Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Spectral observation of conversion between ionized versus non-ionized proton-coupled electron transfer interfaces

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Experimental Procedures

Materials. Solvents were purchased from VWR Scientific Products or Sigma Aldrich and dried using standard solvent drying techniques.[1] Other reagents were purchased from Aldrich, Acros or Strem Chemicals and used as received. Purpurin-amidinium (**1**) and tetrabutylammonium phenylsulfonate (**3**) were prepared as described previously.[2] Tetrabutylammonium acetate (**4**) was purchased from Aldrich and used without further purification.

Physical methods. ^{1}H-NMR spectra were recorded at the MIT Department of Chemistry Instrumentation Facility (DCIF) on a Varian Mercury 300 spectrometer. All chemical shifts are reported using the standard δ notation in parts-per-million; positive chemical shifts are to higher frequency from the given reference. UV-visible absorption spectra were recorded on a Spectral Instruments 440 diode array spectrophotometer with greater than 1 nm band-width. Soret peak positions for all titrations were within 1 nm for a given solvent for at least three different experiment al runs.

Samples of purpurin-amidinium (**1**) used for absorption spectroscopy were contained within a high-vacuum cell consisting of a 1-cm pathlength clear fused-quartz cell (Starna cells), which was connected to a 10-cm^3 solvent reservoir via a graded seal. The two chambers were isolated from the environment and from each other by high-vacuum Teflon valves. An aliquot of **1** (~6×10^{-8} mol) was added to the cell, and an initial aliquot of **2**, **3**, **4**, **5**, **6** or DMAP (4-dimethylaminopyridine) was added to the solvent reservoir. The transferring solvent was removed from both compartments on a high-vacuum manifold (10^{-5} torr). Three milliliters of dry THF, DCM or ACN was subject to at least three freeze-pump-thaw cycles (10^{-5} torr) and added to the cell by vacuum transfer to make a 20 μM solution of **1**. Both chambers were sealed and removed from vacuum. In this configuration, the first absorption spectrum of **1** was recorded. The valve between the two compartments was then open to expose **1** to the binding moiety (BM) while maintaining high vacuum and exactly the same amount of compound and solvent. A second absorption spectrum was recorded. Before a BM was dropped into the vessel, the solvent was transferred into the cuvette with a dry ice/acetone bath and sealed. The solvent reservoir was open and a second addition of BM was added. The same procedure was followed to remove the transferring solvent and expose **1** to a second addition of BM. This procedure was performed for each addition of BM to ensure that the sample remained under vacuum and the solvent volume remained constant.

Compound **1** exhibits spectral shifts with the acidity of the surrounding dielectric environment. The sensitivity of the purpurin chromophore to protons is obviated by reduction of the five-membered isocyclic ring of **1** to form a chlorin**.** As shown by Figure S1the absorption spectrum

1. W. L. F. Armarego and D. D. Perrin, in *Purification of Laboratory Chemicals*; Butterworth-Heinmann: Oxford, 4th ed. 1996.
2. Rosenthal, J.; Hodgkiss, J. M.; Young, E. R.; Nocera, D. G. *J. Am. Chem. Soc.* **2006**, *128*, 10474-10483.

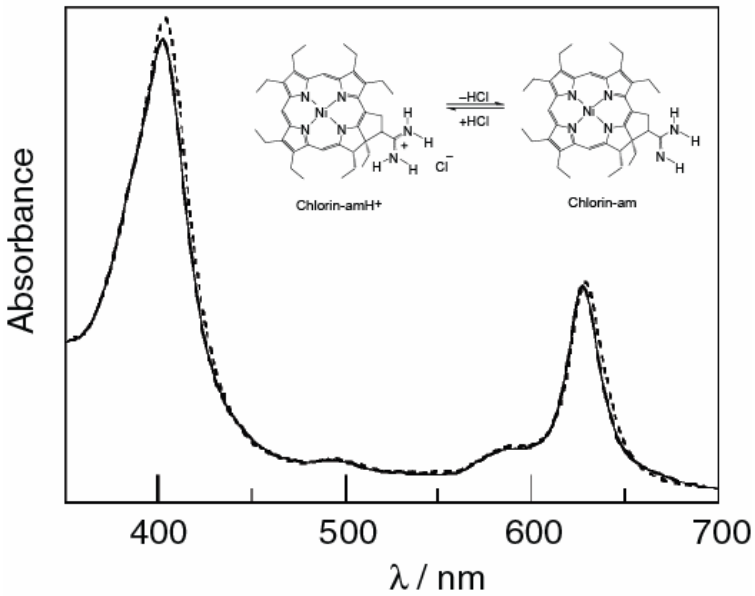


Figure S1. Absorption spectra of chlorin (0.90×10^{-6} M) (i.e., purpurin **1** with a reduced isocyclic ring, in the absence (—) and presence (·····) of 3.00 equivalents of DBU in CH_2Cl_2 (see ref. 10).

of the chlorin, unlike **1,** is invariant to pH. A Benesi-Hildebrand plot was developed for the spectral shift of the final Soret band ($1/\Delta A_{Soret}$ vs. 1/[BM]) of **1** upon its titration with each BM in each solvent. The binding constant K_{assoc} is obtained from the ratio of the *y*-intercept and slope.[3] Linearity of the data points confirms 1:1 binding stoichiometry.

