Acid- and *hydrogen*-bonding-induced switching between 22-π and 18-π electron conjugation in 2-aminothiazolo[4,5c]porphycenes

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1. Further instrumentation and materials

1.1 Techniques for the characterization and identification of compounds

^{1}H and ^{13}C-NMR spectra were recorded on a Varian 400-MR spectrometer working at 400 MHz for ^{1}H or 100.6 MHz for ^{13}C. All NMR data were obtained in $CDCl_3$. Chemical shifts are reported in parts per million (ppm, δ) and are referenced to the residual signal of the solvent. Coupling constants are reported in Hertz (Hz). Spectral splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (complex multiplet).

HPLC-MS analysis was carried out in an Agilent 1260 infinity Series chromatograph equipped with photodiode array detector (200–600 nm) and coupled to an Agilent 6130 quadrupole LC/MS. Separation was achieved using a Discovery® C18 (15m x 4.6 mm, 5µm particle size) column and an ACN:MeOH 85:15 mixture at 1.0 mL/min flow rate. The DAD detector was set at 400 nm matching the Soret band of porphycenes. API-ES positive ionization mode at 80V cone voltage was used. Fragmentations were scanned from 500 to 2500 m/z. Peaks were identified by their characteristic MS fragmentations.

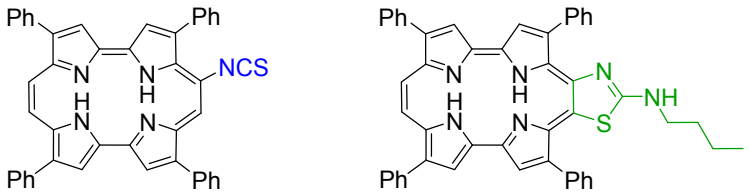
1.2 Fluorescence emission of porphycene-labelled conjugates

Fluorescence emission of porphycene-labelled tetraethylen-glycol undecyl-thiol stabilized gold nanoclusters at different pH were measured by dissolving the conjugate in citric acid/Na_2HPO_4 buffer of different concentrations. Table S1 shows the proportions of solutions of citric acid 0.1 M and Na_2HPO_4 0.2 M to prepare 100 mL of buffer at different pH.

Table S1: Amounts of citric acid 0.1 M and Na_2HPO_4 0.2 M to prepare 100 mL of buffer at different pH

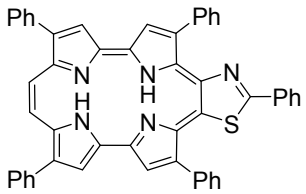
pH	Citric acid 0.1 M solution / mL	Na_2HPO_4 0.2 M solution / mL
2.6	89.10	10.90
3.0	79.45	20.55
3.6	67.80	32.20
4.0	61.45	38.55
4.6	53.25	46.75
5.0	48.50	51.50
5.6	42.00	58.00
6.0	36.85	63.15
6.6	27.25	72.75
7.0	17.65	82.35
7.6	6.35	93.65

2. Synthesis of porphycene derivatives

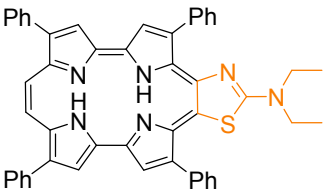


PoITC **1**

ATAZPo **2**



TAZPo **3**



ATAZPo **4**

Figure S1: Chemical structures of 9-isothiocyanate-2,7,12,17-tetraphenylporphycene, 2-(*N*-butylamino)-thiazolo[4,5-c]2,7,12,17-tetraphenylporphycene, 2-phenylthiazolo[4,5-c]2,7,12,17-tetraphenyl-porphycene and 2-(*N,N*-diethylamino)thiazolo[4,5-c]2,7,12,17-tetraphenyl-porphycene; PoITC **1**, ATAZPo **2**, TAZPo **3**, and ATAZPo **4** respectively.

2.1 Synthesis of 9-isothiocyanate-2,7,12,17-tetraphenylporphycene

9-isothiocyanate-2,7,12,17-tetraphenylporphycene (PoITC **1** in Figure S1) was prepared in agreement with previously reported synthetic procedures.[1] Briefly, 9-amino-2,7,12,17-tetraphenylporphycene (50 mg, $7.5 \cdot 10^{-2}$ mmol) was stirred with 1,1′-thiocarbonyldi-2(1H)-pyridone (53 mg, 3 eq, 0.23 mmol) in 10 mL of CH_2Cl_2 for 16 h at room temperature. The solvent was evaporated and the mixture purified by silica gel chromatography eluting with CH_2Cl_2. The product was then crystallized by dissolving it in toluene (5 mL) and pouring it in acetonitrile (50 mL), to provide a blue-greenish product (38 mg, $5.6 \cdot 10^{-2}$ mmol, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm = 9.70 – 9.61 (ABq, 2H, J_{AB} = 11.0 Hz), 9.55 (s, 1H), 9.43 (s, 1H), 9.39 (s, 2H), 9.30 (s, 1H), 8.29 – 8.19 (m, 6H), 8.08 – 8.00 (m, 2H), 7.88 – 7.59 (m, 12H), 3.77 (s, 1H), 3.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm = 145.5, 145.2, 144.8, 143.6, 143.1, 143.0, 139.9, 138.0, 137.4, 136.1, 135.8, 135.2, 134.8, 134.0, 133.5, 131.5, 131.5, 131.5, 130.9, 129.5, 129.3, 129.3, 128.7, 128.4, 128.2, 127.9, 127.3, 124.1, 124.1, 118.3, 115.6, 115.2, 114.8. MS (API-ES) Calculated for $C_{45}H_{30}N_5S$ [$(M+H)^+$]: 672.22. Found: *m/z*=672.2. Retention time: 21.49 min.

