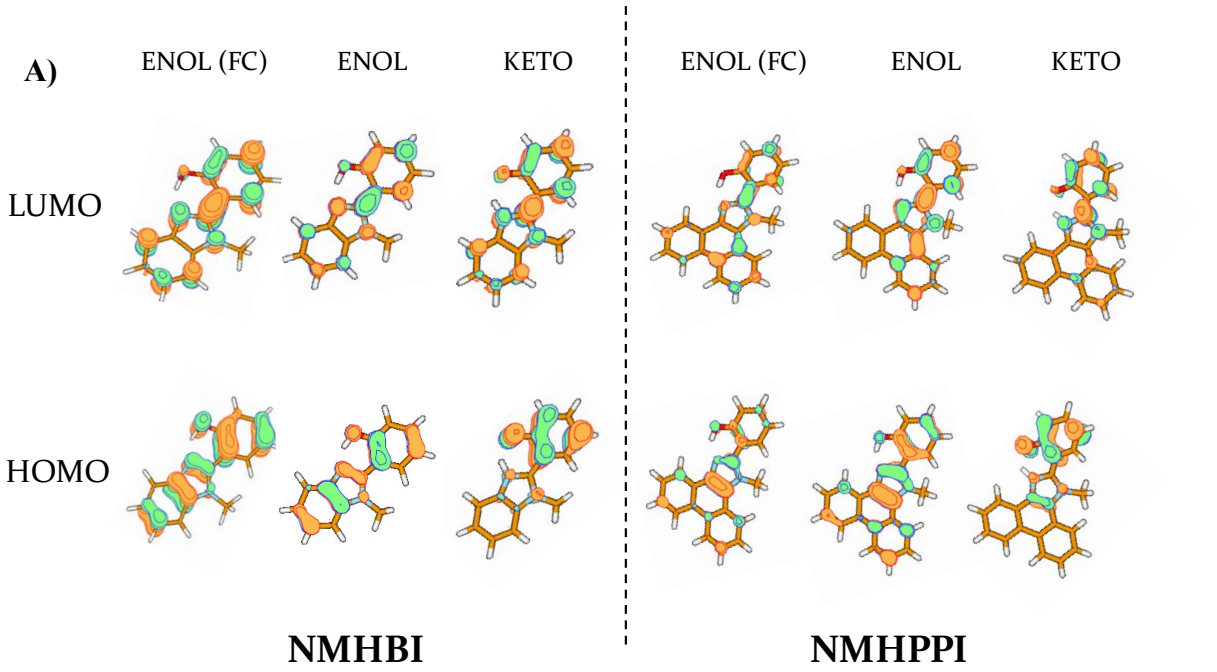
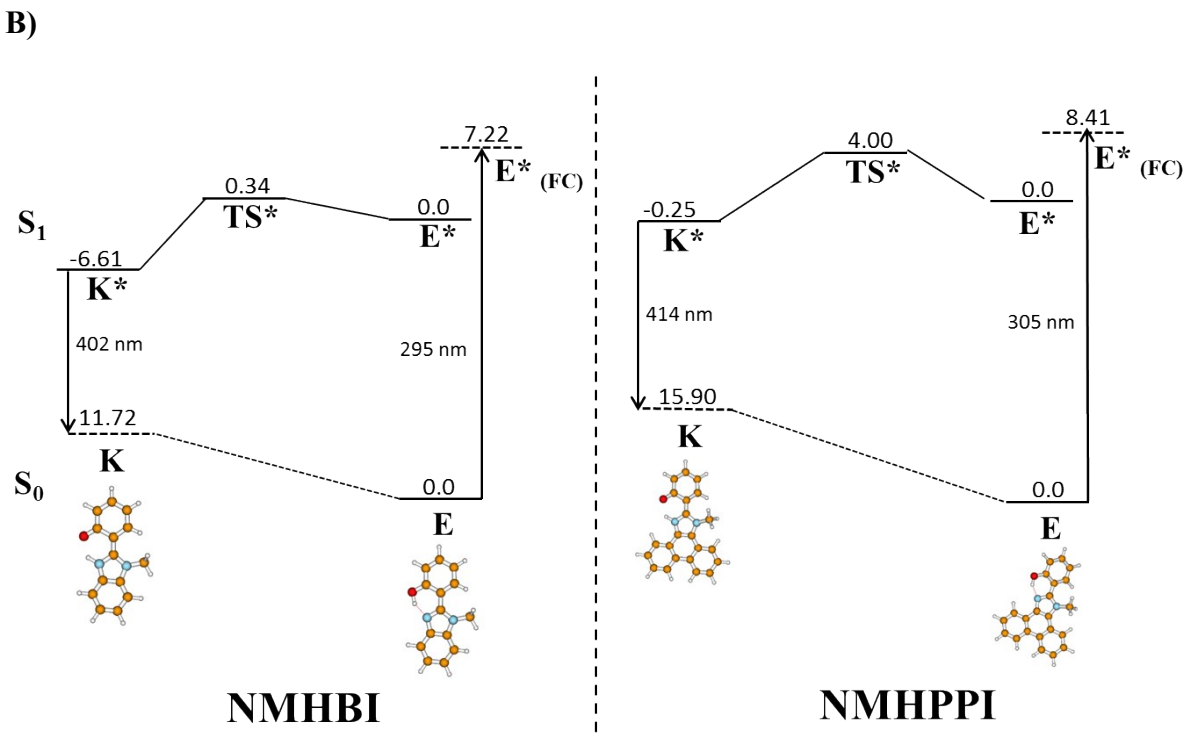
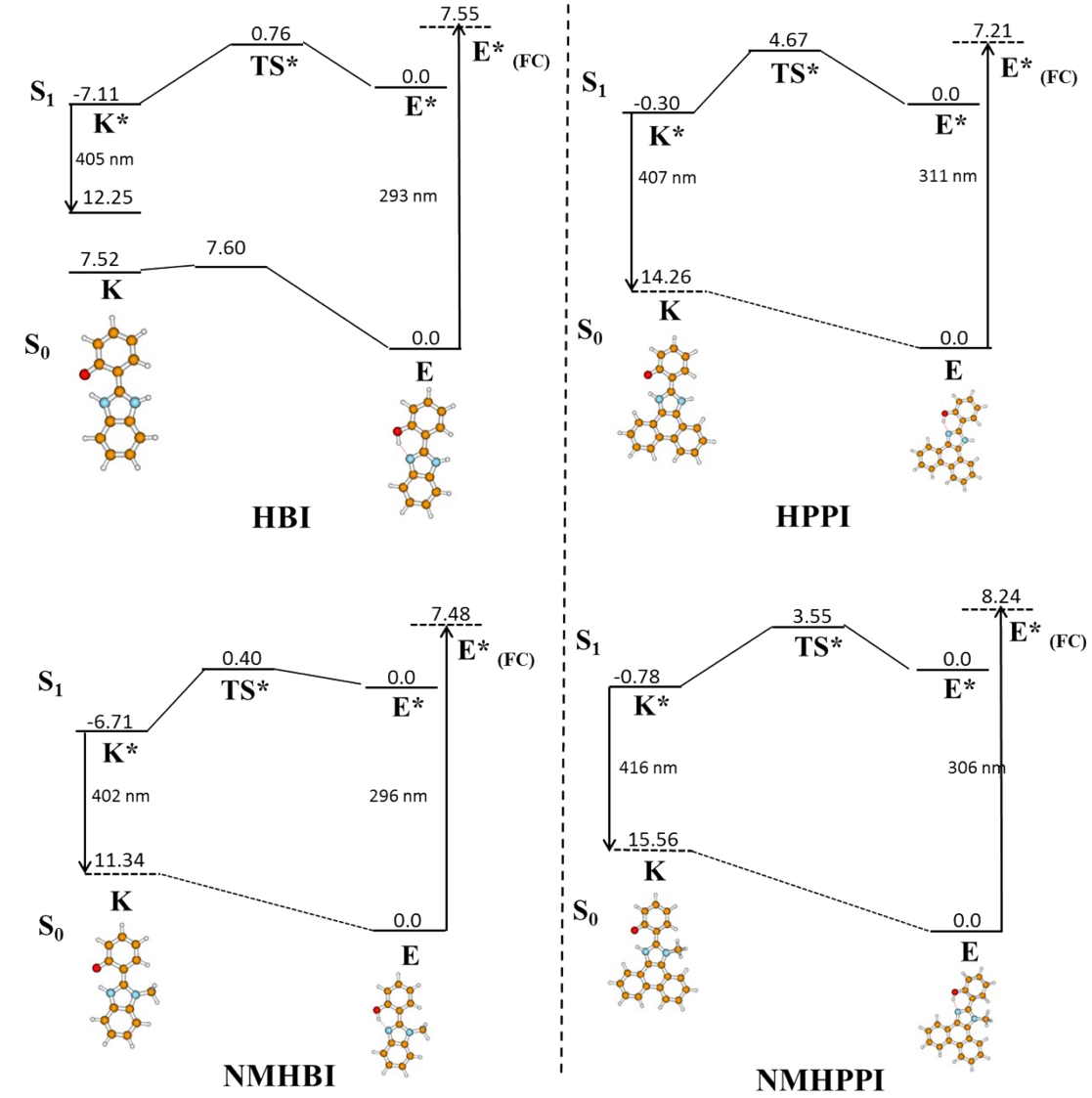
***Synthesis and characterization part are shown in page 15.**





C


S1
-7.11
K*
405 nm
12.25
0.76
TS*
0.0
E*
7.55
E* (FC)
293 nm
7.52
K
7.60
S0
0.0
E
HBI
S1
-0.30
K*
407 nm
14.26
K
4.67
TS*
0.0
E*
7.21
E* (FC)
311 nm
S0
0.0
E
HPPI
S1
-6.71
K*
402 nm
11.34
K
0.40
TS*
0.0
E*
7.48
E* (FC)
296 nm
S0
0.0
E
NMHBI
S1
-0.78
K*
416 nm
15.56
K
3.55
TS*
0.0
E*
8.24
E* (FC)
306 nm
S0
0.0
E
NMHPPI