Spectral analysis was performed to aid assignment the end-point configuration of the interface for each BM titration: ionized or non-ionized. The spectral contribution of the unbound **1-amH**$^+$ species was removed to leave a residual trace indicative of the bound species. In the cases where the residual peaks of the BM titration matched to within 1 nm of the DMAP difference trace, the interface was categorized as non-ionized. When the difference spectra showed greater variation compared to the deprotonated standard, DMAP, the interface was characterized at ionized. In all cases, the magnitude of the peak shift obtained for difference spectra analysis matches the raw Soret peak differences except for **4** in DCM. The Soret peak shift for this latter system is ~2 nm and the difference analysis yields <1 nm shift. The interface has been classified as non-ionized based on (1) the general characteristics of the final spectrum i.e. disappearance of the shoulder to the blue of the Soret and (2) the less than 1 nm shift of the difference spectrum. Significant contribution of the unbound **1** in the final spectrum, which is removed upon difference spectra analysis may lead to this discrepancy. We note that the data presented for THF and DCM was qualitative in nature; all quantitative analysis was performed on the ACN system for which there was no discrepancy between difference analysis and raw data.

Tetrabutylammonium 3,5-Dinitrobenzoate (2). To a flask containing 3,5-dinitrobenzoic acid (0.47 g, 1.5 mmol) in 100 mL diethyl ether was added 1.5 mL of a 1.0 M solution of

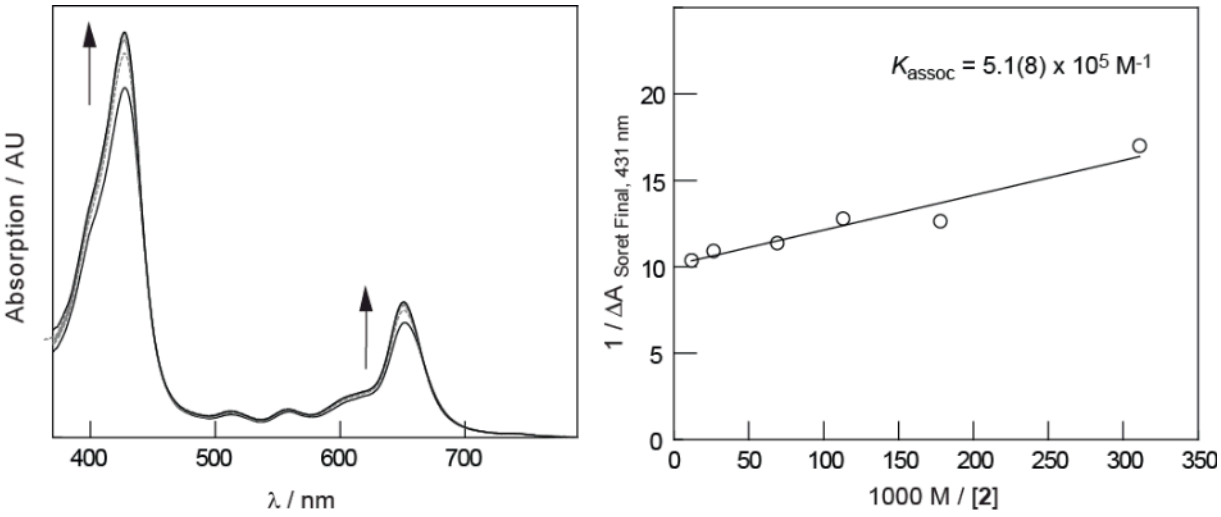
3. Connors, Kenneth A. In Binding Constants: A Measurement of Molecular Complex Stability; Wiley: New York, 1987.

tetrabutylammonium hydroxide in methanol (1.5 mmol tetrabutylammonium hydroxide). The mixture was stirred for ten minutes or until the acid was completely dissolved. After removal of the solvent under reduced pressure, a viscous oil persisted. The oil was dissolved in benzene and lyopholized to produce a white solid. The solid was triturated with diethyl ether to remove additional impurities. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C), δ/ppm: 8.88 (s, 2H), 8.75 (s, 1H), 3.13 (m, 8H), 1.58 (m, 8H), 1.30 (m, 8H), 0.93 (t, 12H).

