Supporting Information

Conformationally Adaptable Macrocyclic Receptors for Ditopic Anions: Analysis of Chelate Cooperativity in Aqueous Containing Media

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General Remarks

All starting materials and solvents were purchased from commercial sources and used without further purification unless stated otherwise. All NMR data were recorded on Bruker Avance III 400 or Bruker Avance III 500 spectrometers and referenced to the indicated solvent at 298 K. Chemical shifts are reported on the delta scale and abbreviations used for spin multiplicity of peaks include: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad.
High resolution ESI spectra were recorded on a Bruker BioApex Qe 7T Fourier Transform Ion Cyclotron Resonance mass spectrometer (FTICR) with an Apollo Dual source. Analytical TLC was performed using precoated silica gel plates (Merck Kieselgel 60 F254). Fluorescence spectra were recorded on a Cary Eclipse fluorescence spectrophotometer and UV-Vis spectra were recorded on a Cary 4000 UV-Vis spectrophotometer at 298 K. Compounds **4**,[1] **6** and **7**[2] were prepared according to literature procedures.

1 – Overview of Compounds

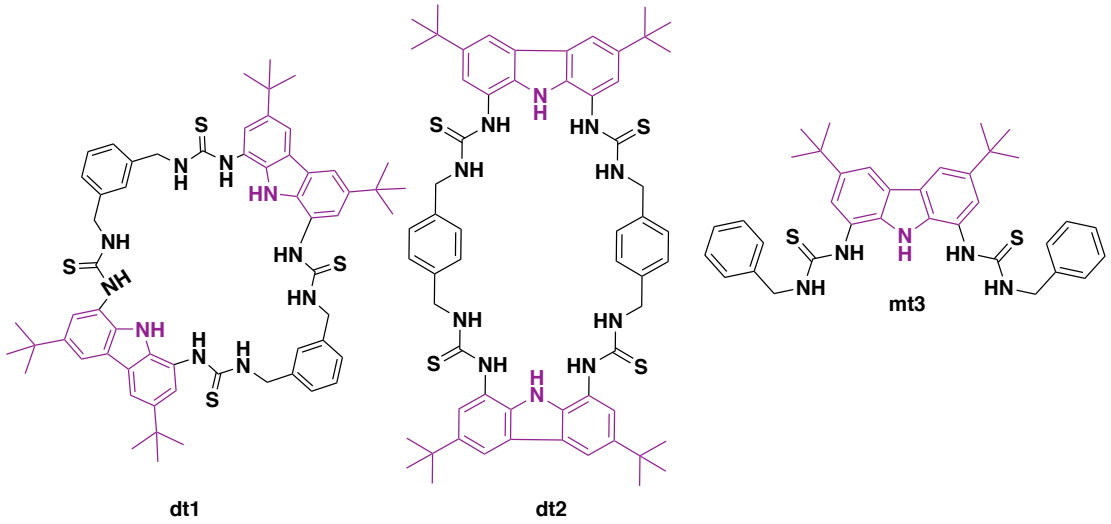
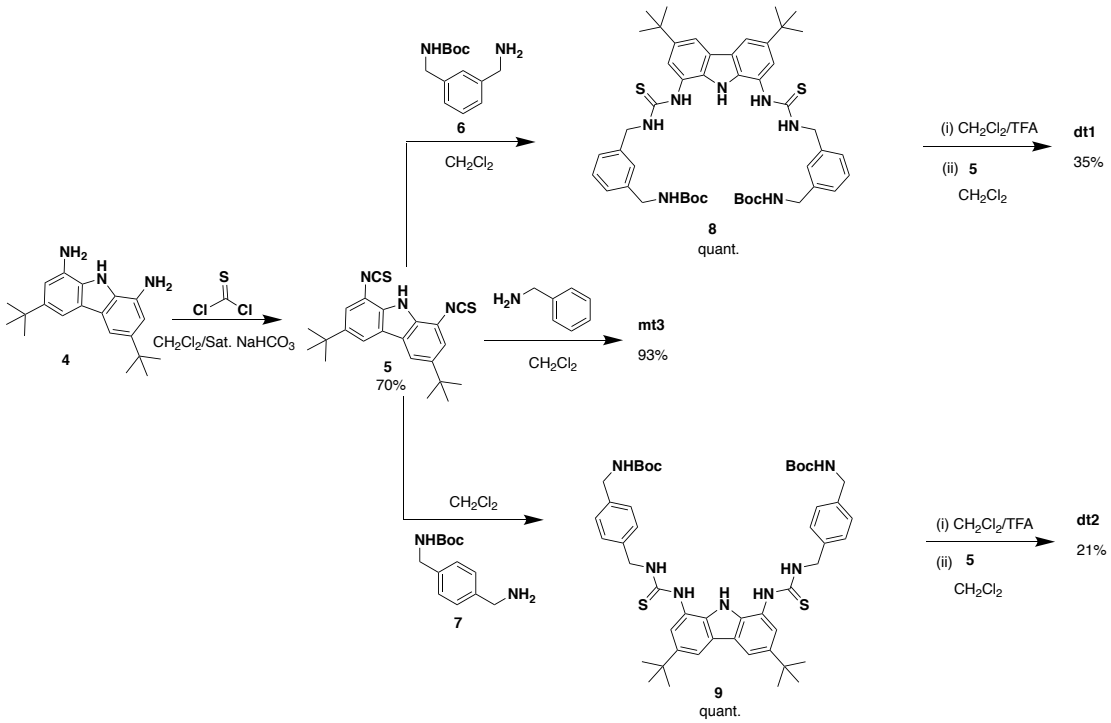


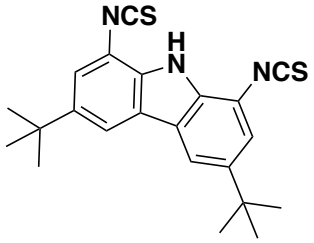
Figure S1: Structures of thiourea macrocycles **dt1** and **dt2** and open thiourea **mt3**.

2 – Synthesis



Scheme S1: Synthesis of thiourea macrocycles **dt1** and **dt2** and open thiourea **mt3**.

Synthesis of 3,6 di-*tert*butyl carbazole 1,8 diisothiocyanate (5):



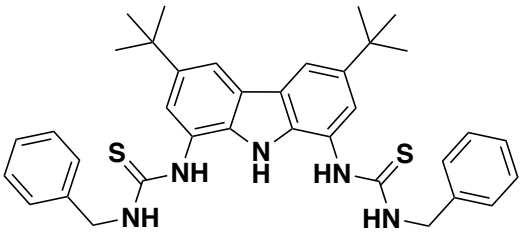
3,6 di-tertbutyl, 1,8 diaminocarbazole **4**[1] (0.4 g) was dissolved in dichloromethane (125 mL). Added to this was sat. $NaHCO_3$ (125 mL) and the biphasic mixture rapidly stirred. Thiophosgene (0.3 mL, 3 equivs) was added dropwise and the reaction stirred overnight. The organic phase was separated and washed with H_2O (3 x 100 mL) and the solvent removed under pressure. The residue was purified by column chromatography in hexane/30% ethyl acetate to give the product as a white solid (0.35 g, 68%).

^{1}H NMR (400 MHz, $CDCl_3$): δ: 8.35 (s, 1H), 7.95 (d, 2H, J = 1.24 Hz), 7.40 (d, 2H, J = 1.56 Hz), 1.53 (2, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): 139.8, 128.4, 120.2, 117.1, 113.3, 111.5, 110.0, 30.2, 27.1.

HRMS (ESI) calcd. for $C_{22}H_{22}N_3S_2$ $[M-H]^-$ 392.1261, found 392.1260.

Synthesis of 3,6 di*tert*butyl carbazole, 1,8 di(benzyl thiourea) (mt3)



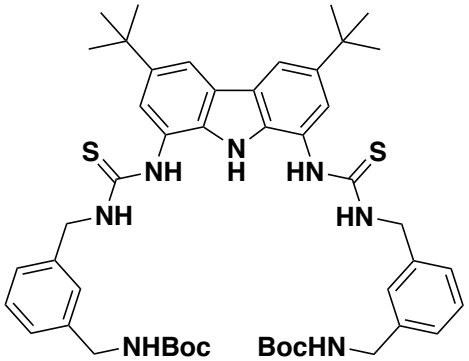
Compound **5** (60 mg, 0.15 mmol) was dissolved in dichloromethane (20 mL). Benzylamine (35 μL, 0.3 mmol) was diluted in dichloromethane and added dropwise to the isothiocyanate solution. The reaction was stirred overnight at rt before the solvent was removed. Purification by column chromatography using 4% dichloromethane/methanol as eluent yielded **mt3** as a white powder (87.3 mg, 93%).

^{1}H NMR (400 MHz, DMSO-d_6): δ: 10.33 (s, 1H), 9.64 (s, 2H), 8.04 (d, 4H, J = 1.52 Hz), 7.45 (br s, 2H), 7.38-7.32 (m, 8H), 7.25 (tt, J_1 = 6.88 Hz, J_2 = 3.24 Hz), 4.79 (d, 4H, J = 5.6 Hz), 1.37 (s, 18H).

^{13}C NMR (100 MHz, DMSO-d_6): 181.4, 142.5, 139.5, 133.5, 128.7, 127.9, 127.3, 125.3, 122.5, 120.5, 114.6, 48.2, 35.0, 32.2.

HRMS (ESI) calcd. for $C_{36}H_{42}N_5S_2$, $[M+H]^+$, 608.2876, found 608.2874.

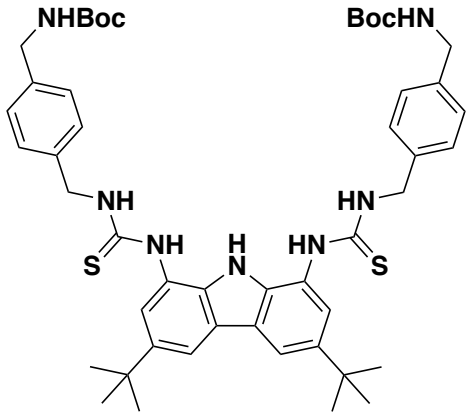
Synthesis of 3,6 di*tert*butyl carbazole, 1,8 di(thiourea-*m*-xylyl *N*-Boc-amine) (8):



Compound **6**[2] (108 mg, 0.46 mmol) was dissolved in dichloromethane (5 mL) and added dropwise to a stirred solution of **5** (75 mg, 0.2 mmol) in 50 mL dichloromethane. After stirring overnight, the solvent was removed under reduced pressure and the compound purified under column chromatography using 2% CH_2Cl_2/MeOH as an eluent, affording **8** as a white solid. (180 mg, quantitative yield)

^{1}H NMR (400 MHz, DMSO-d_6): δ: 10.32 (s, 1H), 9.61 (s, 2H), 8.03 (d, 4H, J = 1.44 Hz), 7.47 (br. s, 2H), 7.37 (t, 2H, J = 5.96 Hz), 7.32-7.20 (m, 6H), 7.13 (d, 2H, J = 7.32 Hz), 4.77 (d, 4H, J = 5.28 Hz), 4.12 (d, 4H, J = 6.00 Hz), 1.40 and 1.37 (overlapping br. s, 36 H).
^{13}C NMR (125 MHz, DMSO-d_6): 181.6, 156.4, 142.6, 140.8, 139.5, 128.8, 126.7, 126.4,126.0, 125.4, 122.7, 114.6, 78.4, 48.4, 44.0, 35.1, 32.4, 28.9.
HRMS (ESI) calcd. for $C_{48}H_{63}N_7O_4S_2$, $[M+Na]^+$, 888.42752, found 888.42676.

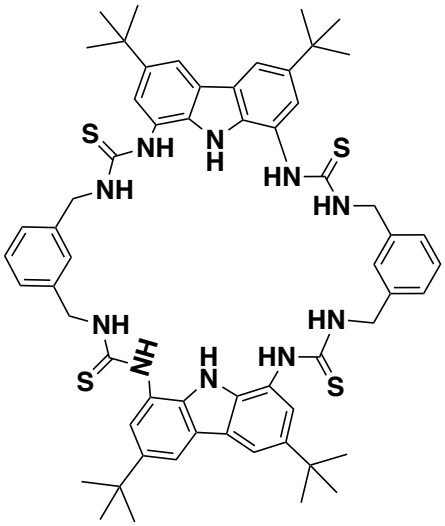
Synthesis of 3,6 di*tert*butyl carbazole, 1,8 di(thiourea-*p*-xylyl *N*-Boc-amine) (9):



Compound **7**[2] (108 mg, 0.46 mmol) was dissolved in dichloromethane (5 mL) and added dropwise to a stirred solution of **5** (75 mg, 0.2 mmol) in 50 mL dichloromethane. After stirring overnight, the solvent was removed under reduced pressure and the compound purified under column chromatography using 2% CH_2Cl_2/MeOH as an eluent, affording **9** as a white solid (180 mg, quantitative yield).

^{1}H NMR (400 MHz, DMSO-d_6): δ: 10.32 (s, 1H), 9.60 (s, 2H), 8.04 (d, 4H, J = 1.44 Hz), 7.47 (br. s, 2H), 7.37 (t, 2H, J = 5.96 Hz), 7.32-7.20 (m, 6H), 7.13 (d, 2H, J = 7.32 Hz), 4.77 (d, 4H, J = 5.28 Hz), 4.12 (d, 4H, J = 6.00 Hz), 1.40 and 1.37 (overlapping br. s, 36 H).
^{13}C NMR (100 MHz, $CDCl_3$): 180.9, 156.0, 155.9, 144.2, 138.5, 136.3, 134.1, 128.2, 127.9, 127.7, 127.6, 125.7, 122.0, 119.5, 116.3, 79.6, 48.9, 44.1, 34.8, 32.4, 29.7, 28.4.
HRMS (ESI) $C_{48}H_{63}N_7O_4S_2$, $[M+Na]^+$, 888.42752, found 888.42658.

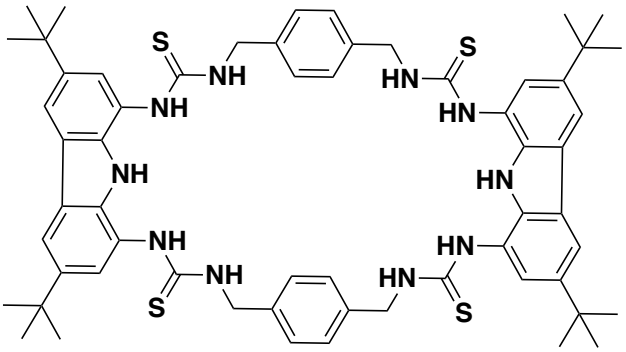
Synthesis of macrocycle (dt1):



Compound **8** (175 mg, 0.2 mmol) was suspended in dichloromethane (5 mL) and TFA (5 mL) was added dropwise. The reaction was allowed to stir for 1 hour before the solvent was removed under a stream of nitrogen. The resultant TFA salt was dissolved in dichloromethane (100 mL) and washed with sat. $NaHCO_3$ solution 3 times. The dichloromethane phase was subsequently rapidly stirred and a solution of **5** (75 mg, 0.2 mmol, dissolved in 10 mL dichloromethane) was added dropwise over the course of 30 mins. The solution was stirred overnight and the resultant precipitate was collected by filtration and washed with dichloromethane, yielding the pure macrocycle as a white solid. A further crop of macrocycle was isolated by column chromatography on the filtrate. Total mass: 73 mg, 35%

^{1}H NMR (400 MHz, DMSO-d_6): δ: 10.51 (s, 1.2H, major conformer), 10.30 (s 0.8H (minor conformer), 9.76 (s, 2.3H, major conformer), 9.63 (s, 1.7H, minor conformer), 8.07 (d, 2.3H, J = 1.24 Hz, major conformer), 8.02 (s, 1.7H, minor conformer), 7.99 (br. t, 4H), 7.49 (s, 4H), 7.35-7.23 (m, 6H) 7.19 (s, 1.3H minor conformer), 4.79 (m, 8H), 1.39 (s, 20H, major conformer), 1.36 (s, 12H, minor conformer).
^{13}C NMR (100 MHz, DMSO-d_6): 181.1, 142.6, 142.5, 139.6, 139.4, 133.8, 133.5, 128.8, 128.7, 127.1, 126.4, 125.5, 125.4, 125.3, 122.3, 120.8, 114.9, 114.5, 48.2, 48.0, 35.0, 32.3.
HRMS (ESI) calcd. for $C_{60}H_{70}N_{10}S_4$, $[M+Na]^+$, 1081.4560 found 1081.4571.

Synthesis of macrocycle (dt2):



Compound **9** (175 mg, 0.2 mmol) was suspended in dichloromethane (5 mL) and TFA (5 mL) was added dropwise. The reaction was allowed to stir for 1 hour before the solvent was removed under a stream of nitrogen. The resultant TFA salt was dissolved in dichloromethane (100 mL) and washed with sat. $NaHCO_3$ solution 3 times. The dichloromethane phase was subsequently rapidly stirred and a solution of **5** (75 mg, 0.2 mmol), dissolved in 10 mL dichloromethane) was added dropwise over the course of 30 mins. The solution was stirred overnight and the resultant precipitate was collected by filtration and washed with dichloromethane, yielding the pure macrocycle as a white solid. A further crop of macrocycle was isolated by column chromatography on the filtrate, total mass: 42.3 mg (20 %)

^{1}H NMR (400 MHz, DMSO-d_6): δ: 10.09 (br. s, 2H), 9.77 (s, 4H), 8.01 (d, 4H, J = 1.36 Hz), 7.63 (br. s, 4H), 7.53 (br. s, 4H), 7.32 (s, 8H), 4.71 (br. d, 8H), 1.36 (s, 36H).
^{13}C NMR (100 MHz, DMSO-d_6): 181.0, 142.6, 137.7, 133.4, 128.1, 127.9, 125.3, 122.4, 120.3, 114.7, 48.5, 35.0, 32.3.
HRMS (ESI) calcd. for $C_{60}H_{70}N_{10}S_4$, $[M+Na]^+$, 1081.4560 found 1081.4571.

3 – Characterisation

3.1 – NMR Spectra

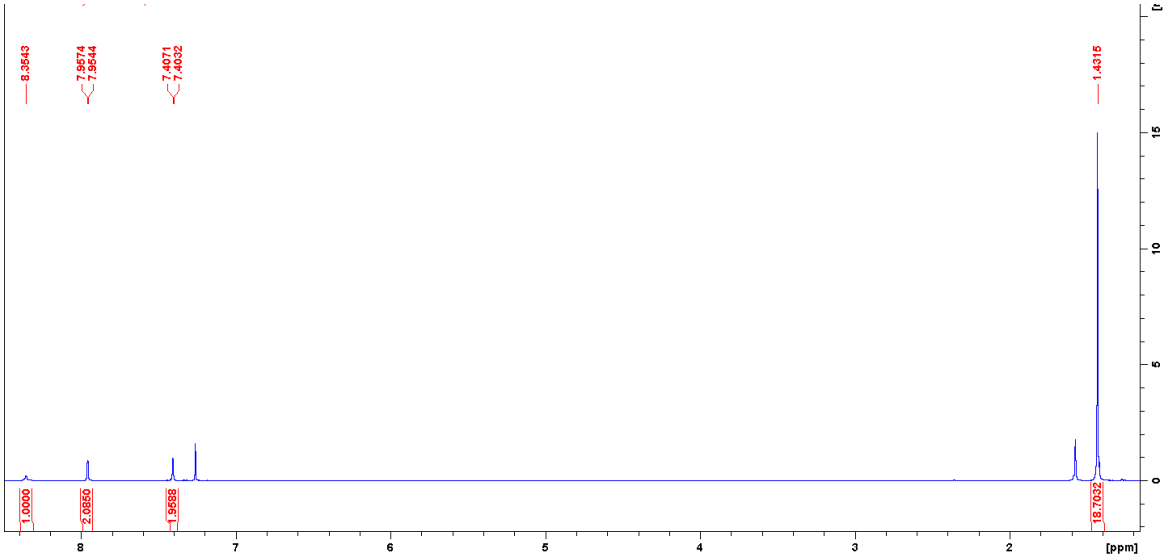


Figure S2: ^{1}H NMR spectra of **5** (400 MHz, $CDCl_3$, 298 K).