2.2 Synthesis of 2-(*N*-butylamino)thiazolo[4,5-c]2,7,12,17-tetraphenylporphycene

2-(*N*-butylamino)thiazolo[4,5-c]2,7,12,17-tetraphenylporphycene (ATAZPo **2** in Figure S1) was prepared in agreement with previously reported synthetic procedures.[1] Briefly, PoITC **1** (10 mg, $1.5 \cdot 10^{-2}$ mmol) was stirred with *n*-butylamine (50 μL, 0.6 mmol, 40 eq) in 2 mL of CH_2Cl_2 for 5 h at room temperature. Acidic water was added to the mixture and the product was extracted with CH_2Cl_2. The organic layers were washed three times with brine and then dried with anhydrous Na_2SO_4. The solvent was evaporated and the remaining crude was further purified by silica gel

chromatography eluting with *n*-hexane:toluene 1:1 to provide a green product (10 mg, $1.3 \cdot 10^{-2}$ mmol, 90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm = 9.63 (d, *J* = 11.0 Hz, 1H), 9.54 (d, *J* = 11.0 Hz, 1H), 9.43 (s, 2H), 9.41 (s, 1H), 9.38 (s, 1H), 8.27 (m, 4H), 8.08 (m, 2H), 7.97 – 7.92 (m, 2H), 7.81 – 7.69 (m, 7H), 7.67 – 7.60 (m, 4H), 7.51 (m, 1H), 5.92 (s, 1H), 5.31 (s, 1H), 5.11 (s, 1H), 3.23 (m, 2H), 1.42 – 1.32 (m, 4H), 0.95 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm = 164.1, 145.0, 144.1, 143.9, 143.4, 142.8, 142.7, 142.6, 140.7, 139.6, 137.8, 136.8, 136.6, 136.5, 135.7, 134.4, 133.9, 131.4, 131.4, 131.1, 130.9, 129.3, 129.1, 129.0, 128.7, 128.0, 127.94, 127.8, 127.8, 126.6, 125.6, 123.6, 123.5, 123.2, 115.7, 112.8, 77.5, 77.2 76.8, 44.5, 31.9, 20.1, 14.0. MS (API-ES) Calculated for $C_{49}H_{38}N_6S$ [$(M+H)^+$]: 743.29. Found: *m/z*=743.2. Retention time: 14.50 min.

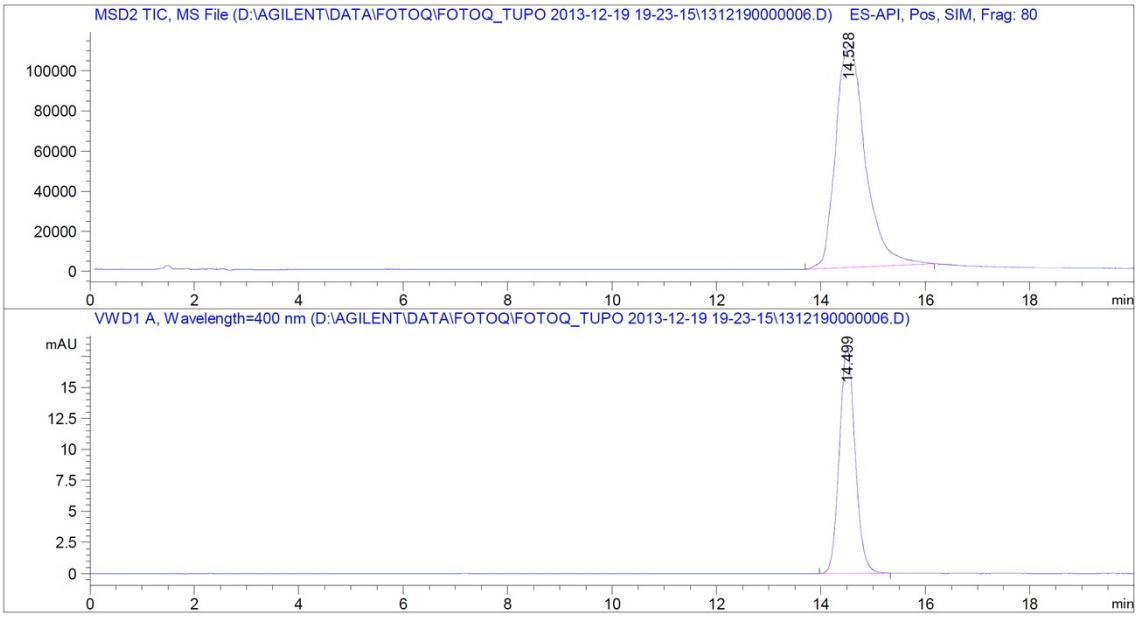


Figure S2: Chromatogram of ATAZPo **2** using mass scan mode (top) and UV/Vis detection at 400 nm (bottom).