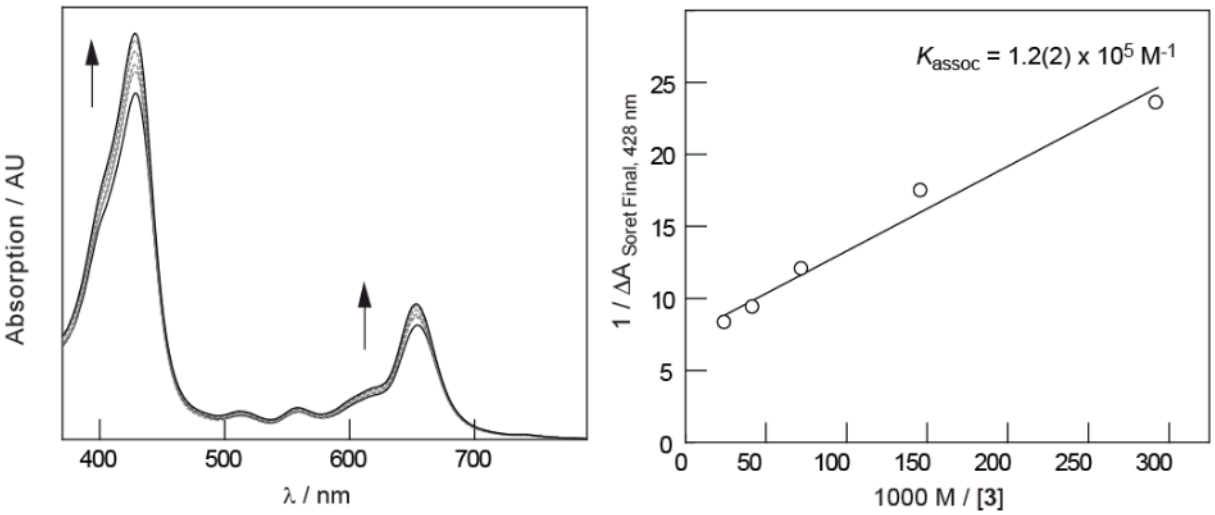
Tetrabutylammonium chloroacetate (5). Deprotonation of chloroacetic acid was accomplished in a manner identical to that outlined for the synthesis of **2**, above, using 0.14 g (1.5 mmol) of chloroacetic acid. ^{1}H NMR (300 MHz, DMSO, 25 ^{o}C), δ/ppm: 3.63 (s, 2H) 3.15 (m, 8H), 1.58 (m, 8H), 1.30 (m, 8H), 0.92 (t, 12H).

Synthesis of Tetrabutylammonium dichloroacetate (6) Deprotonation of dichloroacetic acid was accomplished in a manner identical to that outlined for the synthesis of **2**, above, using 0.19 g (1.5 mmol) of dichloroacetic. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C), δ/ppm: 3.15 (m, 8H), 2.08 (s, 2H), 1.54 (m, 8H), 1.30 (m, 8H), 0.93 (t, 12H)

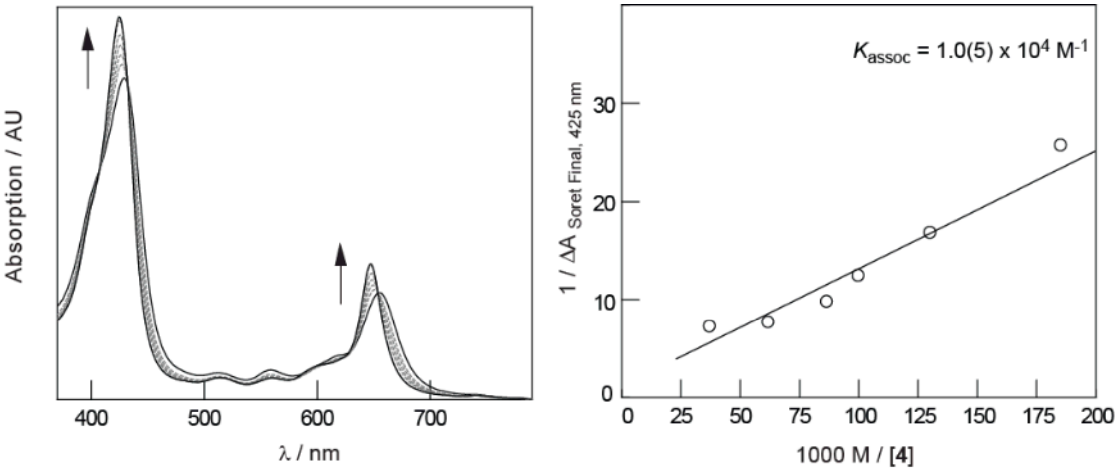
Figure S2. Spectral shifts and Benesi-Hildebrand plots for titrations in THF



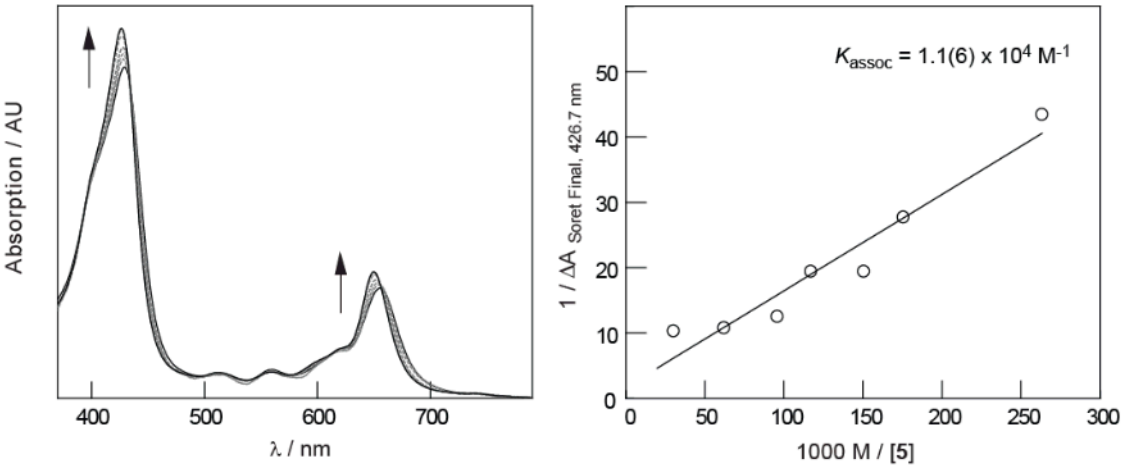
Titration of **1** with **2** in THF a) absorption band shifts upon addition of **2**, b) Benesi-Hildebrant (B-H) Plot. Spectra and B-H shown for addition of 0.4, 0.7, 1.1, 1.8, 4.7 and 10.5 equivalents of **2**.