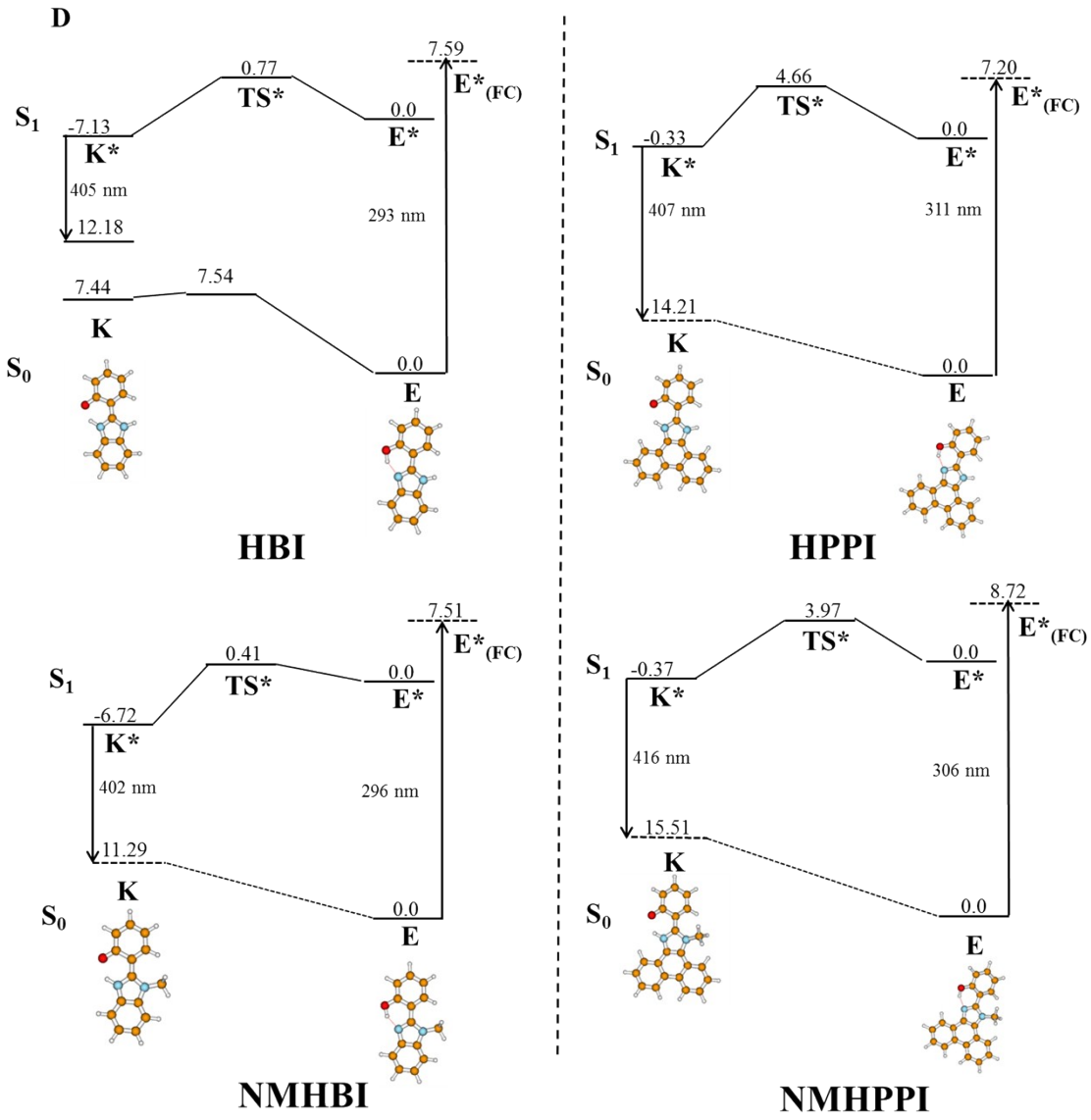


Figure S1. A) Shape of the NMHBI and NMHPPI HOMO/LUMO involved in the electronic excitation from the ground to the lowest singlet excited electronic state. B) Energy diagram not in scale of NMHBI and NMHPPI at S_0 and S_1 states in DCM solution. C) Energy diagram not in scale of HBI, HPPI, NMHBI and NMHPPI at S_0 and S_1 states in ACN solutions. D) Energy diagram not in scale of HBI, HPPI, NMHBI and NMHPPI at S_0 and S_1 states in water solutions.

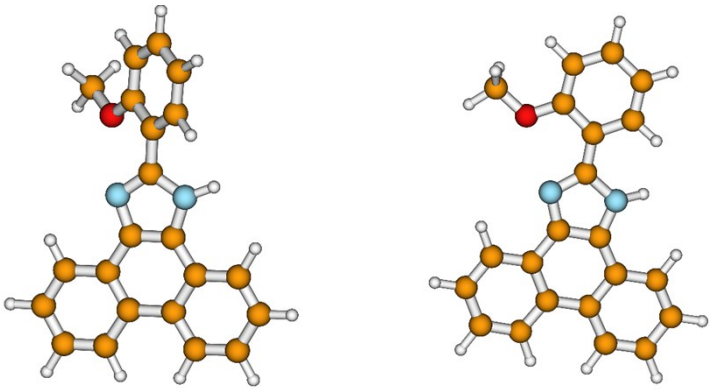


Figure S2: Molecular structure of MPPI at the ground electronic state (left) and the first singlet excited electronic state (right).

Table S1. Dipole moment variations (Δμ in Debye) for the studied molecules after the indicated transitions in (A) DCM and (B) water media. (C) Total Mulliken charges (in a.u.) of the phenanthroimidazole and methoxyphenyl parts for MPPI at different electronic states.

(A)

Δμ/D	**E → E*(FC)**	**E*(FC) → E***	**E* → K***
HBI	-0.95	0.26	1.36
HPPI	-0.50	0.49	2.01
NMHBI	-1.09	0.21	1.17
NMHPPI	-0.57	0.41	1.47

(B)

Δμ/D	**E → E*(FC)**	**E*(FC) → E***	**E* → K***
HBI	-0.94	0.23	1.35
HPPI	-0.53	0.48	1.91
NMHBI	-1.07	0.18	1.16
NMHPPI	-0.57	0.38	1.32

(C)

Moieties Part	**S_0**	**S_1 (FC)**	**S_1 (Relaxed)**
Methoxyphenyl	0.072	0.025	-0.002
Phenanthroimidazole	-0.072	-0.025	0.002

Calculation of pKa

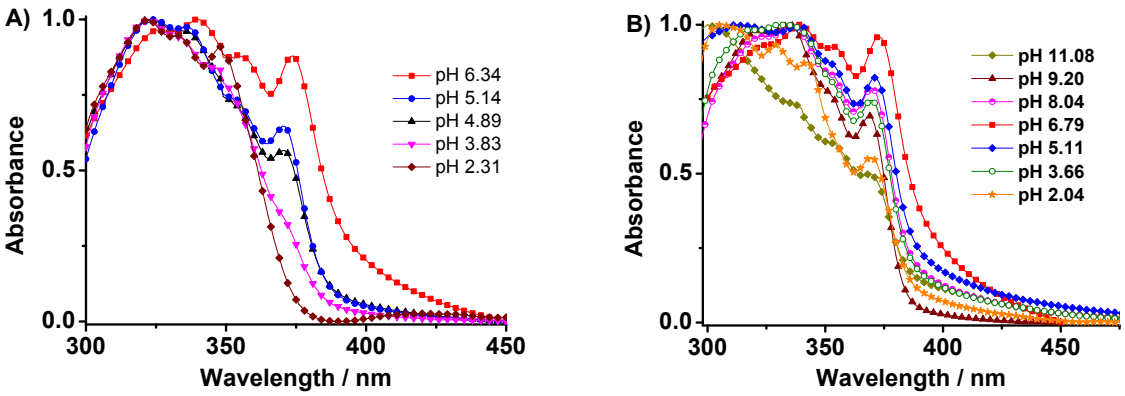


Figure S3. Normalized UV-visible absorption spectra of (A) MPPI and (B) NMHPPI in water solutions at different pHs.

We calculated the pK_a of the species using:

$$pKa = pH + log\ r \qquad \text{Eq.S1}$$

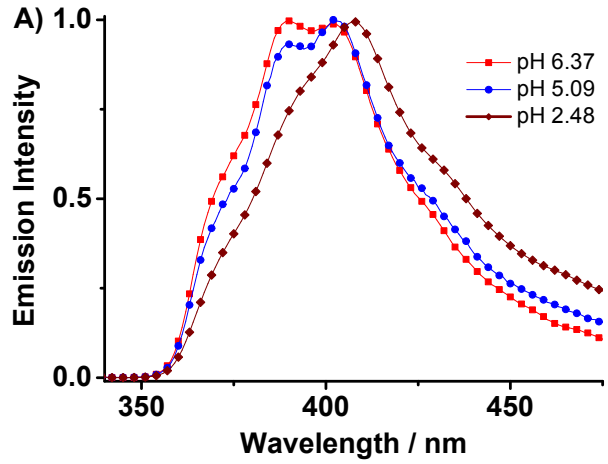
$$r = \frac{A - A_N}{A_I - A} \qquad \text{Eq.S2}$$

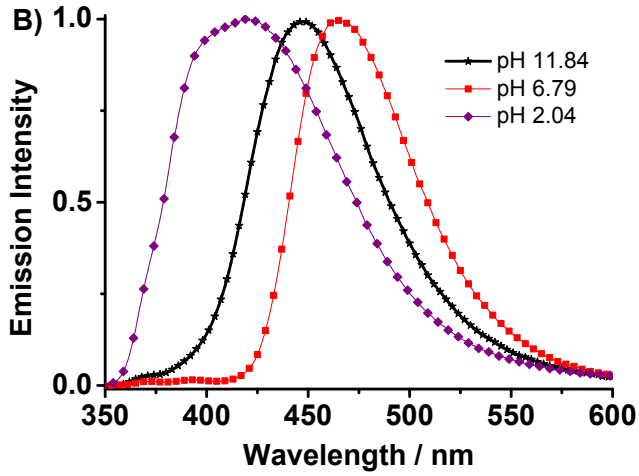
A_N : Absoption intensity of the neutral specie (at pH 7).

A_I: Absoption intensity of the ionic specie (cationic or anionic, at pH 2 and 12, respectively).

To get the values of pKa (-NH^+ of the benzoxazole ring) in MPPI and NMHPPI, and pKa (-OH of the phenyl ring) in NMHPPI, absorption intensity (A) were taken at 370 nm.

Calculation of pKa*





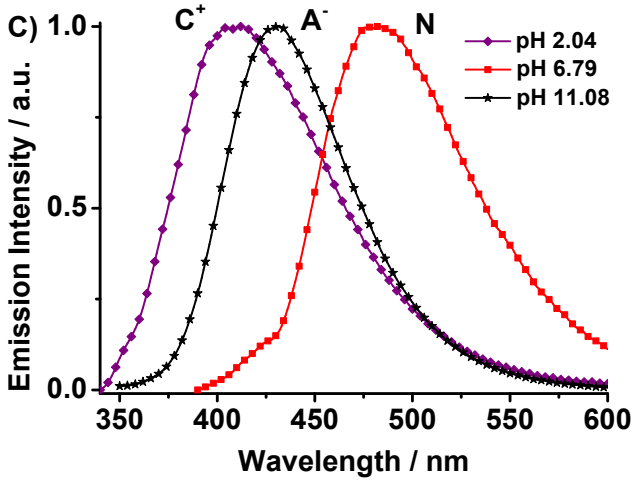


Figure S4. Normalized fluorescence spectra of (A) MPPI, (B) HPPI and (C) NMHPPI in water solutions at different pHs and upon excitation at 330 nm.

