A Hybrid Bis(Amino-Styryl) Substituted Bodipy Dye and its Conjugate Diacid: Synthesis, Structure, Spectroscopy and Quantum Chemical Calculations

Adela Nano,[a] Pascal Retailleau,[b] Jerry P. Hagon,[c,] Anthony Harriman[c,] and Raymond Ziessel[a,]

[a]*Laboratoire de Chimie Organique et Spectroscopies Avancées (ICPEES-LCOSA), UMR 7515 au CNRS, Ecole Européenne de Chimie, Polymères et Matériaux, Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg Cedex 02, France.*

[b]*Centre de Recherche de Gif, Institut de Chimie des Substances Naturelles, UPR2301-CNRS, Bâtiment 27, 1 avenue de la Terrasse, 91198 Gif sur Yvette Cedex, France.*

[c] *Molecular Photonics Laboratory, School of Chemistry, Bedson Building, Newcastle University, Newcastle upon Tyne, NE1 7RU, United Kingdom.*

SUPPORTING INFORMATION

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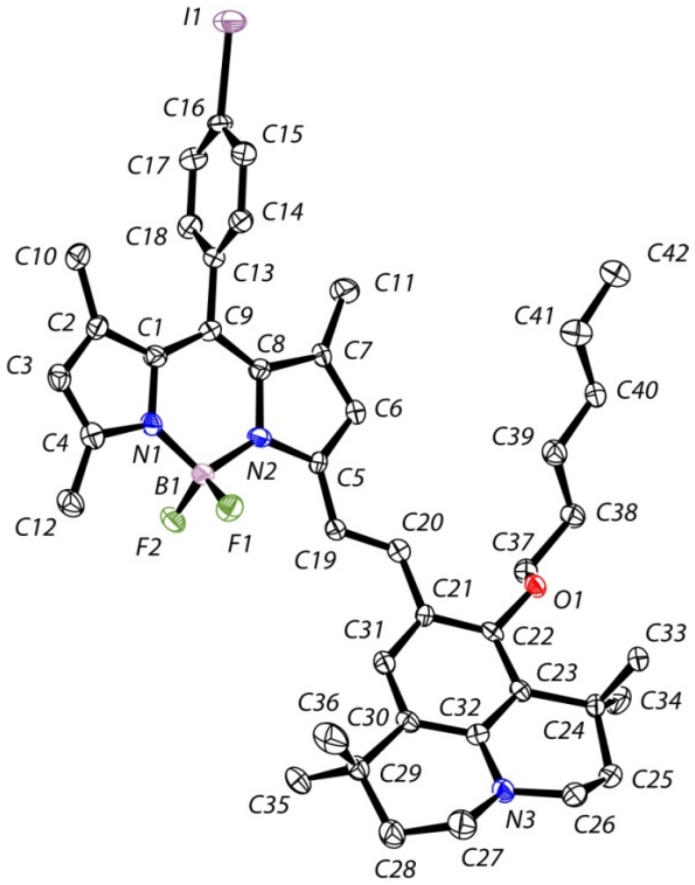

Figure S1. ORTEP view of **4**. Thermal ellipsoids are plotted at 30%. B1–N1, B1–N2, B1–F1, B1–F2, N1–C1, N2–C8, N1–C4 and N2–C5 bond lengths are 1.520(10), 1.542(10), 1.397(9), 1.408(10), 1.426(10), 1.357(10) and 1.382(9) Å, respectively and the F–B–F, N–B–F, and N–B–N angles are 107.2 (6), 111.4(6) /110.4 (6) /108.7(6)/ 111.4(6) and 107.7 (6)°.

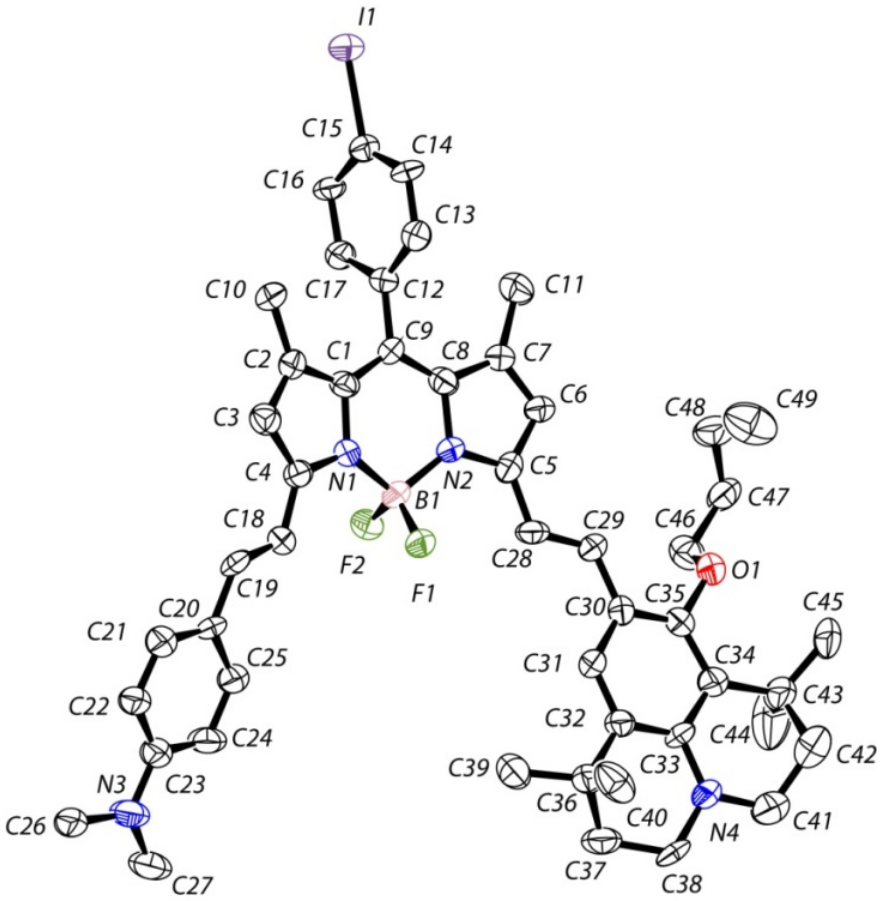

Figure 2. ORTEP view of **5**. Thermal ellipsoids are plotted at the 30% level. B1–N1, B1–N2, B1–F1, B1–F2, N1–C1, N2–C8, N1–C4 and N2–C5 bond lengths are 1.523(7), 1.554(7), 1.393(6), 1.396(6), 1.406(6), 1.412(7), 1.360(6) and 1.382(9) Å, respectively and the F–B–F, N–B–F, and N–B–N angles are 107.8 (4), 111.4(4) /110.2 (4) /109.7(4)/ 110.0(4) and 107.6 (4)°.

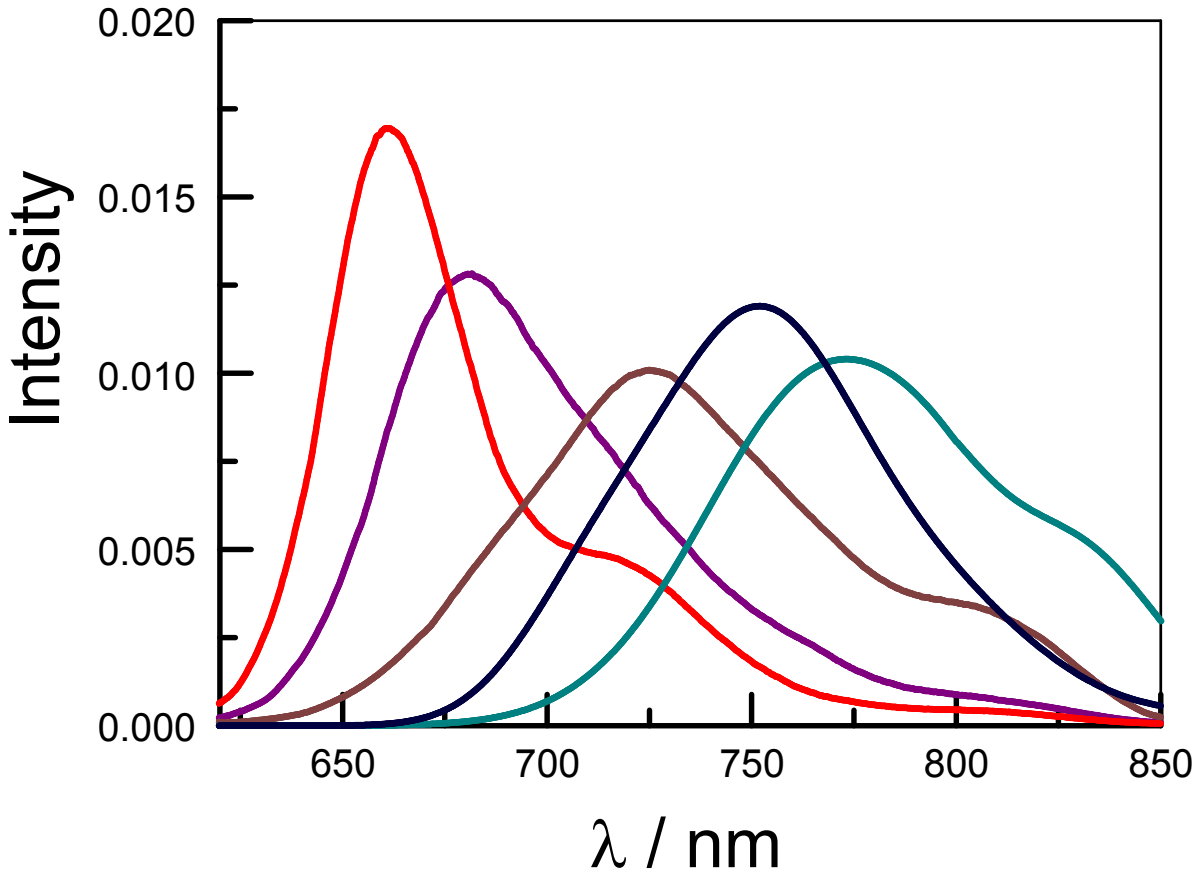

Figure S3. Effect of solvent on the emission spectrum of **4**: spectra were recorded in cyclohexane (red curve) dibutyl ether (plum curve), ethyl acetate (brown curve), butyronitrile (dark blue curve) and acetonitrile (pale blue curve). Spectra were normalized to unit area.

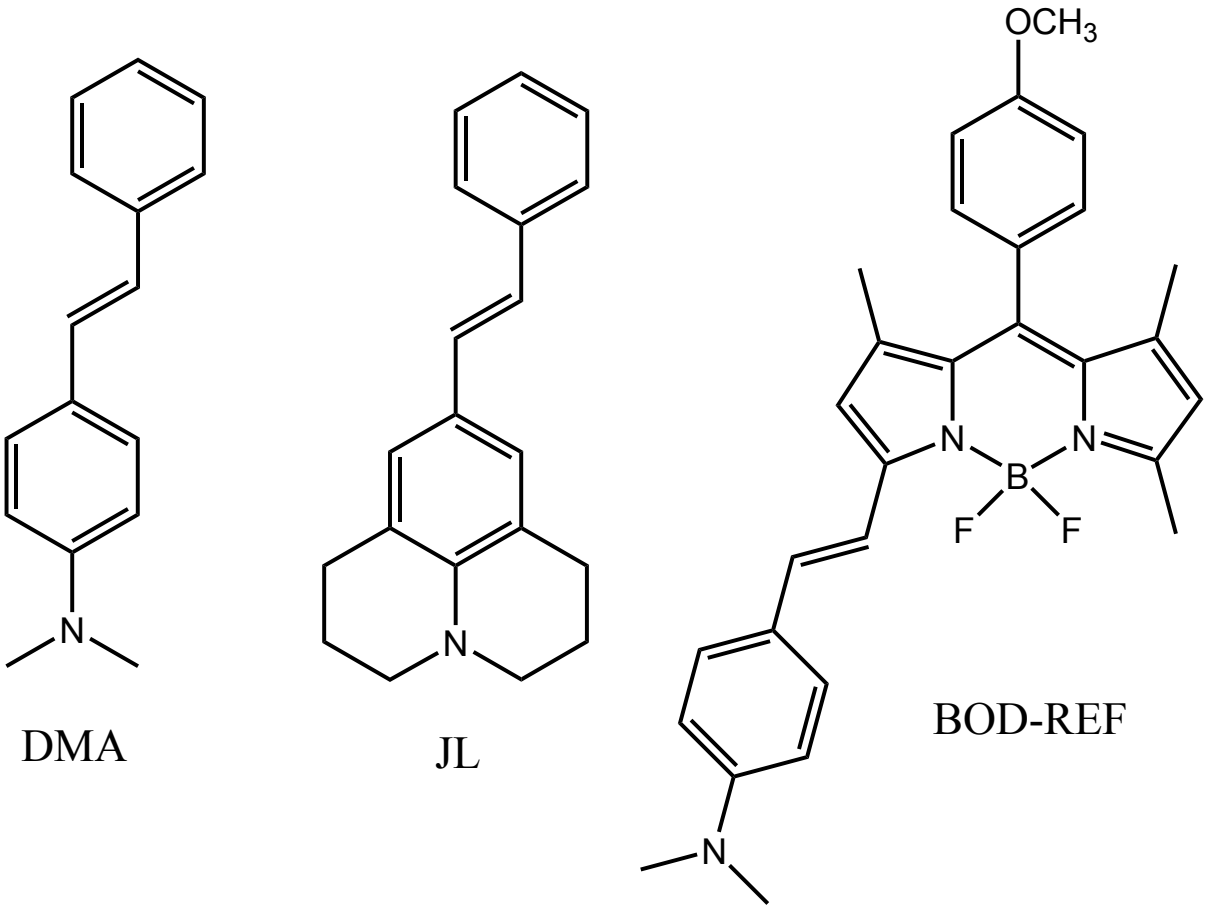

Figure S4. Chemical formulae for DMA, JL and BOD-REF reference compounds.