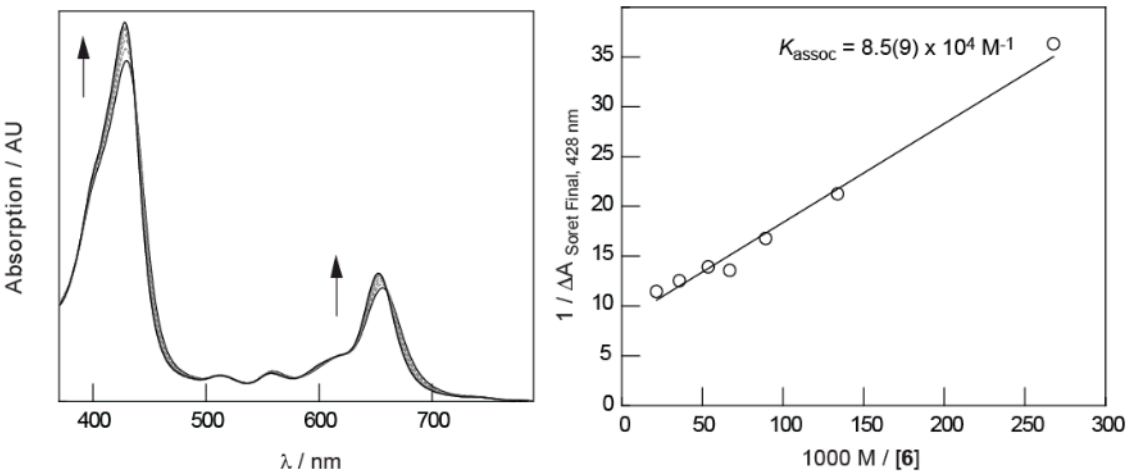
Titration of **1** with **3** in THF a) absorption band shifts upon addition of **3**, b) Benesi-Hildebrant (B-H) Plot. Spectra and B-H shown for addition of 0.4, 0.8, 1.6, 2.8 and 4.8 equivalents of **3**.



Titration of **1** with **4** in THF a) absorption band shifts upon addition of **4**, b) Benesi-Hildebrant (B-H) Plot. Spectra and B-H shown for addition of 0.7, 1.0, 1.3 , 1.5, 2.1 and 3.5 equivalents of **4**.

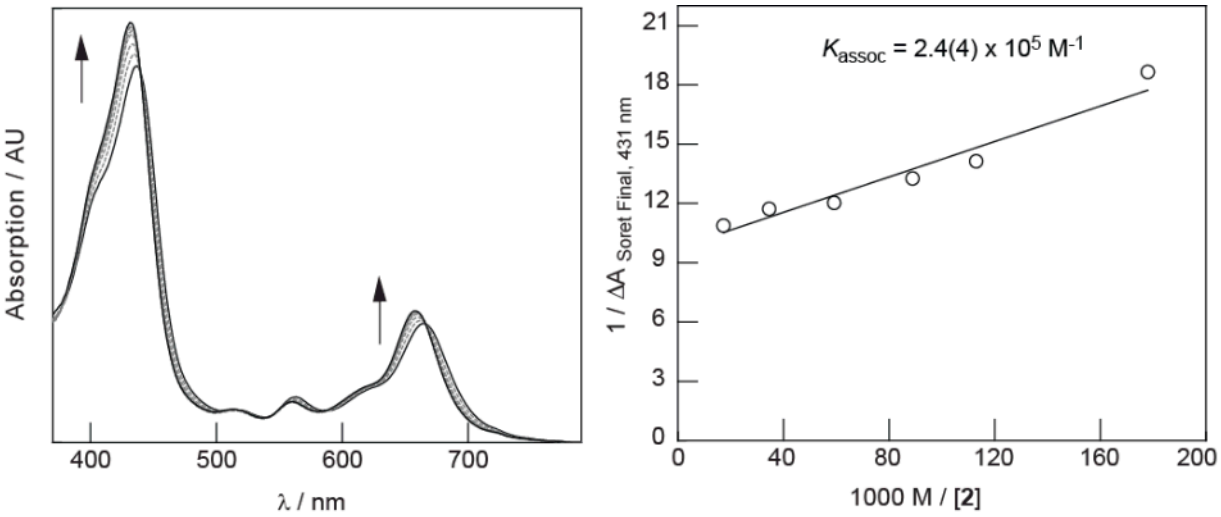


Titration of **1** with **5** in THF a) absorption band shifts upon addition of **5**, b) Benesi-Hildebrant (B-H) Plot. Spectra and B-H shown for addition of 0.4, 0.6, 0.7, 0.9, 1.1, 1.7 and 3.5 equivalents of **5**.