To calculate pK_a* (at S_1) we used the following equation,[1] where ν_{AH+}, ν_{A-} and ν_{AH} are the frecuency of the 0-0 transition (cm^{-1}) of the cationic, anionic and neutral forms, respectively. The term 2.4 x 10^{-3} is for T=293K. The error for the pKa and pHa* values is about ±0.4.

$$pK_a^* - pK_a = 2.4x10^{-3}(\nu_{AH+/A-} - \nu_{AH}) \quad \text{Eq.S3}$$

For MPPI in water solutions we got:

pKa ($-NH^+$)=4.50; pKa* ($-NH^+$)=5.78

For HPPI in water solutions we got:

pKa ($-NH^+$)=3.02[2]; pKa* ($-NH^+$)=6.96

pKa (-OH)=11.10[2]; pKa* (-OH)=3.28

For NMHPPI in water solutions we got:

pKa ($-NH^+$)=3.40; pKa* ($-NH^+$)=7.20

pKa (-OH)= 10.6; pKa* (-OH)=3.45

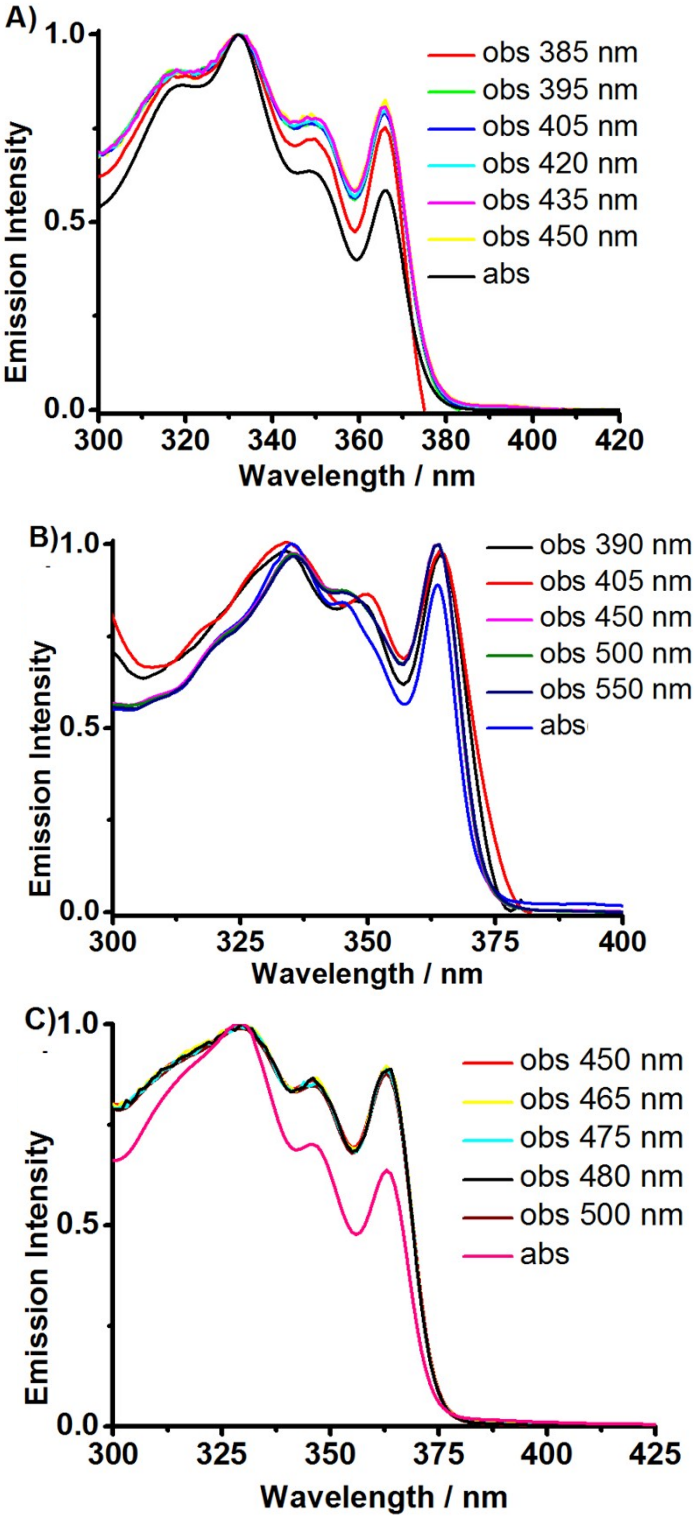


Figure S5. Excitation spectra of A) MPPI, B) HPPI and C) NMHPPI in DCM solutions, at indicated observation wavelengths.

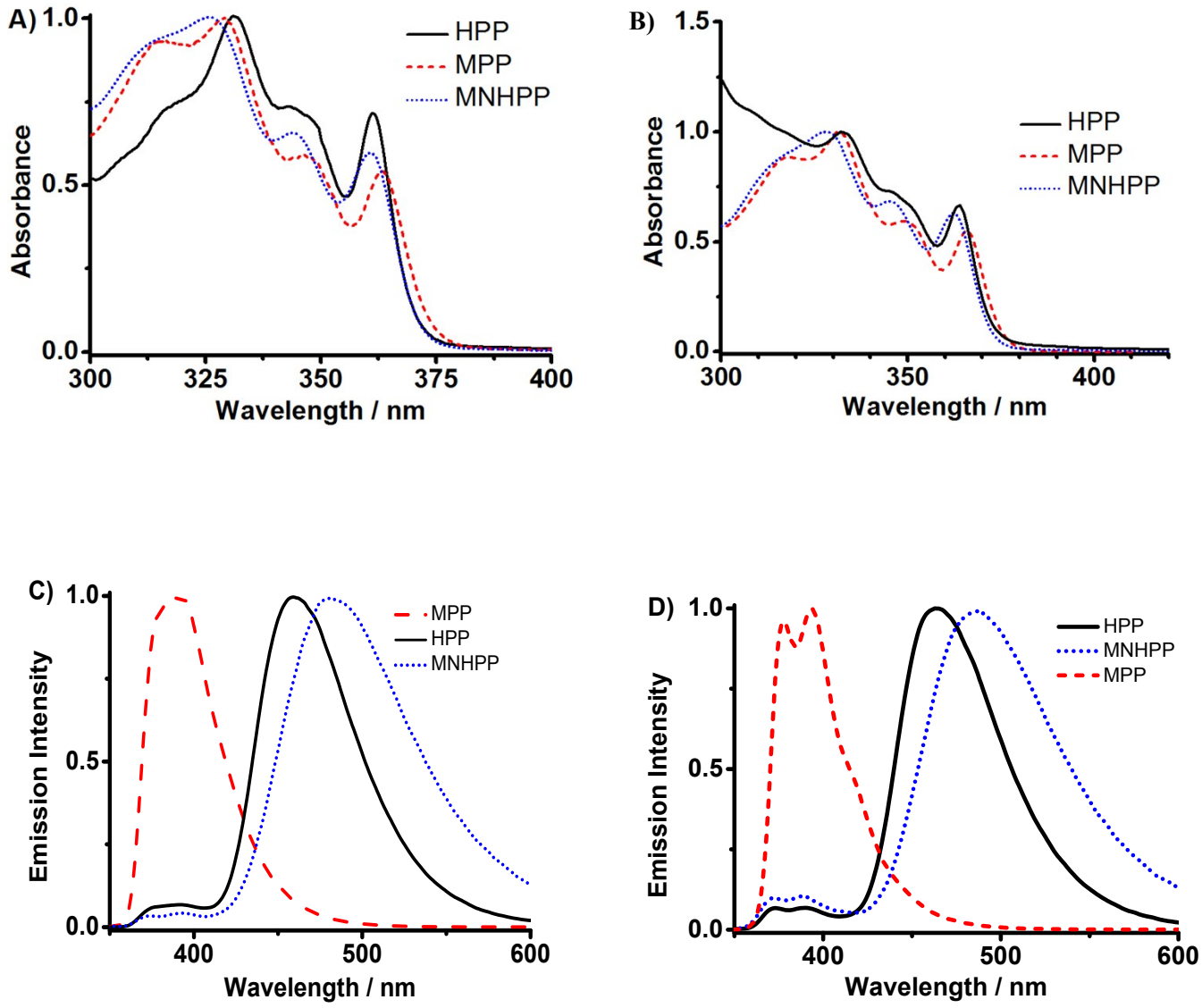


Figure S6. Normalized (A and B) UV-visible absorption and (C and D) emission spectra of MPPI, HPPI and NMHPPI, in ACN (A, C) and TAC (B, D) solutions, respectively. For emission spectra, the excitation wavelength was 320 nm.