2.3 Synthesis of 2-phenylthiazolo[4,5-c]2,7,12,17-tetraphenylporphycene

2-phenylthiazolo[4,5-c]2,7,12,17-tetraphenylporphycene (TAZPo **3** in Figure S1) was prepared in agreement with previously reported synthetic procedures.[1] Briefly, to a solution of 9-benzamido-2,7,12,17-tetraphenylporphycene (3 mg, $4.0 \cdot 10^{-3}$ mmol) in 0.4 mL of toluene were added 4 mg of the Lawesson's reagent ($1.0 \cdot 10^{-2}$ mmol, 2.5 eq). The mixture was stirred and heated at 120 ºC using microwaves for 1.5 h. Then, the solvent was reduced under reduced pressure and the crude was purified by thin layer silica chromatography eluting with toluene to provide a blue-greenish product (2.5 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 2H), 9.43 (d, J = 1.0 Hz, 1H), 9.38 (s, 1H), 9.36 (d, J = 1.0 Hz, 1H), 9.35 (s, 1H), 8.21 – 8.17 (m, 4H), 8.09 – 8.04 (m, 2H), 7.94 (m, 3H), 7.76 – 7.69 (m, 8H), 7.68 – 7.64 (m, 4H), 7.62 – 7.57 (m, 4H), 5.99 (s, 1H), 5.32 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) 174.3, 144.8, 144.7, 142.6, 141.8, 140.5, 139.0, 137.4, 137.4, 136.9, 136.1, 136.0, 133.8, 132.1, 131.2, 131.1, 130.5, 129.5, 129.0, 128.8, 128.1, 127.9, 127.7, 127.1,

126.5, 126.2, 124.3, 123.8, 115.4, 114.7, 114.7. MS (API-ES) Calculated for $C_{51}H_{34}N_5S$ [(M+H)$^+$]: 748.9, $C_{102}H_{67}N_{10}S_2$ [(2M+H)$^+$]: 1496.8, Found: *m*/*z*=748.2, 1496.4. Retention time: 3.37 min.

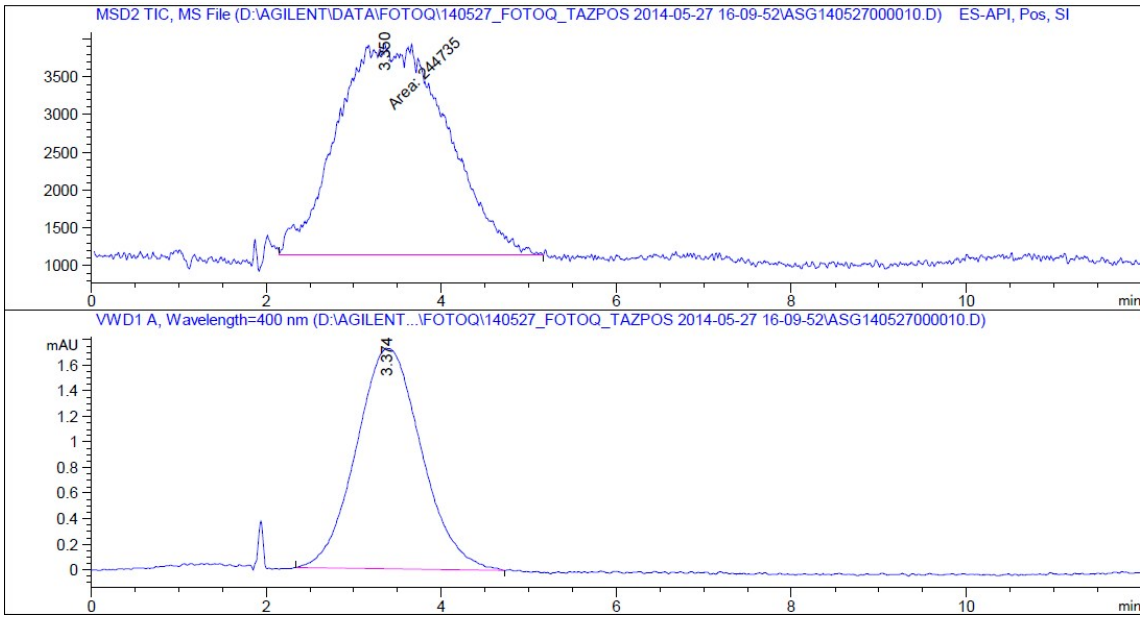


Figure S3: Chromatogram of TAZPo **3** using mass scan mode (top) and UV/Vis detection at 400 nm (bottom).

2.4 Synthesis of 2-(*N,N*-diethylamino)thiazolo[4,5-c]2,7,12,17-tetraphenylporphycene

2-(*N,N*-diethylamino)thiazolo[4,5-c]2,7,12,17-tetraphenylporphycene (ATAZPo **4** in Figure S1) was prepared in agreement with previously reported synthetic procedures.[1] Briefly, PoITC **1** (3 mg, $4{,}6\cdot10^{-3}$ mmol) was stirred with diethylamine (4 µg, 0.04 mmol, 10 eq) in 2 mL of CH_2Cl_2 for 5 h at room temperature. Acidic water was added to the mixture and the product was extracted with CH_2Cl_2. The organic layers were washed three times with brine and then dried with anhydrous Na_2SO_4. The solvent was evaporated and the remaining crude was further purified by silica gel chromatography eluting with *n*-hexane:toluene in gradient mode, starting from a 3:1 ratio to 0:1 to provide a green product (3 mg, $3{,}9\cdot10^{-3}$ mmol, 90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm = 9.61 (d, *J* = 11.0 Hz, 1H), 9.49 (d, *J* = 11.0 Hz, 1H), 9.41 (d, *J* = 1.0 Hz, 1H), 9.39 (s, 1H), 9.37-9.36 (s, 2H), 8.28-8.24 (m, 4H), 8.04-8.02 (m, 2H), 7.98 – 7.92 (m, 2H), 7.81 – 7.59 (m, 12H), 7.56 – 7.48 (m, 2H), 6.09 (s, 1H), 5.49 (s, 1H), 3.36 (q, *J* = 7.0 Hz, 4H), 1.13 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm = 165.0, 145.1, 144.6, 143.6, 143.6, 143.0, 142.9, 140.9, 140.9, 137.6, 136.8, 136.5, 136.2, 135.0, 134.3, 134.0, 131.3, 131.2, 130.8, 130.5, 129.0, 128.9, 128.8, 128.5, 127.9, 127.7, 127.7, 127.5, 126.2, 125.1, 123.4, 115.8, 112.1, 52.8, 29.7. MS (API-ES) Calculated for $C_{49}H_{38}N_6S$ [(M+H)$^+$]: 743,29. Found: *m/z*=743.2. Retention time: 20.03 min.