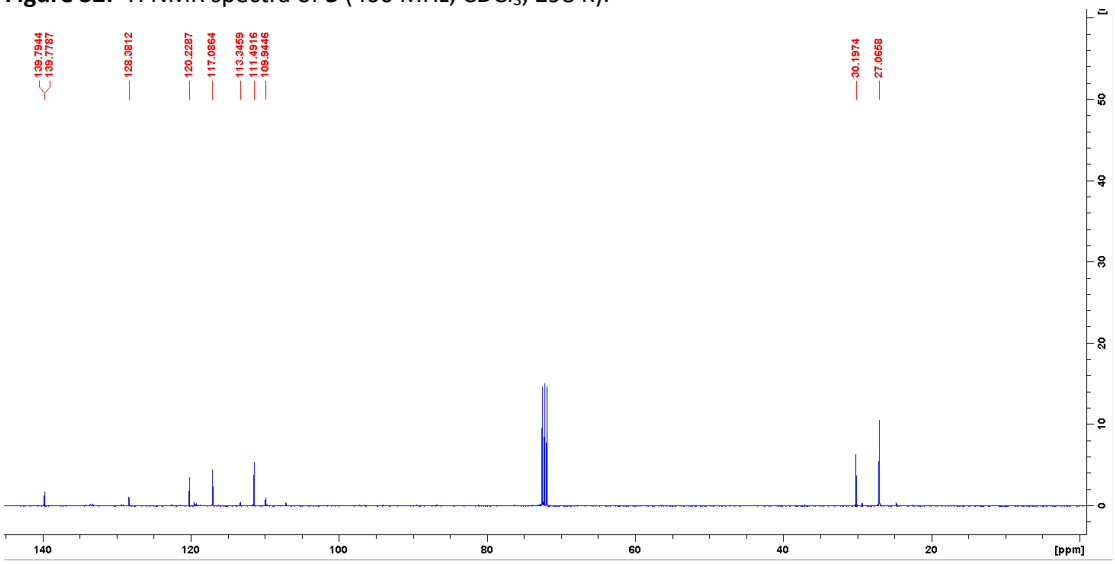


Figure S3: ^{13}C NMR spectra of **5** (100 MHz, $CDCl_3$, 298 K).

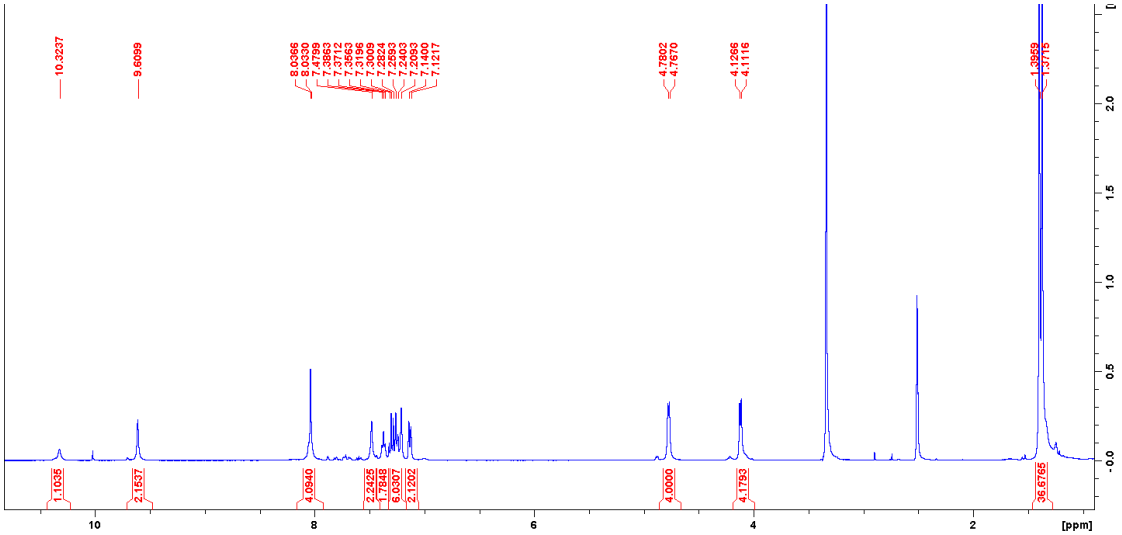


Figure S4: ^{1}H NMR spectra of **8** (400 MHz, $CDCl_3$, 298 K).

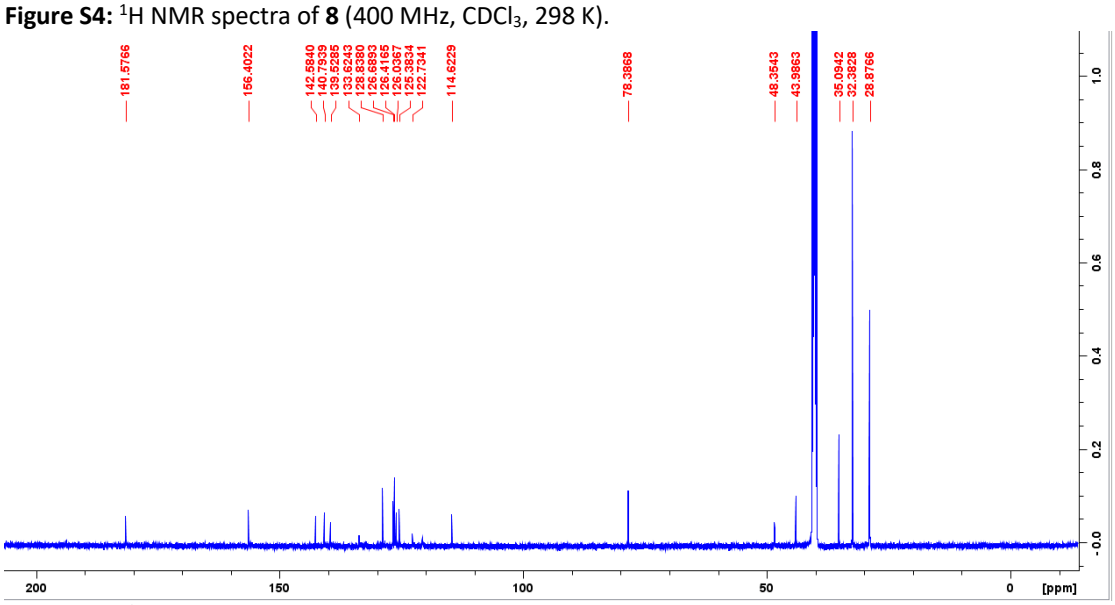


Figure S5: ^{13}C NMR spectra of **8** (125MHz, DMSO-d_6, 298 K).

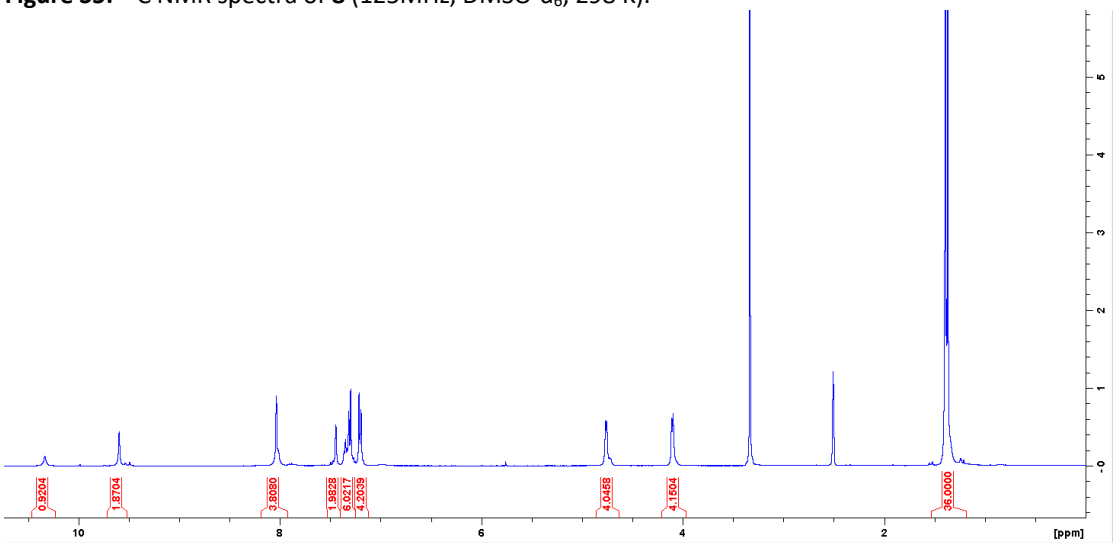


Figure S6: ^{1}H NMR spectra of **9** (400 MHz, $CDCl_3$, 298 K).

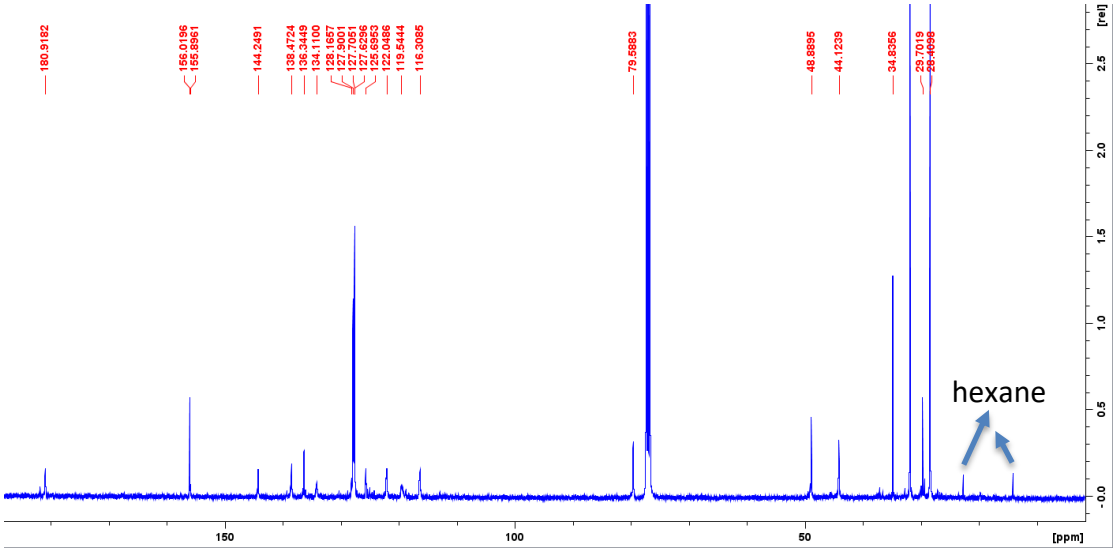


Figure S7: ^{13}C NMR spectra of **9** (100 MHz, $CDCl_3$, 298 K).

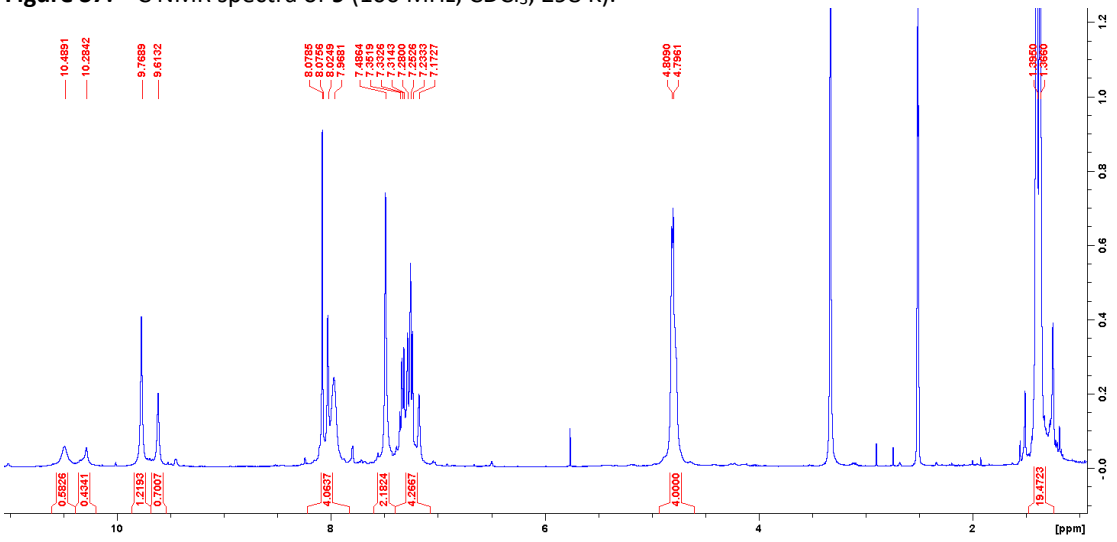


Figure S8: ^{1}H NMR spectra of **dt1** (400 MHz, DMSO-d_6, 298 K).

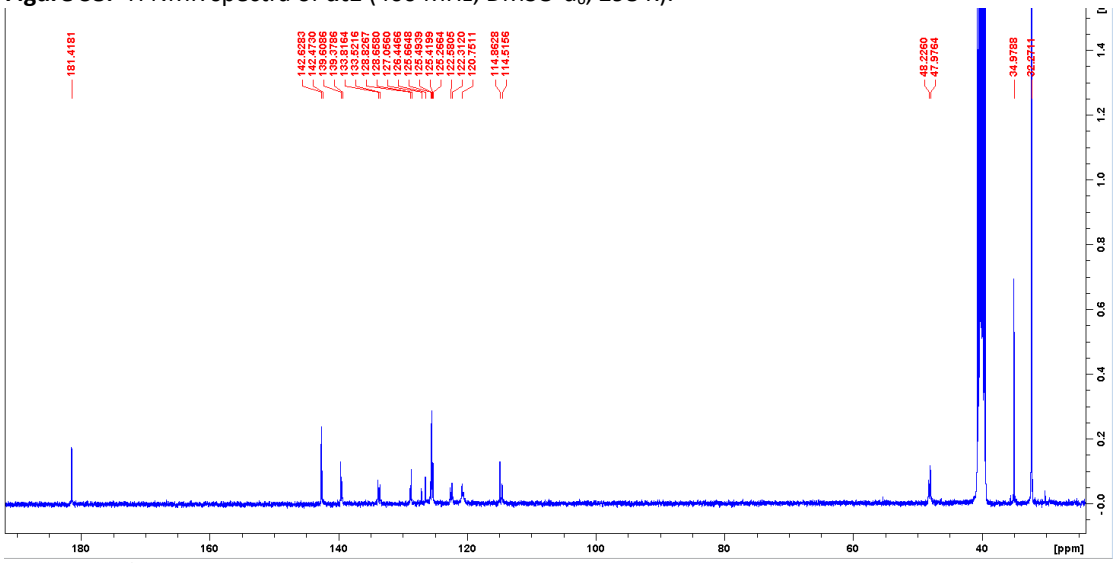


Figure S9: ^{13}C NMR spectra of **dt1** (100 MHz, DMSO-d_6, 298 K).

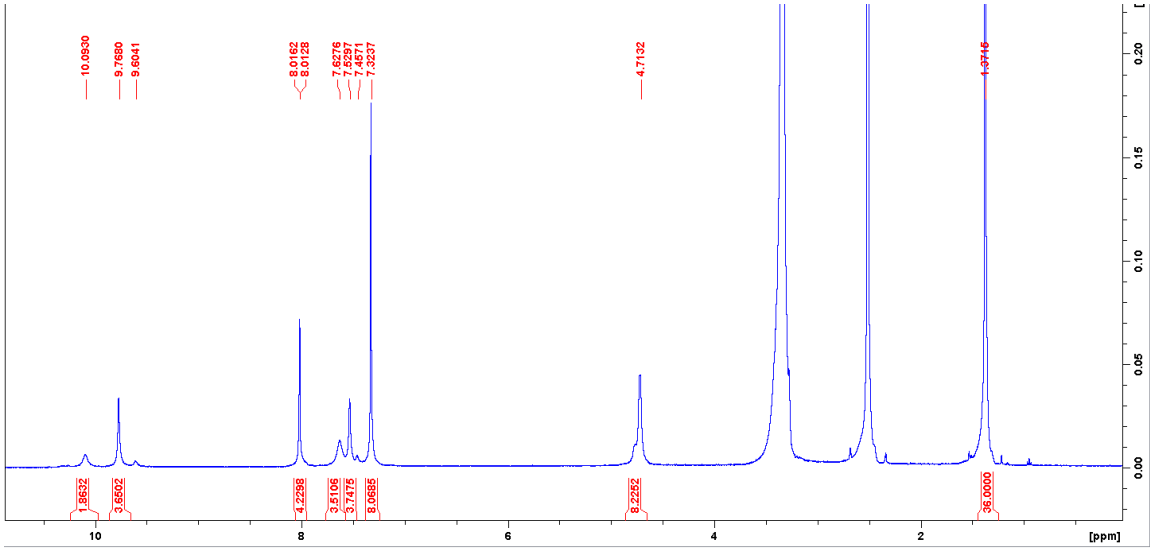


Figure S10: ^{1}H NMR spectra of **dt2** (400 MHz, DMSO-d_6, 298 K).

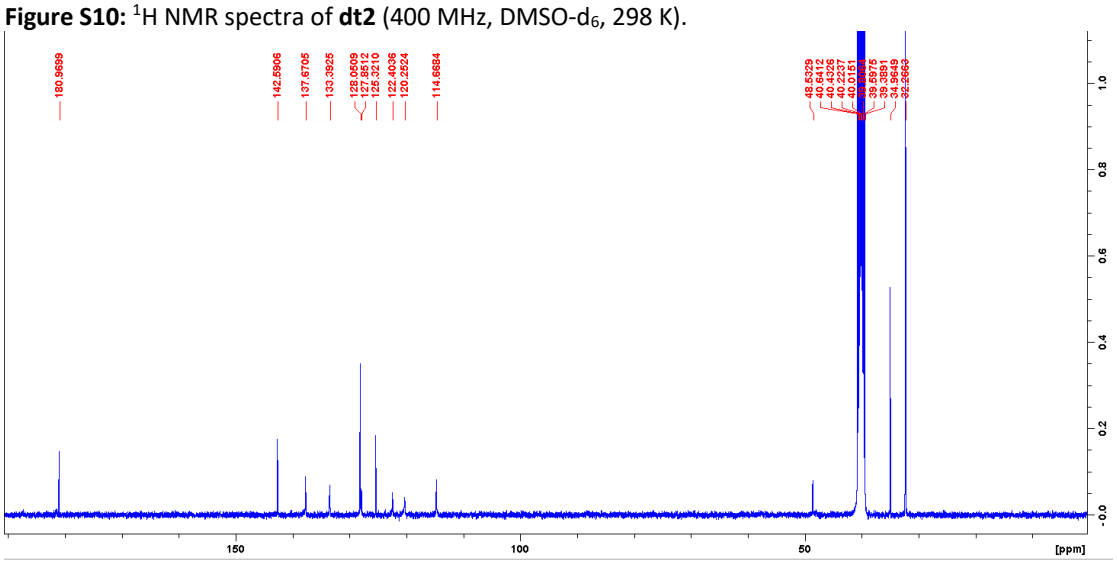


Figure S11: ^{13}C NMR spectra of **dt2** (100 MHz, DMSO-d_6, 298 K).