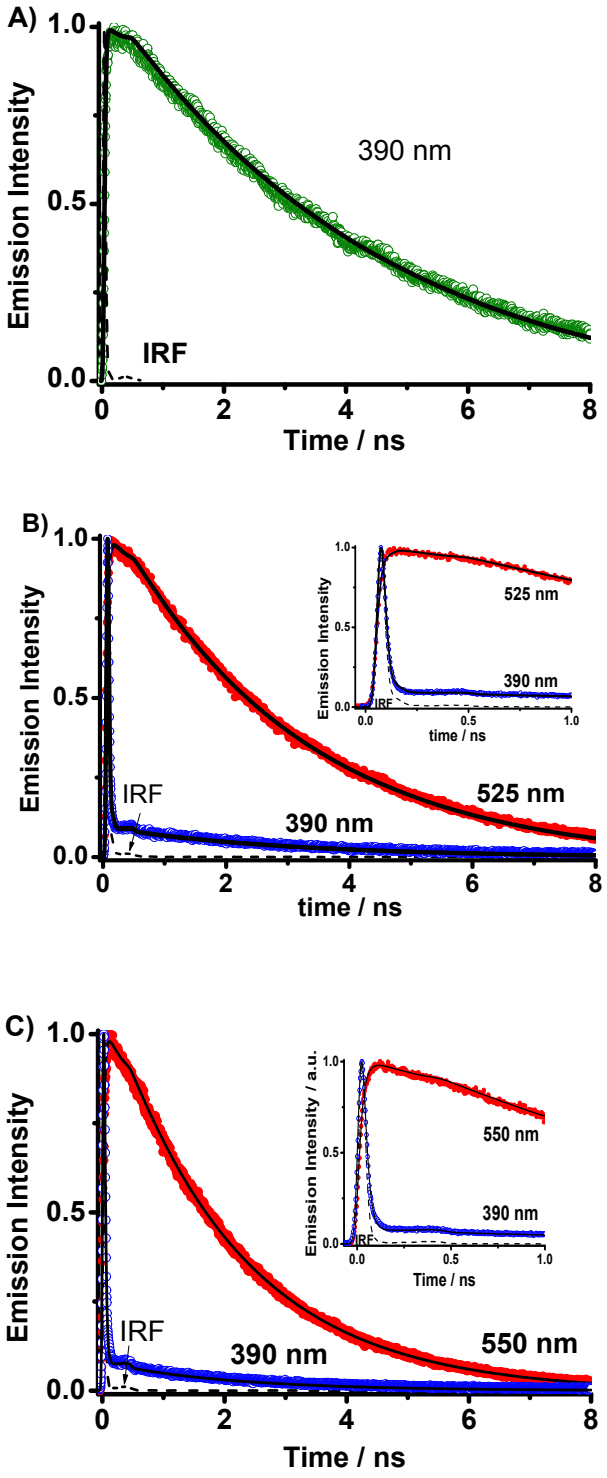


Figure S7. Magic-angle ps-emission decays of A) MPPI, B) HPPI and C) NMHPPI in DCM solution, upon excitation at 320 nm. The observation wavelengths are indicated in the inset. The solid lines are from the best fit using a multiexponential function and IRF is the instrumental response function.

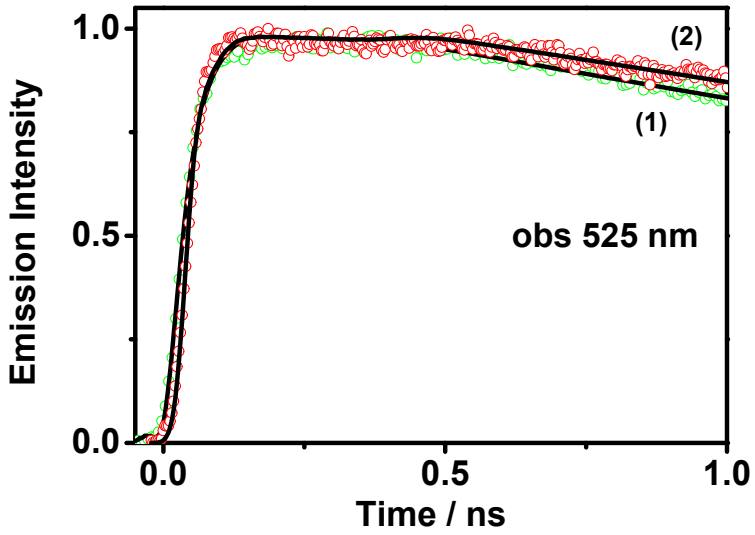


Figure S8. Magic-angle emission decays of HPPI in DCM (1) and DPPI in DCM-d_2 (2) solutions. The samples were excited at 320 nm and observed at 525 nm. The solid lines are from the best-fit using multiexponential functions.

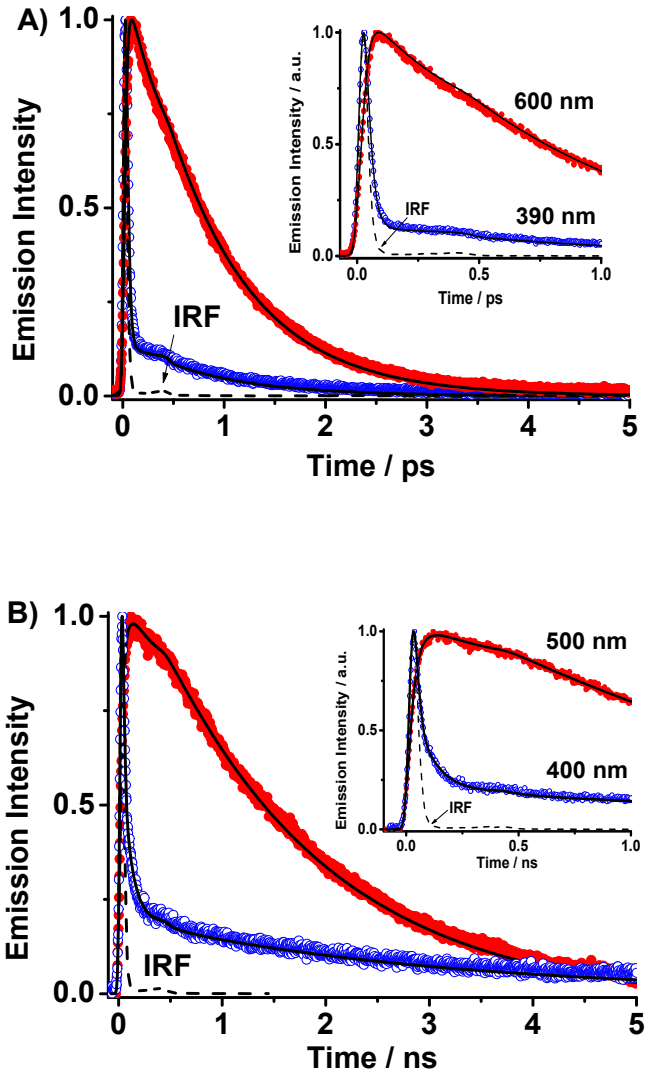


Figure S9. Magic-angle emission decays of NMHPPI in A) ACN and B) TAC solutions, upon excitation at 320 nm. The solid lines are from the best-fit using a multiexponential function. IRF in the instrumental response function.

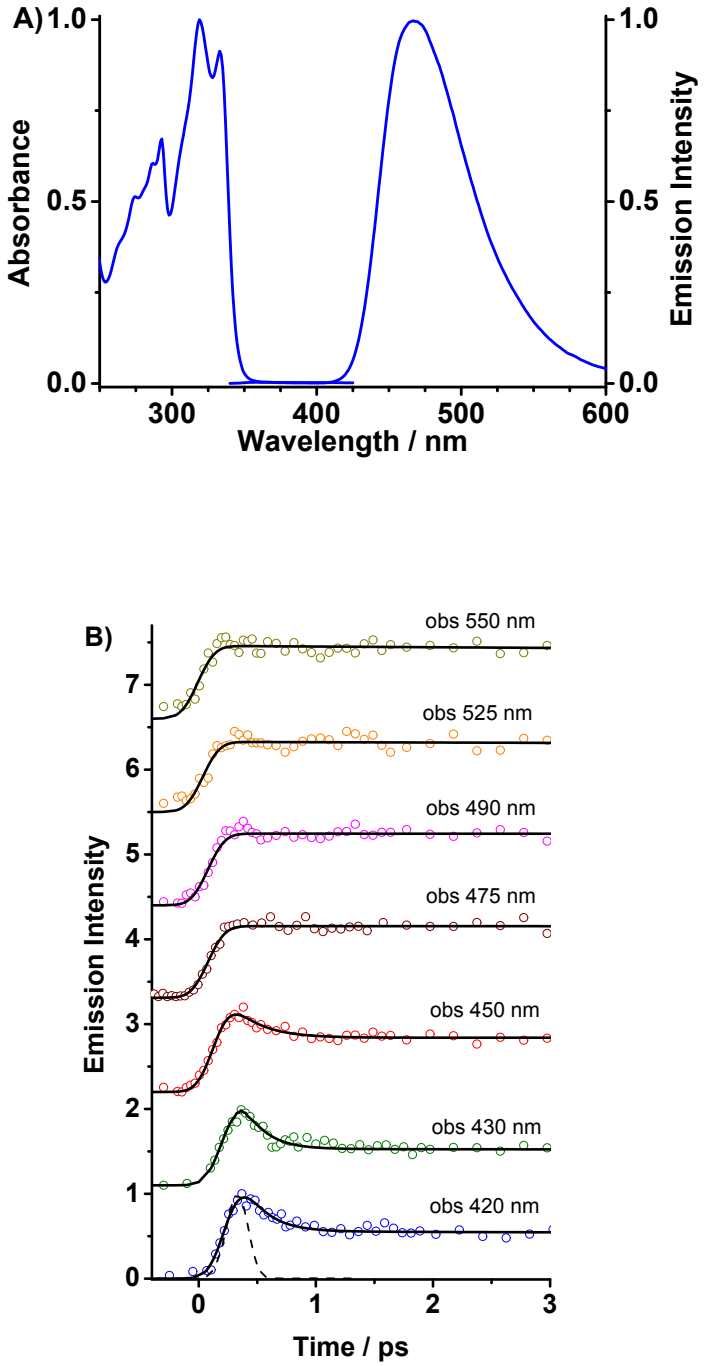


Figure S10. A) UV-Visible absorption and emission spectra of HBI in DCM solutions. For emission, the excitation wavelength was at 320 nm. B) Representative fs-emission transients of HBI in DCM solution, upon excitation at 350 nm. The observation wavelengths are indicated in the inset. The solid lines are from the best-fit using a multiexponential function and the dash signal is the instrumental response function.

Table S2. Values of time constants (τ_i) and normalized (to 100) pre-exponential factors (a_i) obtained from the best fit of the emission decays of HPPI in A) DCM and B) ACN solutions, upon excitation at 370 and 390, nm and observation as indicated. The negative sign of a_1 indicates a rising component in the emission signal.