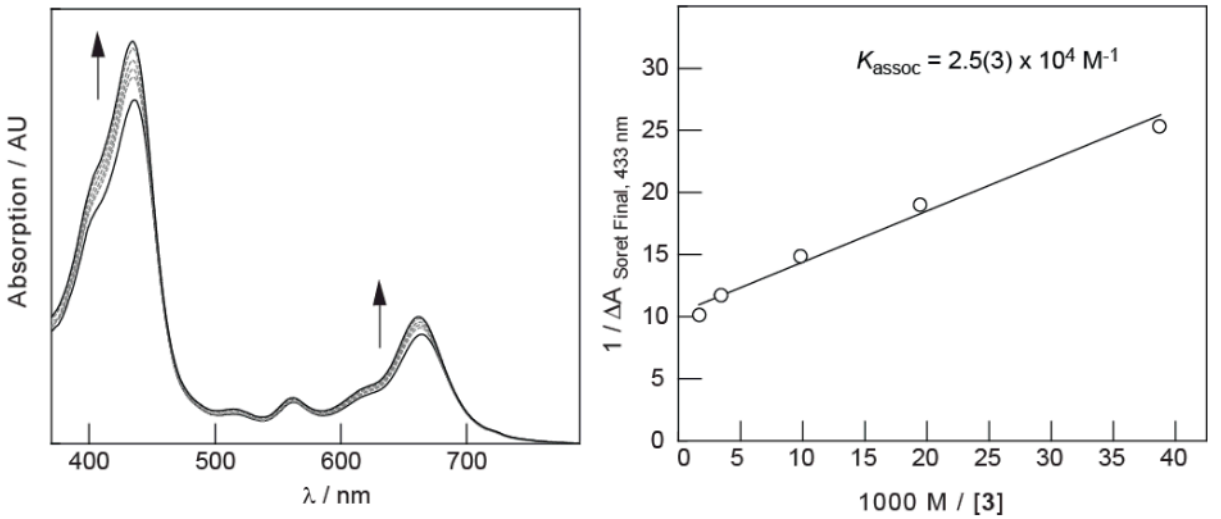


Titration of **1** with **6** in THF a) absorption band shifts upon addition of **6**, b) Benesi-Hildebrant (B-H) Plot. Spectra and B-H shown for addition of 0.4, 0.8, 1.2, 1.6, 2.0, 3.0 and 5.0 equivalents of **6**.

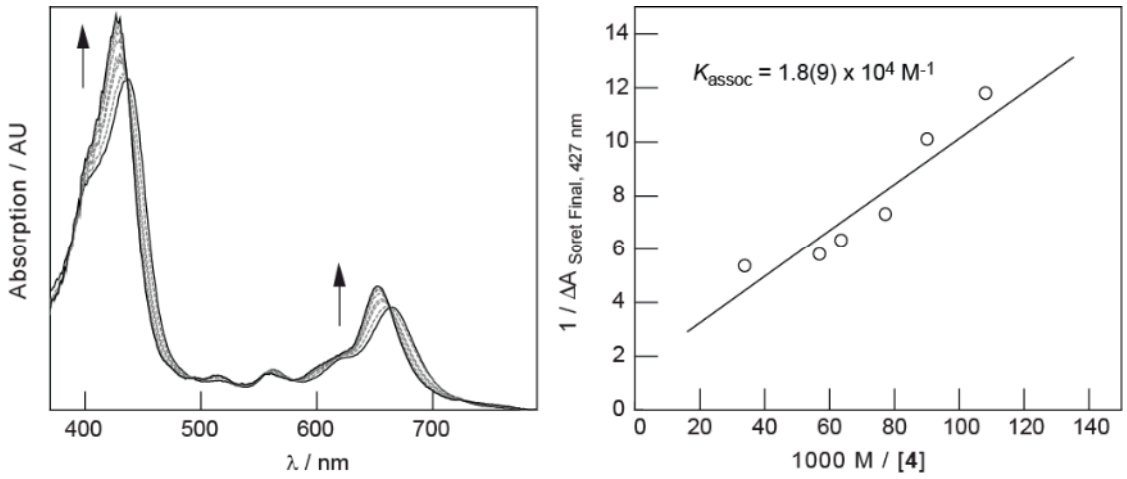
Figure S3. Spectral shifts and Benesi-Hildebrand plots for titrations in DCM