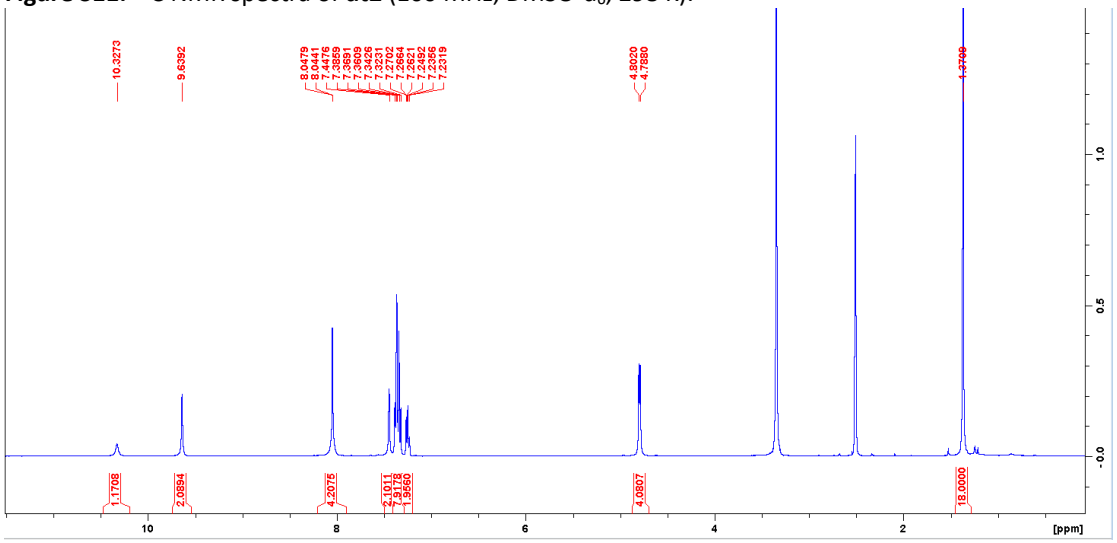


Figure S12: ^{1}H NMR spectra of **mt3** (400 MHz, DMSO-d_6, 298 K).

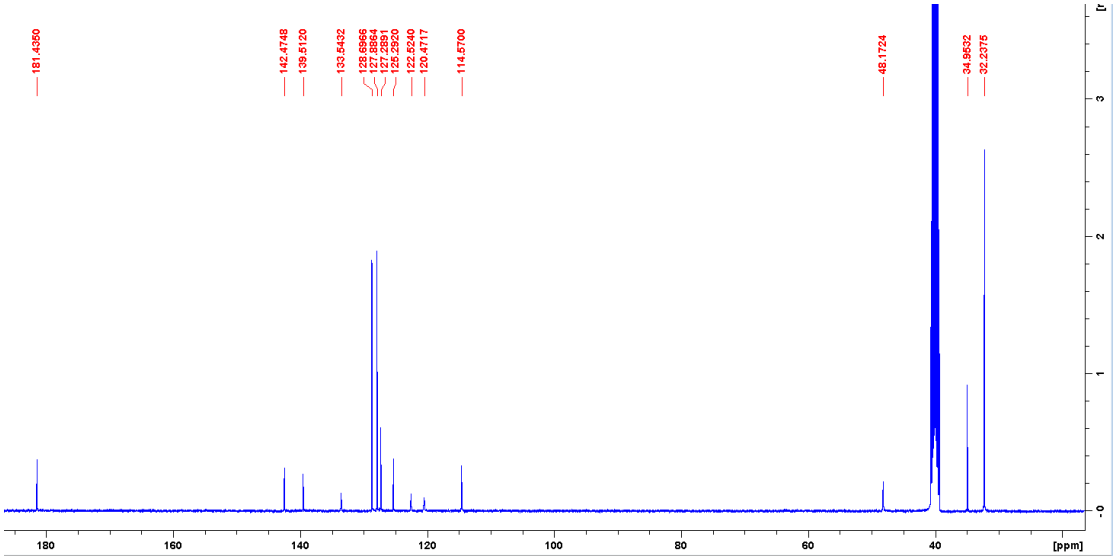


Figure S13: ^{13}C NMR spectra of **mt3** (100 MHz, DMSO-d_6, 298 K).

3.2 – Conformation Effects of Macrocycle dt1

Variable temperature NMR studies were performed on macrocycle **dt1** in DMSO-d_6 and significant chemical exchange was detected (**figure S15**). At 298 K, clear peaks corresponding to major and minor conformers were observed in both the aromatic and aliphatic region and coalescence of the aromatic protons was observed as the compound was heated to 343 K indicating that chemical exchange was occurring. The protons corresponding to the tertiary-butyl groups do not ever fully coalesce even at 343 K. NMR studies at higher temperatures were not possible. Characterisation data is provided at both 298 K and 343 K. These conformational effects were less prominent for **dt2**. Conformational splitting was also observed in the ^{13}C spectra of **dt1**. The conformational effects are resolved upon saturation of binding to an anion, indicating formation of a symmetrical 1:1 complex (see **section 7**).

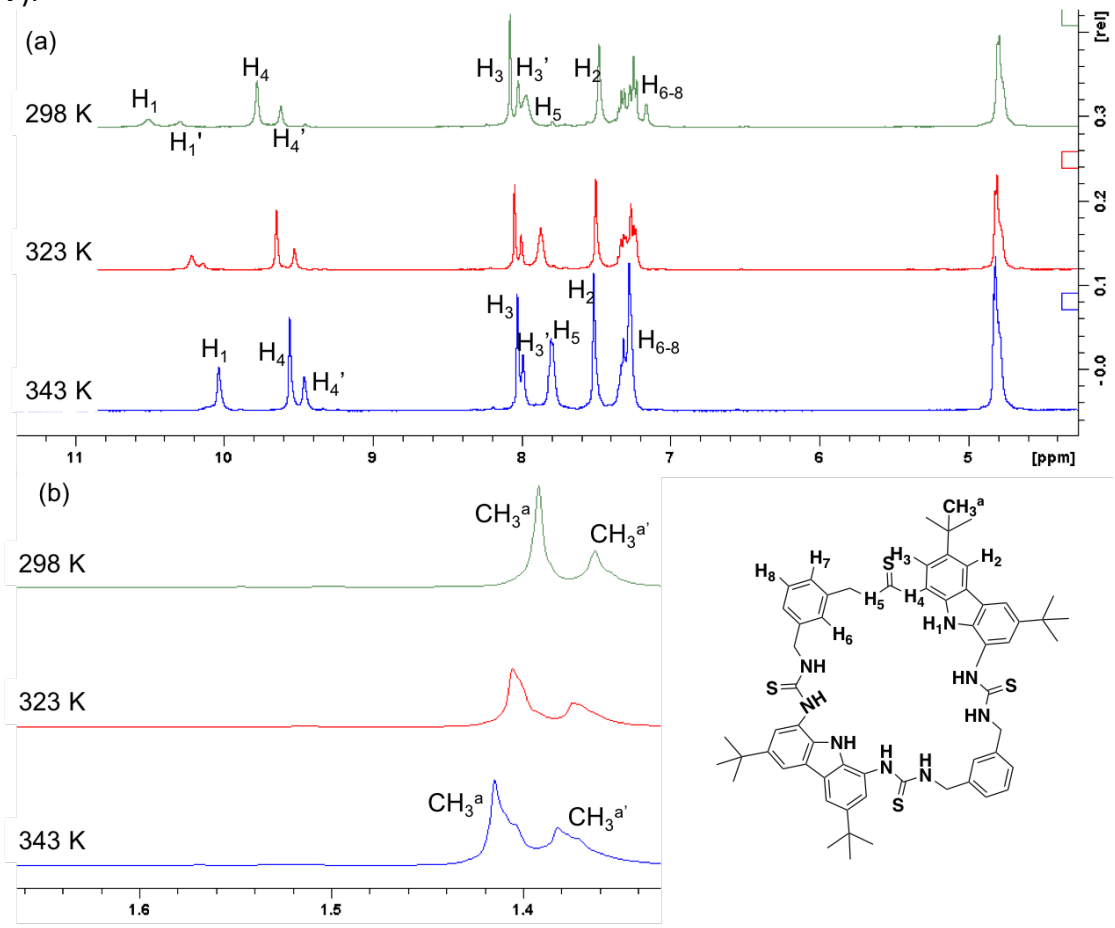


Figure S14: Snapshot of (a) aromatic region of the ^1H NMR spectra of **dt1** in DMSO-d_6 at various temperatures and (b) the aliphatic region at the same temperatures.

3.3 – High Resolution Mass Spectrometry (HRMS)

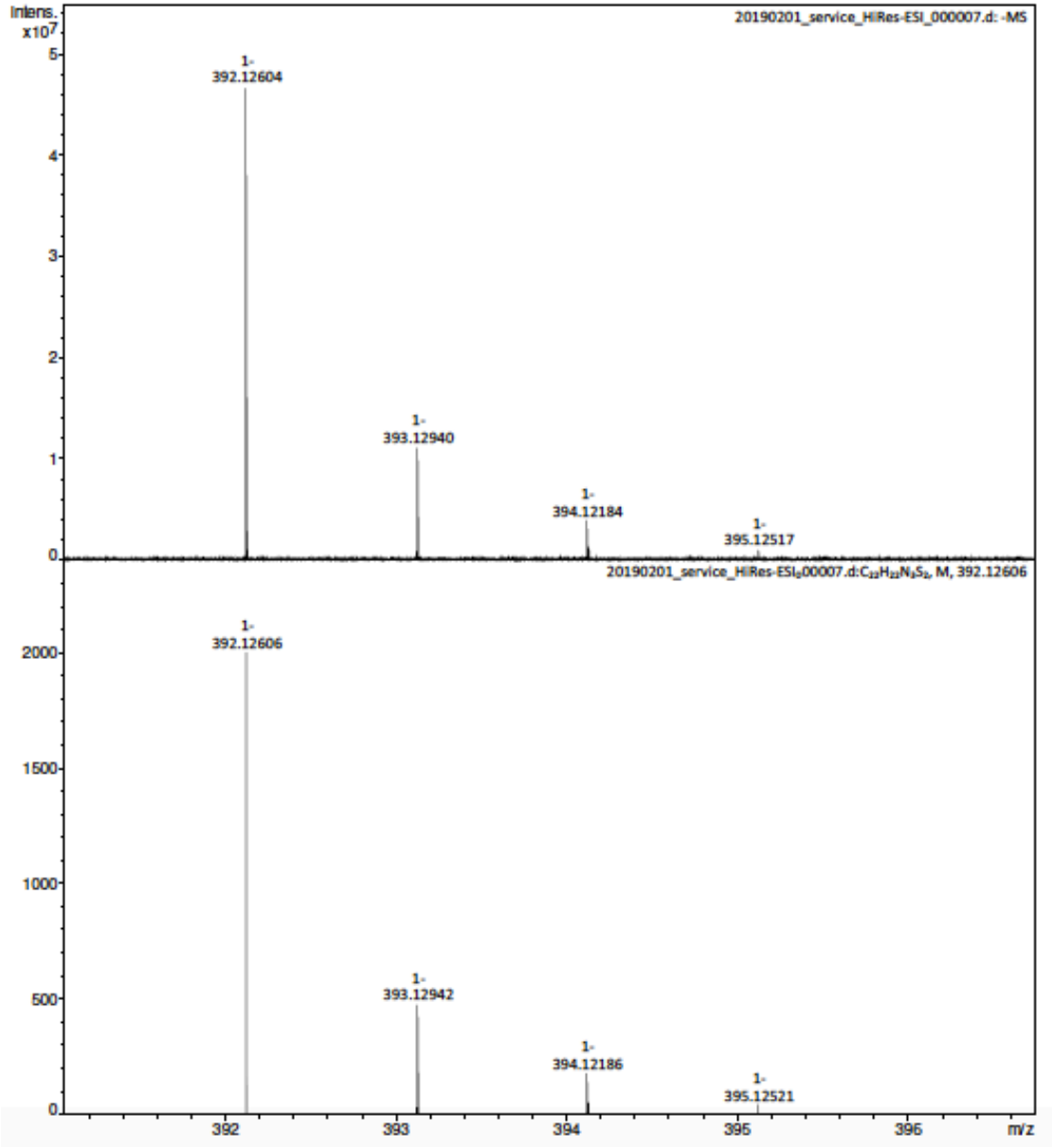


Figure S15: HRMS of compound **5** showing $[M-H]^-$.

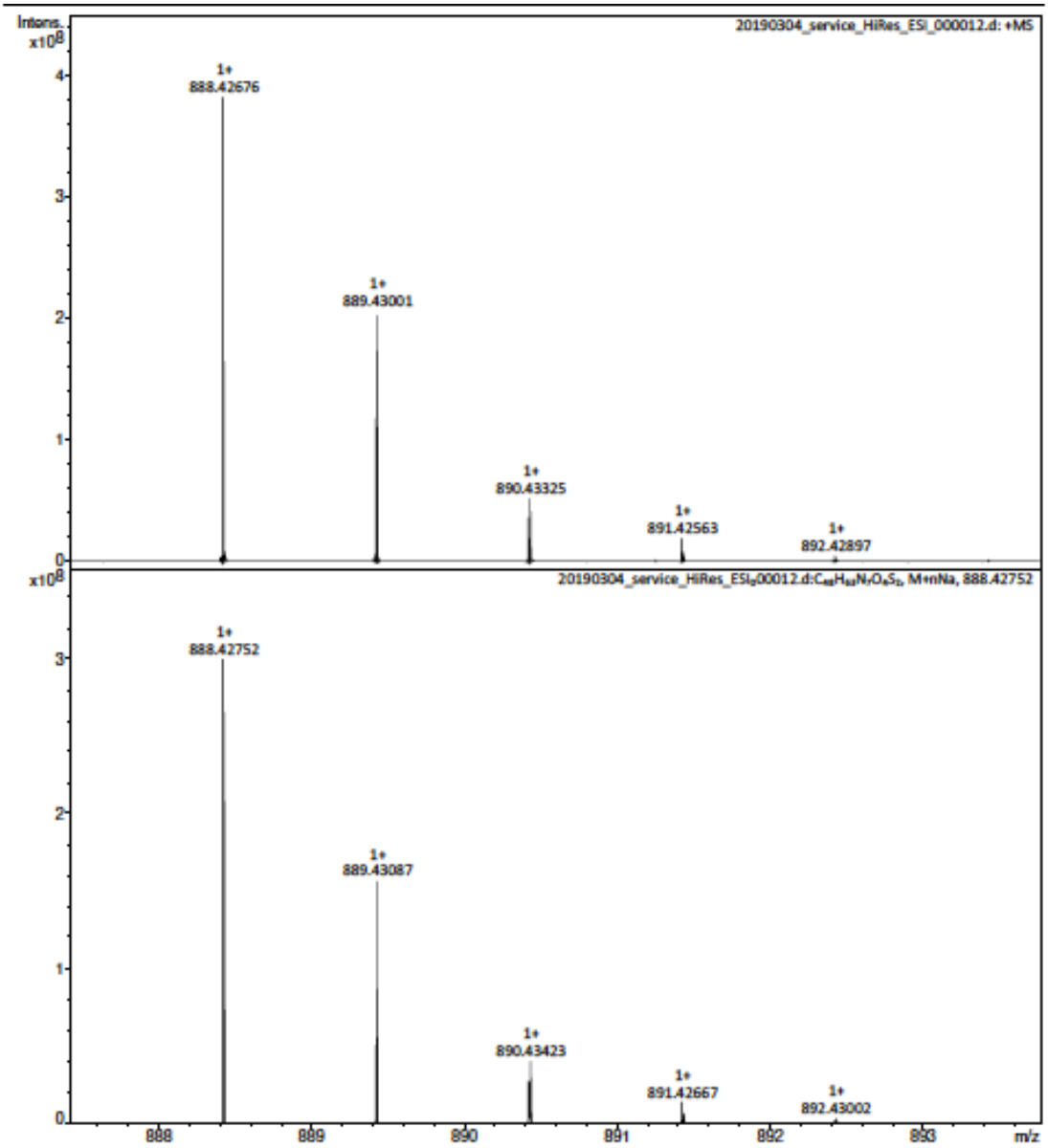


Figure S16: HRMS of compound **8** showing $[M+Na]^+$.

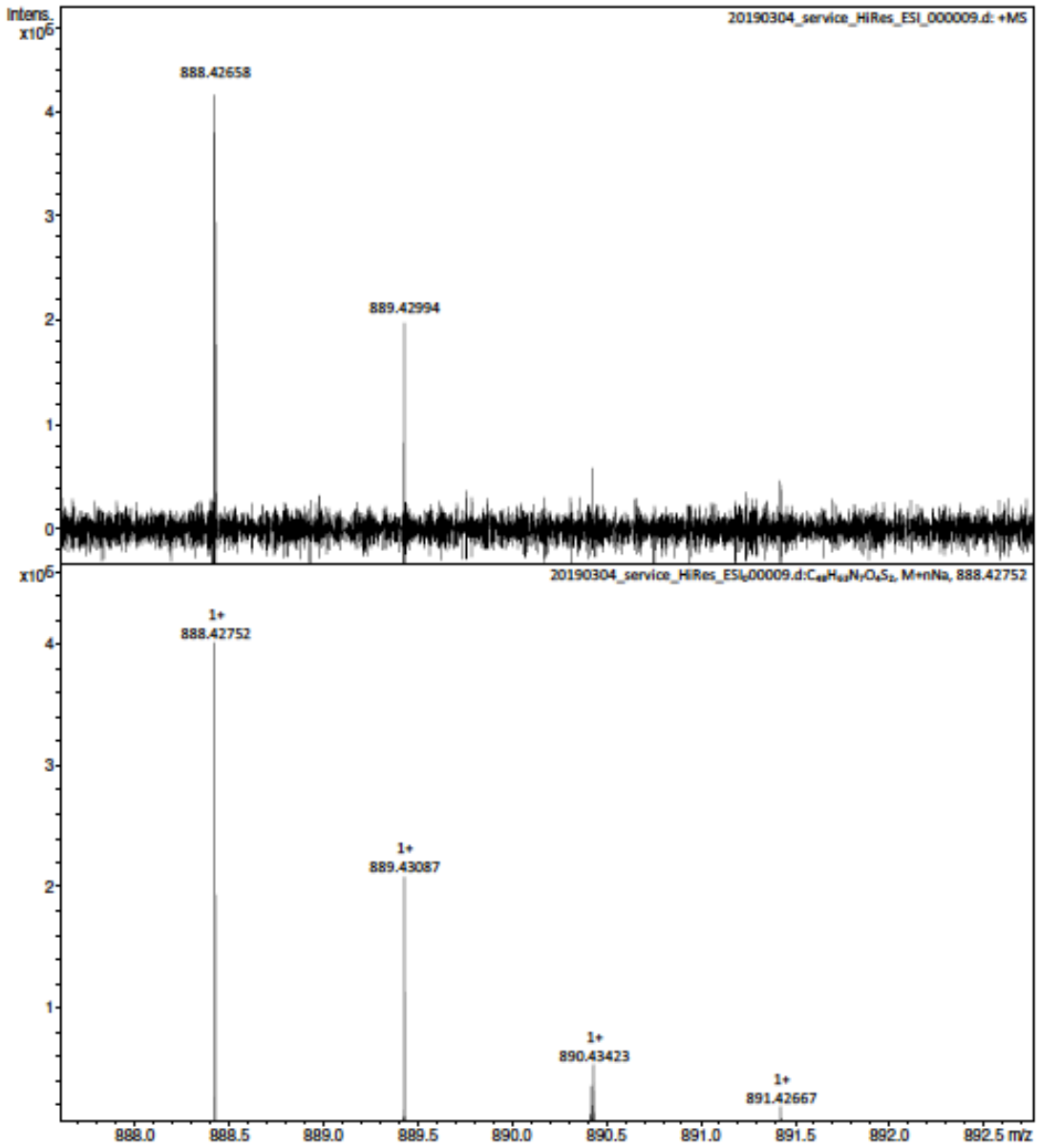


Figure S17: HRMS of compound **9** showing $[M+Na]^+$.