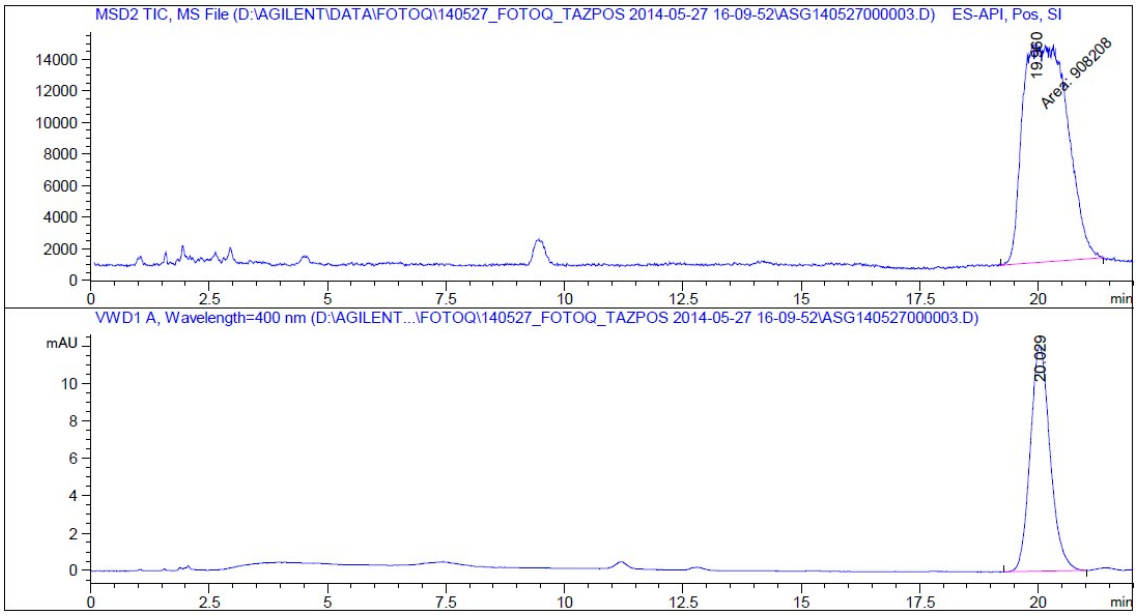


Figure S4: Chromatogram of ATAZPo **4** using mass scan mode (top) and UV/Vis detection at 400 nm (bottom).

3. Additional experiments

3.1 HFIP effects on the absorption and fluorescence emission spectra of ATAZPo 2

ATAZPo **2** (1.34 μM) was dissolved in 1 mL of methanol and the absorption and fluorescence spectra were collected after the addition of increasing amounts of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) 5.9 M. Dilution-corrected absorption and fluorescence emission spectra of the titration experiments are presented below (Figure S5).

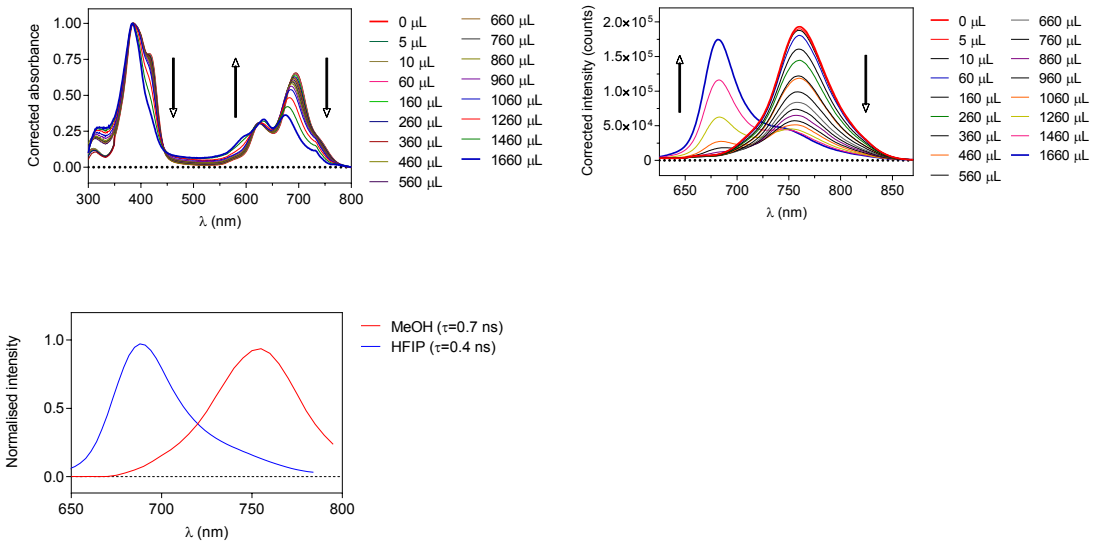


Figure S5: Dilution-corrected absorption (top-left) and normalized fluorescence emission spectra (top-right) of ATAZPo **2** in MeOH with increasing volumes of HFIP 5.9 M. Bottom: time-resolved fluorescence emission spectra of ATAZPo **2** in MeOH (red line) and in HFIP (blue).