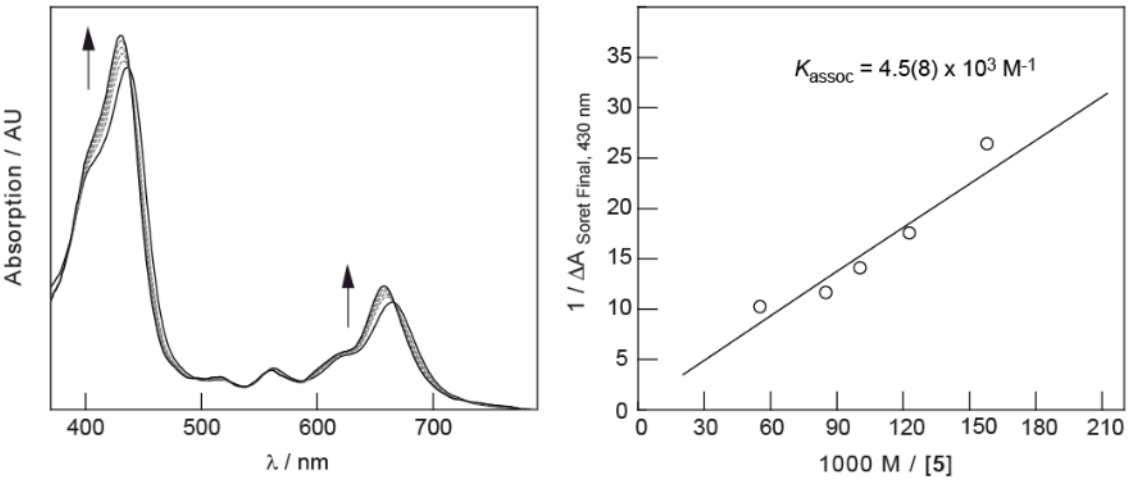
Titration of **1** with **2** in DCM a) absorption band shifts upon addition of **2**, b) Benesi-Hildebrant (B-H) Plot. Spectra and B-H shown for addition of 0.4, 0.7, 1.1, 1.4, 2.1, 3.6 and 7.2 equivalents of **2**.



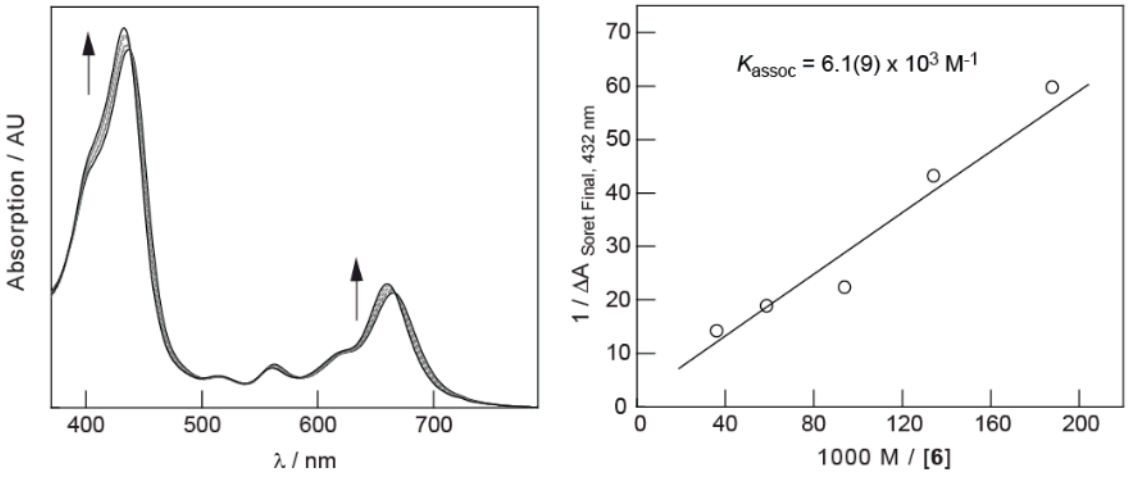
Titration of **1** with **3** in DCM a) absorption band shifts upon addition of **3**, b) Benesi-Hildebrant (B-H) Plot. Spectra and B-H shown for addition of 3.5, 7, 14, 42 and 84 equivalents of **3**.



Titration of **1** with **4** in DCM a) absorption band shifts upon addition of **4**, b) Benesi-Hildebrant (B-H) Plot. Spectra and B-H shown for addition of 1.0, 1.2, 1.4, 1.7, 1.9, and 3.2 equivalents of **4**.