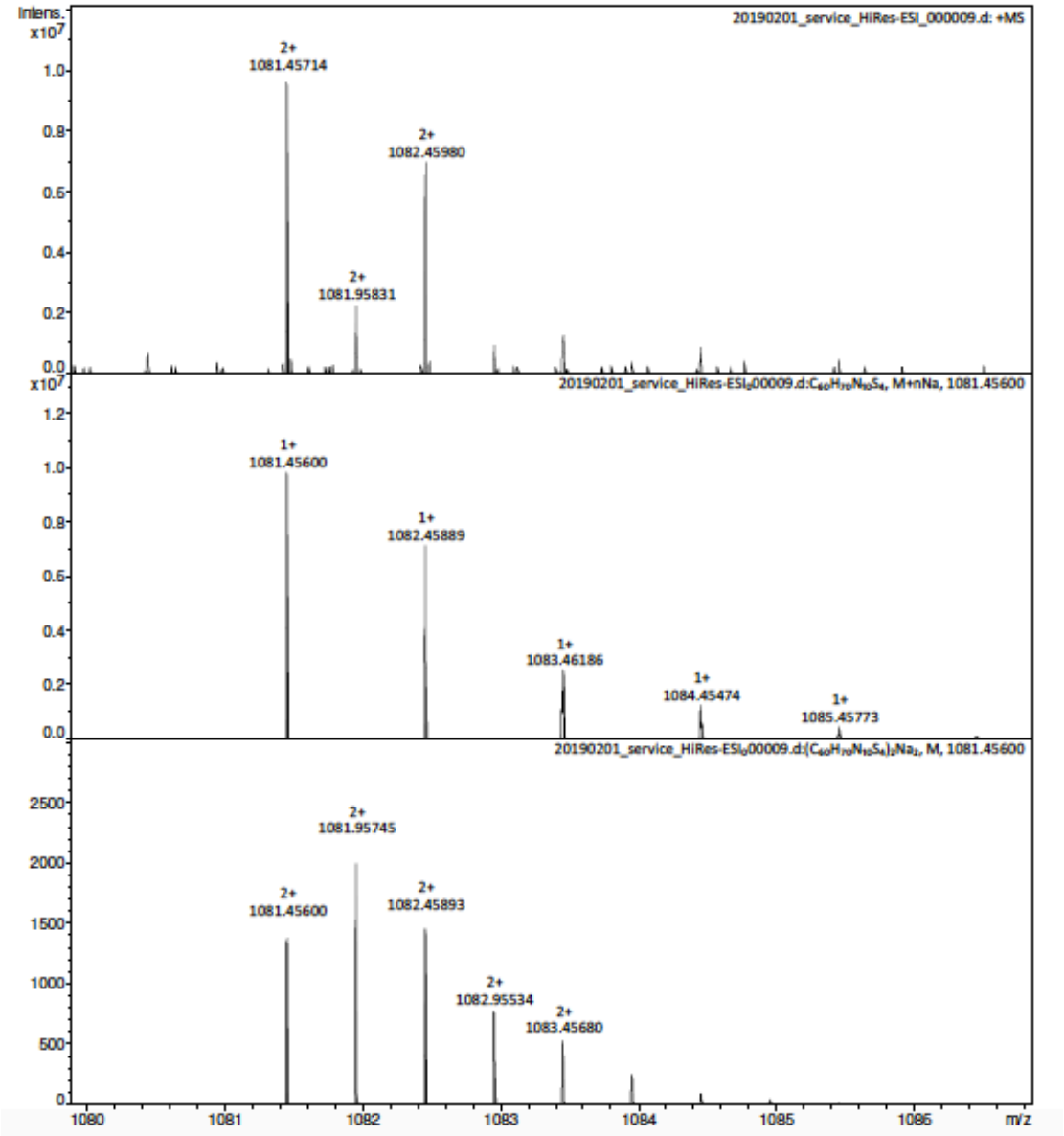


Figure S18: HRMS of compound **dt1** showing $[M+Na]^{+}$ and $[2M+2Na]^{2+}$.

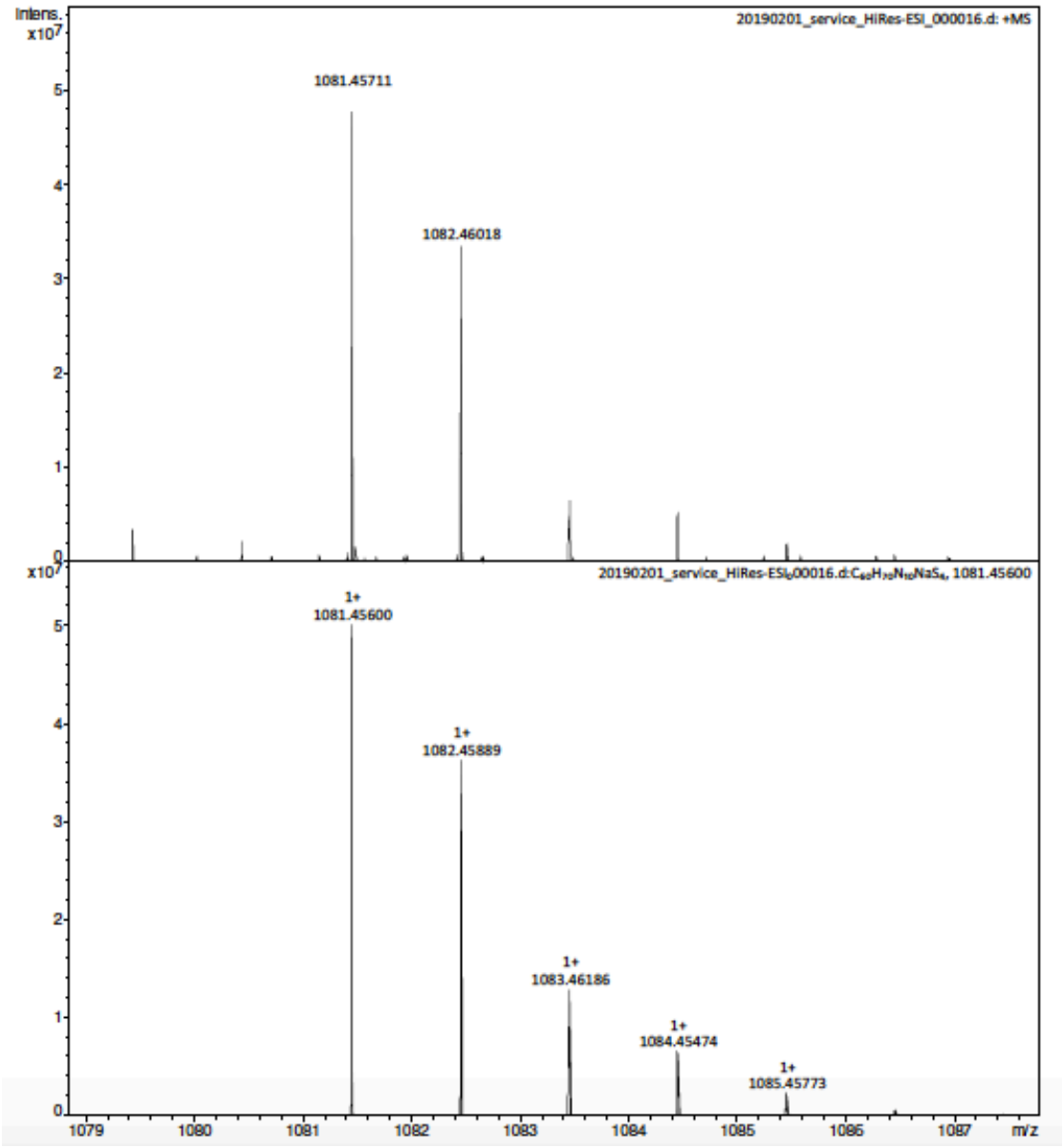


Figure S19: HRMS of compound **dt2** showing $[M+Na]^+$.

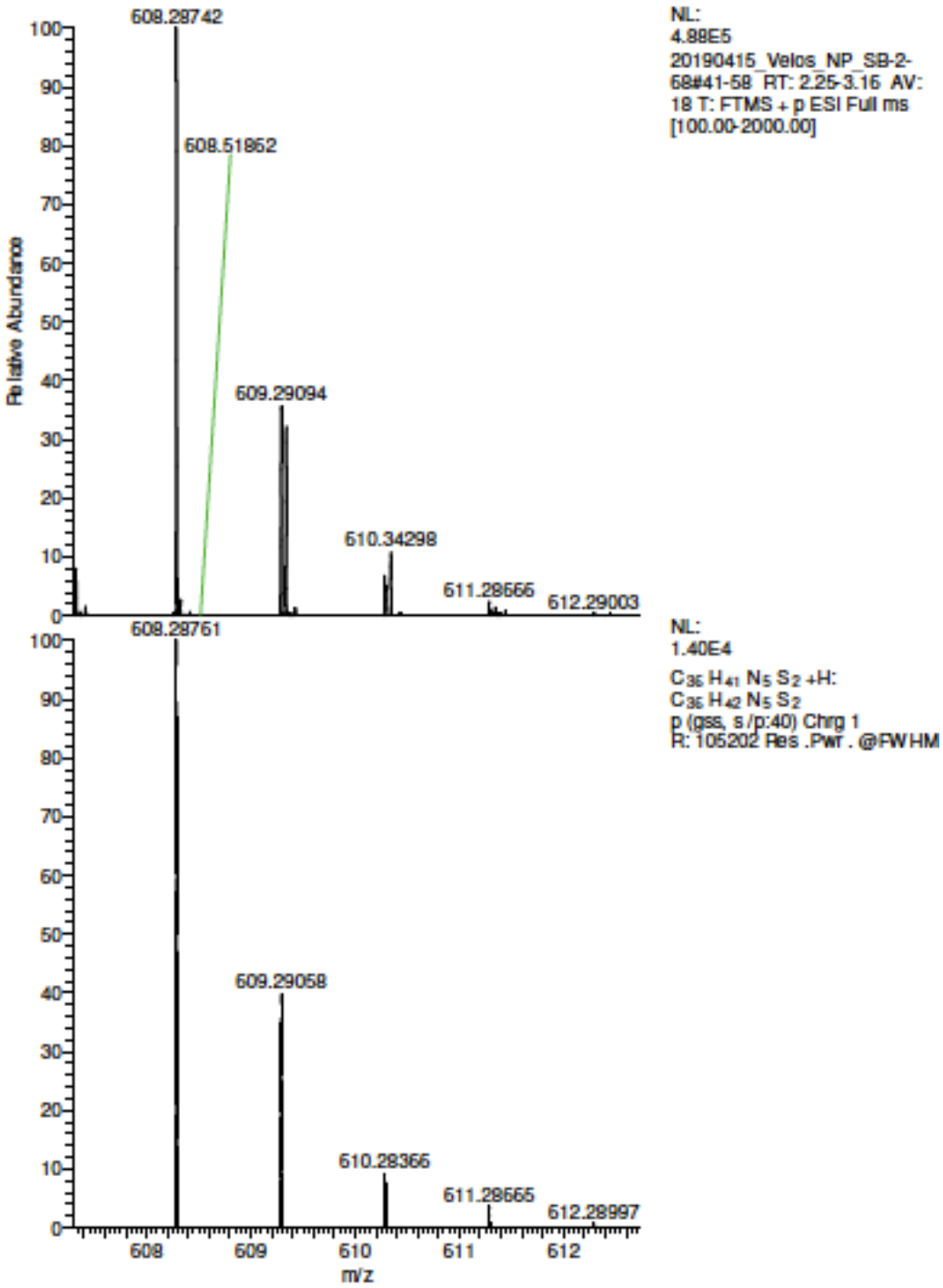


Figure S20: HRMS of compound **mt3** showing $[M+H]^+$.

3.4 – Single Crystal X-Ray Diffraction

Data was collected at the University of Sydney on either a Bruker APEX-II CCD diffractometer (**dt2·Mal** and **dt2·Aze**) or a Rigaku SuperNova Duo Atlas diffractometer (**dt2·Adi**). All crystals were grown from slow evaporation of DMSO solutions of hosts with approximately 5 equivalents of TBA_2Guest salts. Suitable crystals were mounted in paratone-N on a micromount and kept at 100(2) K during data collection.

For **dt2·Mal** and **dt2·Adi**, using Olex2[3], the structure was solved with the olex2.solve[4] structure solution program using Charge Flipping and refined with the ShelXL[5] refinement package using Least Squares minimisation.

For **dt2·Aze**, using Olex2[3], the structure was solved with the ShelXT[6] structure solution program using Intrinsic Phasing and refined with the ShelXL[5] refinement package using Least Squares minimisation.

Further details of the structure refinement can found in the CIFs for these structures, which have been deposited in the Cambridge Crystallographic Data Centre, CCDC numbers: 1954830-1954832.

4 – UV-Vis Binding Studies

4.1 – Overview and Procedure

UV-Vis titrations were performed as follows: A 10 mL solution of macrocycle (10-75 μM) was prepared in H_2O/DMSO (1:9 v:v). From this, 2.5 mL was added to a quartz cuvette. The remaining 7.5 mL was used to make a 5-20 mM stock solution of the relevant anion. All anions were used as their TBA_2 (tetrabutylammonium) salts. UV-Vis spectra were obtained on a Cary 4000 UV-Vis spectrophotometer (Agilent Technologies) equipped with a peltier temperature controller. All spectra were obtained at by scanning from 400 nm – 250 nm at 298 K using a blank sample (H_2O/DMSO 1:9 v/v) as a reference and after background subtraction. Small aliquots of guest were added to the host cuvette using a microsyringe (Hamilton) and the cuvette stirred for at least 30 s before spectra were taken. Data was fitted by performing a global fit on *Bindfit*[7] to an appropriate binding model. Only data fittings for the 3 peaks, 300, 345 and 360 nm are shown. Full fits for the 1:1 binding of **dt1** and **dt2** to dicarboxylates can be accessed online at the appropriate Bindfit link. For titrations with TBA_2 Terephthalate (**Ter**) or TBA_2trans,trans-muconate (**ttM**), spectra are only shown to ~280 nm, due to interfering absorbance from the titrated guest. For this reason, in these cases, no isosbestic points were observed.

4.2 – Fitted Binding Isotherms to Dicarboxylate Anions

4.2.1 – Compound dt1

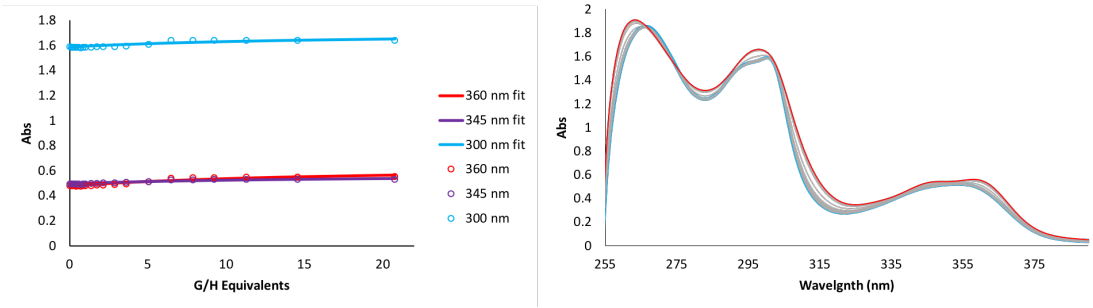


Figure S21: (right) UV-Vis titration of **dt1** with increasing amounts of TBA_2Malonate in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 2284.79 M^{-1}. Full fitted data is available online at:
http://app.supramolecular.org/bindfit/view/a7c299ba-7067-470d-bf48-cecac76b4185

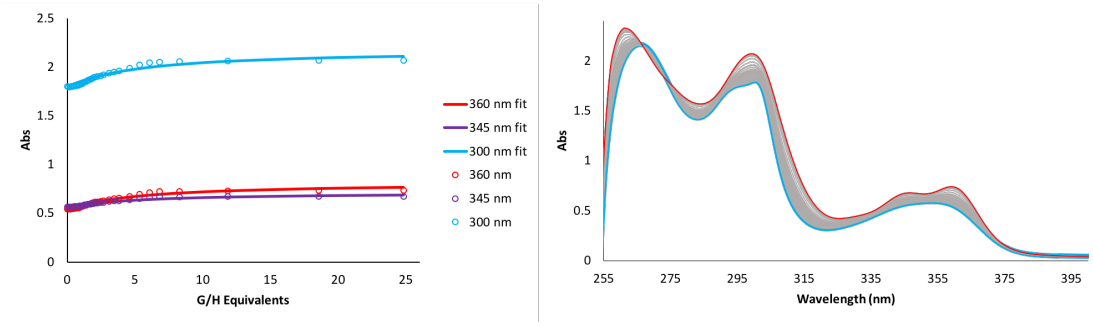


Figure S22: (right) UV-Vis titration of **dt1** with increasing amounts of TBA_2Succinate in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 7885.78 M^{-1}. Full fitted data is available online at:
http://app.supramolecular.org/bindfit/view/f5cc2822-8f58-4f92-b947-d1b2cce86d36

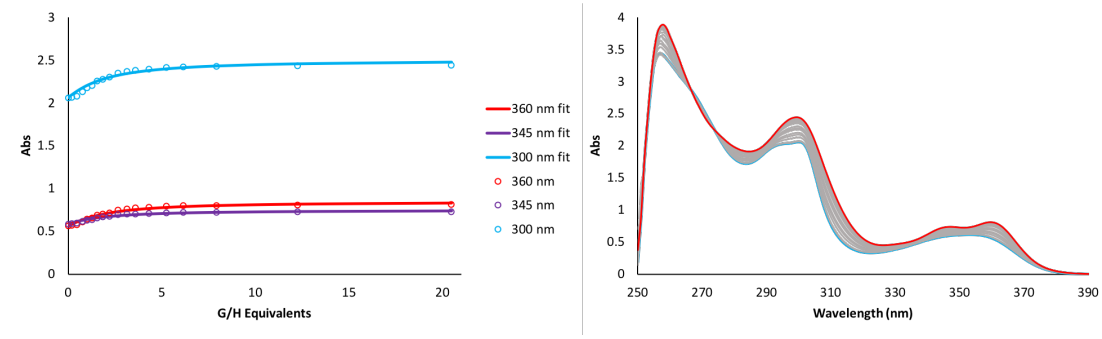


Figure S23: (right) UV-Vis titration of **dt1** with increasing amounts of TBA_2Glutarate in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 35678.38 M^{-1}. Full fitted data is available online at:
http://app.supramolecular.org/bindfit/view/658f9b91-8e05-443f-9fc2-32a329e85688