A)

λ_{Exc} / nm	λ_{Obs} / nm	τ_1 / ps (±5)	a_1 %	c_1 %	τ_2 / ns (±0.3)	a_2 %	c_2 %	τ_3 / ns (±0.5)	a_3 %	c_3 %
370	390	**12**	98	15	**1.2**	1	25	**3.3**	1	60
	410		89	4		3	12		8	85
	440		17	1		5	2		78	97
	470		-100	-100		4	2		96	98
	500		-100	-100		-	-		100	100
	550		-100	-100		-	-		100	100
	600		-100	-100		-	-		100	100
390	410	**12**	68	13	**1.2**	28	62	**3.3**	4	25
	430		64	2		29	66		7	32
	450		26	1		56	48		18	51
	470		-100	-100		51	33		49	67
	500		-100	-100		34	19		66	81
	525		-100	-100		24	13		76	87
	550		-100	-100		16	8		84	92

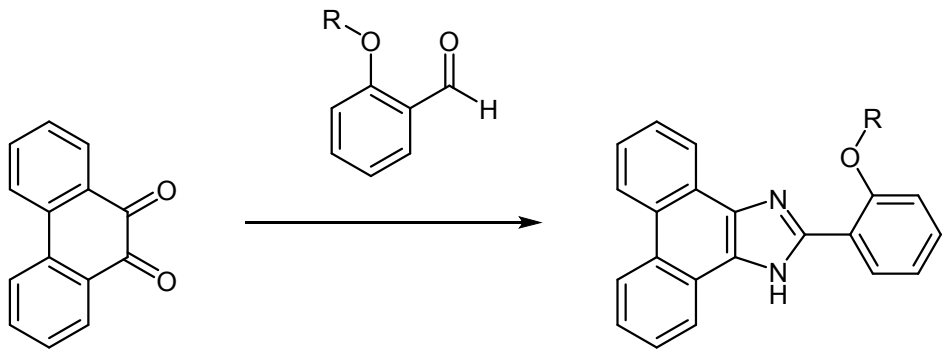
B)

λ_{Exc} / nm	λ_{Obs} / nm	τ_1 / ps (±5)	a_1 %	c_1 %	τ_2 / ns (±0.3)	a_2 %	c_2 %	τ_3 / ns (±0.5)	a_3 %	c_3 %
370	390	**15**	92	5	**1.7**	3	35	**2.75**	5	60
	410		89	4		6	27		5	69
	450		-100	-100		22	17		78	83
	470		-100	-100		18	11		82	89
	500		-100	-100		7	5		93	95
	550		-100	-100		-	-		100	100
	600		-100	-100		-	-		100	100
390	410	**15**	38	1	**1.7**	39	44	**2.75**	23	55
	430		20	1		37	21		43	78
	450		10	1		27	17		63	83
	470		-100	-100		30	8		70	92
	500		-100	-100		18	5		82	95
	525		-100	-100		11	3		89	97
	550		-100	-100		6	2		94	98
	600		-100	-100		5	2		95	98

Table S3. Values of time constants (τ_i) and normalized (to 100) pre-exponential factors (a_i) of the function used in fitting the fs-emission transient of HBI in DCM solutions, upon excitation at 350 nm and observation as indicated.

Sample	λ_{Obs} **/ nm**	τ_1 **/ fs** (±50)	a_1 **%**	τ_2 **/ ns**	a_2 **%**
	420	190	66		34
	430	200	74		26
	450	230	51		49
HBI	475	-	-	3.6*	100
	500	-	-		100
	525	-	-		100
	550	-	-		100

Synthesis and characterization of the different molecules (MPPI, HPPI and NMHPPI)



Scheme S1. Simplified steps of synthesis of MPPI and HPPI.

2-(2-methoxyphenyl)-1H-phenanthro[9,10-d]imidazole (3a=MPPI)

Method A[3]

A mixture of phenantrene-9,10-dione (1.4 mmol, 300 mg), 2-methoxybenzaldehyde (1.6 mmol, 216 mg) and ammonium acetate (10.8 mmol, 833 mg) in acetic acid (6 mL) was refluxed under argon for four hours. The reaction was monitored by TLC using chloroform as eluent. To induce the precipitation of the final product, water (6 mL) was added. The crude product was filtered, washed with water and dried by suction. The obtained solid was recrystallized from toluene and dried in vacuum to give a slightly brown solid (68%; m.p. 215 ºC, Lit. 214-215 ºC[4]).

Method B[5]

A mixture of phenantrene-9,10-dione (4.8 mmol, 1.0 g), and ammonium acetate (36 mmol, 2.7 g) were dissolved in a hot mixture of dichloromethane and ethanol (1:1) (30 mL). After ten minutes, 2-methoxybenzaldehyde (5.3 mmol, 721 mg) and few drops of acetic acid (2-3 drops) were added to the reaction mixture. The reaction was monitored by TLC using heptane/ethyl acetate (2:1). Forty-five minutes later the product

precipitated as a solid and it was warmed to room temperature. After removing dichloromethane by rotary evaporation, the product was filtrated, washed with methanol and dried in vacuum to give compound MPPI as a light brown solid (85%).

^{1}H-NMR (300 MHz, DMSO-d_6) δ 12.75 (s, 1H), 8.87 (d, J = 9.0 Hz, 2H), 8.68 (dd, J = 8.0, 1.4 Hz, 1H), 8.59 (dd, J = 7.9, 1.5 Hz, 1H), 8.22 (dd, J = 7.6, 1.8 Hz, 1H), 7.72 (d, J = 7.4 Hz, 2H), 7.67 – 7.60 (m, 2H), 7.50 (td, J = 7.7, 1.8 Hz, 1H), 7.27 (d, J = 8.2 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 4.03 (s, 3H).

^{1}H NMR (400 MHz, Chloroform-d) δ 11.20 (s, 1H), 8.92 – 8.61 (m, 4H), 8.01 (s, 1H), 7.79 – 7.55 (m, 4H), 7.42 (ddd, J = 8.6, 7.3, 1.8 Hz, 1H), 7.24 – 7.16 (m, 1H), 7.10 (d, J = 8.3 Hz, 1H), 4.16 (s, 3H).

FT-IR (KBr) δ (cm^{-1}) = 3430 (br, w), 3052 (m), 2939 (m), 2840 (m), 1614 (m), 1588 (m), 1472 (w), 1236 (w), 1024 (m), 756 (w), 743 (w).

MS (EI): *m/z* = 324 (100) M^+, 306 (74), 294 (29), 281 (22), 219 (15), 190 (18).

2-(2-hydroxyphenyl)-1H-phenanthro[9,10-d]imidazole (3b=HPPI)[5]

A mixture of ethanol and dichloromethane (1:1, 4.2 mL) was added to phenantrene-9,10-dione (1.4 mmol, 300 mg) and ammonium acetate (10.8 mmol, 833 mg) was initially refluxed for ten minutes in a mixture of dichloromethane and ethanol (1:1) (4 mL). Then 2-hydroxybenzaldehyde (**2b**) (1.6 mmol, 169 μL) was added and three drops of acetic acid as catalyst. The reaction mixture was refluxed for another three hours. The reaction was monitored by TLC using chloroform as eluent. The cold mixture was collected by filtration and dried by suction. The solid obtained was recrystallized from ethanol and dried in vacuum to give a light brown solid (35%; m.p. 260ºC, Lit. 260º,[3] 158ºC[3]).

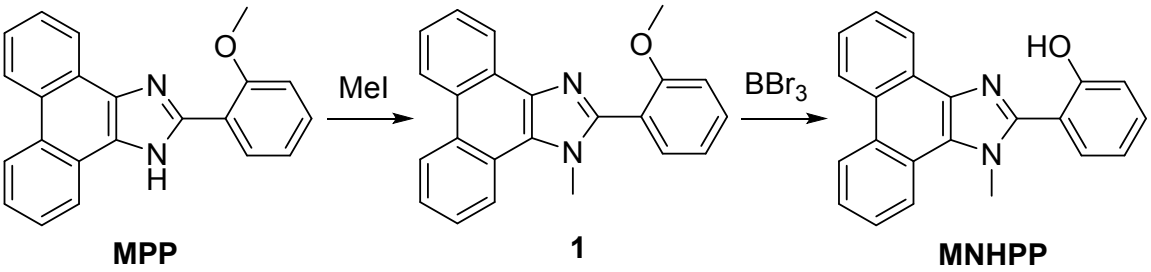
^{1}H-NMR (300 MHz, DMSO-d_6) δ 13.70 (s, 1H), 13.15 (s, 1H), 8.88 (d, J = 8.3 Hz, 2H), 8.66 – 8.42 (m, 2H), 8.24 (dd, J = 8.1, 1.6 Hz, 1H), 7.77 (t, J = 7.5 Hz, 2H), 7.67 (t, J = 7.7 Hz, 2H), 7.39 (td, J = 7.4, 1.6 Hz, 1H), 7.12 – 7.04 (m, 2H).

^{1}H NMR (400 MHz, Chloroform-d) δ 8.74 (d, J = 8.2 Hz, 2H), 8.35 (s, 2H), 7.78 – 7.61 (m, 7H), 7.38 (t, J = 7.8 Hz, 1H), 7.18 (d, J = 8.3 Hz, 1H), 7.01 (t, J = 7.6 Hz, 1H).

FT-IR (KBr) δ (cm^{-1}) = 3369 (br, m), 3052 (m), 1615 (m), 1592 (m), 1485 (w), 756 (w), 746 (w).

MS (EI): *m/z* = 310 (100) M^+, 281 (14).

To OH/OD exchange, a solution of HPPI (30 mg) in 2 mL of a mixture of DMSO-d_6-D_2O (10:1) was stirred at 40^{0}C for 5 minutes for a total OH/OD exchange. Then, 3 mL of D_2O was added to precipitate the deuterated compound, the solid was filtered under vacuum, washed with 1 mL of D_2O, and finally, dried under reduced pressure (50ºC/0.01 mmHg-12h). To confirm that HPPI is deuterated (DPPI), we recorded the FT-IR spectrum (Figure S13D), which does not display the O-H vibration band at 3360 cm^{-1}. In addition to that, the ^{1}H-NMR spectrum of the deuterated sample in DMSO-d_6 does not exhibit the peaks at 13.7 (O-H) and 13.15 (N-H) ppm observed in HPPI/ DMSO-d_6 (Figure S11A), confirming the efficiency of the OH/OD exchange process (Figure S11D).



Scheme S2. Steps of synthesis of NMHPPI.

2-(2-methoxyphenyl)-N-methyl-1H-phenanthro[9,10-d]imidazole **(1)**

2-(2-methoxyphenyl)-1H-phenanthro[9,10-d]imidazole (3.09 mmol, 1.0 g) was dissolved in dry THF (40 mL) and cooled to 0 ºC. HNa (3.40 mmol, 136 mg, 60 %

dispersion in mineral oil) was added during ten minutes under same conditions. Then, MeI (3.40 mmol, 483 mg, 212 µL) was added dropwise and after addition the reaction mixture was stirred to room temperature. The reaction was monitored by TLC using heptane/ethyl acetate (2:1). The solvent was removed by rotary evaporation and water was added. The aqueous layer was extracted with EtOAc and the organic layer washed with water, a saturated solution of NaCl and dried over Na_2SO_4. After removing the solvent by rotary evaporation to give compound **1** as a yellow solid (86% m.p.: 230ºC).

^{1}H NMR (400 MHz, Chloroform-d) δ 8.87 – 8.76 (m, 2H), 8.70 (d, J = 7.3 Hz, 1H), 8.49 (d, J = 7.3 Hz, 1H), 7.74 – 7.58 (m, 5H), 7.53 (d, J = 7.3 Hz, 1H), 7.16 (d, J = 7.3 Hz, 1H), 7.06 (d, J = 8.5 Hz, 1H), 4.10 (s, 3H), 3.85 (s, 3H).