3.2 Excitation spectra of ATAZPo 2 in different solvents

Excitation spectra of ATAZPo **2** were measured in MeOH, HFIP and TFE by observing at 675 and 790 nm. Results are presented in figure S6.

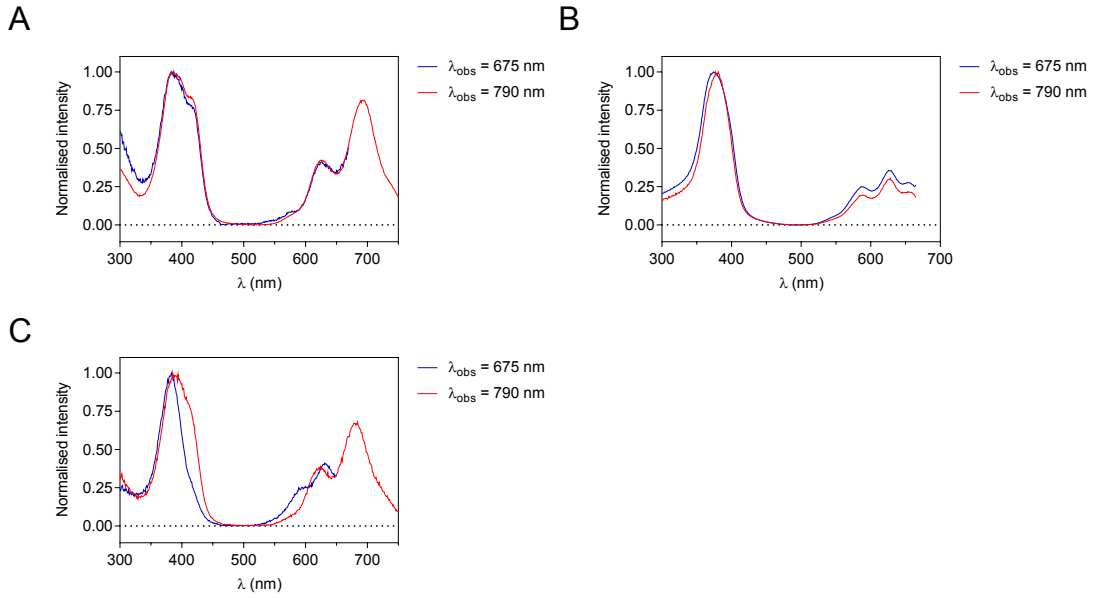


Figure S6: Excitation spectra of ATAZPo **2** in MeOH (A), HFIP (B) and TFE (C) by observing at 675 (blue line) and 790 nm (red line).

3.3 Linear solvation energy relationships

Fitting values of the linear solvation energy relationships with the Kamlet-Taft and Catalan parameters are presented in Table S2. Fittings of Eq.1 and Eq.2 are presented in Figure S7.

Table S2. Fitting values for the dependence of λ_{Max}^{Abs} (expressed in cm^{-1}) of ATAZPo **2** on the Kamlet-Taft and Catalan solvent parameters.

$\bar{\nu}_A = \bar{\nu}_0 + a\pi^* + d\delta + b\alpha + c\beta$				
	$\bar{\nu}_0$	*a*	*b*	c
Coeff.	14574.9	-123.1	27.4	-327.6
±	24.9	33.6	18.4	27.9
t-stat	585.5	-3.7	1.5	-11.7
P(2-tail)	<0.0001	<0.0023	0.159	<0.0001
N = 19		R = 0.96	F = 55.7	
$\bar{\nu}_A = \bar{\nu}_0 + aSPP + bSA + cSB$				
	$\bar{\nu}_0$	*a*	*b*	*c*
Coeff.	14839.6	-439.8	99.1	-301.1
±	81	107.3	38.3	42.1
t-stat	183.3	-4.1	2.6	-7.2
P(2-tail)	<0.0001	0.0009	0.021	<0.0001
N= 19		R= 0.94	F= 36.6	