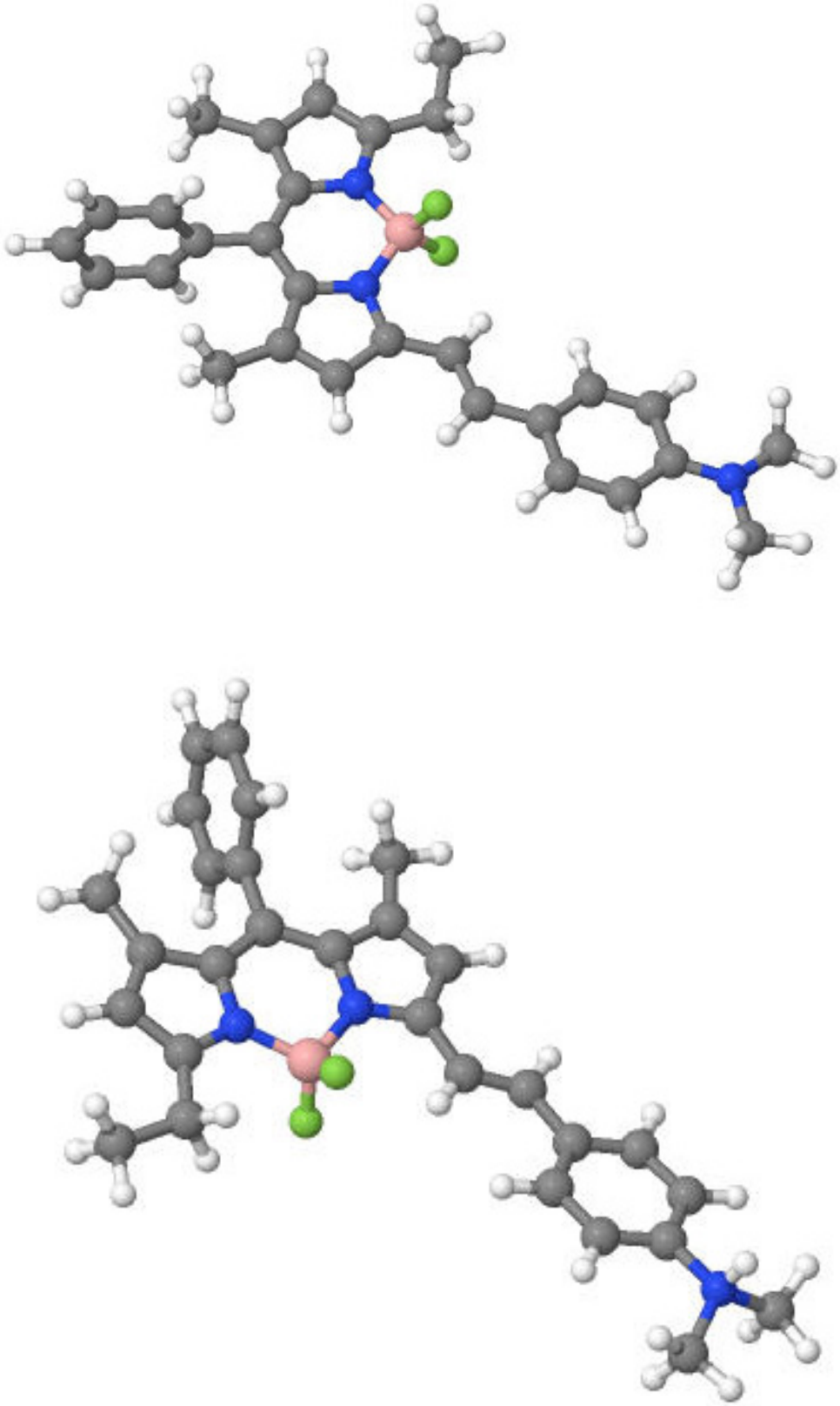

Figure S5. DFT energy-minimized geometries for BOD-DMA (upper panel) and BOD-DMAH$^+$ (lower panel).

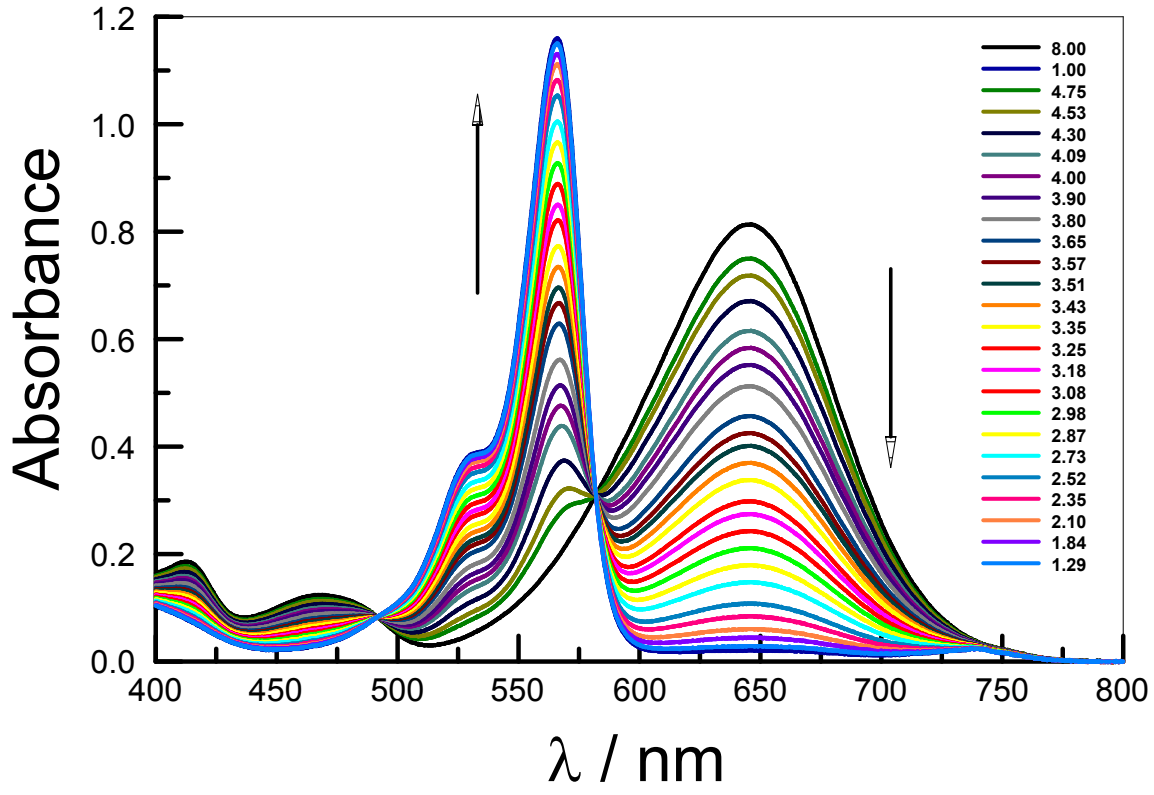

Figure S6. Absorption spectral titration carried out for **4** (9 μM) in CH_3CN by addition of HCl (effective pH values given in the accompanying legend). The arrows indicate the course of reaction as increasing amounts of HCl are added to the solution. The spectra are corrected for minor effects of dilution.

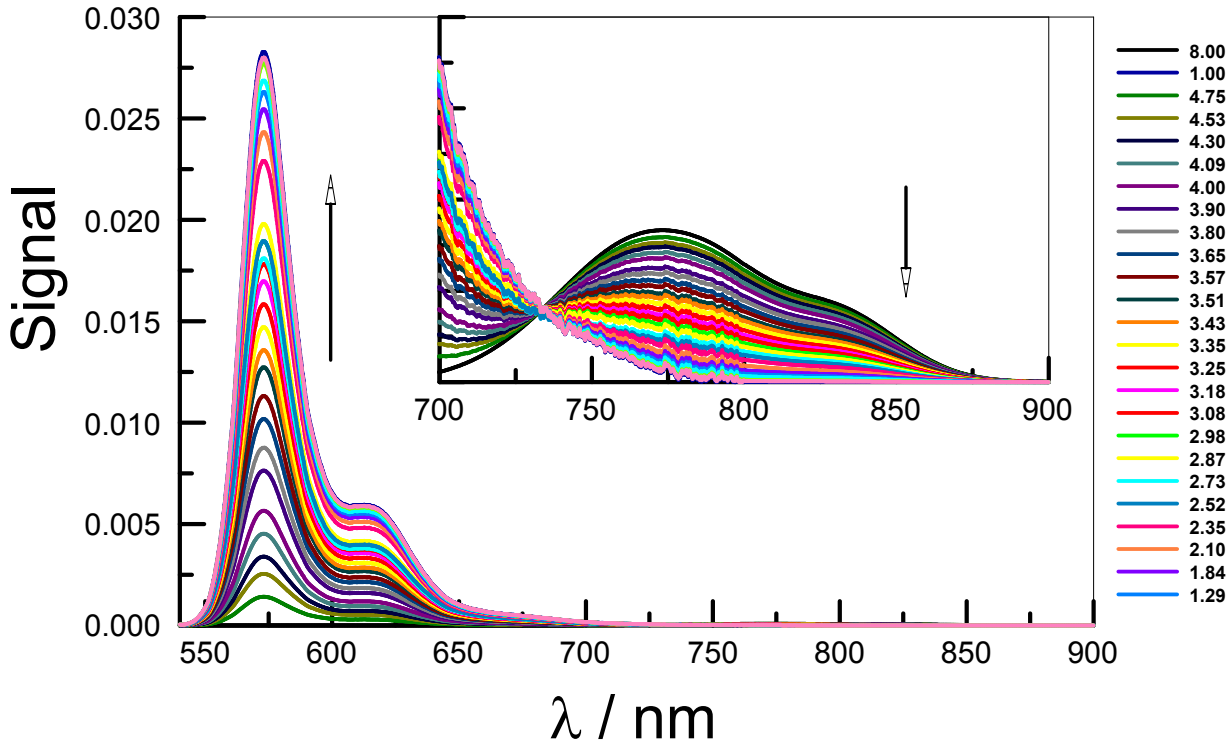

Figure S7. spectral titration carried out for **4** (2 μM) in CH_3CN by addition of HCl (effective pH values are given in the accompanying legend). The arrows indicate the course of reaction as increasing amounts of HCl are added to the solution. The spectra are corrected for minor effects of dilution while the inset shows an expansion of the region where the neutral dye emits. Excitation was made at the isosbestic point around 490 nm.

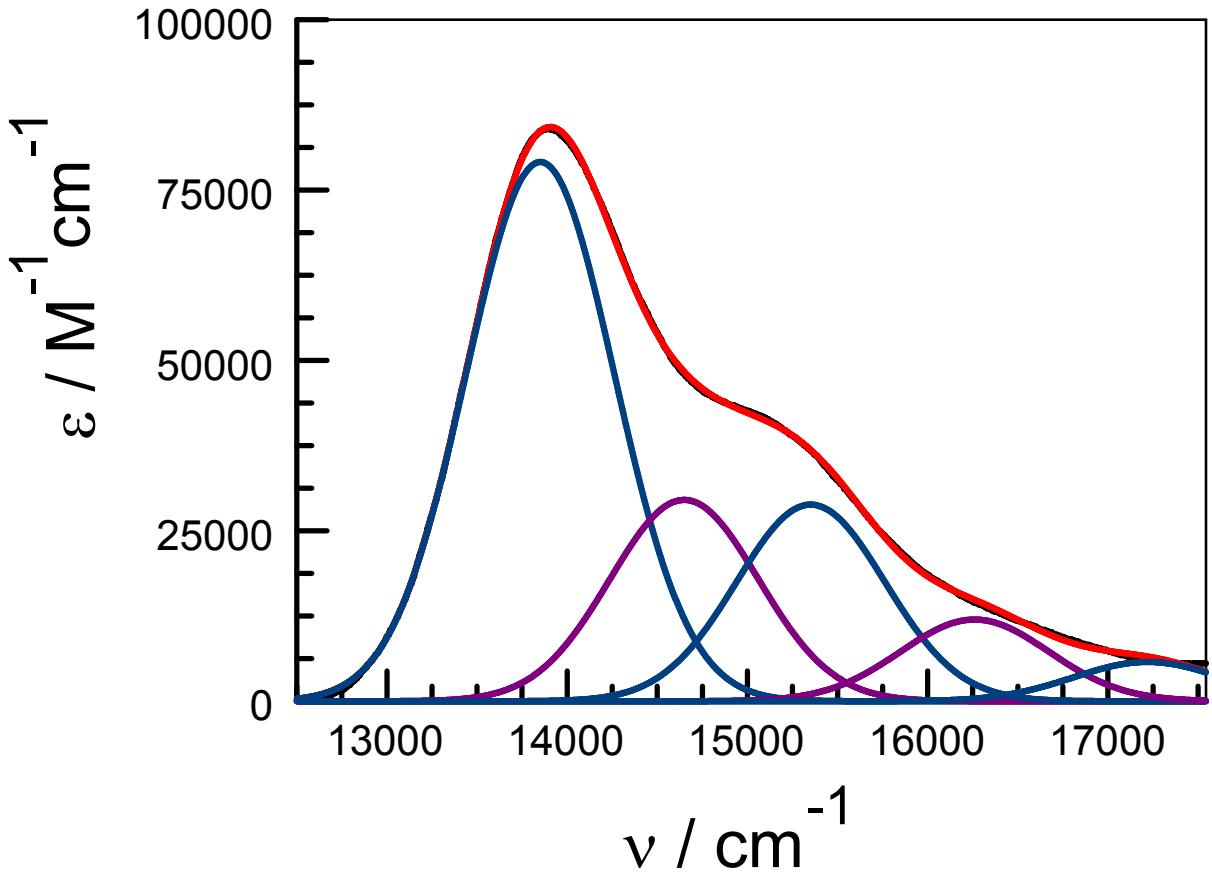

Figure S8. Deconstruction of absorption spectrum recorded for **5** in Bu_2O. The black curve is the experimental spectrum while the calculated spectrum is shown as a red overlay. Two sets of Gaussian-shaped components are shown as plum and blue curves. Deconstruction of the experimental spectrum was accomplished with PEAKFIT.®

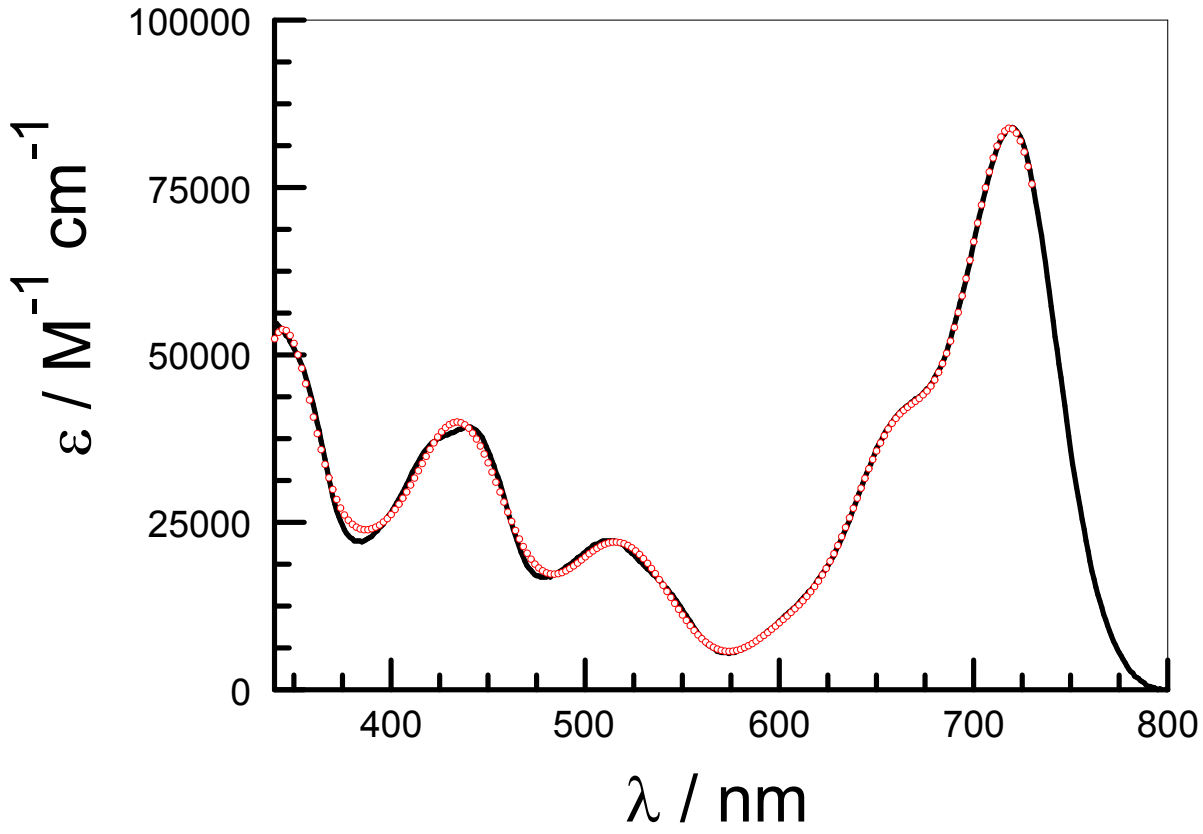

Figure S9. Comparison of absorption (black solid curve) and excitation (open red circles) spectra recorded for **5** in MTHF.