FT-IR (KBr) δ (cm^{-1}) = 2955 (m), 2923 (m), 2853 (m), 1472 (m), 1252 (m), 1241 (m), 1021 (m), 750 (m), 721 (m).

MS (EI): *m/z* = 328 (100) M^+, 307 (57), 233 (47).

2-(2-hydroxyphenyl)-N-methyl-1H-phenanthro[9,10-d]imidazole **(NMHPPI)**

2-(2-methoxyphenyl)-1-methyl-1*H*-phenantrene[9,10-d]imidazole **(1)** (1.5 mmol, 500 mg) was dissolved in dry dichloromethane (25 mL) and cooled to -78 ºC. A solution of 1M boron tribromide in dichloromethane (6.7 mmol, 6.7 mL) was added dropwise. The reaction was monitored by TLC using heptane/ethyl acetate (2:1). After five hours at -78 ºC, 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 EtOAc and the organic layer washed with water, a saturated solution of NaCl and dried over Na_2SO_4. After removing the solvent by rotary evaporation to give compound **NMHPPI** as a slightly yellow solid (76%; m.p.: 216ºC).

^{1}H NMR (300 MHz, DMSO-d_6) δ 10.42 (s, 1H), 8.95 (dd, J = 8.2, 1.4 Hz, 1H), 8.84 (d, J = 8.2 Hz, 1H), 8.65 – 8.54 (m, 2H), 7.81 – 7.56 (m, 5H), 7.43 (td, J = 8.6, 1.6 Hz, 1H), 7.10 (d, J = 8.2 Hz, 1H), 7.04 (t, J = 7.7 Hz, 1H), 4.18 (s, 3H).

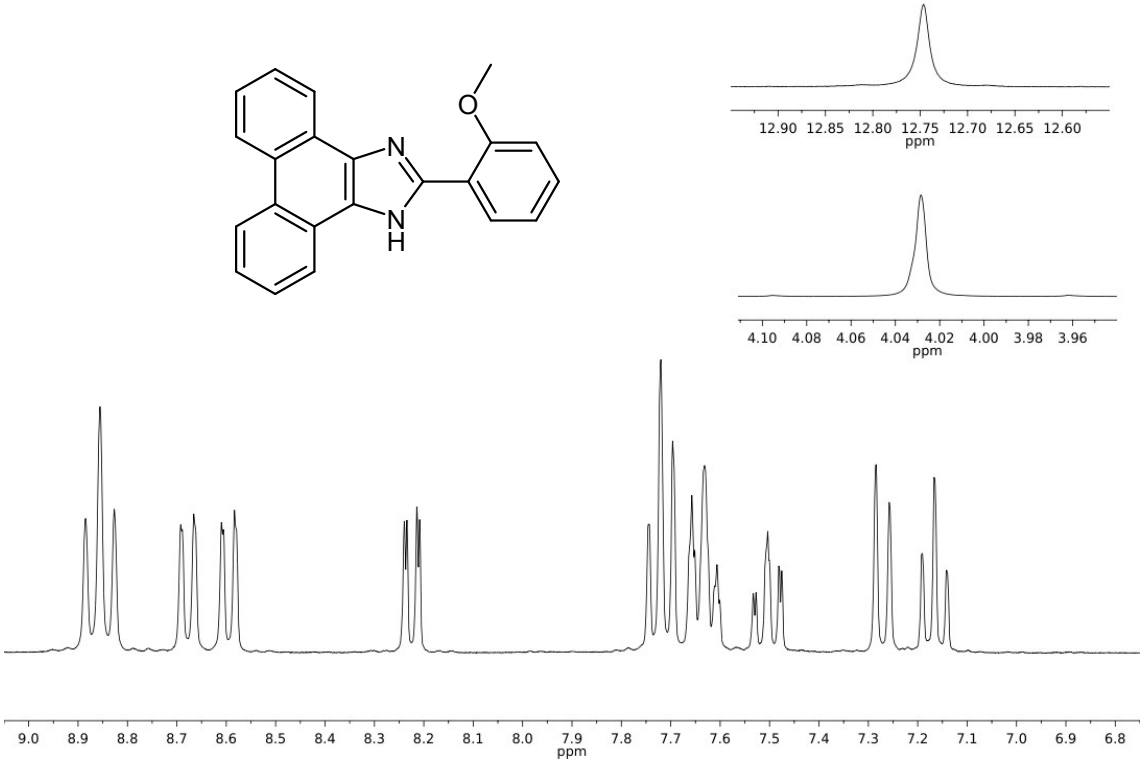
^{1}H NMR (400 MHz, Chloroform-d) δ 12.39 (s, 1H), 8.80 – 8.71 (m, 1H), 8.68 – 8.57 (m, 2H), 8.38 – 8.28 (m, 1H), 7.71 (t, J = 7.5 Hz, 1H), 7.63 (dh, J = 5.9, 3.3 Hz, 4H), 7.44 – 7.32 (m, 1H), 7.19 (d, J = 8.2 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 4.37 (s, 3H).

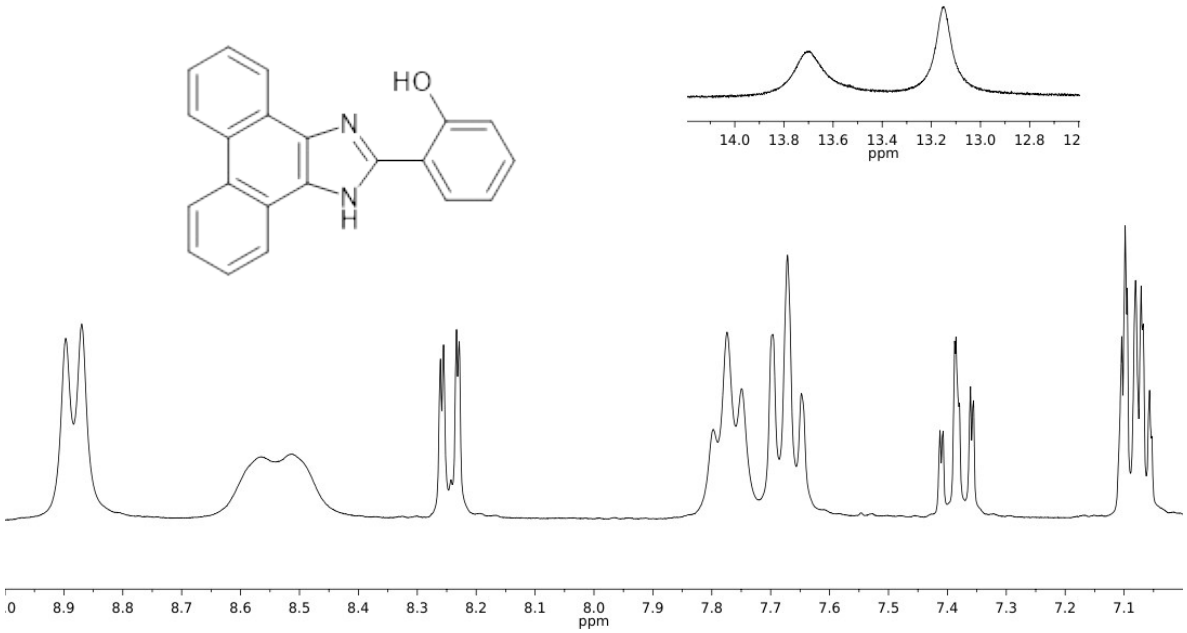
FT-IR (KBr) δ (cm^{-1}) = 3430 (br, m), 2924 (m), 2853 (m), 1252 (m), 1256 (m), 751 (m), 722 (m).

MS (EI): *m/z* = 328 (98) M^+, 323 (100), 307 (32).

Table S4 gives the values of the chemical shift of the protons in the phenyl part of the studied compounds.

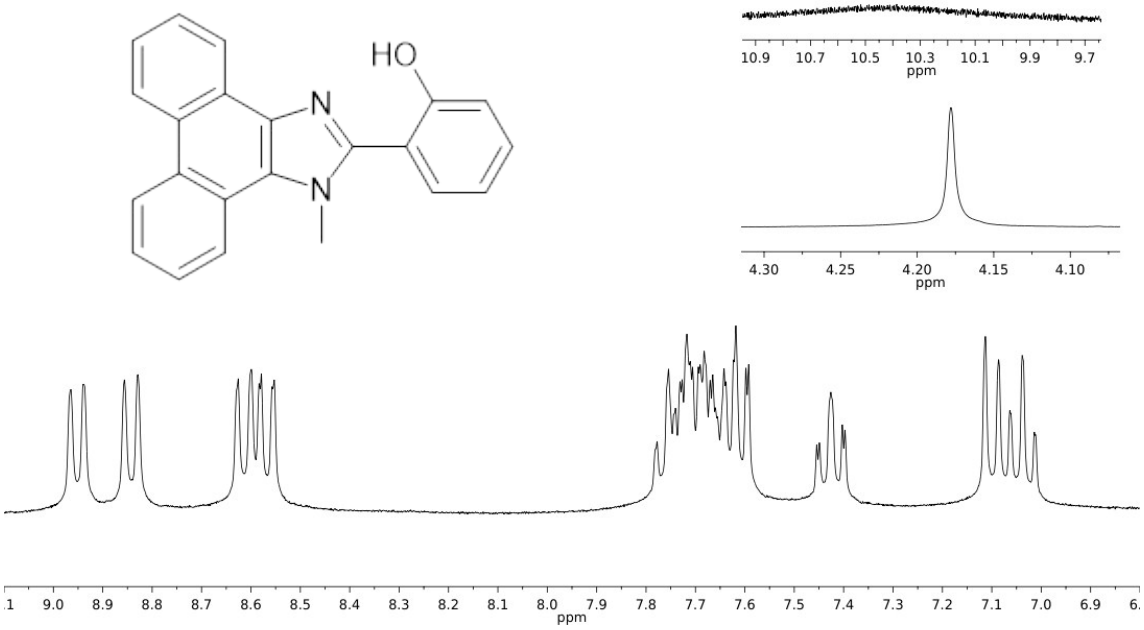
A)




HO
N
N
H
14.0 13.8 13.6 13.4 13.2 13.0 12.8 12
ppm
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
ppm

B)

C)


HO
N
N
10.9 10.7 10.5 10.3 10.1 9.9 9.7
ppm
4.30 4.25 4.20 4.15 4.10
ppm
9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
ppm

D)