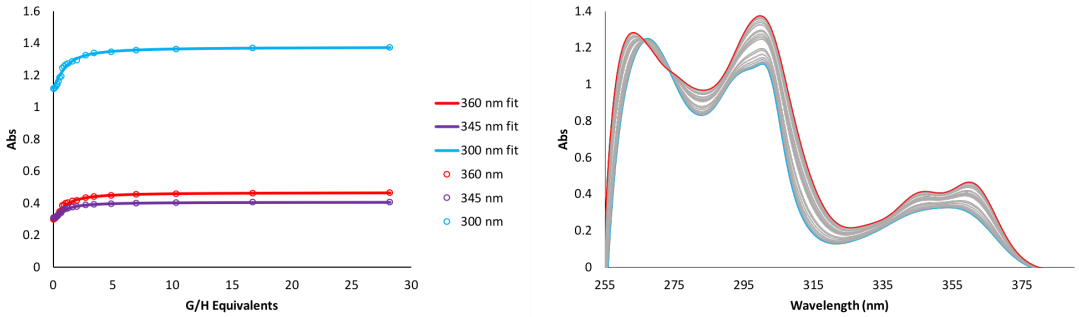


Figure S24: (right) UV-Vis titration of **dt1** with increasing amounts of $TBA_2Adipate$ in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 74984.26 M^{-1}. Full fitted data is available online at:
http://app.supramolecular.org/bindfit/view/0cbbf45f-5b63-4113-99bd-e89451fea28e

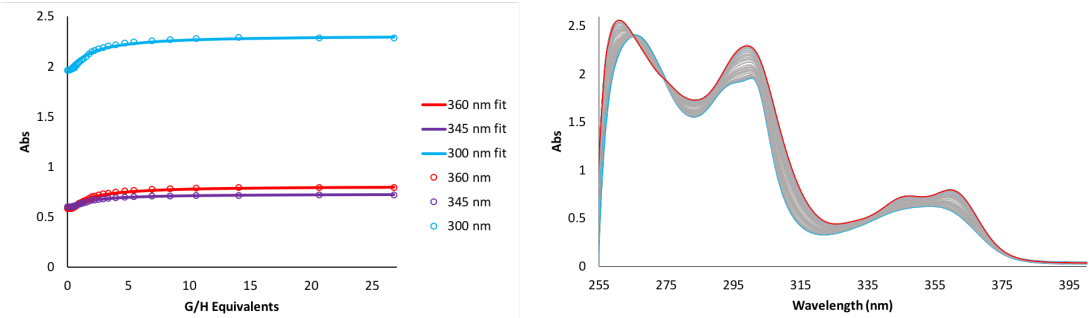


Figure S25: (right) UV-Vis titration of **dt1** with increasing amounts of $TBA_2Pimelate$ in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 26949.12 M^{-1}. Full fitted data is available online at:
http://app.supramolecular.org/bindfit/view/edcc9c96-cbac-4e24-a318-75d1a44e5d6e

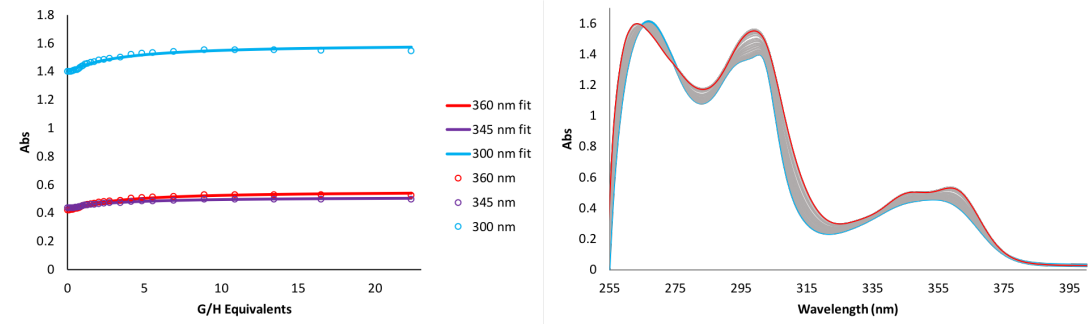


Figure S26: (right) UV-Vis titration of **dt1** with increasing amounts of $TBA_2Suberate$ in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 12886.50 M^{-1}. Full fitted data is available online at:
http://app.supramolecular.org/bindfit/view/58c009b3-a594-4488-a917-19f7c70a40a0

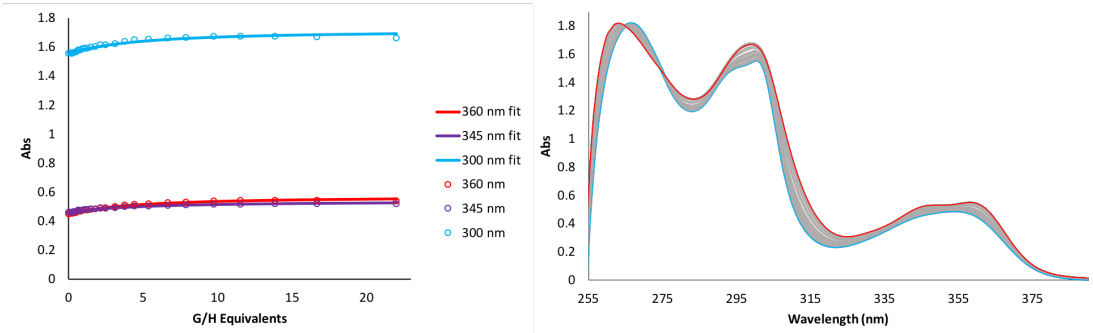


Figure S27: (right) UV-Vis titration of **dt1** with increasing amounts of TBA_2Azelate in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 9167.82 M^{-1}. Full fitted data is available online at:
http://app.supramolecular.org/bindfit/view/321820e2-f6e7-4049-b916-a1475fac6931

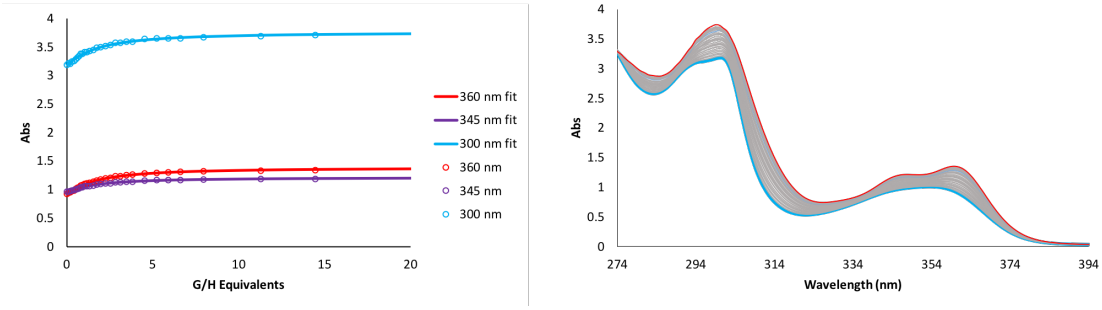


Figure S28: (right) UV-Vis titration of **dt1** with increasing amounts of TBA_2Terephthalate in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 30203.02 M^{-1}. Full fitted data is available online at:
http://app.supramolecular.org/bindfit/view/0a9a4c05-219e-46fc-a1f7-9854f303f60e

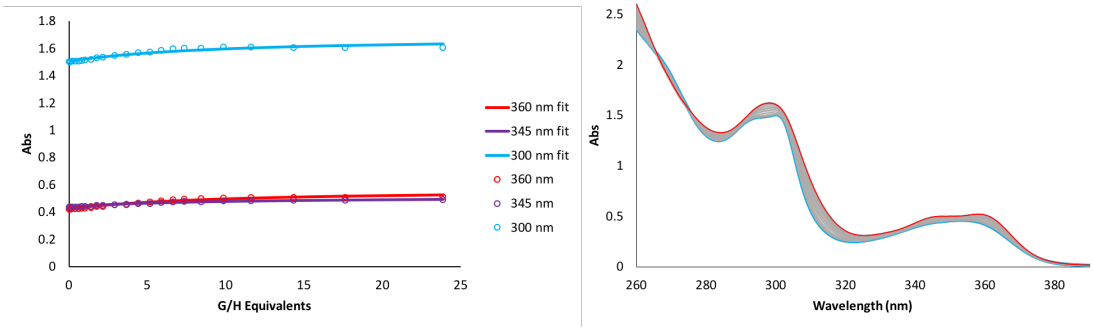


Figure S29: (right) UV-Vis titration of **dt1** with increasing amounts of $TBA_2\alpha$-keto glutarate in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 7498.26 M^{-1}. Full fitted data is available online at:
http://app.supramolecular.org/bindfit/view/aab13990-8df4-4f03-8b0a-a59f73d7e08c

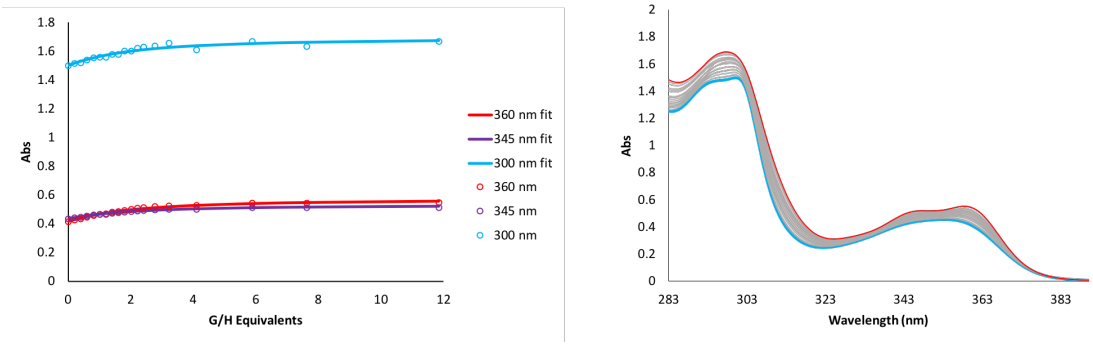


Figure S30: (right) UV-Vis titration of **dt1** with increasing amounts of TBA_2trans,trans-mucconate in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 27835.96 M^{-1}. Full fitted data is available online at: http://app.supramolecular.org/bindfit/view/ae6dc433-24fa-4052-813c-967c9129e63e

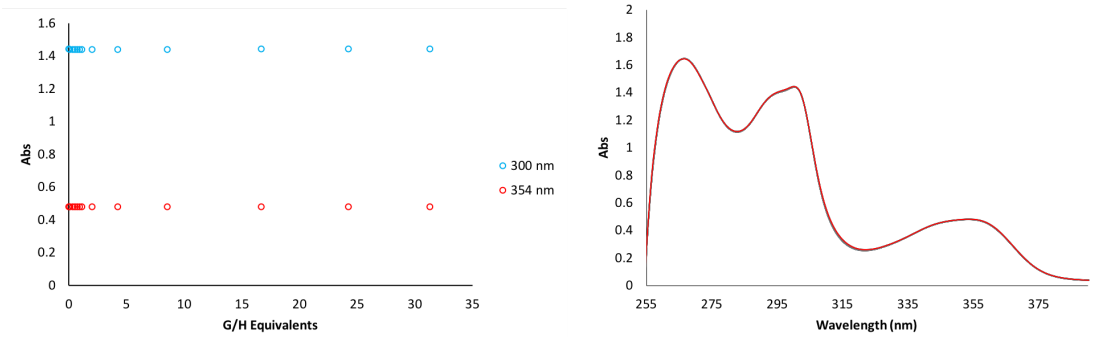


Figure S31: (right) UV-Vis titration of **dt1** with increasing amounts of TBA Acetate in H_2O/DMSO (1:9 *v/v*). (left) plot of change in absorbance vs equivalents of Acetate confirming no binding interaction.

4.2.2 – Compound dt2

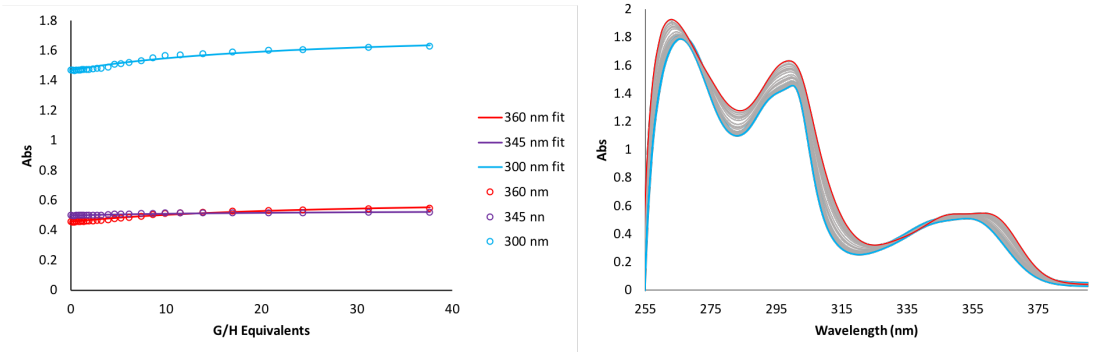


Figure S32: (right) UV-Vis titration of **dt2** with increasing amounts of TBA_2Malonate in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 1582.55 M^{-1}. Full fitted data is available online at: http://app.supramolecular.org/bindfit/view/c586c56f-39ec-4b4c-b1ef-42015b3016bf

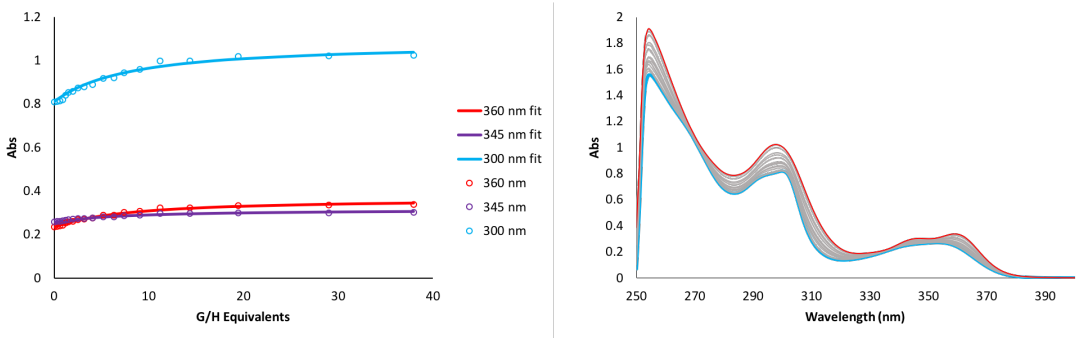


Figure S33: (right) UV-Vis titration of **dt2** with increasing amounts of TBA_2Succinate in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 5773.02 M^{-1}. Full fitted data is available online at:
http://app.supramolecular.org/bindfit/view/2f40bf7d-5792-43a0-93f7-be2cd626219a

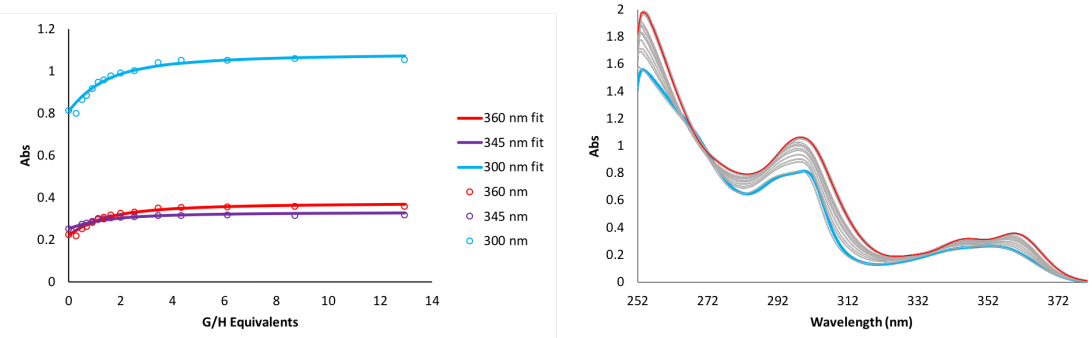


Figure S34: (right) UV-Vis titration of **dt2** with increasing amounts of TBA_2Glutarate in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 51050.94 M^{-1}. Full fitted data is available online at:
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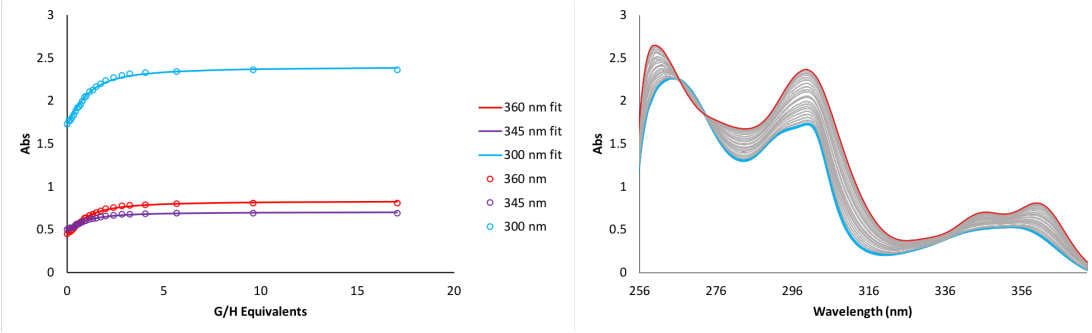

Figure S35: (right) UV-Vis titration of **dt2** with increasing amounts of TBA_2Adipate in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 87188.85 M^{-1}. Full fitted data is available online at:
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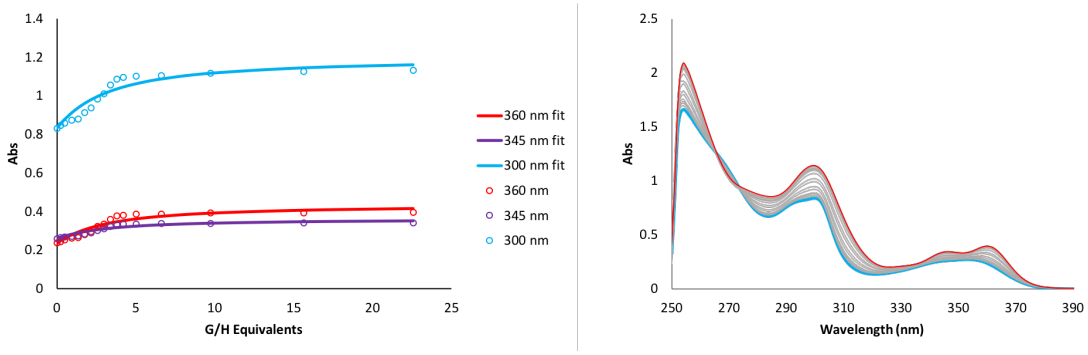

Figure S36: (right) UV-Vis titration of **dt2** with increasing amounts of TBA_2Pimeate in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 15696.96 M^{-1}. Full fitted data is available online at:
http://app.supramolecular.org/bindfit/view/393aba0e-b0f7-4ac7-b92c-da3ee6641077