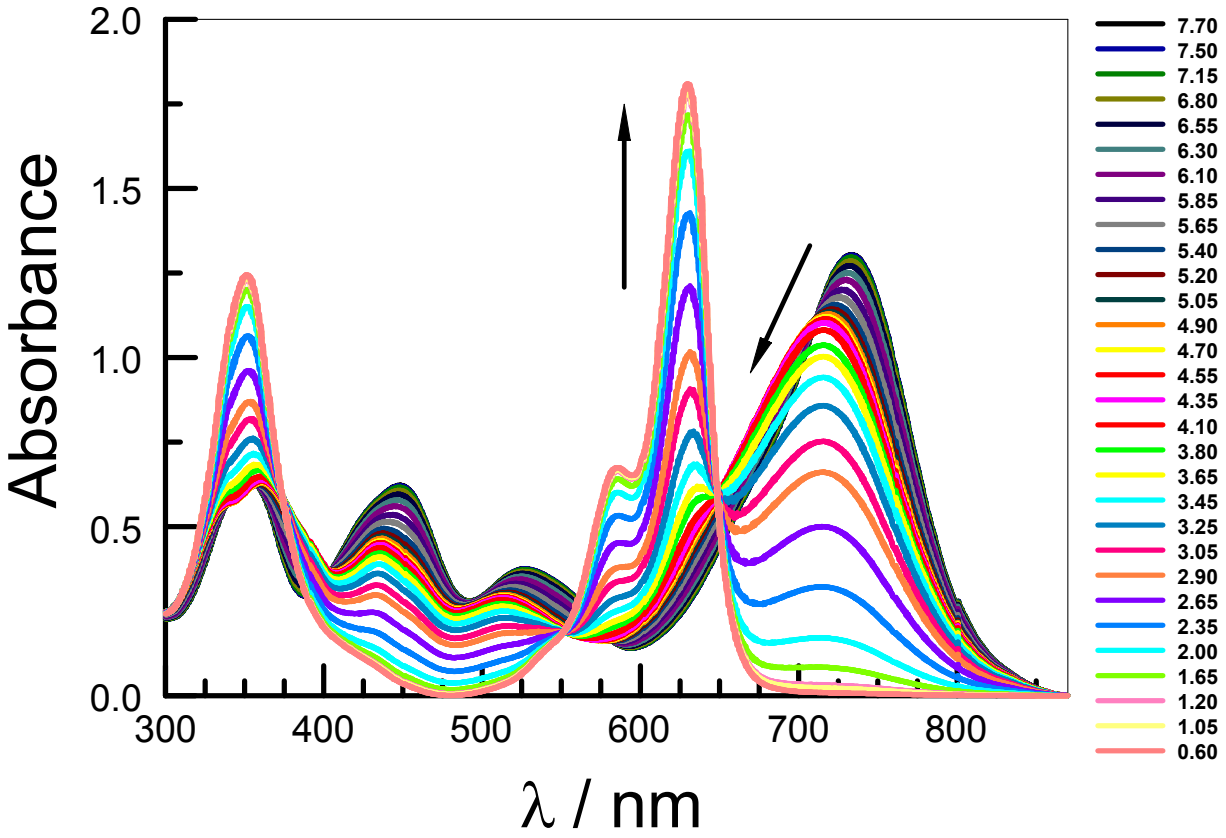

Figure S10. Absorption spectral titration carried out for **5** (15 μM) in CH_3CN by addition of HCl (effective pH values are given in the accompanying legend). The arrows indicate the course of reaction as increasing amounts of HCl are added to the solution. The spectra are corrected for minor effects of dilution.

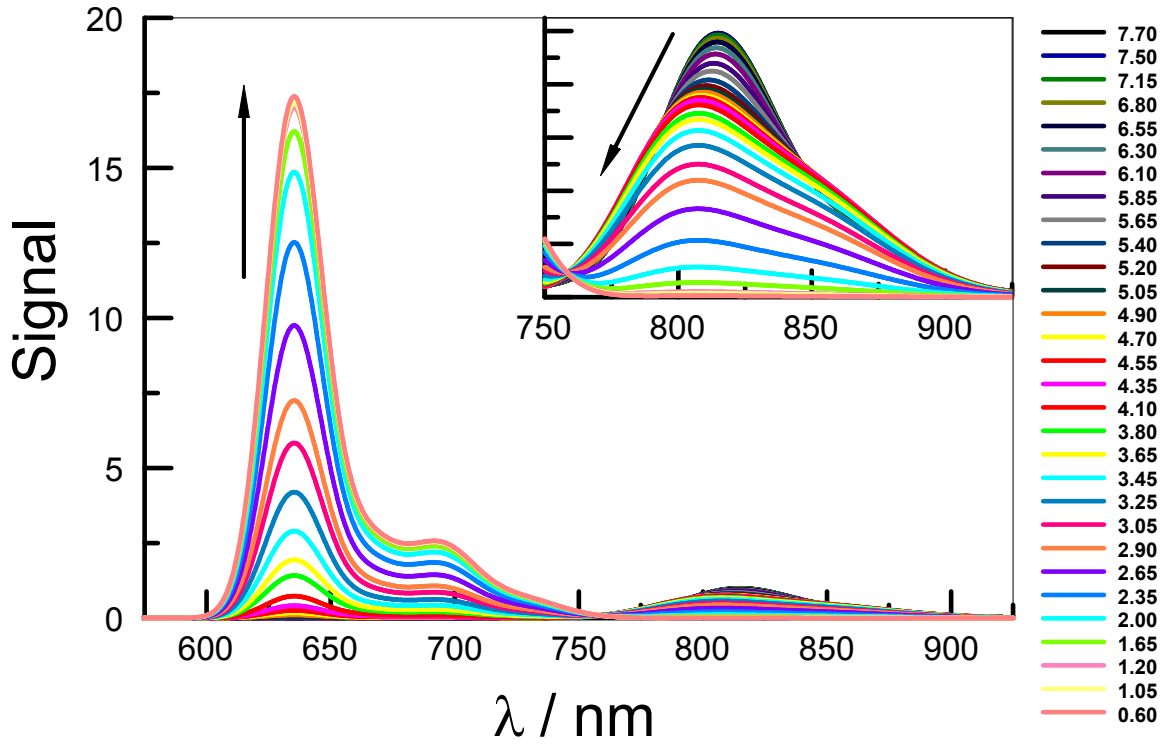

Figure S11. Fluorescence spectral titration carried out for **5** (3 μM) in CH_3CN by addition of HCl (effective pH values are given in the accompanying legend). The arrows indicate the course of reaction as increasing amounts of HCl are added to the solution. The spectra are corrected for minor effects of dilution while the inset shows an expansion of the region where the neutral dye emits. Excitation was made at 365 nm.

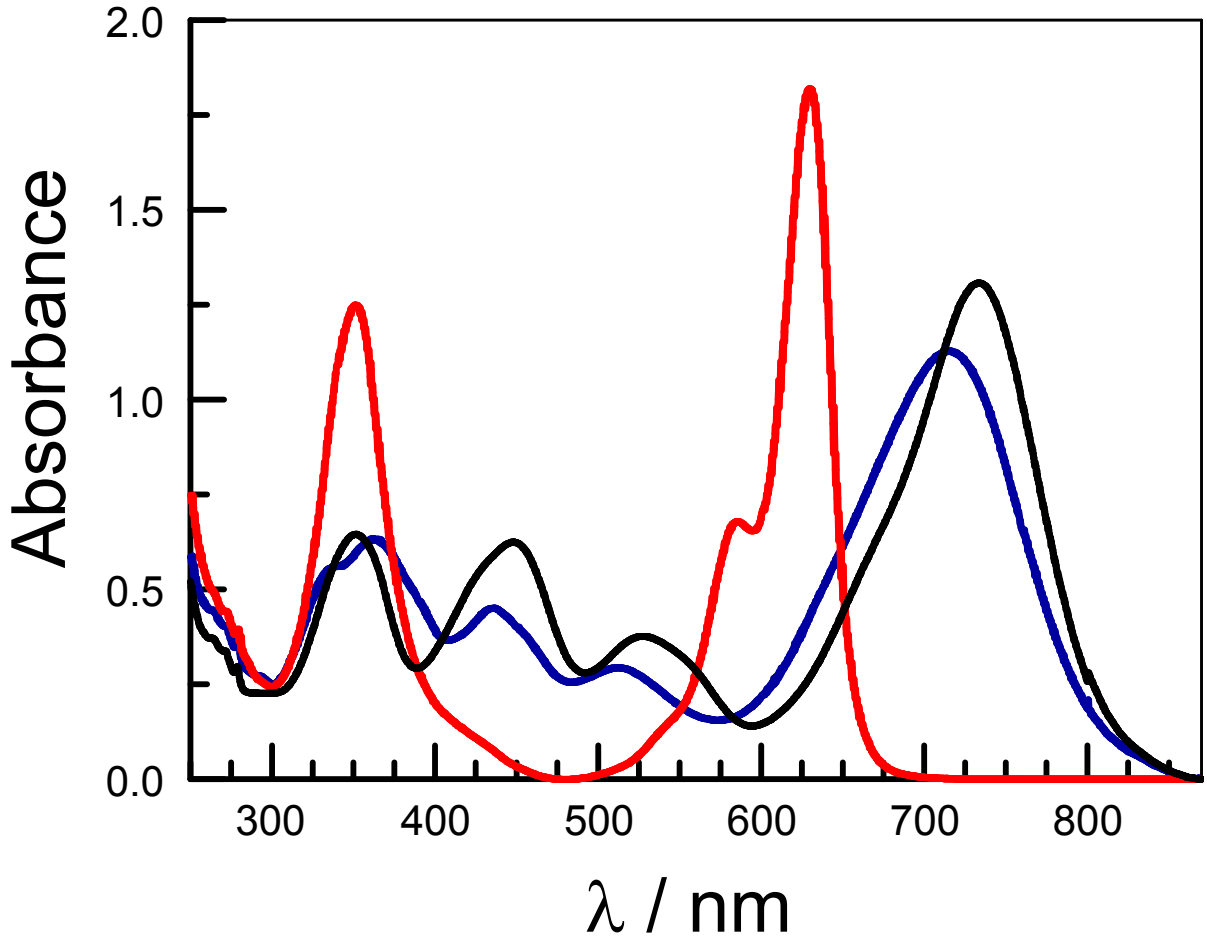

Figure S12(a). Absorption spectra recorded in CH_3CN for the neutral (black curve), mono-protonated form (blue curve) and di-protonated form (red curve) of compound **5**. The spectrum for the mono-protonated species was derived using SPECFIT.®

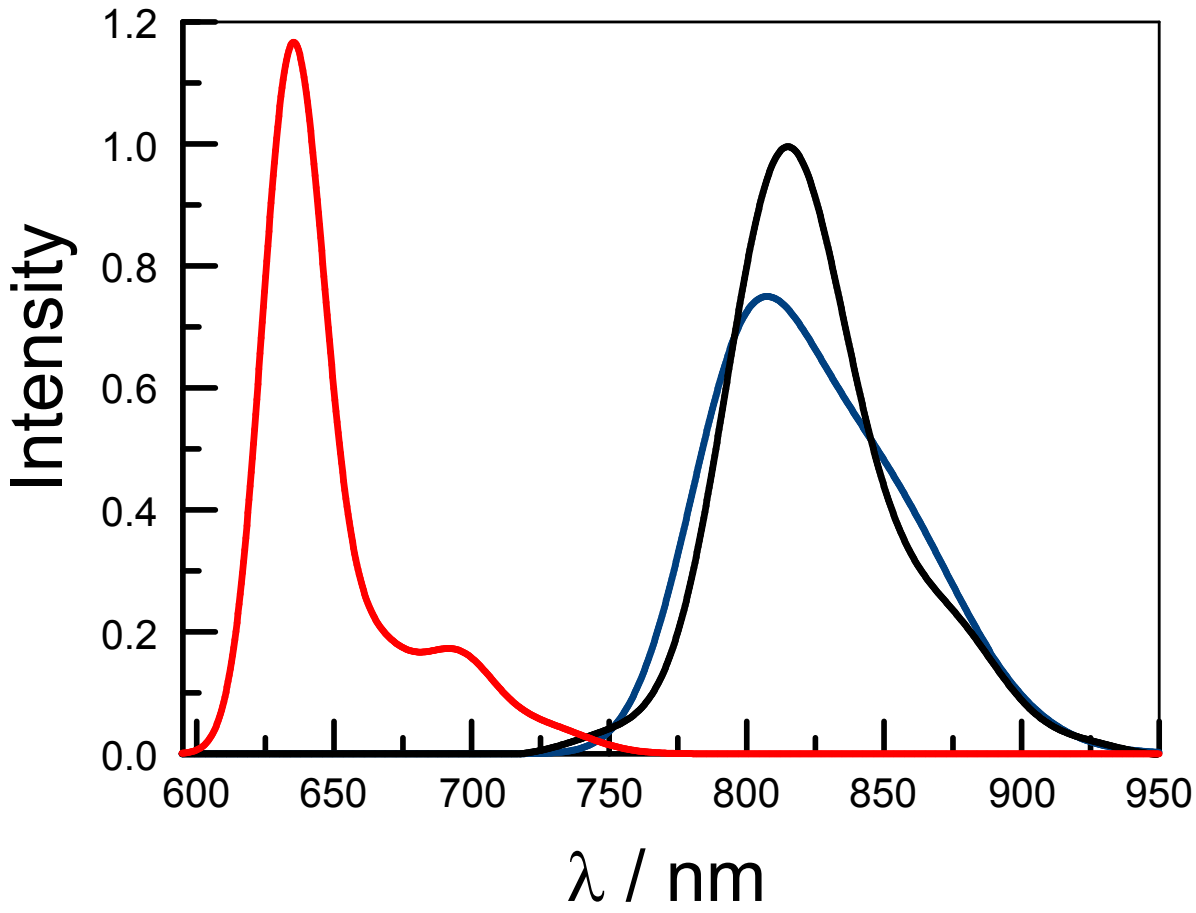

Figure S12(b). Fluorescence spectra recorded in CH_3CN for the neutral (black curve), mono-protonated form (blue curve) and di-protonated form (red curve) of compound **5**. The spectrum for the mono-protonated species was derived using SPECFIT.®