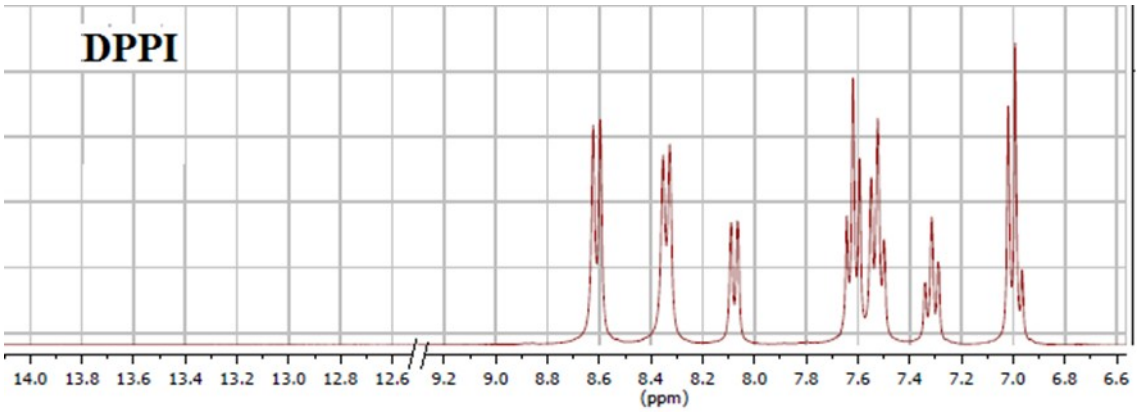
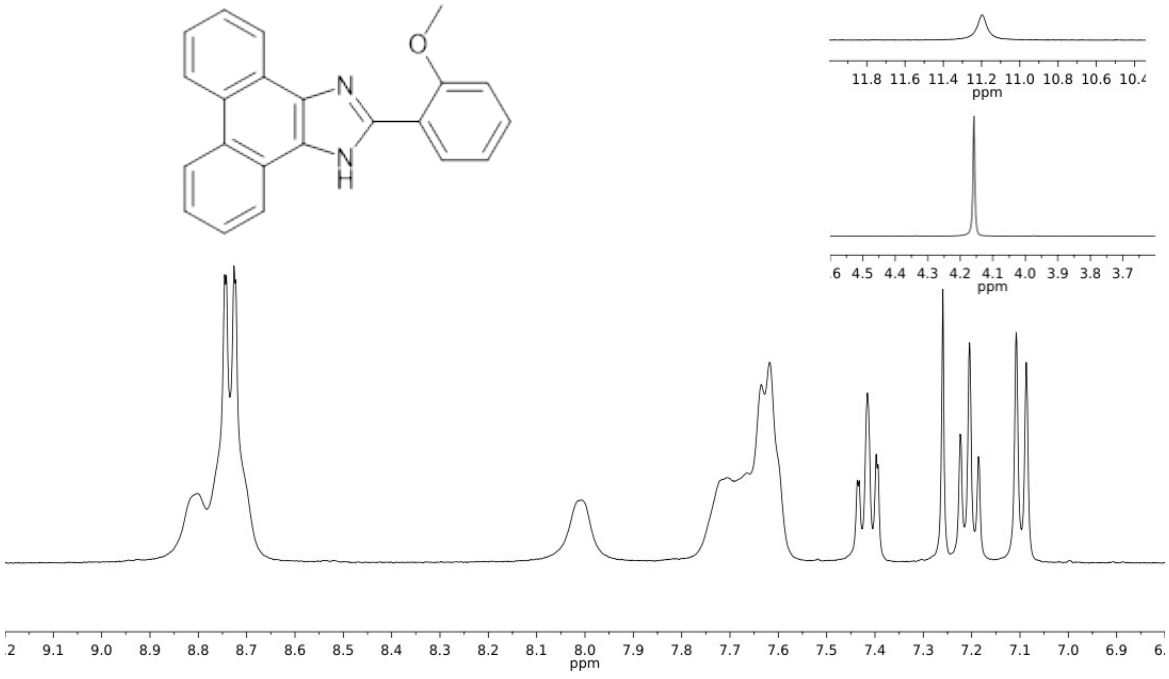
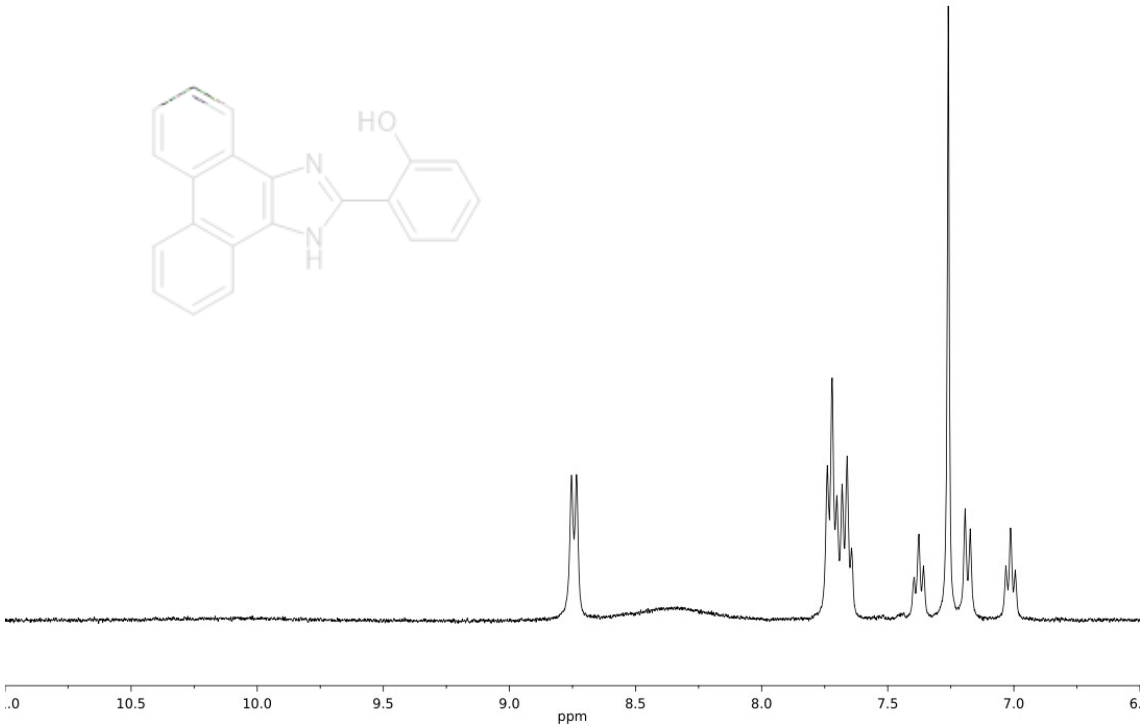


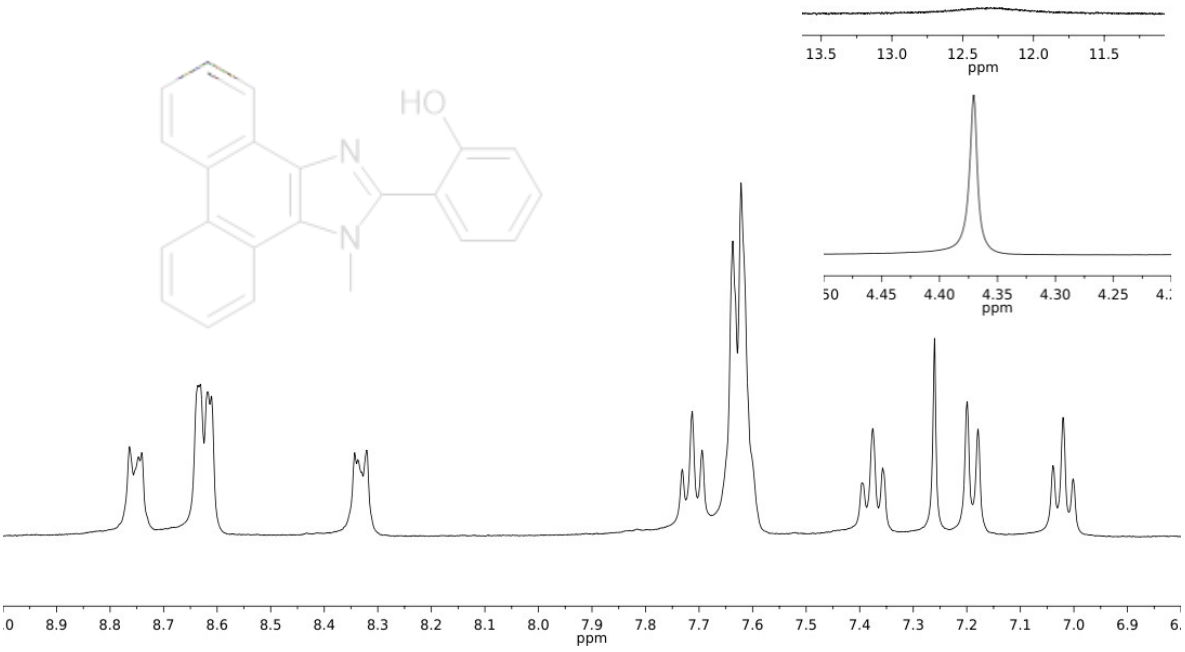
Figure S11. ^{1}H NMR spectra of A) MPPI, B) HPPI and C) NMHPPI and D) DPPI in DMSO-d_6. Note that the absence of the O-H and N-H signal, compared with B), confirm that the molecule is deuterated.



A)


HO
N
N
H
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
ppm

B)


HO
N
N
13.5
13.0
12.5
12.0
11.5
ppm
4.45
4.40
4.35
4.30
4.25
ppm
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
ppm

C)

Figure S12. [1]H NMR spectra of A) MPPI, B) HPPI and C) NMHPPI in Chloroform-d.