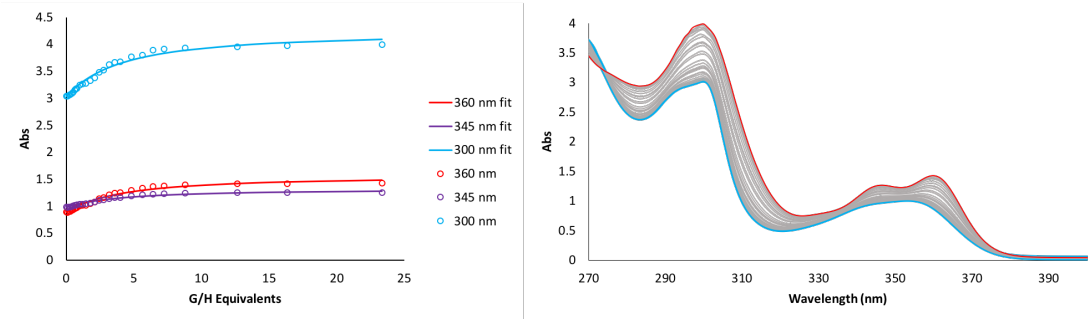

Figure S37: (right) UV-Vis titration of **dt2** with increasing amounts of TBA_2Suberate in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 12114.96 M^{-1}. Full fitted data is available online at:
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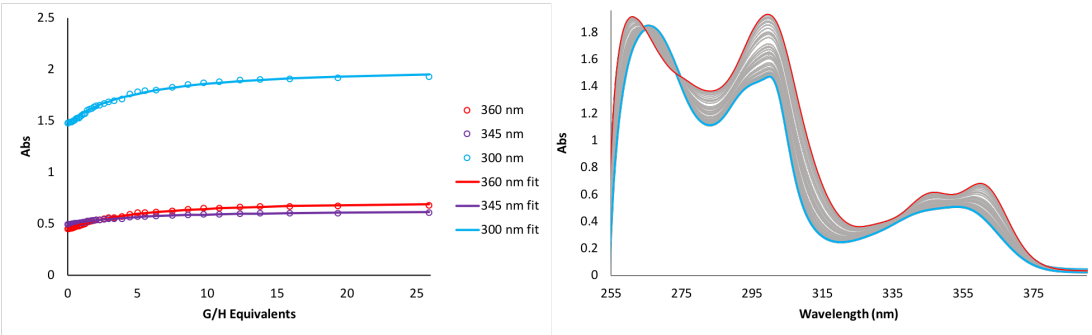

Figure S38: (right) UV-Vis titration of **dt2** with increasing amounts of TBA_2Azelate in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 9841.39 M^{-1}. Full fitted data is available online at:
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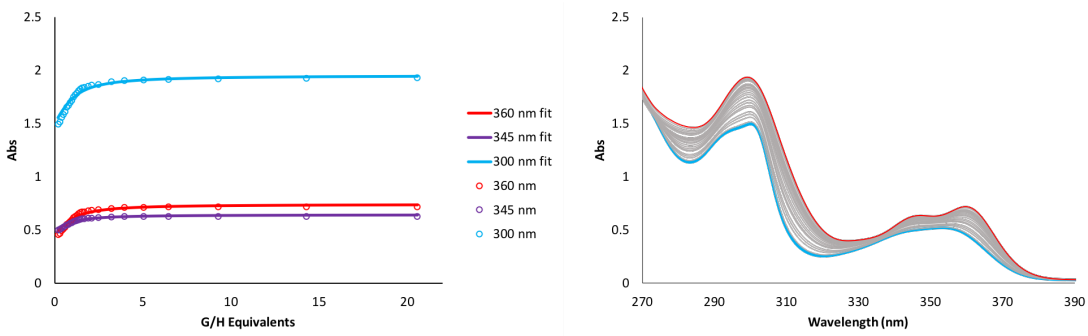

Figure S39: (right) UV-Vis titration of **dt2** with increasing amounts of TBA_2Terephthalate in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 86899.90 M^{-1}. Full fitted data is available online at: http://app.supramolecular.org/bindfit/view/5039c358-7b60-4a3a-9daf-6d917297a201

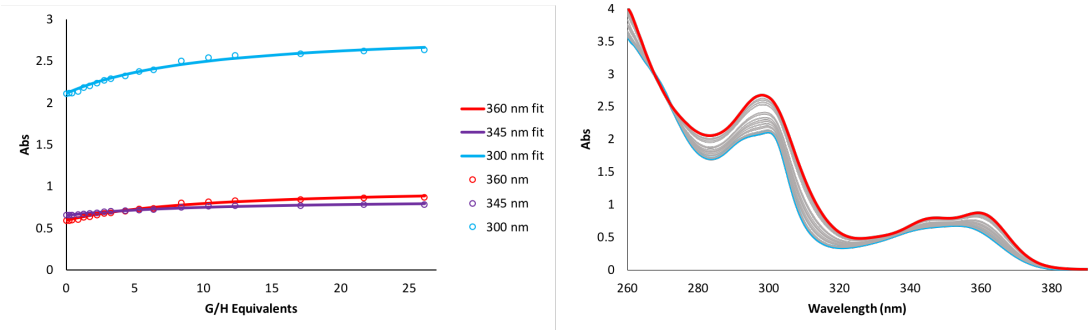

Figure S40: (right) UV-Vis titration of **dt2** with increasing amounts of $TBA_2\alpha$-keto glutarate in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 4908.96 M^{-1}. Full fitted data is available online at: http://app.supramolecular.org/bindfit/view/8561af17-ed6e-4d72-ab69-f9cb2a6aea0f

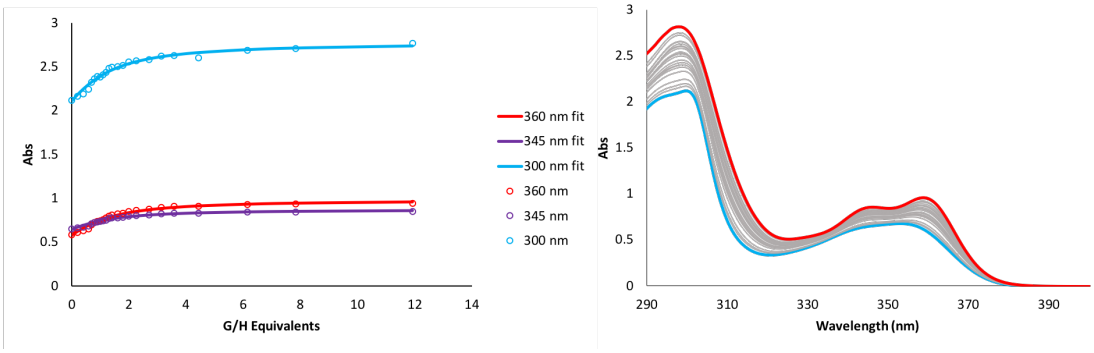

Figure S41: (right) UV-Vis titration of **dt2** with increasing amounts of TBA_2Trans,trans-mucconate in H_2O/DMSO (1:9 *v/v*). (left) Fitted binding isotherm from bindfit to a 1:1 model $Ka_{1:1}$ = 57546.53 M^{-1}. Full fitted data is available online at: http://app.supramolecular.org/bindfit/view/d67c493e-c9e6-4b88-989e-28641bbda568

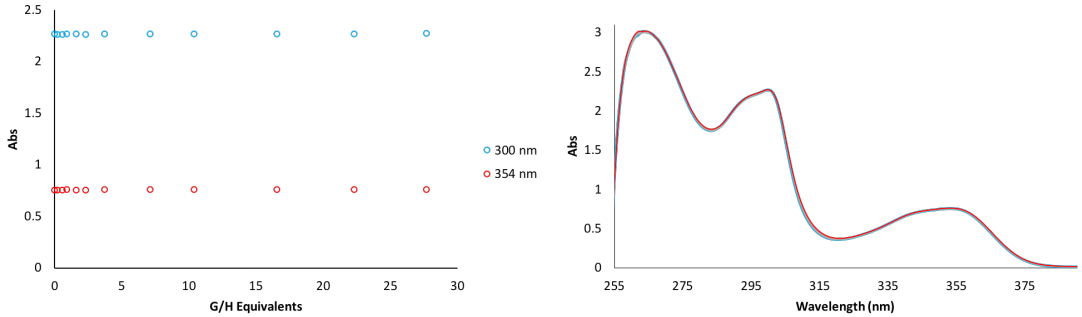

Figure S42: (right) UV-Vis titration of **dt2** with increasing amounts of TBA Acetate in H_2O/DMSO (1:9 *v/v*). (left) plot of change in absorbance vs equivalents of Acetate confirming no binding interaction.

5 – Double Mutant Cycle Analysis

DMC analysis, as first described by Jencks[8] was conducted following literature procedures[9] and is described briefly in the following section. The divalent host-guest binding event was subjected to two mutations which allows the binding to be deconvoluted. Each of the mutations allow the equilibrium constants to be expressed by statistical factors (**section 5.1**), the monovalent reference constant (K_{ref}) and Effective Molarity (*EM*).

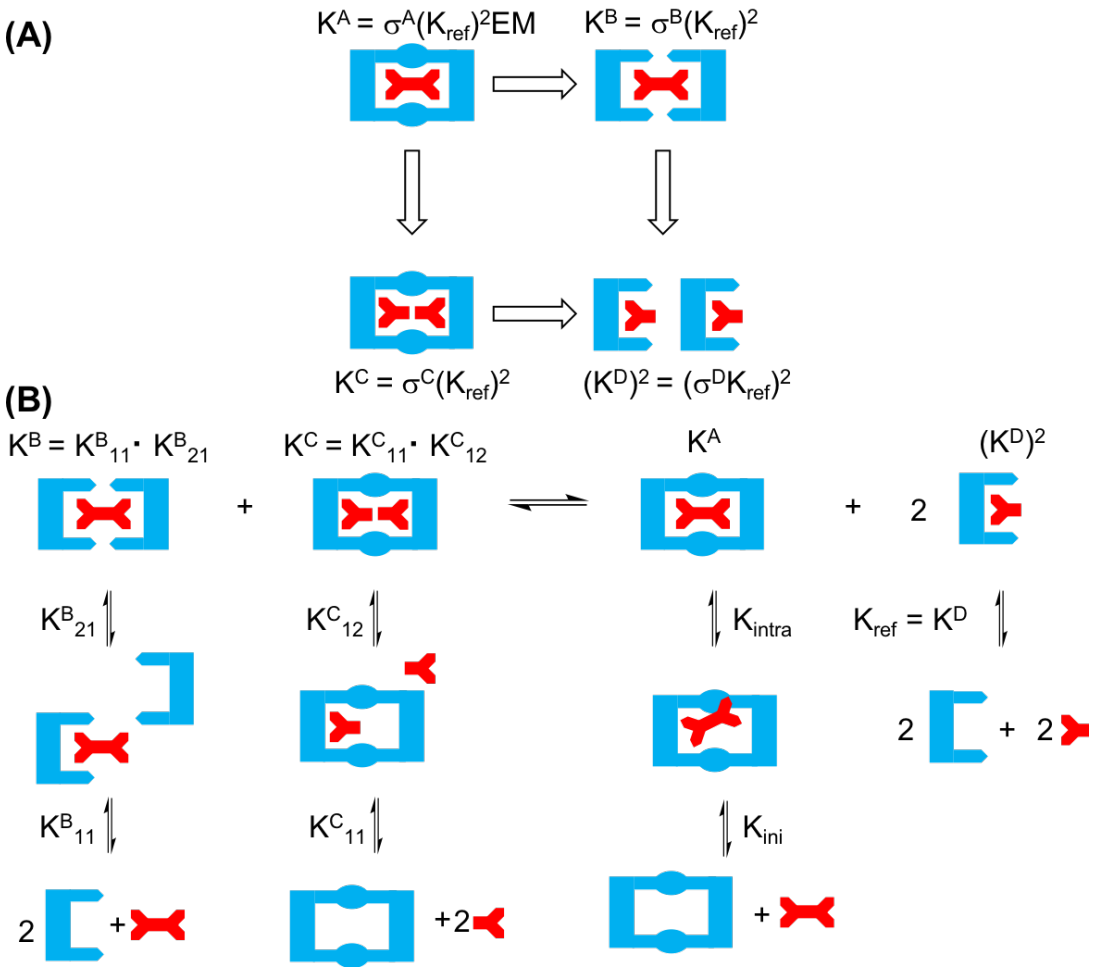

Figure S43: A) Double mutant cycle analysis schematic for **dt1** and **dt2** showing the relationship between binding constant (K^X), statistical factors (σ^x), the monovalent reference (K_{ref}) and effective molarity (EM). B) Double mutant cycle equilibria, showing how experimentally determined binding constants can be combined to an overall binding equilibria.

Each of the experimentally determinable individual binding constants can be expressed by the following equations (S1-S4) where the statistical factors are represented by (σ^X):

$$K^A = \sigma^A(K_{ref})^2EM \quad \text{(S1)}$$
$$K^B = K^B_{11} \cdot K^B_{21} = \sigma^B(K_{ref})^2 \quad \text{(S2)}$$
$$K^C = K^C_{11} \cdot K^C_{12} = \sigma^C(K_{ref})^2 \quad \text{(S3)}$$
$$(K^D)^2 = (\sigma^D K_{ref})^2 \quad \text{(S4)}$$

The overall binding constant, and therefore EM can be calculated by considering the overall DMC equilibria and combining the above equations to get equations (S5 and S6):

$$K = \frac{K^A(K^D)^2}{K^B K^C} = \frac{\sigma^A(K_{ref})^2 EM(\sigma^D K_{ref})^2}{\sigma^B(K_{ref})^2\sigma^C(K_{ref})^2} = \frac{\sigma^A\sigma^D}{\sigma^B\sigma^C}EM \quad \text{(S5)}$$

$$EM = \frac{\sigma^B\sigma^C}{\sigma^A\sigma^D}K \quad \text{(S6)}$$

5.1 – Determination of Statistical Factors

Statistical factors were determined using Benson's symmetry number method whereby for each step in the DMC equilibria, the product of the reactant symmetry numbers is divided by the product of the product symmetry numbers. Each symmetry number is derived from the point group of the species and a summary of this method for our study is provided (**Figure S45**).

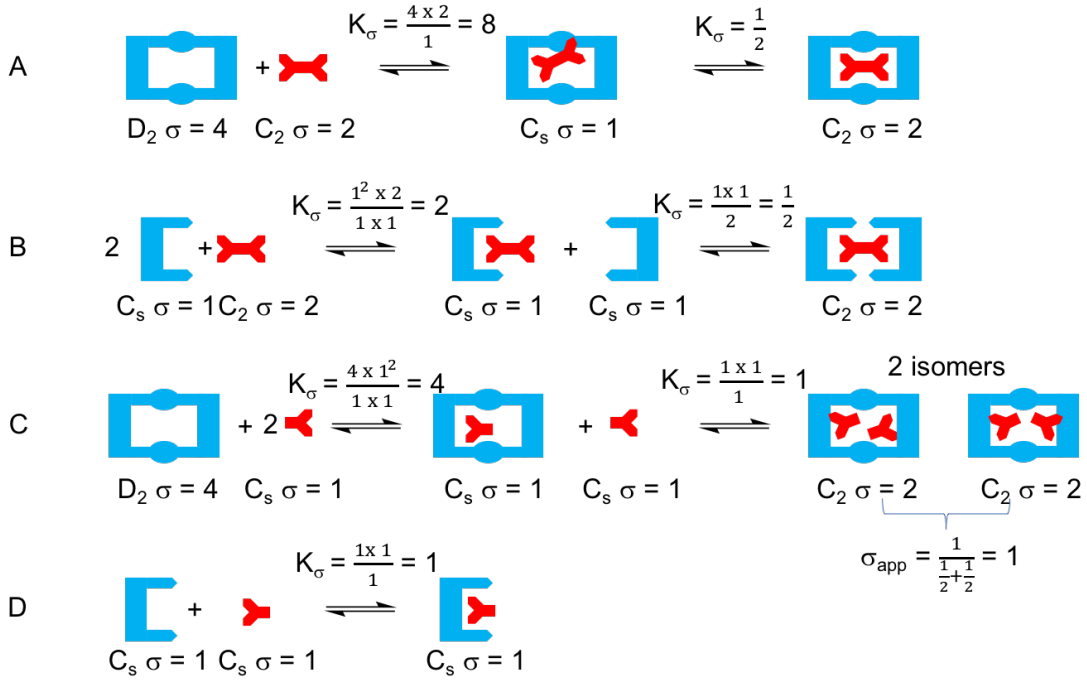

Figure S44: Point groups and symmetry numbers as determined by Benson's symmetry number method represented for each species in this DMC analysis.

Taken together, equations (S1-S6) can be re-written with the appropriate statistical factor added in to give equations (S7-S11) which describe EM for this DMC:

$$K^A = 4(K_{ref})^2 EM \qquad \text{(S7)}$$
$$K^B = K^B{}_{11} \cdot K^B{}_{21} = (K_{ref})^2 \qquad \text{(S8)}$$
$$K^C = K^C{}_{11} \cdot K^C{}_{12} = 4(K_{ref})^2 \qquad \text{(S9)}$$
$$(K^D)^2 = (K_{ref})^2 \qquad \text{(S10)}$$

$$K = \frac{K^A (K^D)^2}{K^B K^C} = \frac{4(K_{ref})^2 EM (K_{ref})^2}{(K_{ref})^2 4 (K_{ref})^2} = EM \qquad \text{(S11)}$$

The Benson's symmetry number method in **Figure S45** (top line) also allows equation 3 (main text) to be calculated from equation 1 (main text) as follows:

$$K_{intra} = \sigma' K_{ref} \cdot \mathrm{EM} = {}^1\!/_2\, K_{ref} \cdot \mathrm{EM} \qquad (3)$$

5.2 – DMC Analysis for dt1

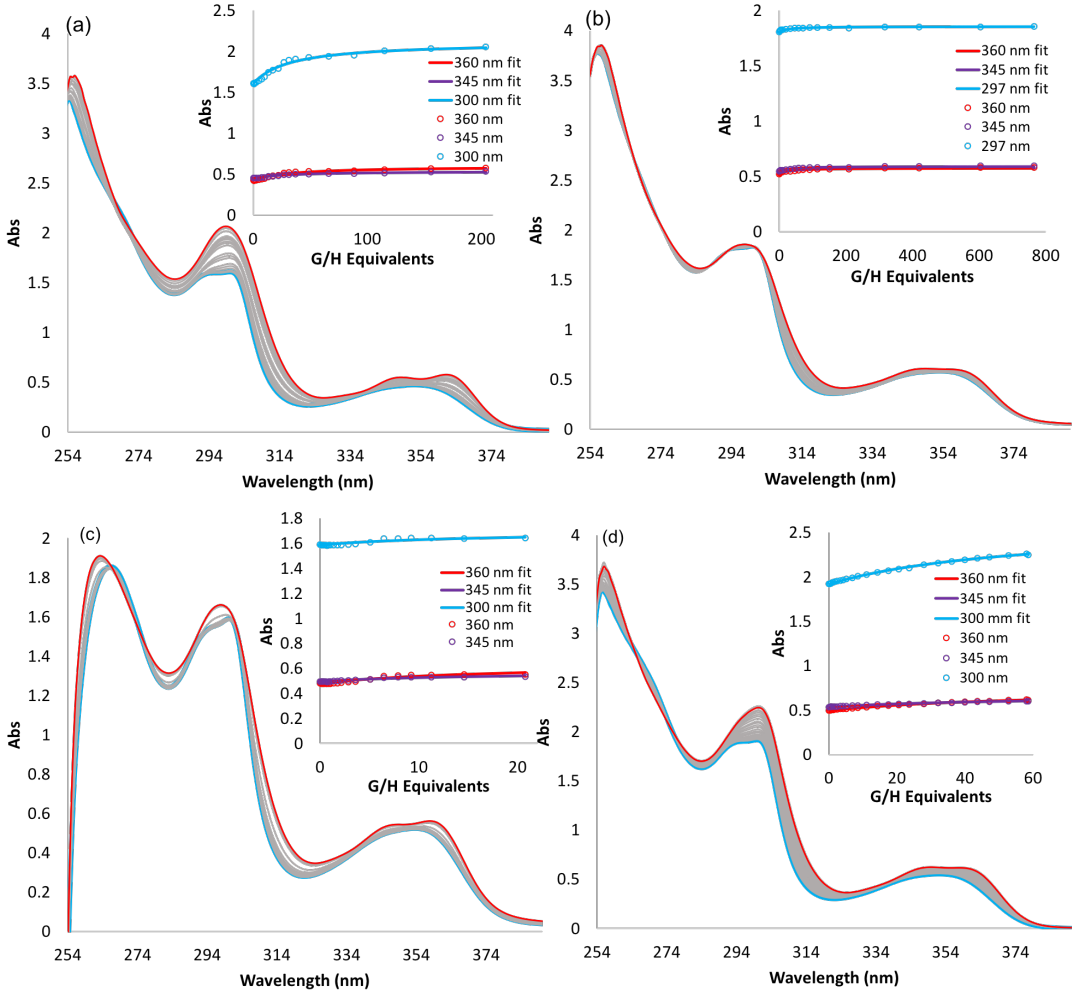

Figure S45: DMC analysis for **dt1** with TBA_2Malonate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 Malonate, inset: global fitting analysis to 2:1 statistical model. (b) Titration of **dt1** with TBA Propionate, inset: global fitting analysis to 1:2 statistical model. (c) Titration of **dt1** with TBA_2 Malonate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Propionate, inset: global fitting analysis to 1:1 model.