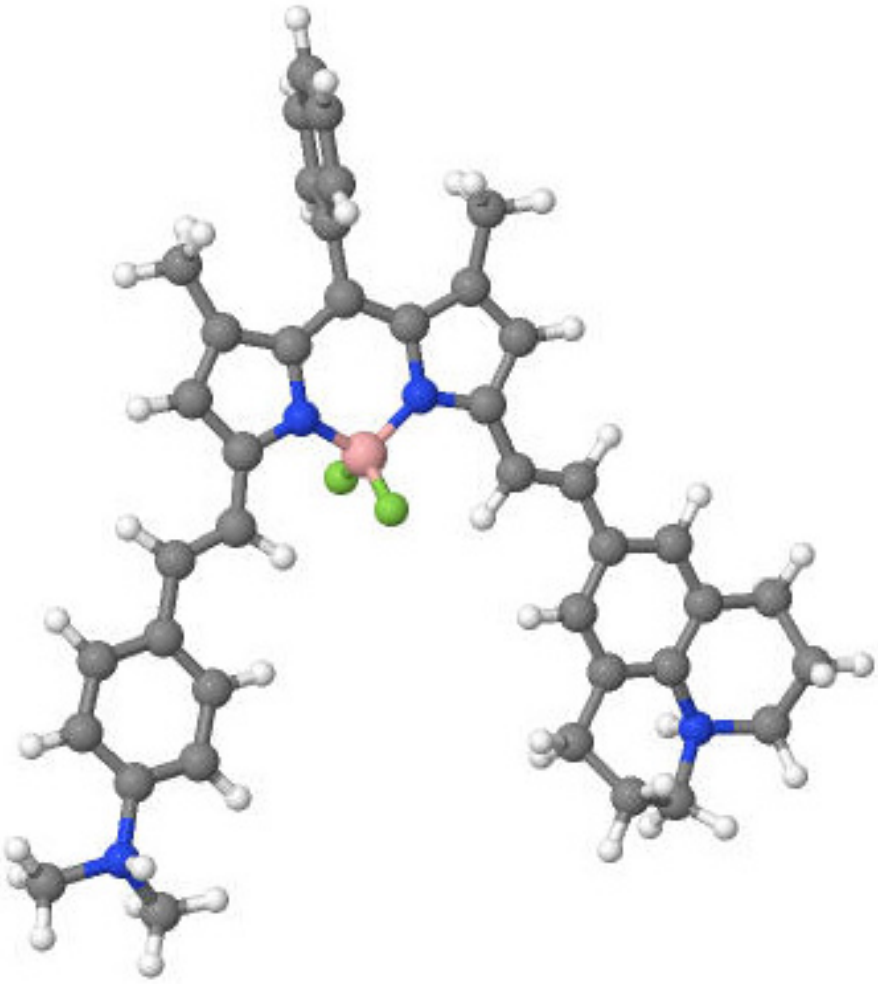

Figure S13. DFT energy-minimized geometry for the conjugate diacid, $H_2\mathbf{5}^{2+}$.

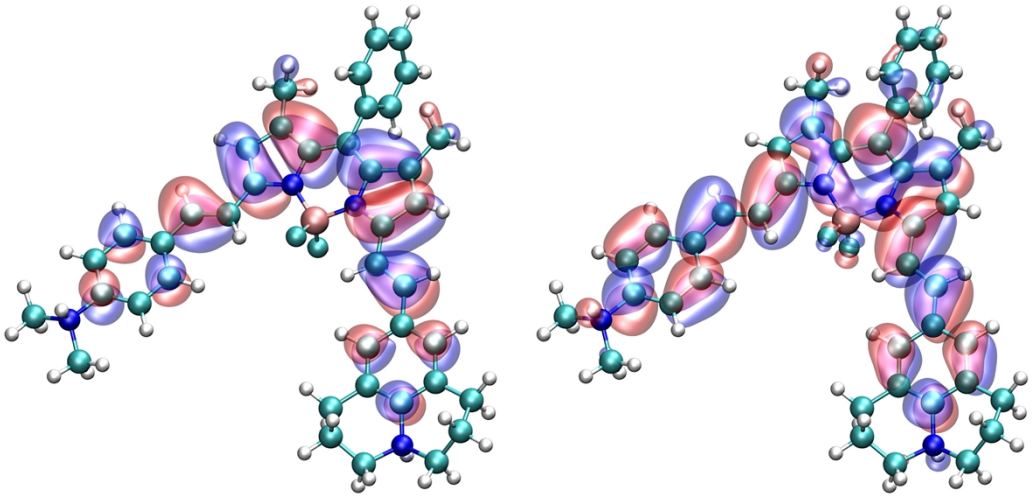

Figure S14. Computed Kohn-Sham distributions for the HOMO (left panel) and LUMO (right panel) isosurfaces for the conjugate diacid $\mathbf{H_2 5^{2+}}$. The surface contains 90% of the orbital charge.

Table S1(a). Summary of the photophysical properties determined for **4** in solvents of differing polarity at room temperature.

Solvent	ε_S [(a)]	λ_{ABS} /nm	λ_{FLU} /nm	Φ_F	SS /cm^{-1}	τ_S / ns	k_{RAD} /10^8 s^{-1}	k_{NR} /10^8 s^{-1}
C_6H_{12}	2.02	638	661	0.92	513	3.7	2.50	0.22
Bu_2O	3.18	640	682	0.82	820	3.9	2.10	0.46
EtOAc[(b)]	6.03	637	725	0.45	1010	3.15	1.43	1.75
CH_2Cl_2	9.02	642	766	0.003	2520	1.1	0.25	9.2
C_3H_7CN[(c)]	24.56	645	750	0.13	1890	1.6	0.81	5.4
CH_3CN	35.94	644	775	0.023	2625	0.88	0.26	11.0

(a) static dielectric constant of the solvent. (b) ethyl acetate. (c) butyronitrile.

Table S1(b). Summary of the photophysical properties[(a)] determined for **BOD-REF** in solvents of differing polarity at room temperature.

Solvent	λ_{ABS} /nm	λ_{FLU} /nm	Φ_F	SS /cm^{-1}	τ_S / ns	k_{RAD} /10^8 s^{-1}	k_{NR} /10^8 s^{-1}
C_6H_{12}	597	612	0.97	411	3.50	2.77	0.09
Bu_2O	596	627	0.91	830	NA	NA	NA
EtOAc	596	665	0.59	1741	3.31	1.78	1.24
C_3H_7CN	600	695	0.27	2278	2.26	1.19	3.23
CH_3CN	597	717	0.090	2803	1.20	0.75	7.58

(a) All data taken from: M. Baruah, W. Qin, C. Flors, J. Hofkens, R. A. L. Vallée, D. Beljonne, M. Van der Auweraer, W. De Borggraeve and N. Boens, *J. Phys. Chem. A*., 2006, **110**, 5998-6009.

Table S1(c). Effect of solvent polarity on the molar absorption coefficient of compound **4** at room temperature.

Solvent	ε_S [a]	λ_{ABS} /nm	ε_{MAX} /M^{-1} cm^{-1}	f [d]	FWHM /cm^{-1} [e]
C_6H_{12}	2.02	638	119,850	0.98	1,025
Bu_2O	3.18	640	108,860	1.00	1,325
EtOAc[b]	6.03	637	94,500	1.00	1,550
CH_2Cl_2	9.02	642	92,000	1.03	1,600
C_3H_7CN[c]	24.56	645	86,790	1.05	1,755
CH_3CN	35.94	644	85,370	1.06	1,825

(b) static dielectric constant of the solvent. (b) ethyl acetate. (c) butyronitrile. (d) oscillator strength. (e) full width at half-maximum of the lowest-energy absorption band after deconstruction into Gaussian-shaped components.

Table S2. Selected structural data taken from the DFT output for **4** and BOD-DMA and for their corresponding conjugate acids.

Parameter	**4**	**4H$^+$**	**BOD-DMA**	**BOD-DMAH$^+$**
Dihedral [(a)] /°	1.4	7.8	10.9	7.6
C_A-N-H /°	-	104.1	-	106.8
C_A-N-CH_3 /°	122.4	116.6	119.8	113.8
N-B /Å	9.084	9.141	9.065	9.139
N-C_1 /Å	8.024	8.080	8.040	8.107
C_B-C_1 /Å	1.437	1.441	1.439	1.440
C_1-C_2 /Å	1.359	1.356	1.357	1.358
C_2-C_3 /Å	1.450	1.454	1.452	1.451
C_A-N /Å	1.384	1.504	1.384	1.510
N-H /Å	-	1.025	-	1.027
N-CH_3 /Å	1.461	1.550	1.454	1.511

(a) Dihedral angle between Bodipy nucleus and the aryl ring of the amine.

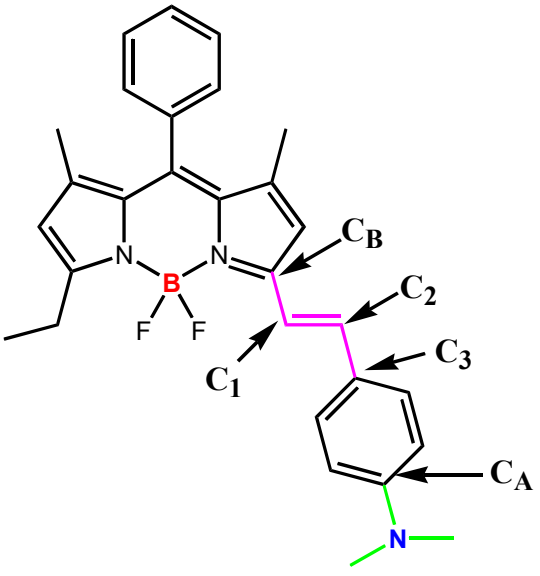

Table S3. Selected structural data taken from the DFT output for **5** and for its corresponding conjugate diacid, $\mathbf{H_2 5^{2+}}$.

Parameter	**DMA** [(b)]	**JL** [(b)]	**DMAH$^+$** [(c)]	**JLH$^+$** [(c)]
Dihedral [(a)] /°	4.5	4.4	1.0	8.3
C_A-N-CH_3 /°	125.0	125.2	114.7	116.0
C_A-N-N /°	NA	NA	105.7	103.4
N-B /Å	9.225	9.235	9.266	9.139
N-C_1 /Å	8.154	8.146	8.118	8.079
C_B-C_1 /Å	1.462	1.467	1.442	1.443
C_1-C_2 /Å	1.381	1.386	1.356	1.356
C_2-C_3 /Å	1.485	1.492	1.455	1.457
C_A-N /Å	1.395	1.382	1.513	1.509
N-CH_3 /Å	1.474	1.474	1.512	1.555
N-H /Å	NA	NA	1.027	1.022

(a) Ddihedral angle between Bodipy nucleus and the aryl ring of the amine. (b) Refers to the neutral molecule. (c) Refers to the conjugate diacid.

Table S4. Selected structural data taken from the DFT output for the mono-protonated species derived from **5**.

Parameter	**DMA**	**DMAH$^+$**	**JL**	**JLH$^+$**
Dihedral [(a)] /°	2.2	4.1	10.7	8.2
C_A-N-H /°	121.1	114.3	120.7	115.7
C_A-N-CH_3 /°	-	106.9	-	104.0
N-B /Å	9.209	9.211	9.151	9.094
N-C_1 /Å	8.031	8.110	8.012	8.092
C_B-C_1 /Å	1.432	1.433	1.432	1.435
C_1-C_2 /Å	1.364	1.363	1.366	1.360
C_2-C_3 /Å	1.444	1.446	1.441	1.450
C_A-N /Å	1.381	1.506	1.383	1.507
N-H /Å	-	1.026	-	1.022
N-CH_3 /Å	1.454	1.510	1.462	1.554

Table S5. Coordinates for the energy-minimized neutral form of compound **BOD-DMA**.

C	-2.65639	2.32054	0.39824
N	-2.71266	0.93648	0.20638
B	-1.49821	0.00637	-0.06678
N	-0.22153	0.88841	0.10590
C	-0.21491	2.27815	0.23368
C	-1.41538	2.98734	0.38932
C	1.05820	0.45024	-0.01021
C	1.92367	1.57952	0.03717
C	1.15791	2.71852	0.18611
C	-3.99632	2.79101	0.58779
C	-4.81488	1.66764	0.49528
C	-4.00351	0.54082	0.25599
C	1.39063	-0.94464	-0.13317
C	2.64165	-1.39933	-0.39984
C	3.06465	-2.78224	-0.53179
C	4.40823	-3.07139	-0.84029
C	4.87524	-4.36932	-0.98408
C	4.00391	-5.47385	-0.83163
C	2.65262	-5.19053	-0.50587
C	2.20434	-3.88839	-0.36652
N	4.44675	-6.77396	-0.99880
C	3.56658	-7.88584	-0.67834
C	1.71615	4.10875	0.27530
C	-4.49215	4.18311	0.85075
C	-4.40216	-0.89338	0.06520
C	-5.91355	-1.13329	0.07827
C	-1.38075	4.47393	0.55087
C	-1.18579	5.04941	1.81399
C	-1.15507	6.43712	1.96222
C	-1.31676	7.26515	0.84961
C	-1.51212	6.69943	-0.41193
C	-1.54604	5.31184	-0.56083
F	-1.55250	-0.50120	-1.36253
F	-1.48205	-1.04083	0.85941
C	5.86606	-7.03638	-1.16802
H	3.00340	1.54626	-0.01324
H	-5.89178	1.65845	0.59197
H	0.57025	-1.63868	0.00765
H	3.43535	-0.66732	-0.54640
H	5.10776	-2.24830	-0.96882
H	5.92184	-4.52288	-1.21661
H	1.94568	-5.99771	-0.35808
H	1.15967	-3.72731	-0.11862
H	2.64432	-7.84241	-1.26917
H	4.06948	-8.82204	-0.92479
H	3.28701	-7.91525	0.38597
H	2.80070	4.07884	0.13650
H	1.29475	4.77127	-0.48696
H	1.51222	4.57649	1.24350
H	-4.28217	4.86274	0.01849
H	-5.57493	4.16599	1.00526
H	-4.03034	4.62503	1.73915
H	-3.96564	-1.24252	-0.87881
H	-3.91041	-1.49315	0.84027
H	-6.13069	-2.19505	-0.07172
H	-6.36065	-0.83528	1.03280

H	-6.41673	-0.57434	-0.71786
H	-1.05806	4.40402	2.67849
H	-1.00426	6.87048	2.94702
H	-1.29104	8.34493	0.96500
H	-1.63914	7.33768	-1.28191
H	-1.69917	4.87066	-1.54164
H	6.26225	-6.52244	-2.05196
H	6.46300	-6.72350	-0.29758
H	6.01604	-8.10670	-1.31640

Table S6. Coordinates for the energy-minimized protonated form of compound **BOD-DMA** (i.e., **BOD-DMAH$^+$**).