HPPI	H3	H4	H5	H6	NH	OH
DMSO	7.07	7.10	7.38	**7.77**	13.15	13.71
CDCl3	7.01	7.18	7.38	**7.73**	8.34	10.11
MPPI	**H3**	**H4**	**H5**	**H6**	**NH**	**OH**
DMSO	7.17	7.28	7.50	**8.25**	12.58	-
CDCl3	7.10	7.20	7.42	**8.01**	11.20	-
NMHPPI	**H3**	**H4**	**H5**	**H6**	**NH**	**OH**
DMSO	7.04	7.10	7.43	**7.59**	-	10.42
CDCl3	7.02	7.19	7.38	**7.63**	-	12.29

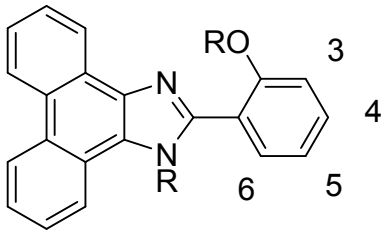
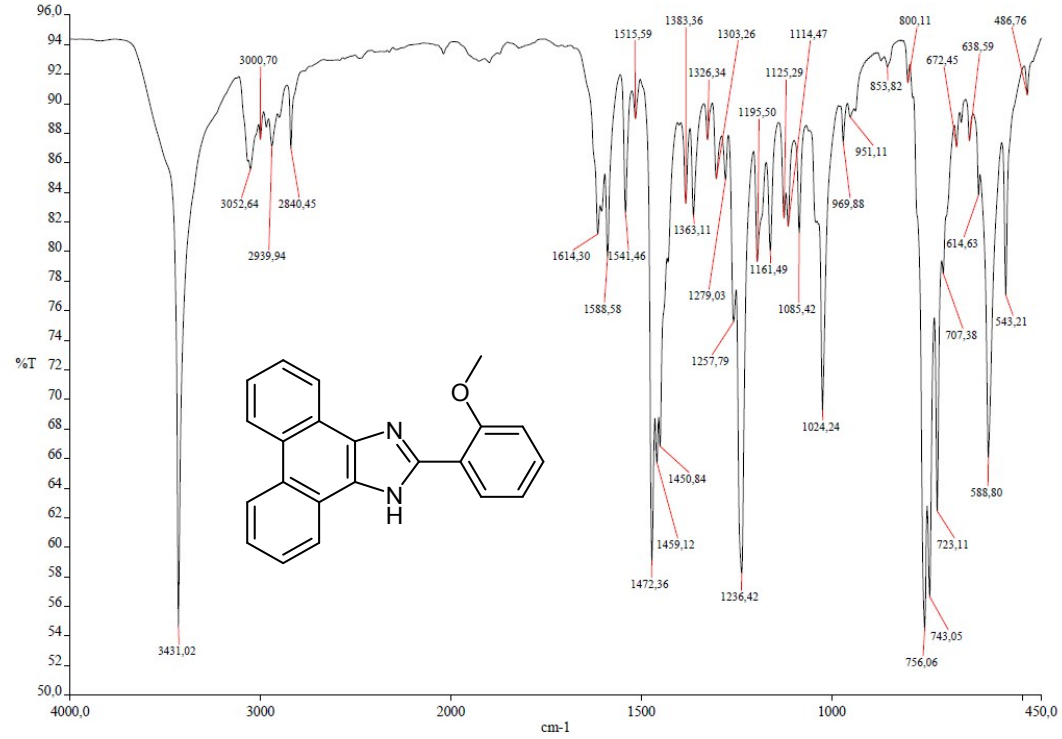
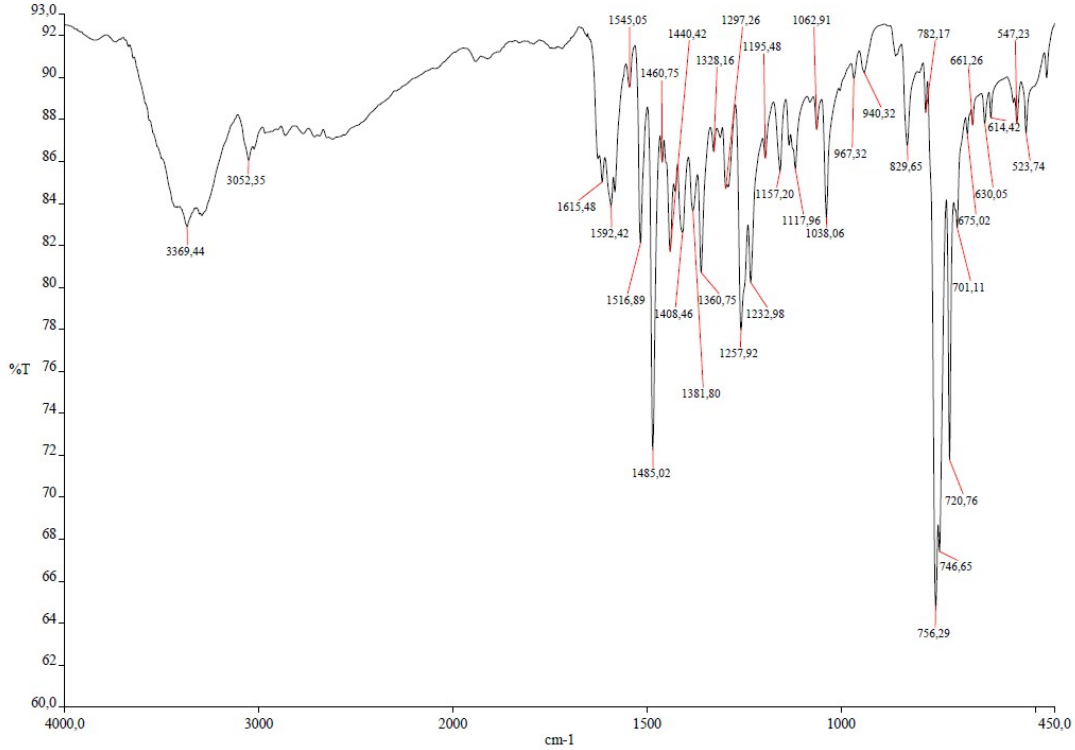


Table S4. Chemical shifts of aromatic protons of 2-phenyl compounds (R= H or Me).

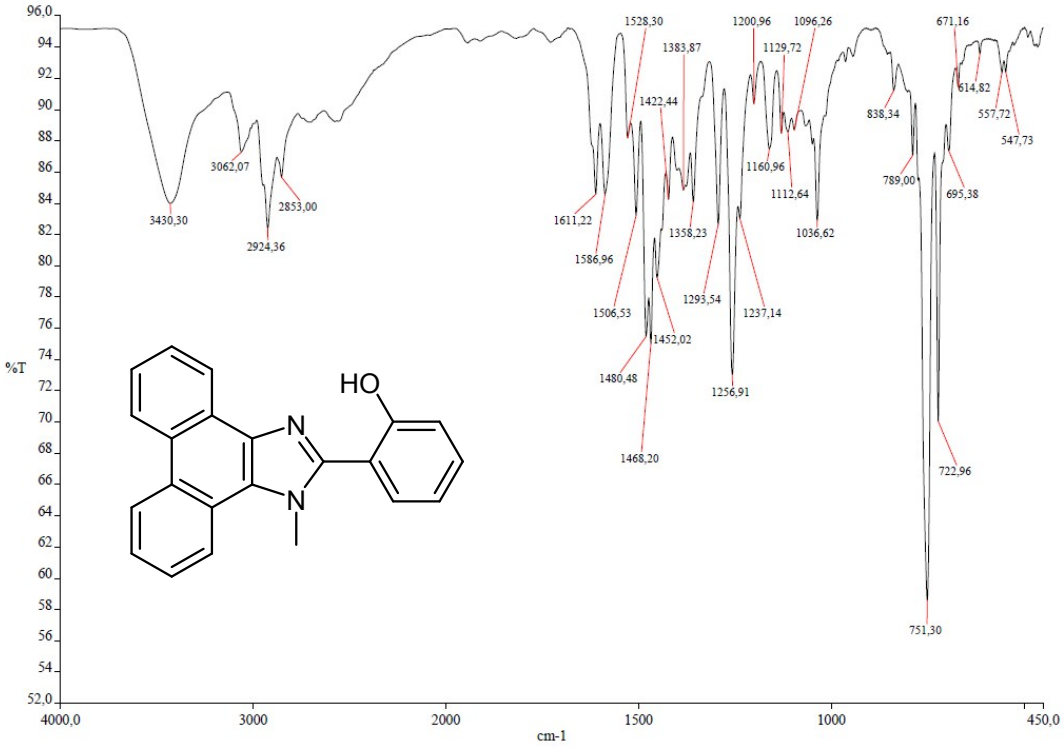
A)


%T
cm-1
3431,02
3052,64
3000,70
2939,94
2840,45
1614,30
1588,58
1541,46
1515,59
1472,36
1459,12
1450,84
1383,36
1363,11
1326,34
1303,26
1279,03
1257,79
1236,42
1195,50
1161,49
1125,29
1114,47
1085,42
1024,24
969,88
951,11
853,82
800,11
756,06
743,05
723,11
707,38
672,45
638,59
614,63
588,80
543,21
486,76
O
N
H


%T
cm-1
3369,44
3052,35
1615,48
1592,42
1545,05
1516,89
1485,02
1460,75
1440,42
1408,46
1381,80
1360,75
1328,16
1297,26
1257,92
1232,98
1195,48
1157,20
1117,96
1062,91
1038,06
967,32
940,32
829,65
782,17
756,29
746,65
720,76
701,11
675,02
661,26
630,05
614,42
547,23
523,74

B)

C)



D)

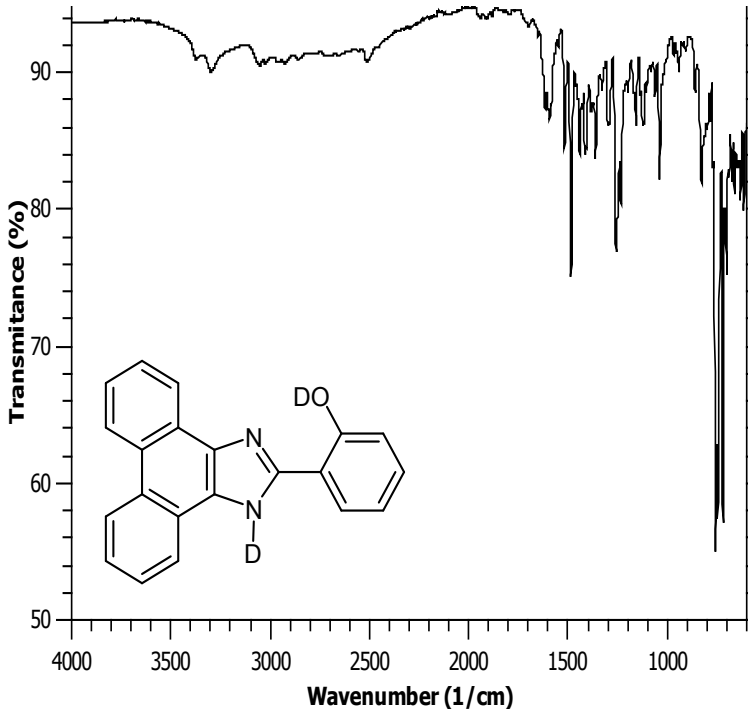


Figure S13. FTIR-spectra of A) MPPI, B) HPPI, C) NMHPPI and D) DPPI in potassium bromide (KBr).

References

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4. E. A. Steck and A. R. Day, *Journal of the American Chemical Society*, 1943, **65**, 452-456.
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