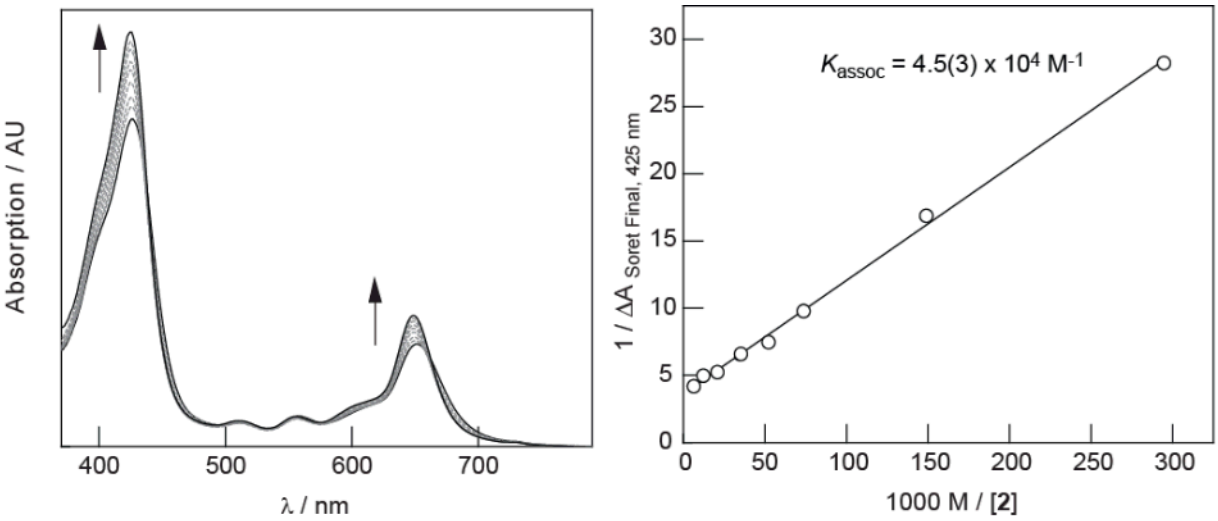


Titration of **1** with **5** in DCM a) absorption band shifts upon addition of **5**, b) Benesi-Hildebrant (B-H) Plot. Spectra and B-H shown for addition of 0.7, 0.9, 1.1 and 1.3 equivalents of **5**.

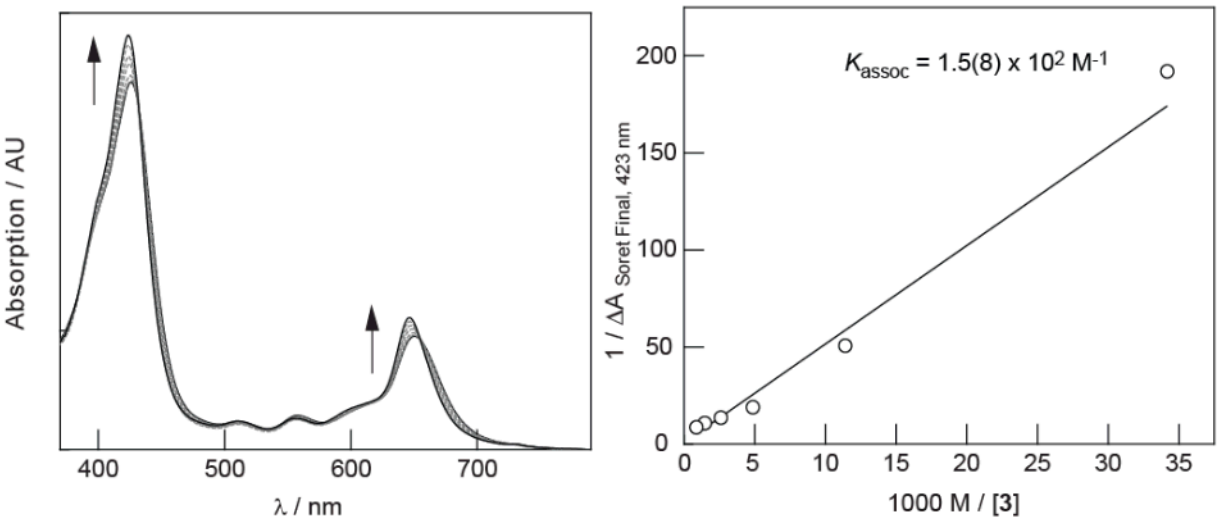


Titration of **1** with **6** in DCM a) absorption band shifts upon addition of **6**, b) Benesi-Hildebrant (B-H) Plot. Spectra and B-H shown for addition of 0.5, 0.7, 1.0, 1.6 and 2.6 equivalents of **6**.

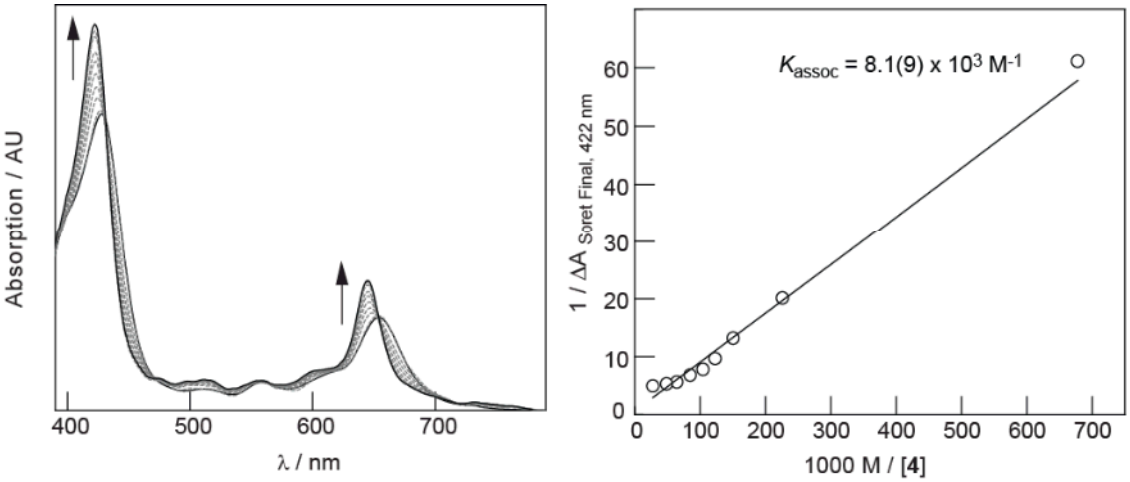
Figure S4. Spectral Shifts and Benesi-Hildebrand plots for titrations in ACN