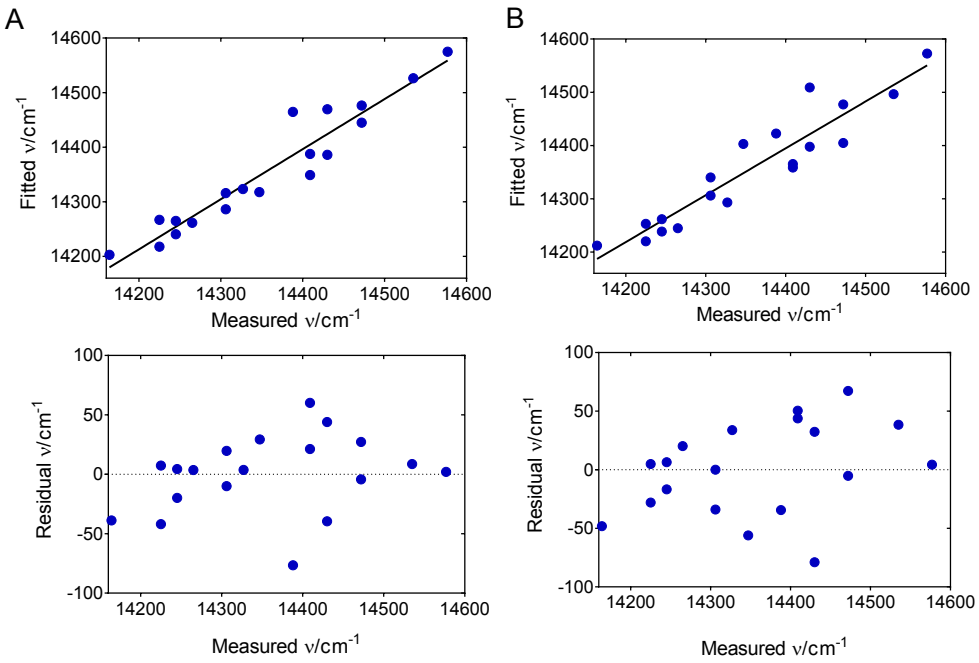


Figure S7: Top: plot of $\bar{\nu}_A$ (exp) vs. $\bar{\nu}_A$ (calc) for the absorption maxima of ATAZPo **2** in several solvents. Calculated $\bar{\nu}_A$ values according to equations $\bar{\nu}_A$ = 14574.9 – 123.1 π* + 27.4 α – 327.6 β (A) and $\bar{\nu}_A$ = 14839.6 – 439.8 SPP + 99.1 SA – 301.1 SB (B). Bottom: Plot of the residuals of $\bar{\nu}_A$ vs. $\bar{\nu}_A$ (exp)

3.4 Acid effect on the absorption and fluorescence emission spectra of ATAZPo 2

ATAZPo **2** (1.34 μM) was dissolved in 1 mL of methanol and the absorption and fluorescence spectra were collected after the addition of increasing amounts of mineral and organic acids. Dilution-corrected absorption and fluorescence emission spectra of the titration experiments are presented below for all acids tested (Figures S8-S9).

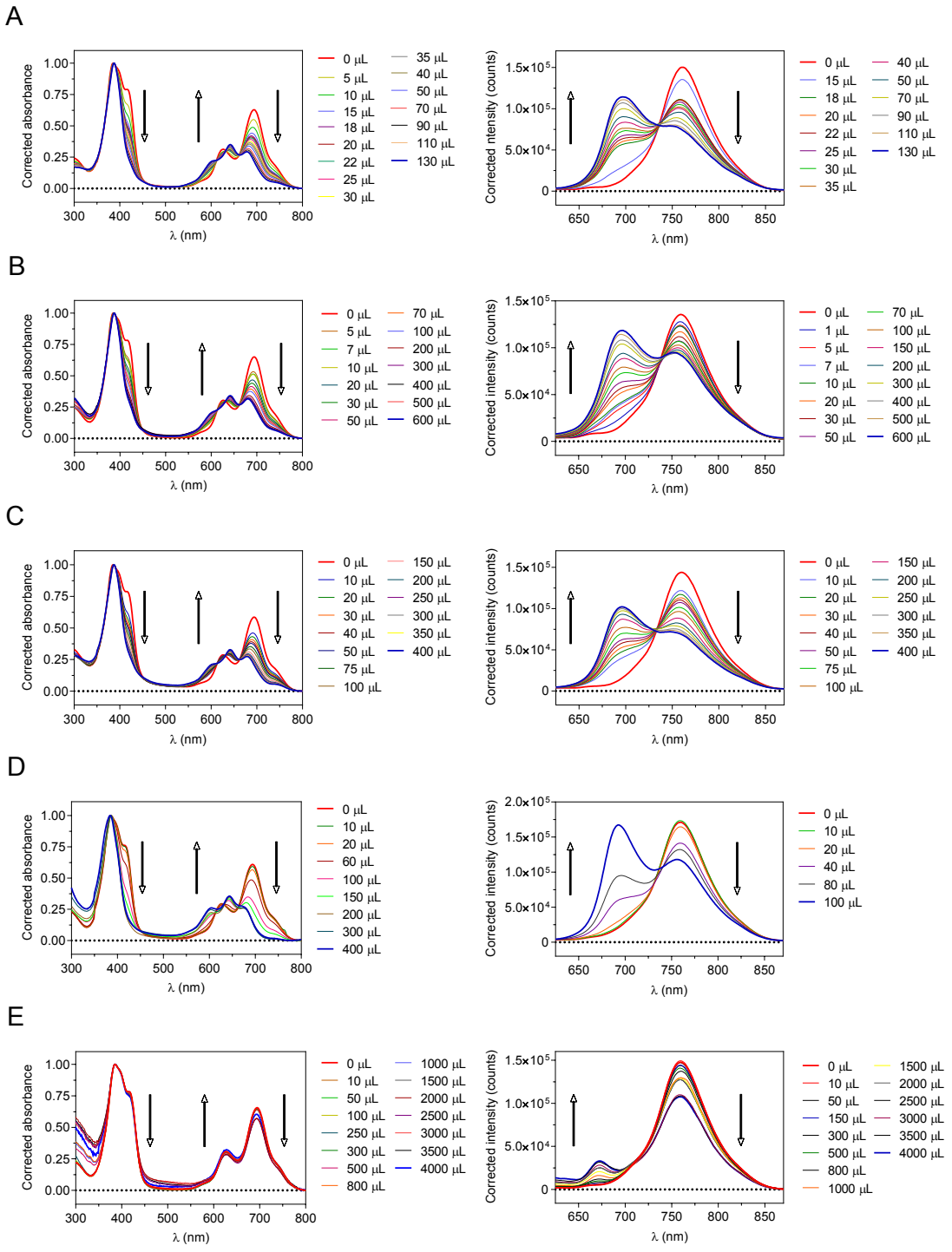


Figure S8: Dilution-corrected absorption (left) and normalized fluorescence emission spectra (right) of ATAZPo **2** in MeOH with increasing volumes of (A) HCl 0.05 M, (B) HNO_3 0.103 M, (C) H_2SO_4 0.01 M , (D) H_3PO_4 8.67 M and (E) H_3BO_3 3.23 M.