Table S1: Summary of DMC Analysis for **dt1** with TBA_2Malonate.

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt1·Mal	K_{11}	2280	0.5	0.14
mt3·Mal	K_{11}	1570		
	K_{21}	390		
dt1·Pro	K_{11}	3310		
	K_{12}	830		
mt3·Pro	K_{11}	600		

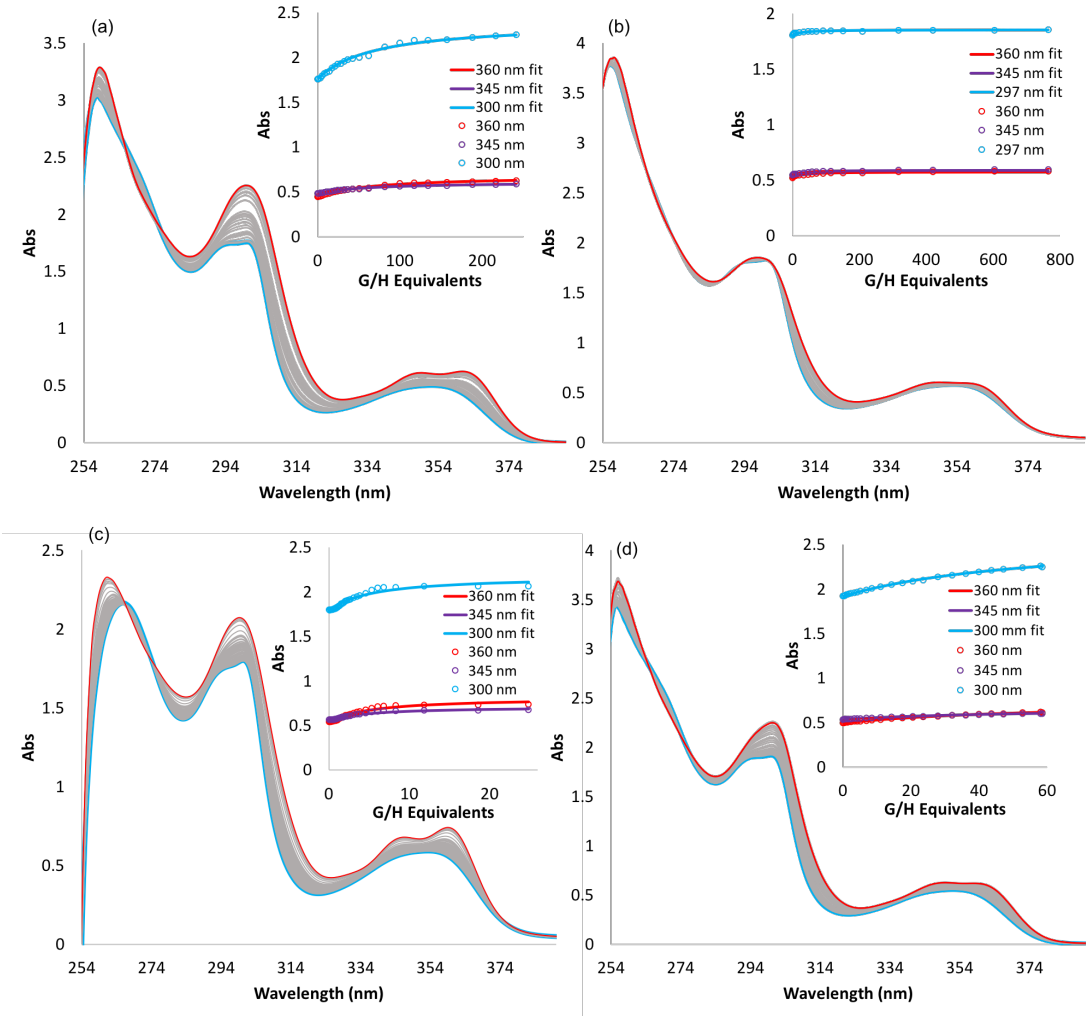

Figure S46: DMC analysis for **dt1** with TBA_2Succinate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 Succinate, inset: global fitting analysis to 2:1 statistical model. (b) Titration of **dt1** with TBA Propionate, inset: global fitting analysis to 1:2 statistical model. (c) Titration of **dt1** with TBA_2 Succinate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Propionate, inset: global fitting analysis to 1:1 model.

Table S2: Summary of DMC Analysis for **dt1** with TBA_2 Succinate.

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt1·Suc	K_{11}	7890	14	4.2
mt3·Suc	K_{11}	550		
	K_{21}	140		
dt1·Pro	K_{11}	3310		
	K_{12}	830		
mt3·Pro	K_{11}	600		

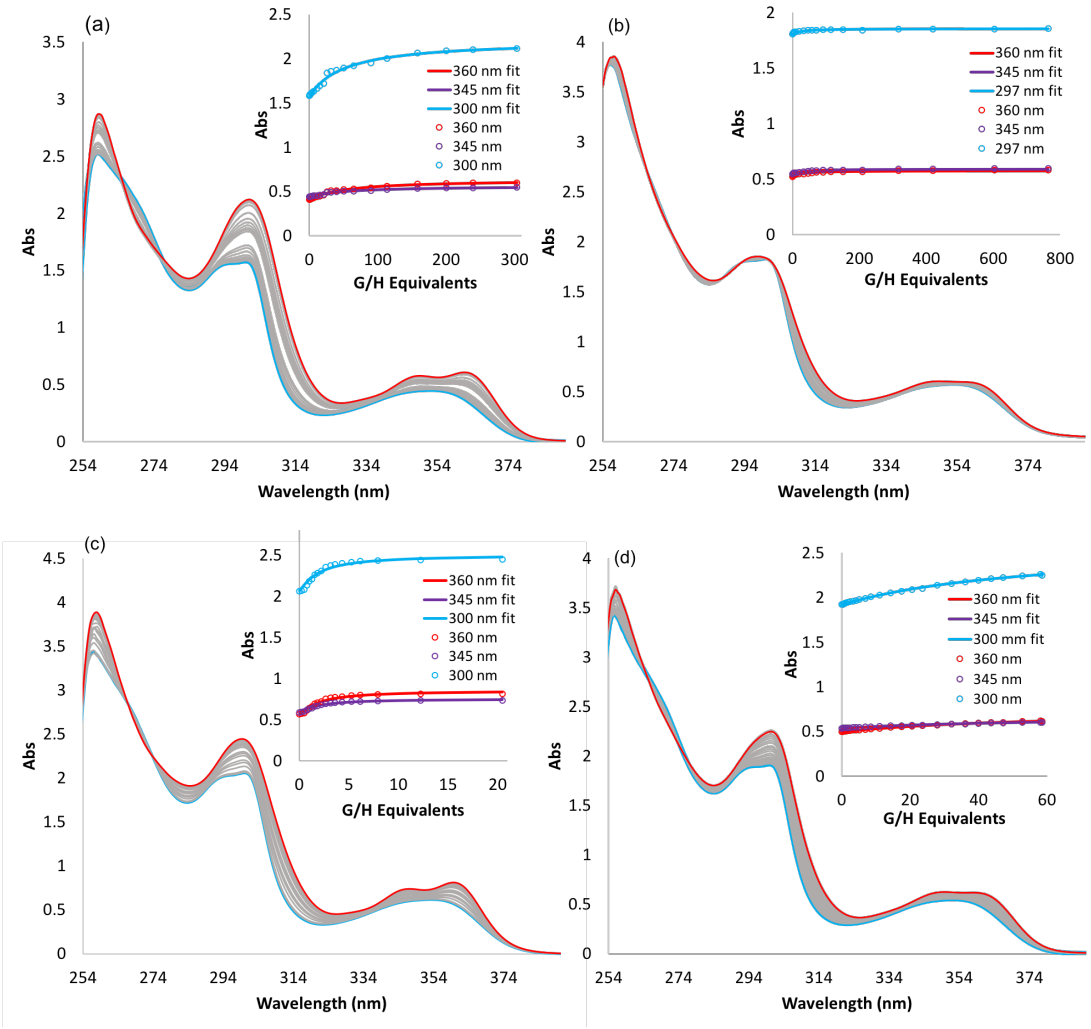

Figure S47: DMC analysis for **dt1** with TBA_2Glutarate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 Glutarate, inset: global fitting analysis to 2:1 statistical model. (b) Titration of **dt1** with TBA Propionate, inset: global fitting analysis to 1:2 statistical model. (c) Titration of **dt1** with TBA_2 Glutarate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Propionate, inset: global fitting analysis to 1:1 model.

Table S3: Summary of DMC Analysis for **dt1** with TBA_2 Glutarate.

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt1·Glu	K_{11}	35680	21	6.2
mt3·Glu	K_{11}	1000		
	K_{21}	660		
dt1·Pro	K_{11}	3310		
	K_{12}	830		
mt3·Pro	K_{11}	600		

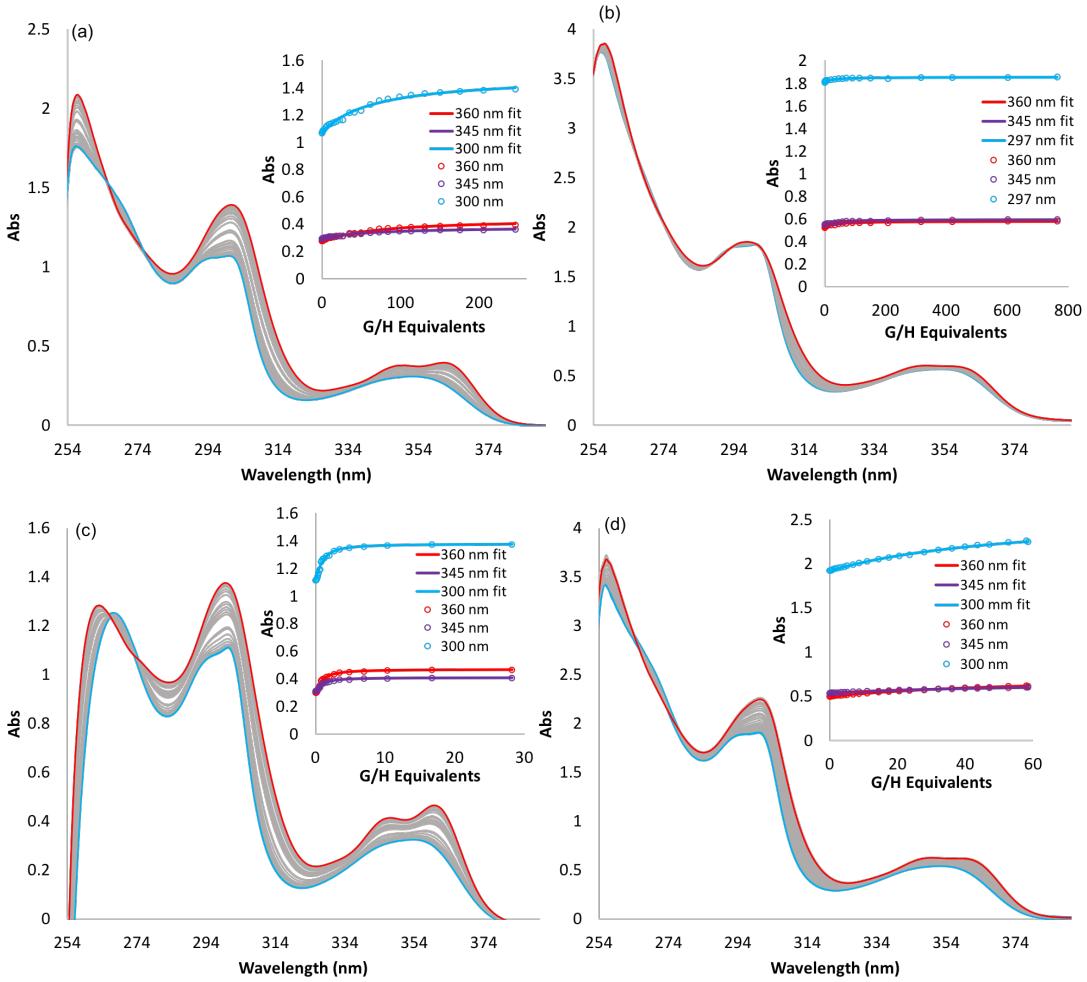

Figure S48: DMC analysis for **dt1** with TBA_2Adipate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 Adipate, inset: global fitting analysis to 2:1 statistical model. (b) Titration of **dt1** with TBA Propionate, inset: global fitting analysis to 1:2 statistical model. (c) Titration of **dt1** with TBA_2 Adipate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Propionate, inset: global fitting analysis to 1:1 model.

Table S4: Summary of DMC Analysis for **dt1** with TBA_2 Adipate.

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt1·Adi	K_{11}	74980	91	27.4
mt3·Adi	K_{11}	660		
	K_{21}	165		
dt1·Pro	K_{11}	3310		
	K_{12}	830		
mt3·Pro	K_{11}	600		

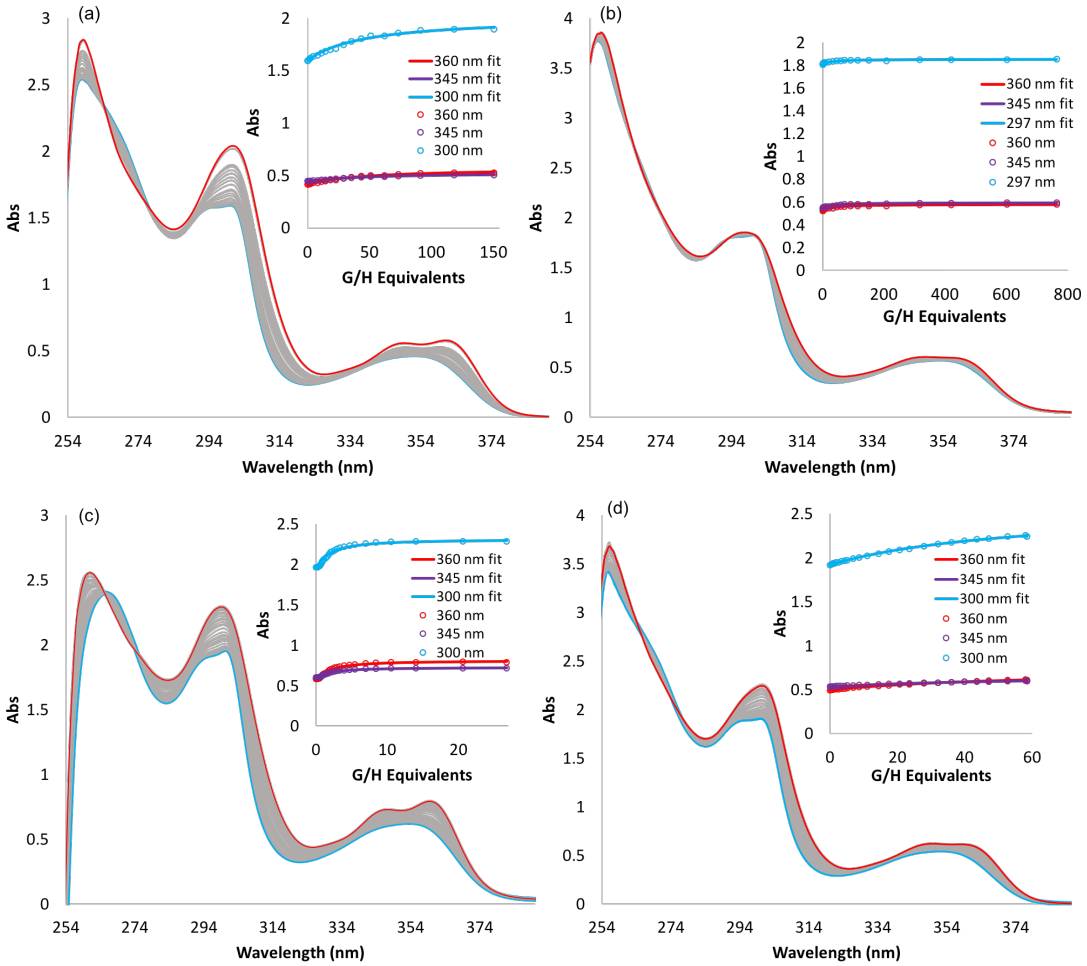

Figure S49: DMC analysis for **dt1** with TBA_2Pimelate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 Pimelate, inset: global fitting analysis to 2:1 statistical model. (b) Titration of **dt1** with TBA Propionate, inset: global fitting analysis to 1:2 statistical model. (c) Titration of **dt1** with TBA_2 Pimelate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Propionate, inset: global fitting analysis to 1:1 model.

Table S5: Summary of DMC Analysis for **dt1** with TBA_2 Pimelate.