C	-2.63827	2.30569	0.38696
N	-2.68228	0.91709	0.18143
B	-1.45438	0.00228	-0.08807
N	-0.19259	0.91229	0.05199
C	-0.20022	2.29006	0.18339
C	-1.42395	2.98800	0.37186
C	1.09841	0.49756	-0.09541
C	1.94174	1.63213	-0.06735
C	1.15409	2.76205	0.09830
C	-3.99440	2.75958	0.59773
C	-4.79244	1.63383	0.49846
C	-3.96369	0.51196	0.24459
C	1.44284	-0.89522	-0.19341
C	2.69083	-1.35774	-0.46327
C	3.09609	-2.75229	-0.49142
C	4.43133	-3.07547	-0.81462
C	4.89171	-4.38724	-0.84074
C	4.01215	-5.42497	-0.52714
C	2.67800	-5.14499	-0.20799
C	2.23229	-3.83133	-0.19305
N	4.50197	-6.85246	-0.45239
C	3.49040	-7.86195	-0.95018
C	1.69189	4.16045	0.18509
C	-4.49783	4.14218	0.88069
C	-4.36181	-0.91904	0.04396
C	-5.87223	-1.16607	0.07387
C	-1.40038	4.47165	0.55499
C	-1.17835	5.02273	1.82516
C	-1.15457	6.40816	1.99596
C	-1.33352	7.25365	0.89911
C	-1.55524	6.70960	-0.36787
C	-1.58450	5.32485	-0.54110
F	-1.50652	-0.52932	-1.37268
F	-1.40483	-1.03059	0.85391
C	5.82202	-7.08934	-1.14549
H	3.02020	1.62271	-0.14668
H	-5.86728	1.60474	0.60652
H	0.62676	-1.58613	-0.00960
H	3.48557	-0.64234	-0.66036
H	5.12612	-2.27693	-1.05555
H	5.93186	-4.56020	-1.08711
H	1.97396	-5.92741	0.05190
H	1.19434	-3.64425	0.05732
H	3.22078	-7.60396	-1.97169
H	3.94678	-8.85214	-0.90504
H	2.61039	-7.84255	-0.31005
H	2.77252	4.14818	0.01856
H	1.24164	4.81964	-0.56257
H	1.50568	4.61819	1.16110
H	-4.29695	4.82905	0.05400
H	-5.57784	4.11576	1.04647
H	-4.02475	4.57403	1.76876
H	-3.93022	-1.25754	-0.90626
H	-3.85630	-1.51732	0.81194
H	-6.08407	-2.22723	-0.08317

H	-6.31023	-0.88023	1.03594
H	-6.38703	-0.60567	-0.71296
H	-1.03701	4.36523	2.67816
H	-0.98568	6.82538	2.98446
H	-1.31039	8.33088	1.03283
H	-1.69688	7.36239	-1.22401
H	-1.75674	4.90153	-1.52679
H	5.71820	-6.81561	-2.19337
H	6.59544	-6.49008	-0.66746
H	6.06938	-8.14714	-1.04836
H	4.65687	-7.05870	0.53553

Table S7. Coordinates for the energy-minimized neutral form of compound **4**.

H	-6.98474	-1.00828	-1.41913
H	-7.91195	-0.02628	-0.28017
H	-8.51467	-2.48107	-0.22527
H	-8.03537	-1.82427	1.34078
H	5.39635	1.17908	-2.50395
H	7.83491	0.75837	-2.68604
H	9.19930	0.43801	-0.63116
H	8.11025	0.54485	1.60145
H	5.67121	0.96477	1.77554
H	0.97347	6.81465	-1.00022
H	1.02549	6.84045	0.76966
H	-0.52913	6.80173	-0.06995
H	-0.01516	4.51865	0.81790
H	-0.07281	4.49710	-0.91954
H	6.12347	3.77830	0.60588
H	5.76049	5.30704	-0.20918
H	6.06600	3.83696	-1.14688
H	5.18100	-1.71798	0.52033
H	5.09661	-1.64275	-1.23111
H	4.32090	-2.98292	-0.37062
H	-3.14756	-0.19804	0.05732
H	-2.27092	-4.40517	0.16218
H	-0.48055	-2.94229	-0.08506
H	-0.97934	0.08522	0.11460
H	3.29305	5.98773	-0.12605
H	1.79418	-2.80313	-0.15272
C	-7.14902	-4.46176	0.63706
C	-6.08627	-5.40328	1.19884
C	-4.81794	-5.32098	0.34441
C	-5.83374	-0.36444	0.29452
C	-7.14856	-0.80810	-0.35339
C	-7.66133	-2.07157	0.33252
N	-6.63932	-3.11037	0.42225
F	0.17728	2.01124	-1.34279
F	0.10194	2.02352	0.93969
C	5.99386	1.03958	-1.60759
C	7.36566	0.80235	-1.70723
C	8.13183	0.62303	-0.55373
C	7.51997	0.68254	0.69977
C	6.14782	0.91957	0.80040
C	5.37165	1.09924	-0.35293
C	0.49738	6.42354	-0.09465
C	0.50209	4.89351	-0.07361
C	5.59257	4.22655	-0.24008
C	4.52658	-1.90919	-0.33601
C	-3.46780	-1.23389	0.13064
C	-4.82445	-1.49037	0.24909
C	-5.28651	-2.83549	0.31713
C	-4.33631	-3.88947	0.27235
C	-2.98611	-3.58430	0.17954
C	-2.50401	-2.26342	0.10250
C	-1.07641	-2.03417	0.00041
C	-0.42635	-0.84043	0.00713
C	1.87237	4.28276	-0.11714
C	3.12841	4.91925	-0.14466
C	4.11957	3.94127	-0.20089
C	3.23439	-1.15109	-0.24553
C	1.98941	-1.73965	-0.16746

C	1.00164	-0.71495	-0.09863
C	3.90106	1.35543	-0.25492
C	3.00975	0.27428	-0.22253
N	1.63249	0.48700	-0.13639
B	0.92946	1.87941	-0.17639
N	2.06148	2.94459	-0.14738
C	3.43377	2.68439	-0.20548
H	-6.02807	-0.07075	1.33700
H	-5.43026	0.52181	-0.20646
H	-4.02951	-5.96244	0.75280
H	-5.03844	-5.70230	-0.66405
H	-5.85228	-5.11825	2.23174
H	-6.48694	-6.42228	1.22251
H	-7.54607	-4.86900	-0.30830
H	-7.99723	-4.39968	1.33235

Table S8. Coordinates for the energy-minimized protonated form of compound **4** (i.e., **4H**$^+$).

H	-7.07346	-0.90382	-1.43560
H	-7.93383	0.00271	-0.19769
H	-8.62757	-2.38567	-0.09264
H	-7.71958	-1.96719	1.38062
H	5.39386	1.18691	-2.50856
H	7.82993	0.75818	-2.68766
H	9.19199	0.43486	-0.63257
H	8.10480	0.54559	1.59996
H	5.66857	0.97235	1.77688
H	0.97360	6.81314	-1.00111
H	1.02742	6.84026	0.76997
H	-0.52567	6.79910	-0.06872
H	-0.01158	4.51567	0.82071
H	-0.07102	4.49272	-0.91755
H	6.11421	3.77304	0.60278
H	5.76215	5.30807	-0.20948
H	6.05570	3.83471	-1.14944
H	5.18400	-1.71086	0.51674
H	5.10195	-1.63426	-1.23533
H	4.32757	-2.97515	-0.37595
H	-3.14524	-0.19583	0.17733
H	-2.25060	-4.40474	0.23657
H	-0.48192	-2.95234	-0.04622
H	-0.96607	0.07966	0.15685
H	3.28719	5.98565	-0.12590
H	1.80421	-2.80815	-0.14891
C	-7.18838	-4.51105	0.64838
C	-6.06681	-5.37536	1.21431
C	-4.82312	-5.32445	0.31951
C	-5.83284	-0.35462	0.26470
C	-7.17198	-0.76802	-0.35028
C	-7.65768	-2.05819	0.29220
N	-6.68588	-3.19077	0.00986
F	0.17122	1.99386	-1.34012
F	0.09225	2.00537	0.93988
C	5.98929	1.04589	-1.61095
C	7.36052	0.80387	-1.70937
C	8.12517	0.62200	-0.55520
C	7.51446	0.68418	0.69886
C	6.14307	0.92545	0.80069
C	5.37056	1.10841	-0.35466
C	0.50075	6.42255	-0.09416
C	0.50272	4.89233	-0.07189
C	5.58912	4.22939	-0.24205
C	4.53205	-1.90155	-0.34099
C	-3.46572	-1.23259	0.20562
C	-4.83432	-1.49439	0.23781
C	-5.24234	-2.83950	0.24059
C	-4.32558	-3.89994	0.24653
C	-2.97049	-3.59095	0.22933
C	-2.50144	-2.26223	0.17008
C	-1.06925	-2.04214	0.04821
C	-0.42057	-0.85057	0.03699
C	1.86715	4.27336	-0.11609
C	3.12981	4.91662	-0.14511
C	4.11779	3.94906	-0.20117

C	3.23868	-1.14594	-0.24861
C	1.99044	-1.74312	-0.16417
C	1.00912	-0.72711	-0.08514
C	3.90083	1.36837	-0.25783
C	3.00100	0.27049	-0.22545
N	1.63504	0.48303	-0.13007
B	0.92257	1.87096	-0.17477
N	2.05192	2.94067	-0.14506
C	3.42971	2.67873	-0.20403
H	-5.99490	-0.04012	1.30572
H	-5.42039	0.51330	-0.25692
H	-4.03812	-5.96999	0.72217
H	-5.06103	-5.71504	-0.68130
H	-5.80421	-5.03554	2.22134
H	-6.45322	-6.39543	1.30679
H	-7.72057	-5.02718	-0.15589
H	-7.91163	-4.23256	1.41608
H	-6.74719	-3.34747	-1.00052

Table S9. Coordinates for the energy-minimized neutral form of the hybrid compound **5** .

C	20.1773	-20.8018	-0.0271
C	18.7982	-21.0822	-0.0354
N	18.3436	-22.3998	0.0508
B	19.2440	-23.6616	-0.1347
N	20.7208	-23.1749	0.0157
C	21.1258	-21.8409	0.0291
C	21.8234	-23.9693	0.0878
C	22.9690	-23.1323	0.1702
C	22.5608	-21.8138	0.1466
C	17.6482	-20.2203	-0.1253
C	16.5421	-21.0472	-0.0643
C	16.9812	-22.3936	0.0401
C	20.6413	-19.3832	-0.0908
C	17.5648	-18.7287	-0.2789
C	16.1851	-23.5913	0.1095
C	23.4931	-20.6423	0.2663
C	21.7617	-25.4086	0.0812
C	14.8284	-23.5745	0.0457
C	22.8653	-26.1983	0.0353
C	13.9134	-24.6999	0.0596
C	22.9208	-27.6503	0.0181
C	12.5260	-24.4627	0.0559
C	11.5920	-25.4863	0.0448
C	11.9885	-26.8458	0.0226
C	13.3881	-27.0879	0.0473
C	14.3085	-26.0526	0.0626
C	21.7846	-28.4825	0.0053
C	21.8754	-29.8664	-0.0183
C	23.1547	-30.4919	-0.0131
C	24.3139	-29.6744	-0.0225
C	24.1716	-28.2922	-0.0005
N	23.2666	-31.8842	0.0356
C	24.5485	-32.5036	-0.2778
C	25.7049	-31.7464	0.3700
C	25.6974	-30.2908	-0.1018
C	20.6129	-30.7022	-0.0999
C	20.8394	-32.1367	0.3818
C	22.0973	-32.7022	-0.2695
N	11.0644	-27.8806	-0.0521
C	9.6263	-27.6803	-0.0230
C	11.4179	-29.2871	-0.0174
C	21.2231	-18.8820	-1.2635
C	21.6496	-17.5556	-1.3335
C	21.5015	-16.7121	-0.2288
C	20.9257	-17.2035	0.9441
C	20.4980	-18.5305	1.0138
F	18.9523	-24.6107	0.8492
F	19.0388	-24.2091	-1.3962
H	23.9902	-23.4735	0.2650
H	15.5128	-20.7218	-0.0998
H	18.3216	-18.3346	-0.9582
H	16.5782	-18.4599	-0.6717
H	17.6928	-18.2042	0.6769
H	16.7268	-24.5232	0.2214
H	24.4822	-20.9954	0.5751
H	23.6144	-20.1077	-0.6813

H	23.1451	-19.9092	0.9982
H	20.7707	-25.8445	0.1142
H	14.3361	-22.6051	-0.0303
H	23.8404	-25.7160	-0.0007
H	12.1667	-23.4359	0.0663
H	10.5457	-25.2119	0.0406
H	13.7765	-28.0979	0.0373
H	15.3654	-26.3045	0.0686
H	20.7928	-28.0369	0.0003
H	25.0738	-27.6806	-0.0030
H	24.5173	-33.5371	0.0877
H	24.7053	-32.5562	-1.3697
H	25.5972	-31.7930	1.4614
H	26.6504	-32.2328	0.1116
H	26.4066	-29.6937	0.4822
H	26.0518	-30.2493	-1.1420
H	19.8093	-30.2238	0.4712
H	20.2661	-30.7287	-1.1438
H	20.9576	-32.1584	1.4708
H	19.9812	-32.7694	0.1291
H	22.2962	-33.7176	0.0958
H	21.9455	-32.7818	-1.3617
H	9.3547	-26.6323	-0.1069
H	9.1548	-28.2132	-0.8596
H	9.1904	-28.0722	0.9094
H	12.4916	-29.4433	-0.0816
H	11.0583	-29.7639	0.9076
H	10.9539	-29.8124	-0.8649
H	21.3373	-19.5397	-2.1207
H	22.0980	-17.1804	-2.2483
H	21.8314	-15.6790	-0.2838
H	20.8065	-16.5533	1.8072
H	20.0467	-18.9113	1.9250

Table S10. Coordinates for the energy-minimized mono-protonated form of compound **5** with the proton localized on the julolidinyl arm.

C	20.1508	-20.8107	-0.0342
C	18.7931	-21.1126	-0.0661
N	18.3464	-22.4379	0.0053
B	19.2754	-23.6766	-0.1877
N	20.7286	-23.1749	0.0853
C	21.1198	-21.8486	0.0811
C	21.8462	-23.9566	0.2059
C	22.9723	-23.1087	0.3092
C	22.5453	-21.7913	0.2338
C	17.6252	-20.2532	-0.1317
C	16.5353	-21.0848	-0.0685
C	16.9881	-22.4407	0.0126
C	20.6112	-19.3904	-0.1056
C	17.5507	-18.7608	-0.2553
C	16.1969	-23.6330	0.0853
C	23.4581	-20.6021	0.3183
C	21.7960	-25.3911	0.1869
C	14.8334	-23.6083	0.0711
C	22.9006	-26.1843	0.1607
C	13.9190	-24.7259	0.0877
C	22.9288	-27.6305	0.0614
C	12.5295	-24.4780	0.0681
C	11.5938	-25.4957	0.0274
C	11.9951	-26.8552	-0.0257
C	13.3921	-27.1113	0.0607
C	14.3138	-26.0818	0.1033
C	21.7746	-28.4431	-0.0161
C	21.8552	-29.8190	-0.1854
C	23.1275	-30.4165	-0.2462
C	24.3040	-29.6625	-0.1384
C	24.1777	-28.2859	0.0223
N	23.1947	-31.8712	-0.6344
C	24.5752	-32.5515	-0.4561
C	25.5259	-31.7463	0.4138
C	25.6590	-30.3295	-0.1437
C	20.6197	-30.6861	-0.2311
C	20.9008	-31.9819	0.5358
C	22.0443	-32.7651	-0.0964
N	11.0801	-27.8775	-0.1828
C	9.6487	-27.6309	-0.0671
C	11.4854	-29.2710	-0.0810
C	21.0710	-18.8591	-1.3193
C	21.5127	-17.5370	-1.3899
C	21.5031	-16.7324	-0.2486
C	21.0486	-17.2546	0.9640
C	20.6046	-18.5760	1.0359
F	18.9395	-24.6835	0.7247
F	19.1756	-24.1610	-1.4856
H	23.9964	-23.4298	0.4436
H	15.5020	-20.7685	-0.0845
H	18.1802	-18.3862	-1.0669
H	16.5184	-18.4592	-0.4526
H	17.8812	-18.2558	0.6577
H	16.7368	-24.5692	0.1614
H	24.4714	-20.9347	0.5603

H	23.5022	-20.0495	-0.6253
H	23.1418	-19.8896	1.0849
H	20.8019	-25.8256	0.1817
H	14.3453	-22.6368	0.0180
H	23.8797	-25.7110	0.1658
H	12.1774	-23.4491	0.0826
H	10.5448	-25.2300	0.0244
H	13.7600	-28.1289	0.0918
H	15.3691	-26.3331	0.1529
H	20.7900	-27.9912	0.0476
H	25.0838	-27.6934	0.1195
H	24.3851	-33.5451	-0.0499
H	24.9889	-32.6687	-1.4612
H	25.1714	-31.7145	1.4504
H	26.4864	-32.2721	0.4160
H	26.3635	-29.7395	0.4487
H	26.0705	-30.3719	-1.1631
H	19.7769	-30.1537	0.2172
H	20.3264	-30.9141	-1.2672
H	21.1480	-31.7406	1.5745
H	20.0261	-32.6398	0.5530
H	22.4875	-33.4620	0.6150
H	21.7053	-33.3344	-0.9673
H	9.3646	-26.7146	-0.5879
H	9.1089	-28.4537	-0.5423
H	9.3134	-27.5571	0.9787
H	12.4180	-29.4477	-0.6214
H	11.6157	-29.6046	0.9603
H	10.7183	-29.8953	-0.5457
H	21.0806	-19.4858	-2.2068
H	21.8656	-17.1368	-2.3360
H	21.8501	-15.7048	-0.3037
H	21.0386	-16.6333	1.8550
H	20.2513	-18.9820	1.9797
H	23.0481	-31.8649	-1.6454

Table S11. Coordinates for the energy-minimized mono-protonated form of compound **5** with the proton localized on the N,N-dimethylaniline arm.