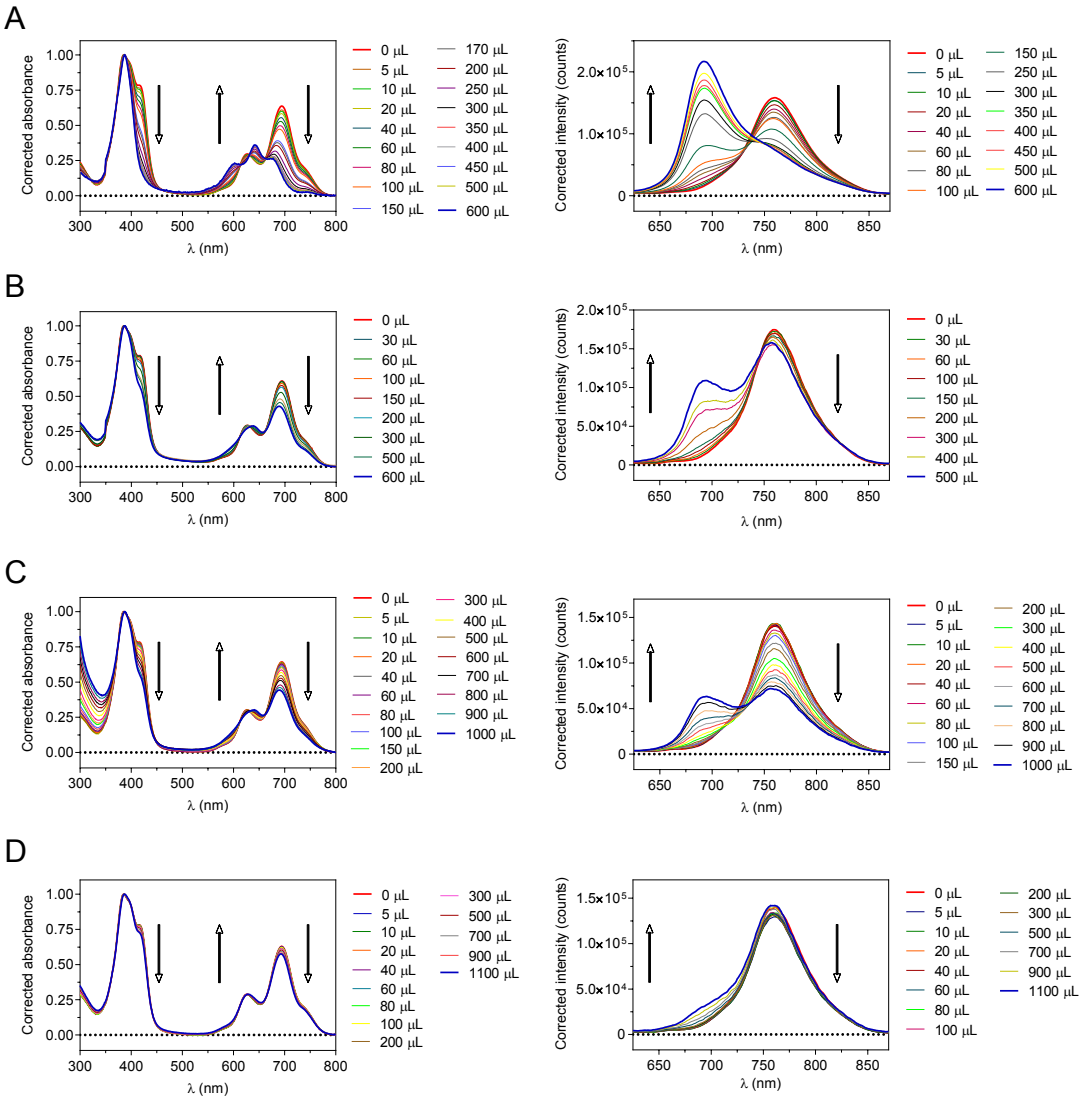


Figure S9: Dilution-corrected absorption (left) and normalized fluorescence emission spectra (right) of ATAZPo **2** in MeOH with increasing volumes of (A) formic acid 22.5 M, (B) acetic acid 16.6 M, (C) propionic acid 9.4 M and (D) lactic acid 13.4 M.

3.5 HFIP and acid effects on the absorption and fluorescence emission spectra of 2,7,12,17-tetraphenylporphycene

2,7,12,17-tetraphenylporphycene (TPPo) was dissolved in 1 mL of MeOH and the absorption and fluorescence spectra were collected after the addition of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) 5.9 M and HCl 0.05 M (Figure S10).

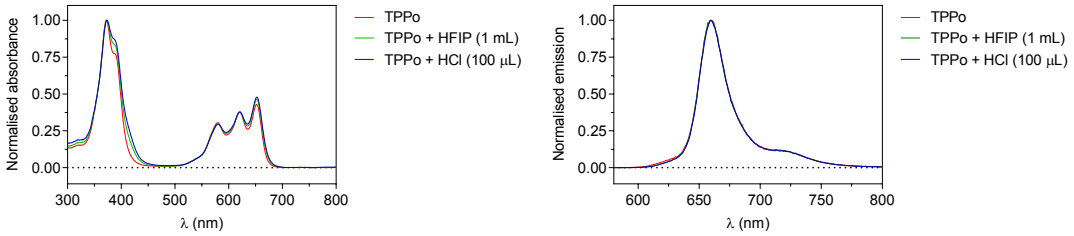


Figure S10: Dilution-corrected absorption (left) and normalized fluorescence emission spectra (right) of TPPo in MeOH (red line) and in MeOH-HFIP (green) and MeOH-HCl (blue) mixtures. The stock concentrations of HFIP and HCl were 5.9 M and 0.05 M respectively.