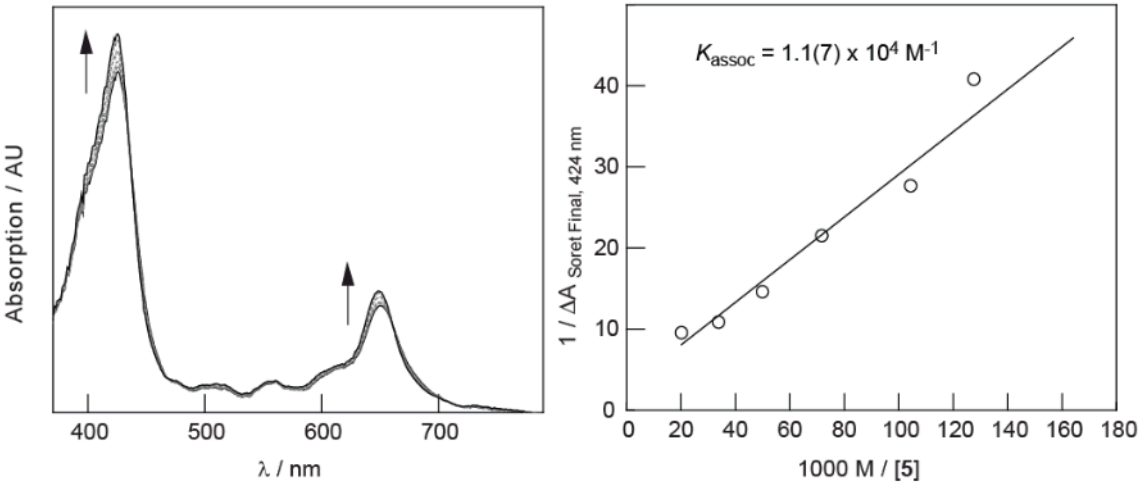
Titration of **1** with **2** in ACN a) absorption band shifts upon addition of **2**, b) Benesi-Hildebrant (B-H) Plot. Spectra and B-H shown for addition of 0.3, 0.6, 1.2, 1.7, 2.6, 4.3, 7.2, and 13 equivalents of **2**.



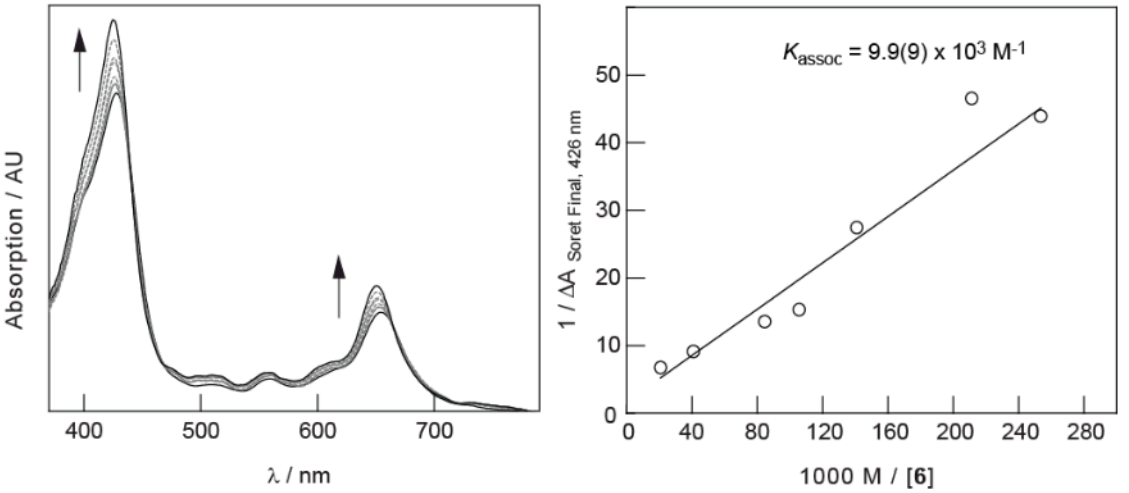
Titration of **1** with **3** in ACN a) absorption band shifts upon addition of **3**, b) Benesi-Hildebrant (B-H) Plot. Spectra and B-H shown for addition of 2.4, 7.2, 16.8, 31.2, 55.2 and 93.5 equivalents of **3**.



Titration of **1** with **4** in ACN a) absorption band shifts upon addition of **4**, b) Benesi-Hildebrant (B-H) Plot. Spectra and B-H shown for addition of 0.1, 0.4, 0.6, 0.9, 1.1, 1.3, 1.6, 2.1, 2.8, and 4.9 equivalents of **4**.



Titration of **1** with **5** in ACN a) absorption band shifts upon addition of **5**, b) Benesi-Hildebrant (B-H) Plot. Spectra and B-H shown for addition of 0.9, 1.1, 1.6, 2.3, 3.4 and 5.7 equivalents of **5**.



Titration of **1** with **6** in ACN a) absorption band shifts upon addition of **6**, b) Benesi-Hildebrant (B-H) Plot. Spectra and B-H shown for addition of 0.5, 0.6, 0.9, 1.2, 1.5, 3.1 and 6.1 equivalents of **6**.