C	20.1694	-20.8194	-0.0668
C	18.7706	-21.0920	-0.1321
N	18.3082	-22.3935	-0.0923
B	19.2081	-23.6572	-0.2682
N	20.6671	-23.1944	0.0326
C	21.0852	-21.8593	0.0388
C	21.7578	-23.9952	0.1529
C	22.9172	-23.1606	0.2721
C	22.5291	-21.8470	0.2071
C	17.6446	-20.2064	-0.2123
C	16.5213	-21.0195	-0.2077
C	16.9376	-22.3679	-0.1320
C	20.6446	-19.4026	-0.1084
C	17.5993	-18.7073	-0.2846
C	16.1355	-23.5528	-0.0611
C	23.4586	-20.6755	0.3116
C	21.6934	-25.4229	0.1429
C	14.7773	-23.5537	-0.1691
C	22.8087	-26.2105	0.1132
C	13.8993	-24.6946	-0.0391
C	22.8756	-27.6493	0.0614
C	12.5010	-24.4933	-0.1050
C	11.5912	-25.5310	0.0433
C	12.0638	-26.8289	0.2554
C	13.4424	-27.0718	0.3253
C	14.3387	-26.0255	0.1704
C	21.7436	-28.4919	0.0227
C	21.8464	-29.8697	-0.0466
C	23.1361	-30.4837	-0.0728
C	24.2929	-29.6532	-0.0448
C	24.1375	-28.2792	0.0305
N	23.2592	-31.8605	-0.0978
C	24.5623	-32.4911	-0.3044
C	25.6726	-31.7095	0.3925
C	25.6777	-30.2654	-0.1125
C	20.5964	-30.7243	-0.1210
C	20.8602	-32.1409	0.3925
C	22.0914	-32.7128	-0.3046
N	11.1031	-27.9634	0.5158
C	9.6770	-27.6698	0.1234
C	11.5318	-29.2701	-0.1114
C	21.0867	-18.8433	-1.3159
C	21.5318	-17.5212	-1.3611
C	21.5366	-16.7425	-0.2020
C	21.0959	-17.2919	1.0039
C	20.6492	-18.6134	1.0510
F	18.8230	-24.6517	0.6417
F	19.1089	-24.1398	-1.5654
H	23.9297	-23.5115	0.4131
H	15.4967	-20.6743	-0.2332
H	18.2483	-18.3106	-1.0699
H	16.5759	-18.3824	-0.4930
H	17.9145	-18.2380	0.6525
H	16.6796	-24.4748	0.1161
H	24.4710	-21.0262	0.5286
H	23.4898	-20.0955	-0.6159

H	23.1564	-19.9840	1.1030
H	20.7030	-25.8617	0.1422
H	14.2700	-22.6085	-0.3471
H	23.7792	-25.7169	0.1154
H	12.1208	-23.4901	-0.2749
H	10.5351	-25.2985	-0.0153
H	13.8396	-28.0654	0.5038
H	15.4001	-26.2446	0.2171
H	20.7492	-28.0540	0.0444
H	25.0319	-27.6594	0.0540
H	24.5027	-33.5094	0.0948
H	24.7839	-32.5814	-1.3815
H	25.5032	-31.7310	1.4753
H	26.6353	-32.1936	0.2002
H	26.3817	-29.6568	0.4657
H	26.0372	-30.2468	-1.1513
H	19.7891	-30.2483	0.4471
H	20.2495	-30.7798	-1.1630
H	21.0342	-32.1256	1.4748
H	19.9999	-32.7924	0.2059
H	22.3309	-33.7047	0.0942
H	21.8881	-32.8423	-1.3816
H	9.3077	-26.8224	0.6974
H	9.6511	-27.4490	-0.9437
H	9.0762	-28.5515	0.3454
H	12.4779	-29.5905	0.3185
H	10.7668	-30.0189	0.0980
H	11.6401	-29.1135	-1.1839
H	21.0863	-19.4510	-2.2164
H	21.8736	-17.1000	-2.3022
H	21.8813	-15.7133	-0.2383
H	21.0984	-16.6909	1.9089
H	20.3075	-19.0405	1.9897
H	11.0934	-28.1182	1.5301

Table S12. Coordinates for the energy-minimized doubly-protonated form of compound **5** (i.e., $\mathbf{H_2 5^{2+}}$).

C	20.1637	-20.8156	-0.0400
C	18.7832	-21.1026	-0.0783
N	18.3290	-22.4169	-0.0181
B	19.2418	-23.6719	-0.1973
N	20.7037	-23.1863	0.0648
C	21.1082	-21.8536	0.0587
C	21.8095	-23.9685	0.1870
C	22.9510	-23.1317	0.2874
C	22.5428	-21.8142	0.2118
C	17.6397	-20.2293	-0.1661
C	16.5311	-21.0548	-0.1375
C	16.9675	-22.4004	-0.0528
C	20.6292	-19.3979	-0.0972
C	17.5734	-18.7356	-0.2810
C	16.1642	-23.5974	-0.0026
C	23.4658	-20.6363	0.3031
C	21.7537	-25.4104	0.1812
C	14.8136	-23.5813	-0.1326
C	22.8614	-26.1916	0.1598
C	13.9048	-24.7152	-0.0562
C	22.9095	-27.6464	0.0749
C	12.5161	-24.4672	-0.0485
C	11.5826	-25.4884	0.0844
C	12.0226	-26.8092	0.1908
C	13.3923	-27.0968	0.1514
C	14.3133	-26.0641	0.0201
C	21.7678	-28.4702	0.0125
C	21.8640	-29.8478	-0.1555
C	23.1439	-30.4235	-0.2382
C	24.3107	-29.6546	-0.1330
C	24.1664	-28.2781	0.0312
N	23.2489	-31.8738	-0.6429
C	24.6249	-32.5560	-0.3886
C	25.5739	-31.7068	0.4385
C	25.6751	-30.3016	-0.1539
C	20.6331	-30.7217	-0.1959
C	20.9444	-32.0506	0.4964
C	22.0627	-32.7883	-0.2222
N	11.0311	-27.9103	0.4951
C	9.6174	-27.6375	0.0333
C	11.4397	-29.2806	0.0081
C	21.1497	-18.8789	-1.2922
C	21.5815	-17.5532	-1.3532
C	21.5043	-16.7373	-0.2224
C	20.9909	-17.2500	0.9710
C	20.5510	-18.5728	1.0341
F	18.8929	-24.6596	0.7327
F	19.1221	-24.1742	-1.4836
H	23.9704	-23.4651	0.4238
H	15.5029	-20.7227	-0.1678
H	18.2588	-18.3515	-1.0403
H	16.5576	-18.4343	-0.5501
H	17.8313	-18.2384	0.6595
H	16.7028	-24.5232	0.1730
H	24.4671	-20.9741	0.5822
H	23.5415	-20.1065	-0.6513

H	23.1295	-19.9050	1.0425
H	20.7606	-25.8462	0.1798
H	14.3209	-22.6246	-0.2856
H	23.8362	-25.7103	0.1654
H	12.1582	-23.4453	-0.1251
H	10.5339	-25.2216	0.1028
H	13.7698	-28.1097	0.2165
H	15.3681	-26.3133	-0.0197
H	20.7778	-28.0311	0.0846
H	25.0650	-27.6731	0.1182
H	24.4164	-33.5137	0.0871
H	25.0451	-32.7498	-1.3784
H	25.2396	-31.6553	1.4802
H	26.5437	-32.2149	0.4349
H	26.3819	-29.6900	0.4130
H	26.0661	-30.3563	-1.1803
H	19.8057	-30.2136	0.3068
H	20.3075	-30.9017	-1.2311
H	21.2225	-31.8678	1.5393
H	20.0745	-32.7153	0.5028
H	22.4797	-33.5805	0.3986
H	21.7045	-33.2349	-1.1536
H	9.2554	-26.7102	0.4699
H	9.6161	-27.5751	-1.0555
H	8.9909	-28.4632	0.3720
H	12.4027	-29.5529	0.4308
H	10.6848	-29.9937	0.3403
H	11.4936	-29.2559	-1.0810
H	21.2121	-19.5134	-2.1719
H	21.9815	-17.1596	-2.2828
H	21.8438	-15.7072	-0.2703
H	20.9305	-16.6196	1.8533
H	20.1498	-18.9699	1.9625
H	10.9878	-27.9712	1.5188
H	23.1806	-31.8406	-1.6620

Protocol used to determine the pK_A for the conjugate acid of 4 in CH_3CN.

As a starting point, it is reasonable to suppose that one proton will be attached to the julolidinyl N atom of **4**, forming the conjugate acid **4H**$^+$. The corresponding expression for the acid dissociation constant, K_A, can be written as Equation 1:

$$4H^+ \; f \quad 4 + H^+$$

$$K_A = \frac{[4][H^+]}{[4H^+]} \qquad (1)$$

Absorption spectra for the two limiting forms were derived in the absence and presence of a slight excess of HCl (Figure S15). Estimates for the pK_A were obtained from analysis of the absorption spectra recorded during the titration with HCl, after automatic correction for the effects of dilution. The commercial software SPECFIT (G. A. Kriss (1994), in *Astronomical Data Analysis Software & Systems III*, A.S.P. Conf. Series, Vol. 61, ed. D. R. Crabtree, R. J. Hanisch, & J. Barnes (Astronomical Society of the Pacific: San Francisco), p. 437) was used to conduct a multi-wavelength analysis on the basis of reversible addition of a single proton to the neutral species. The above limiting spectra were used as input parameters and the software used to determine concentrations of neutral species and conjugate acid at each pH value, the latter being calculated on the basis of complete dissociation of HCl in CH_3CN. Next, the respective concentrations were analysed in terms of the Henderson-Haselbalch equation (Eqn 2) to obtain the required pK_A (pK_A = 3.57 ± 0.05) value (Figure S16). The main error is the uncertainty in the concentration of HCl. Each titration used a total of 30 separate additions of HCl and was repeated a total of three times. The entire dataset was used for analysis. At selected wavelengths, the absorbance data were plotted in the form of the Hill expression (Eqn 3) in order to confirm the stoichiometry (n = 1.04 ± 0.02) of proton addition (Figure 17). In this latter expression, A refers to absorbance at a particular wavelength while A_{MIN} and A_{MAX} are the minimum and maximum absorbance values at that same wavelength recorded during the titration.

$$pH = pK_A + \log_{10} \frac{[4]}{[4H^+]} \qquad (2)$$

$$\log_{10} \frac{A - A_{MIN}}{A_{MAX} - A} = -\log_{10} K_A + n \log_{10} [H^+] \qquad (3)$$

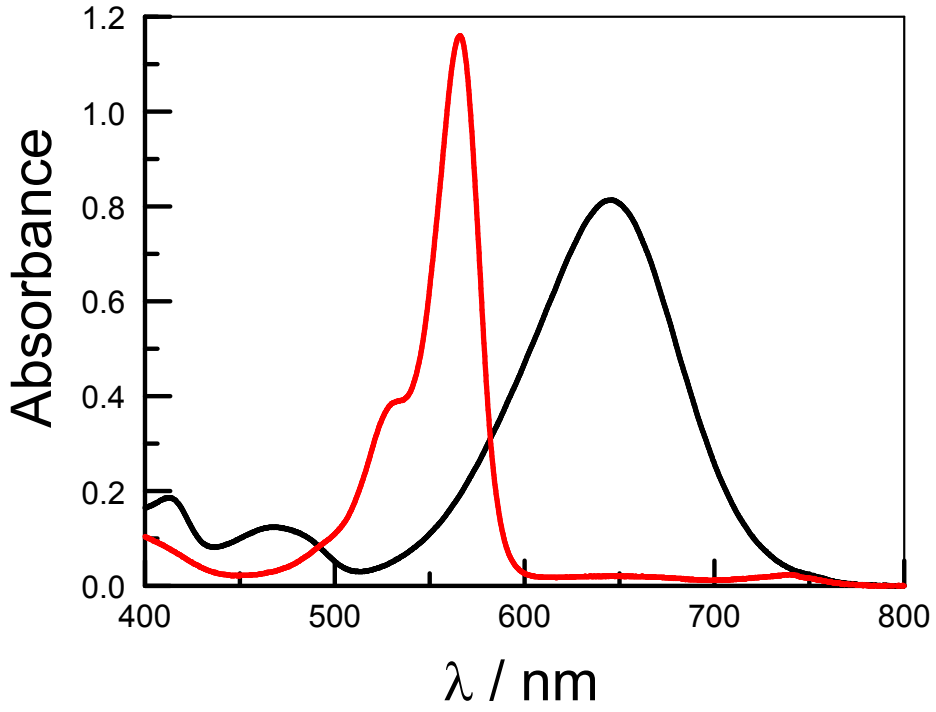

Figure S15. Limiting absorption spectra recorded for **4** (black curve) and **4H**$^+$ (red curve) in CH_3CN in the absence or presence of a slight excess of HCl, respectively.