3.6 HFIP and acid effects on the absorption spectra of 9-amino-2,7,12,17-tetrakis(2-methoxyethyl)porphycene

Absorption spectra of 9-amino-2,7,12,17-tetrakis(2-methoxyethyl)porphycene in THF and HFIP is shown in Figure S11.

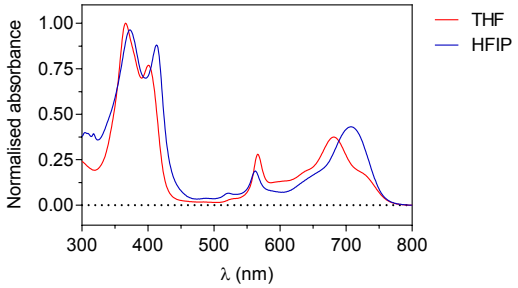


Figure S11: Normalised absorption spectra of 9-amino-2,7,12,17-tetrakis(2-methoxyethyl)porphycene in THF (red line) and HFIP (blue line).

3.7 HFIP effects on the absorption and fluorescence emission spectra of 2-phenylthiazolo[4,5-c]2,7,12,17-tetraphenylporphycene (TAZPo 3)

Absorption spectra and time-resolved emission spectra of 2-phenylthiazolo[4,5-c]2,7,12,17-tetraphenylporphycene in MeOH and HFIP are shown in Figure S12.

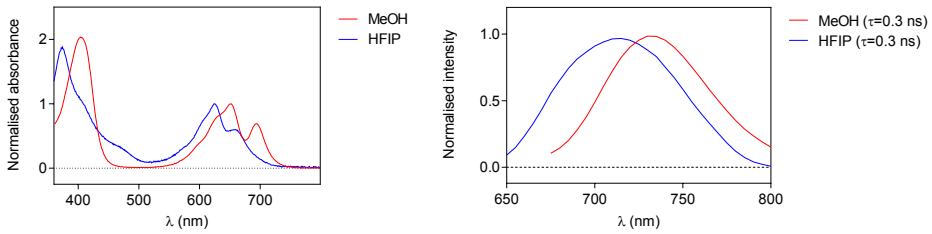


Figure S12: Absorption and time-resolved emission spectra of TAZPo **3** in MeOH and HFIP.

3.8 HFIP and acid effects on the absorption and fluorescence emission spectra of ATAZPo 4

ATAZPo **4** was dissolved in 1 mL of MeOH and the absorption and fluorescence spectra were collected after the addition of 2 mL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) 5.9 M and 100 μL of HCl 12 M (Figure S13).

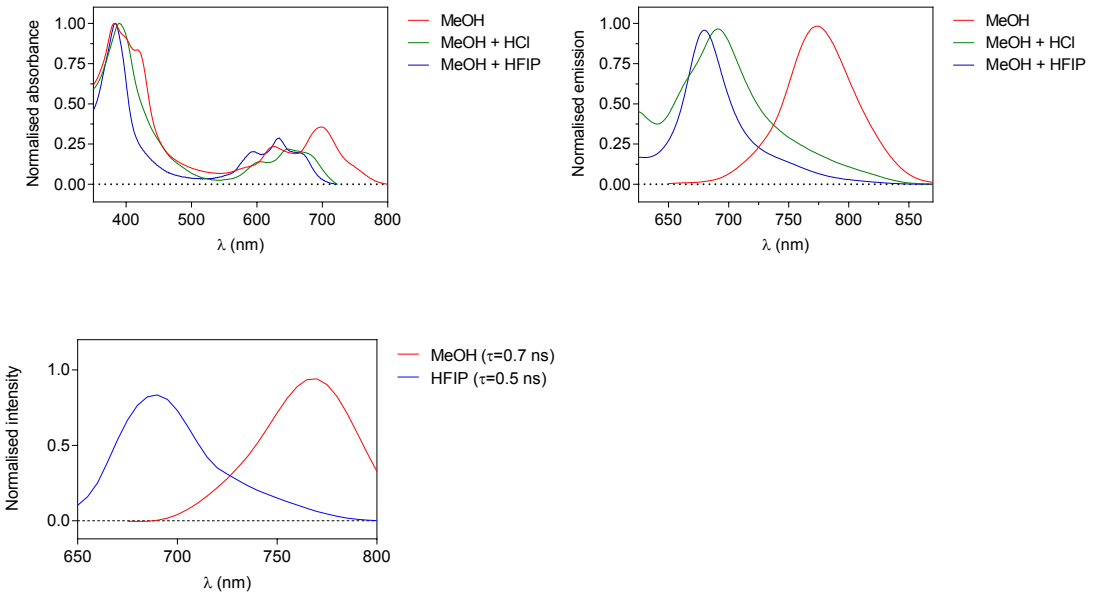


Figure S13: Dilution-corrected absorption (top-left) and normalized fluorescence emission spectra (top-right) of ATAZPo **4** in MeOH (red line) and in MeOH-HCl (green) and MeOH-HFIP (blue) mixtures. The stock concentrations of HFIP and HCl were 5.9 M and 12 M respectively. Bottom: time-resolved fluorescence emission spectra of ATAZPo **4** in MeOH (red line) and in HFIP (blue).

4. References

1. O. Planas, T. Gallavardin, and S. Nonell, *Chem. Commun.*, 2015, **51**, 5586–5589.