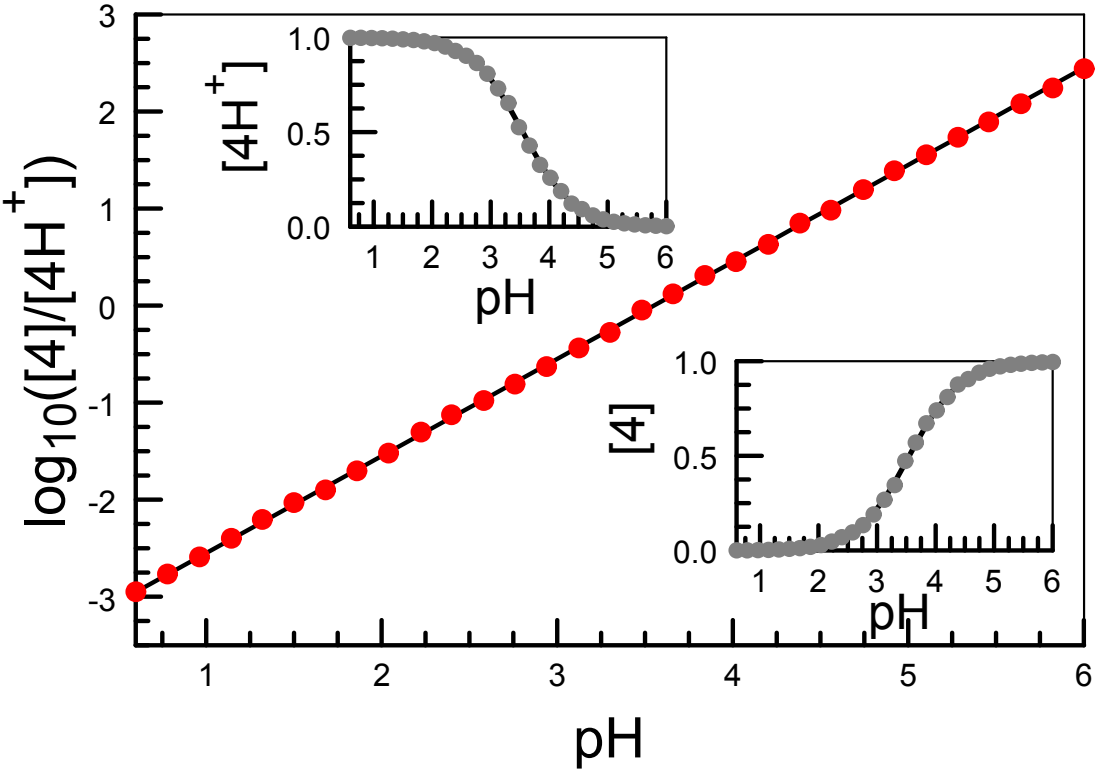

Figure S16. Example of a Henderson-Haselbalch plot constructed for **4** in CH_3CN. The inserts show the effect of pH on the concentrations of neutral species and conjugate acid.

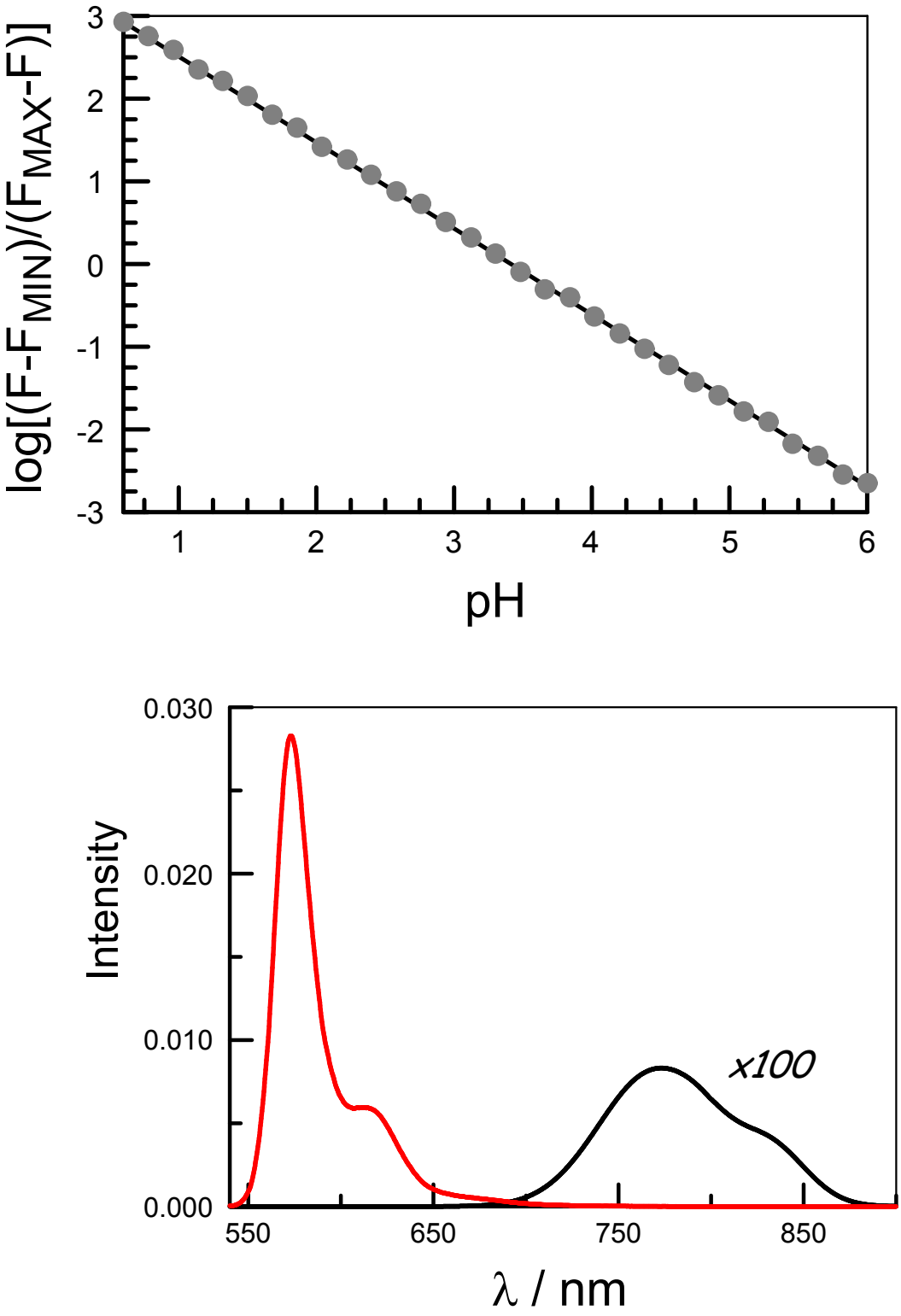

Figure S14. Limiting fluorescence spectra recorded for **4** (black curve) and **4H**$^+$ (red curve) in CH_3CN in the absence or presence of a slight excess of HCl, respectively.

The fluorescence spectral titration was analyzed similarly using global methodology with non-linear, least squares fitting of the entire spectral profile. Data collected at each wavelength were treated in terms of the Benisi-Hildebrand expression (Eqn 4) where F refers to the emission intensity at that wavelength while F_{MIN} and F_{MAX} refer to the initial and final fluorescence intensities at the same wavelength. The plot of the left side of eqn (4) versus the reciprocal of the proton concentration, assuming the stiochiometry factor n to be unity, gives a linear relationship from which the acid dissociation constant can be obtained from the ratio of gradient to intercept. This plot double-reciprocal plot separates the independent and dependent variables but requires knowledge of n and F_{MAX}. Global analysis of three separate titration runs gives pK_A = 3.52 ± 0.05, in excellent agreement with the absorption spectral data. Figure S18 gives a representative plot at a wavelength corresponding to the conjugate acid profile. Confirmation of the fact that n = 1 for this system was obtained from the corresponding Hill plots (Eqn 3, Figure 19). Further confirmation for the veracity of the derived pK_A and n parameters was obtained by fitting the fluorescence data to the Scott expression (Eqn 5).

$$\frac{1}{F - F_{MIN}} = \left(\frac{1}{F_{MAX} - F_{MIN}} \right) \left(1 + \frac{K_A}{\left[H^+ \right]^n} \right) \qquad (4)$$

$$\frac{\left[H^+ \right]^n}{F - F_{MIN}} = \left(\frac{1}{F_{MAX} - F_{MIN}} \right) \left(K_A + \left[H^+ \right]^n \right) \qquad (5)$$

In principle, further analysis could be undertaken using the excitation spectra in place of absorption spectral data but this was not done (for information on this protocol see: N. Boens, V. Leen and W. Dehaen, *Chem. Soc. Rev*., 2012, **41**, 1130-1172). Finally, it should be noted that the fluorescence ratiometric method is a popular analytical protocol for analysis of fluorescence spectral titration data (see, for example: Cielen et al., *J. Chem. Soc., Perkin Trans. 2*, 2002, 1197-1206) but this methodology is not useful here because of the very low emission yield for the neutral species.

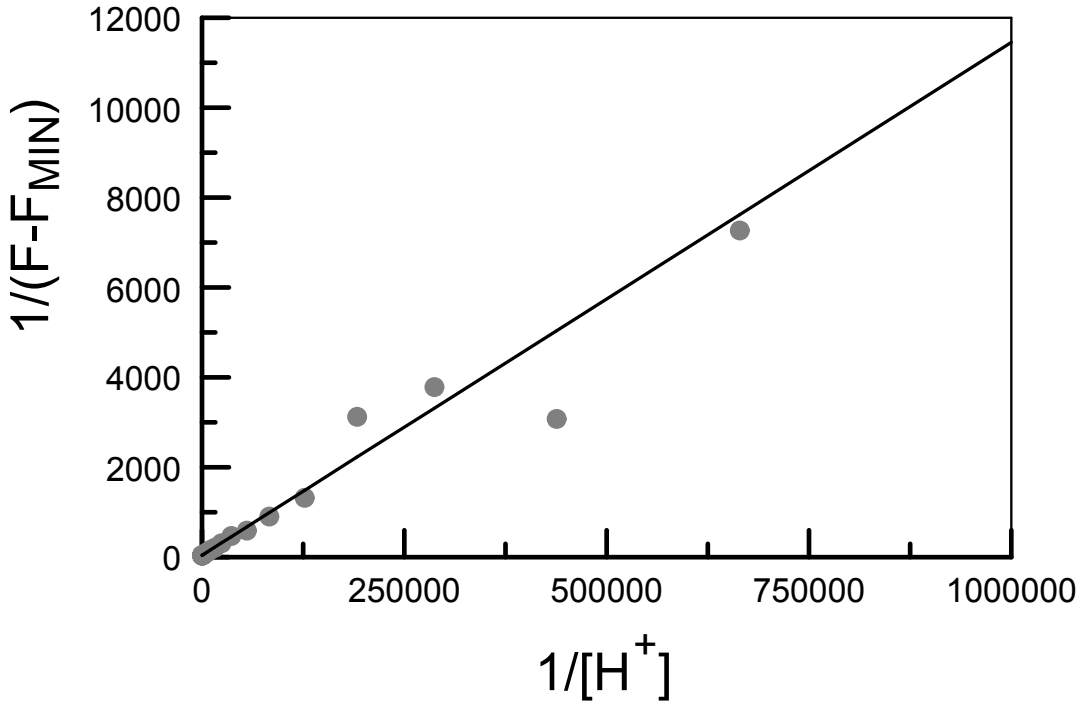

Figure S18. Representative Benesi-Hildebrand plot made for fluorescence from the conjugate acid of **4** in CH_3CN. The emission wavelength was 570 nm.

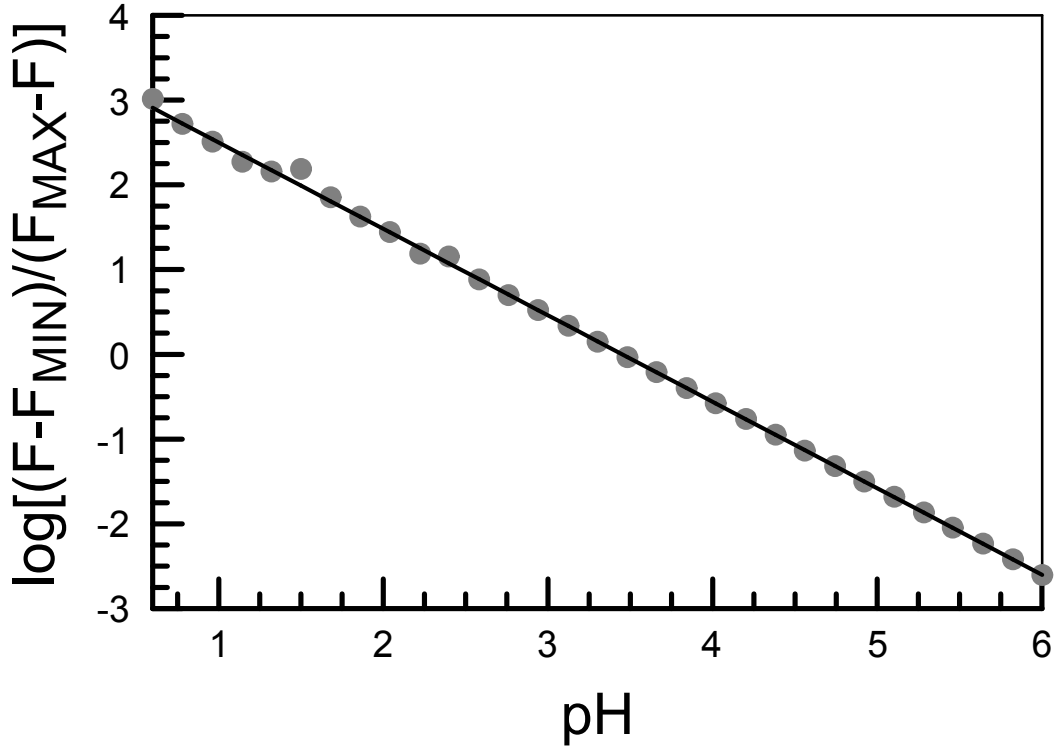

Figure S19. Representative Hill plot for emission from the emergent conjugate acid of **4** during titration with HCl. Fluorescence was collected at 570 nm.

Protocol used to determine the successive pK_A values for protonation of 5 in CH_3CN

Absorption and fluorescence spectral titrations indicate that the hybrid dye **5** undergoes two successive protonation steps in CH_3CN, the two steps being quite well resolved such that spectroscopic information can be collected for the intermediary mono-cation. This situation is similar to that reported earlier for the double protonation of certain porphyrin derivatives (see, for example: T. P. G. Sutter and P Hambright, *Inorg. Chem*., 1992, **31**, 5089-5093), although the two respective pK_A values are closer together for the porphyrins. In establishing the pK_A values for **5**, we have used global methodologies to analyze the entire absorption spectral changes induced on addition of HCl, with data analysis being based on non-linear, least-squares statistics. The starting point was to establish the three absorption and emission spectra by way of SPECFIT (Figure S20). In fact, the relevant absorption spectral profiles are quite distinctive for the three species but only the conjugate diacid emits strongly. The most appropriate analytical method, therefore, involves detailed analysis of the absorption spectrophotometric titration data.

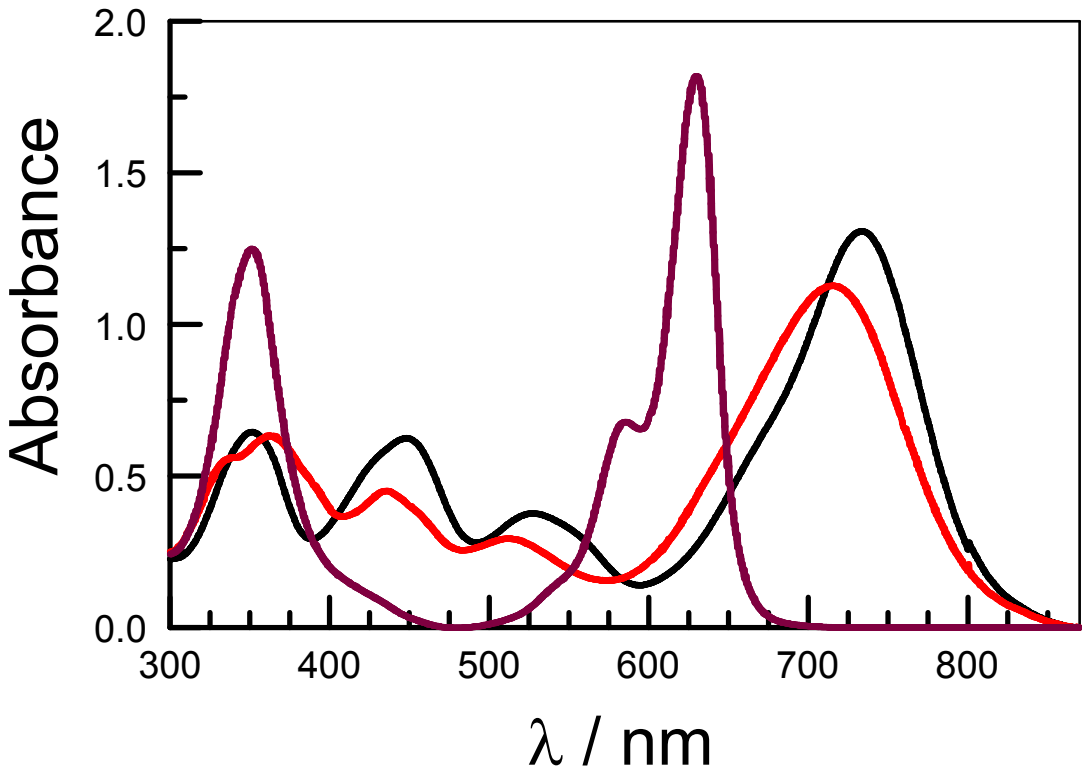

Figure S20. Derived absorption spectra for the neutral (black curve), mono-protonated (red curve), and di-protonated (brown curve) species associated with the hybrid dye **5** in CH_3CN.

It is apparent from Figure S20 that there are spectral windows where the conjugate di-acid does not absorb, notably above 700 nm and around 480 nm, such that the analysis outlined above can be used to determine the pK_A for the mono-acid. Because the molar absorption coefficients for the two species are comparable, the same is also true for the corresponding fluorescence quantum yields, the pK_A can be obtained with good accuracy. There is no spectral region, however, where spectra for the mono-acid and the di-acid are free from contamination from the neutral species. As such, the full spectral records were analyzed in terms of two successive protonation steps according to the following (Eqn. 6):

$$H_2 5^{2+} \; \mathbf{f} \quad H^+ + 5H^+ \; \mathbf{f} \quad 5 + 2H^+$$

$$K_2 = \frac{\left[H^+\right]\left[5H^+\right]}{\left[H_2 5^{2+}\right]} \qquad (6)$$

$$K_1 = \frac{\left[H^+\right]^2 \left[5\right]}{\left[5H^+\right]}$$

It is safe to assume that the total concentration, C_T, remains constant throughout the titration, although there is a very minor build-up of a species absorbing at long wavelength if too much acid is added (Eqn. 7).

$$C_T = \left[5\right] + \left[5H^+\right] + \left[H_2 5^{2+}\right]$$

$$\left[5\right] = C_T \times \frac{K_1 K_2}{K_1 K_2 + K_2\left[H^+\right] + \left[H^+\right]^2}$$

$$\left[5H^+\right] = C_T \times \frac{K_2\left[H^+\right]}{K_1 K_2 + K_2\left[H^+\right] + \left[H^+\right]^2} \qquad (7)$$

$$\left[H_2 5^{2+}\right] = C_T \times \frac{\left[H^+\right]^2}{K_1 K_2 + K_2\left[H^+\right] + \left[H^+\right]^2}$$

At any given wavelength, λ, the absorbance of each species can be determined from the Beer-Lambert law using the molar absorption coefficients extracted from the SPECFIT analysis.

$$A_1 = \varepsilon_1\left[5\right]; A_2 = \varepsilon_2\left[5H^+\right]; A_3 = \varepsilon_3\left[H_2 5^{2+}\right]$$

The total absorbance, A_T, at that wavelength as measured at any point during the titration will be given by:

$$A_T = \frac{A_3\left[H^+\right]^2 + A_2K_2\left[H^+\right] + A_1K_1K_2}{\left[H^+\right]^2 + K_2\left[H^+\right] + K_1K_2} \qquad (8)$$

Here, $A_1 = \varepsilon_1 C_T; A_2 = \varepsilon_2 C_T; A_3 = \varepsilon_3 C_T$. We can also define the following parameters:

$$S_1 = A_1K_1K_2$$
$$S_2 = A_2K_2$$
$$S_3 = A_3$$
$$S_4 = K_4$$
$$S_5 = K_1K_2$$

Now, we are able to define the total absorbance at that wavelength as a function of pH:

$$A_T\left(pH\right) = \frac{S_3 \times 10^{-2\,pH} + S_2 \times 10^{-pH} + S_1}{10^{-2\,pH} + S_4 \times 10^{-pH} + S_5} \qquad (9)$$

Non-linear fitting of the titration data in the form of A_T vs pH was performed using MATLAB with the Marquardt-Levenberg algorithm to extract values for the parameters S_1 to S_5. The entire dataset was used for such analysis, carried out at all wavelengths. Once these parameters had been averaged, it becomes a simple task to derive values for K_1 and K_2. Figure S21 shows a typical fit at a single wavelength. Finally, shown in Figure S22 is the calculated distribution of species as a function of pH. For more detailed information of fitting absorption spectral data to successive protonation steps see: S. Thyagarajan et al., *Inorg. Chem*., 2010, **49**, 9909-9920.

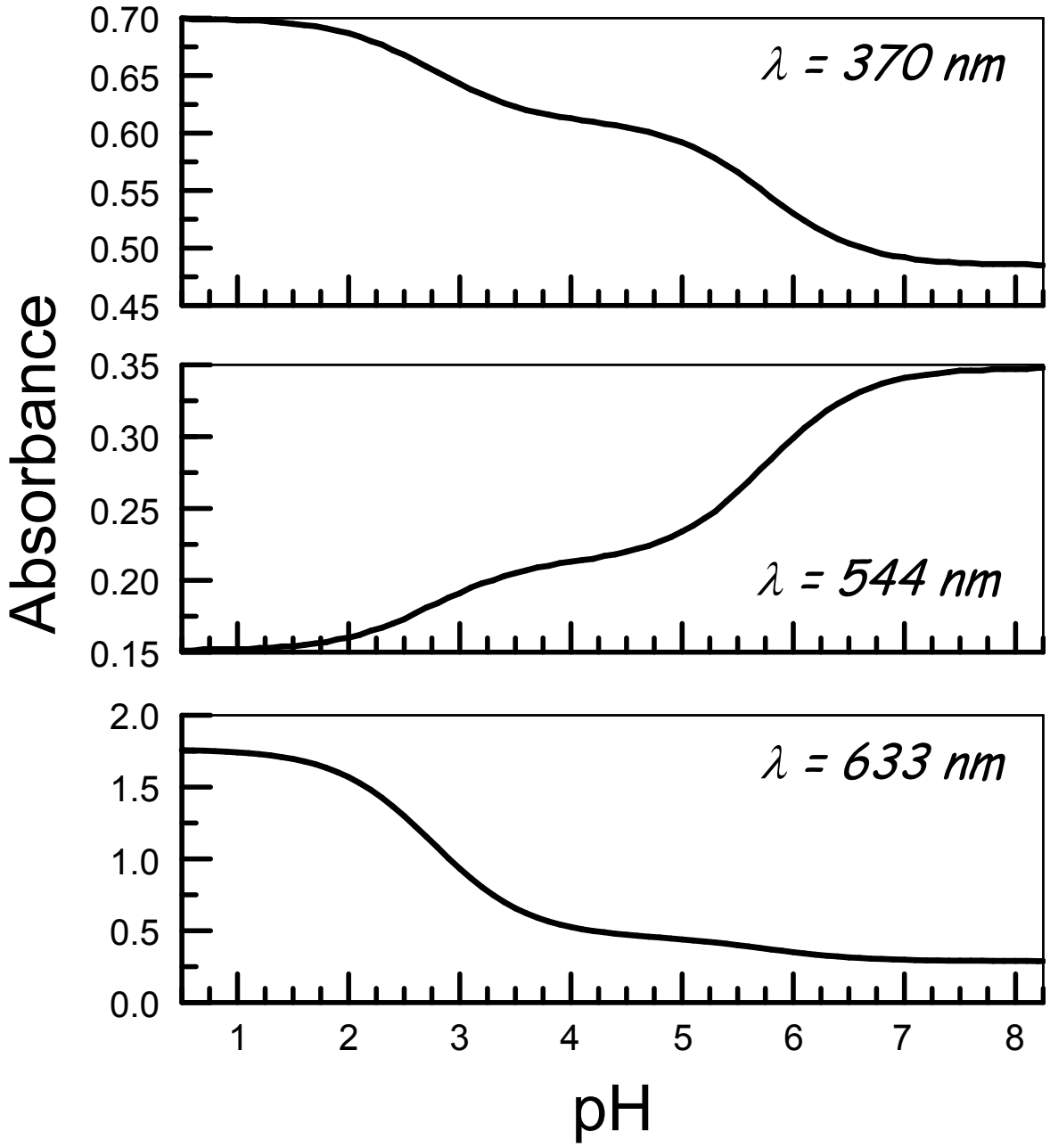

Figure S21. Effect of pH on the solution absorbance at specific wavelengths for titration of **5** with HCl in CH_3CN.

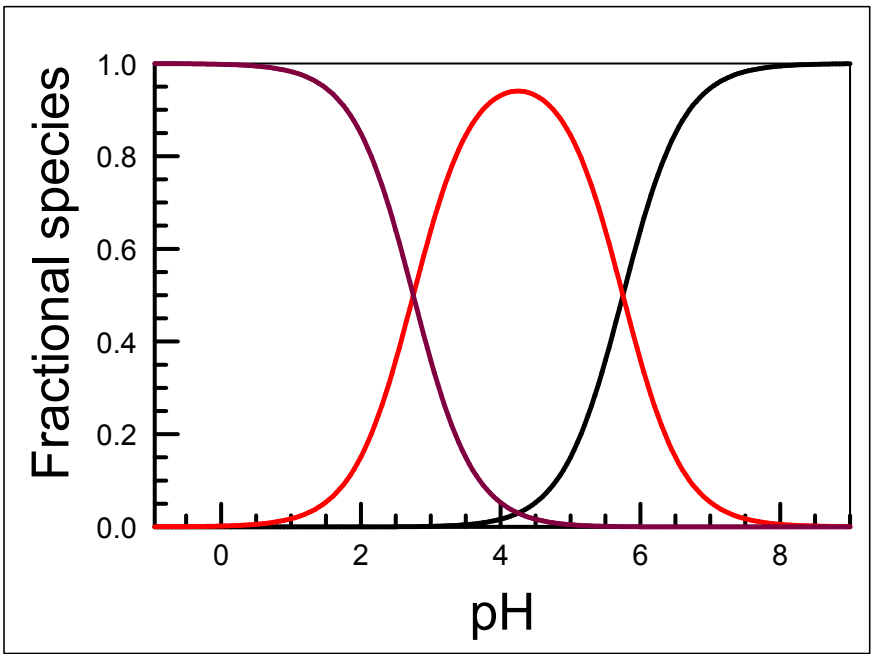

Figure S22. Calculated distribution pattern for the various protonated species relevant to **5** as a function of pH: black curve refers to the neutral species **5**, red curve is for the mono-cation $\mathbf{5H^+}$, and brown curve is for the conjugate diacid $\mathbf{H_25^{2+}}$.

At wavelengths where the conjugate diacid does not absorb or emit, the pK_A for the interconversion between neutral species and mono-cation can be determined from the following expression (Eqn. 10):

$$A_\lambda(pH) = B_1 \frac{10^{pH-pK_A}}{1+10^{pH-pK_A}} + B_2$$
$$B_1 = C_T(\alpha - \beta) \qquad (10)$$
$$B_2 = C_T\beta$$

Here, α and β refer respectively to the molar absorption coefficients for neutral species and mono-cation at that wavelength. Typical absorbance vs pH profiles are shown in Figure S23 for a near isobestics point at 710 nm and for wavelengths where the absorbance is in favour of either the neutral species (i.e., 750 nm) or the mono-cation (i.e., 680 nm). Similar analysis can be made by fluorescence spectroscopy.

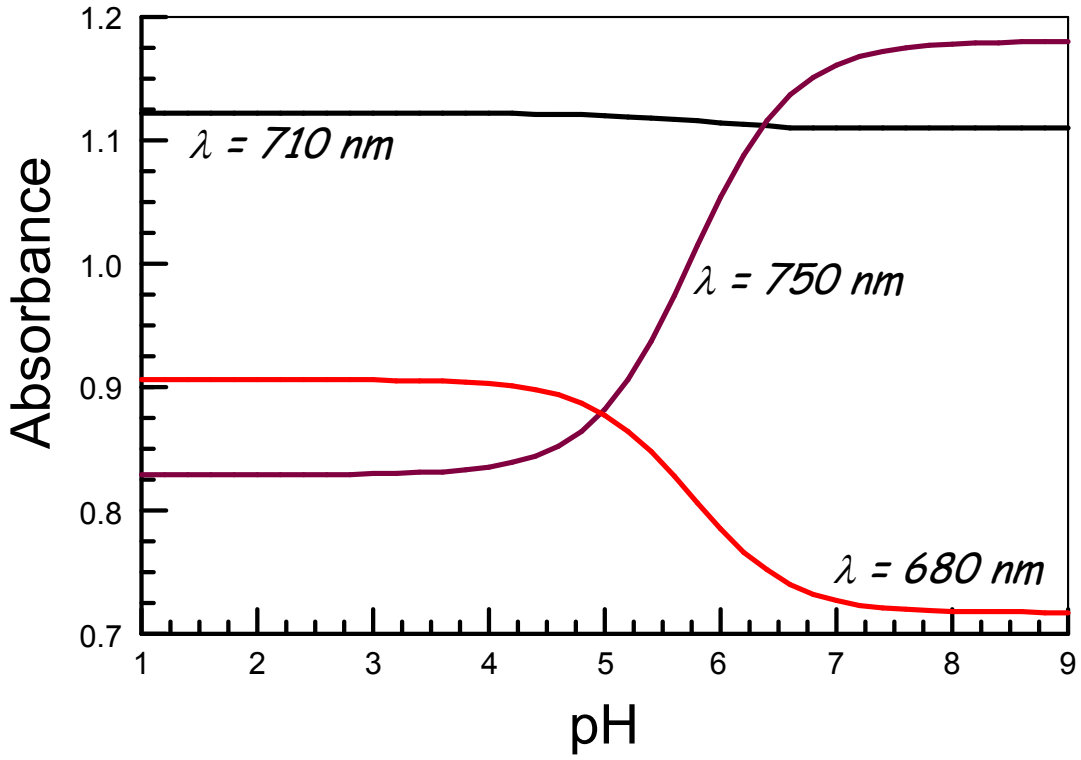

Figure S23. Effect of pH on the solution absorbance at specific wavelengths for titration of **5** with HCl in CH_3CN.