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt1·Pim	K_{11}	26950	12	3.6
mt3·Pim	K_{11}	1080		
	K_{21}	270		
dt1·Pro	K_{11}	3310		
	K_{12}	830		
mt3·Pro	K_{11}	600		

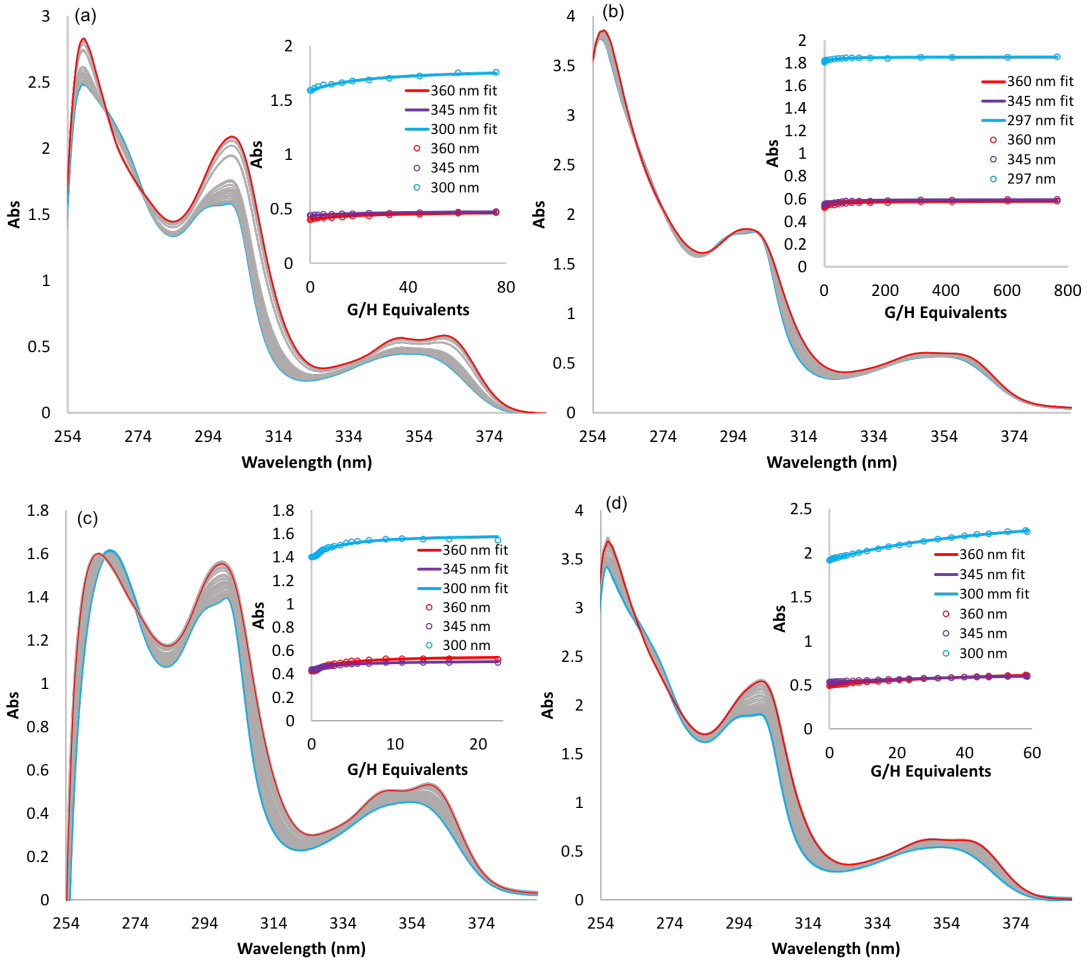

Figure S50: DMC analysis for **dt1** with TBA_2 Suberate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 Suberate, inset: global fitting analysis to 2:1 statistical model. (b) Titration of **dt1** with TBA Propionate, inset: global fitting analysis to 1:2 statistical model. (c) Titration of **dt1** with TBA_2 Suberate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Propionate, inset: global fitting analysis to 1:1 model.

Table S6: Summary of DMC Analysis for **dt1** with TBA_2 Suberate.

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt1·Sub	K_{11}	12890	1.6	0.5
mt3·Sub	K_{11}	2050		
	K_{21}	510		
dt1·Pro	K_{11}	3310		
	K_{12}	830		
mt3·Pro	K_{11}	600		

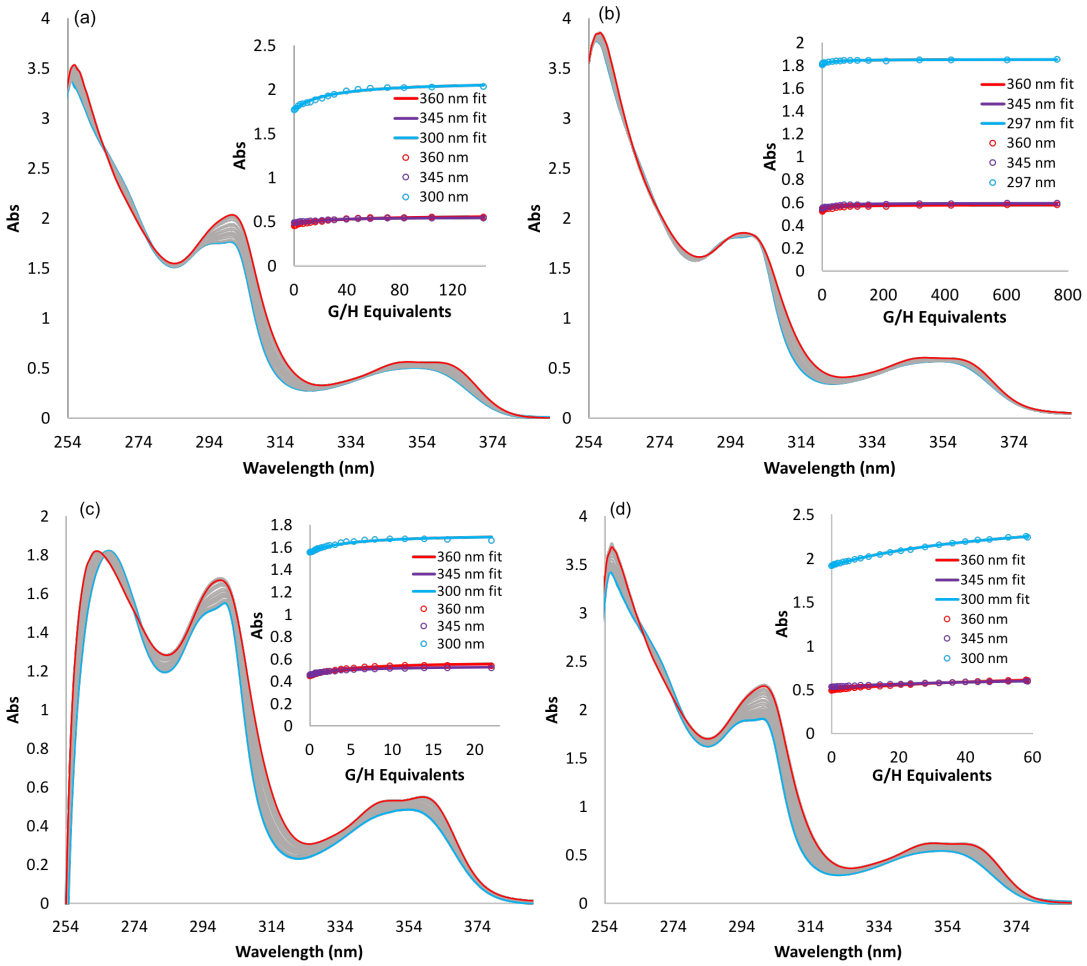

Figure S51: DMC analysis for **dt1** with TBA_2 Azelate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 Azelate, inset: global fitting analysis to 2:1 statistical model. (b) Titration of **dt1** with TBA Propionate, inset: global fitting analysis to 1:2 statistical model. (c) Titration of **dt1** with TBA_2 Azelate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Propionate, inset: global fitting analysis to 1:1 model.

Table S7: Summary of DMC Analysis for **dt1** with TBA_2 Azelate.

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt1·Aze	K_{11}	9170	2.4	0.7
mt3·Aze	K_{11}	1400		
	K_{21}	350		
dt1·Pro	K_{11}	3310		
	K_{12}	830		
mt3·Pro	K_{11}	600		

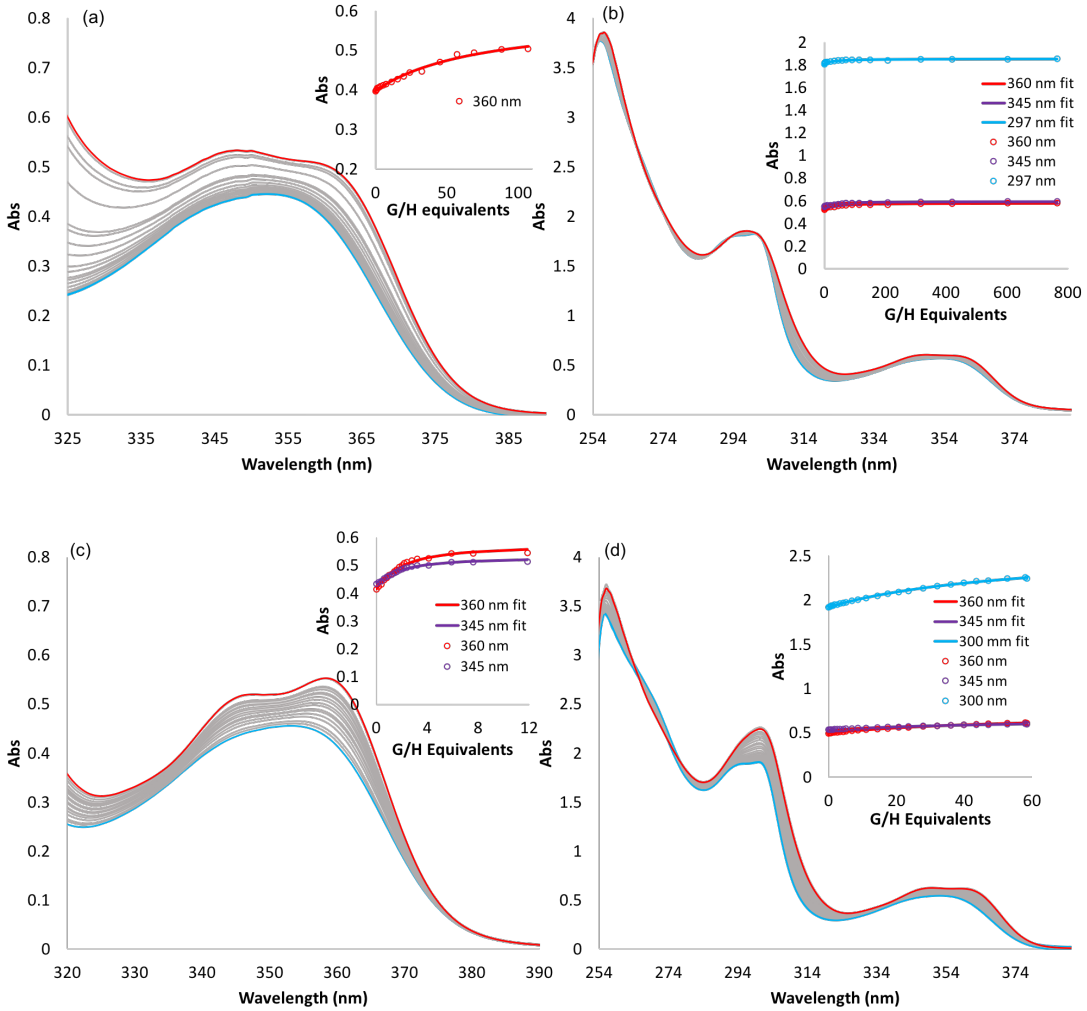

Figure S52: DMC analysis for **dt1** with TBA_2 *trans,trans*-Muconate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 *trans,trans*-Muconate, inset: peak at 360 nm fit to 2:1 statistical model. (b) Titration of **dt1** with TBA Propionate, inset: global fitting analysis to 1:2 statistical model. (c) Titration of **dt1** with TBA_2 *trans,trans*-Muconate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Propionate, inset: global fitting analysis to 1:1 model. For (a) and (c), spectra are only shown to 320 nm due to interference arising from the added *trans,trans*-Muconate anion.

Table S8: Summary of DMC Analysis for **dt1** with TBA_2 *trans,trans*-Muconate.

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt1·ttM	K_{11}	27840	32	9.7
mt3·ttM	K_{11}	680		
	K_{21}	170		
dt1·Pro	K_{11}	3310		
	K_{12}	840		
mt3·Pro	K_{11}	600		

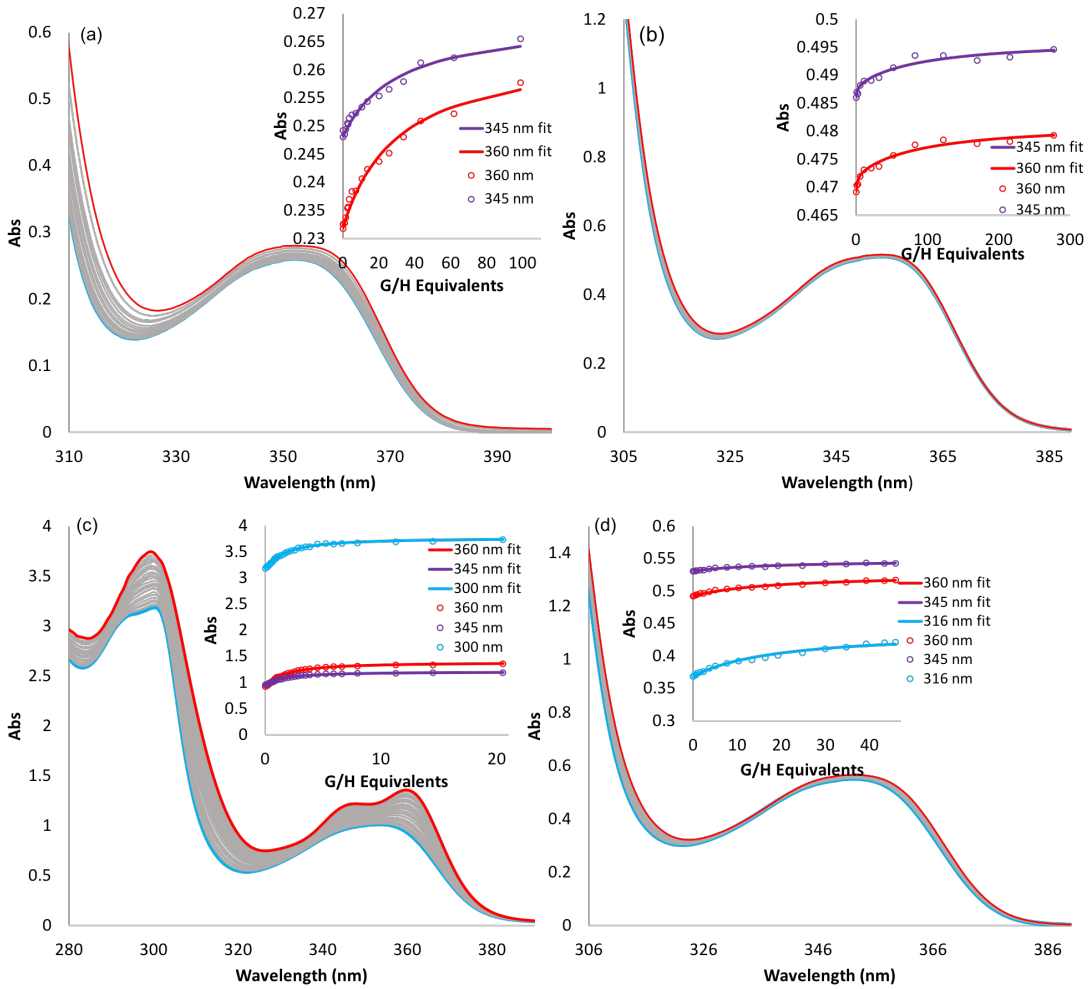

Figure S53: DMC analysis for **dt1** with TBA_2 Terephthalate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 Terephthalate, inset: global fitting analysis to 2:1 statistical model. (b) Titration of **dt1** with TBA Benzoate, inset: global fitting analysis to 1:2 full. (c) Titration of **dt1** with TBA_2 Terephthalate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Benzoate, inset: global fitting analysis to 1:1 model.

Table S9: Summary of DMC Analysis for **dt1** with TBA_2 Terephthalate

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt1·Ter	K_{11}	30200	19	17.4
mt3·Ter	K_{11}	1240		
	K_{21}	310		
dt1·Bnz	K_{11}	30050		
	K_{12}	475		
mt3·Bnz	K_{11}	1840		

5.3 – DMC Analysis for dt2

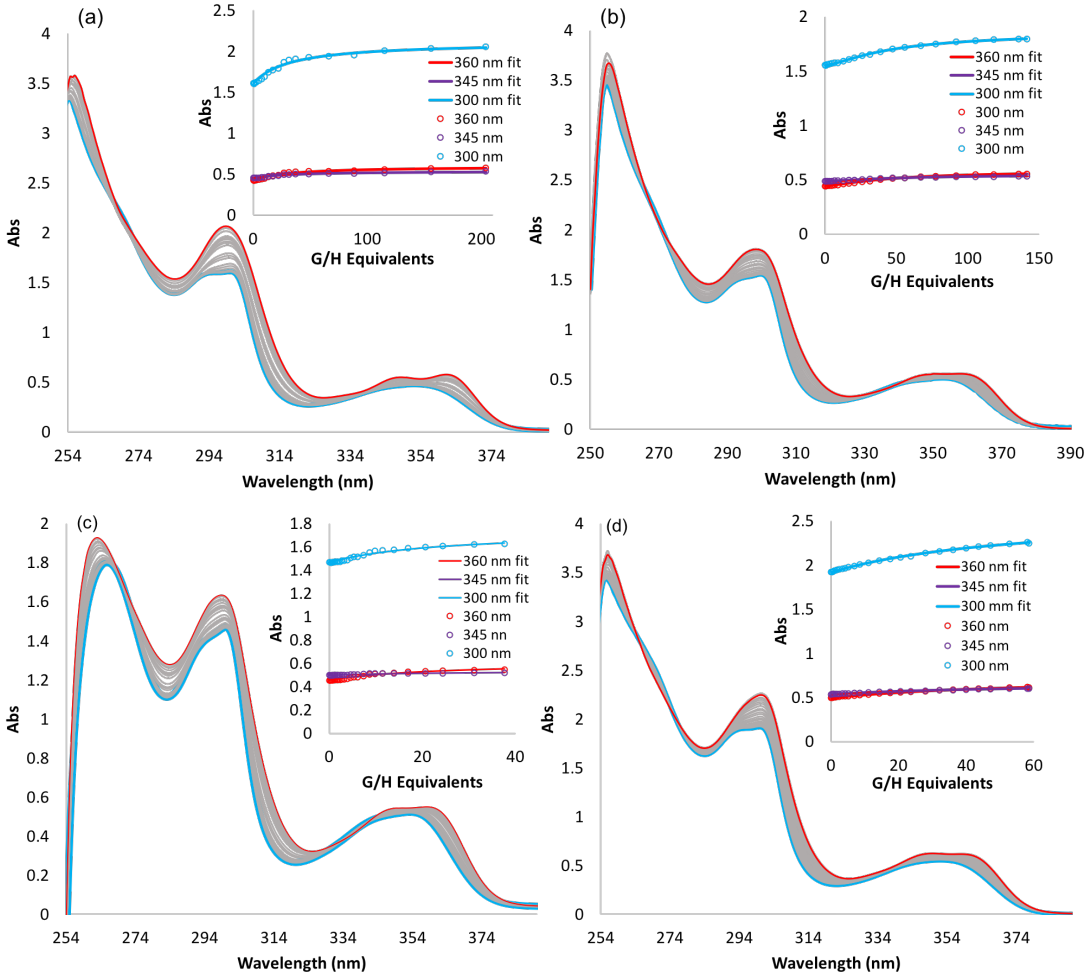

Figure S54: DMC analysis for **dt2** with TBA_2 Malonate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 Malonate, inset: global fitting analysis to 2:1 statistical model. (b) Titration of **dt2** with TBA Propionate, inset: global fitting analysis to 1:2 statistical model. (c) Titration of **dt2** with TBA_2 Malonate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Propionate, inset: global fitting analysis to 1:1 model.

Table S10: Summary of DMC Analysis for **dt2** with TBA_2 Malonate.

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt2·Mal	K_{11}	1850	0.4	0.11
mt3·Mal	K_{11}	1570		
	K_{21}	390		
dt2·Pro	K_{11}	2230		
	K_{12}	1240		
mt3·Pro	K_{11}	600		

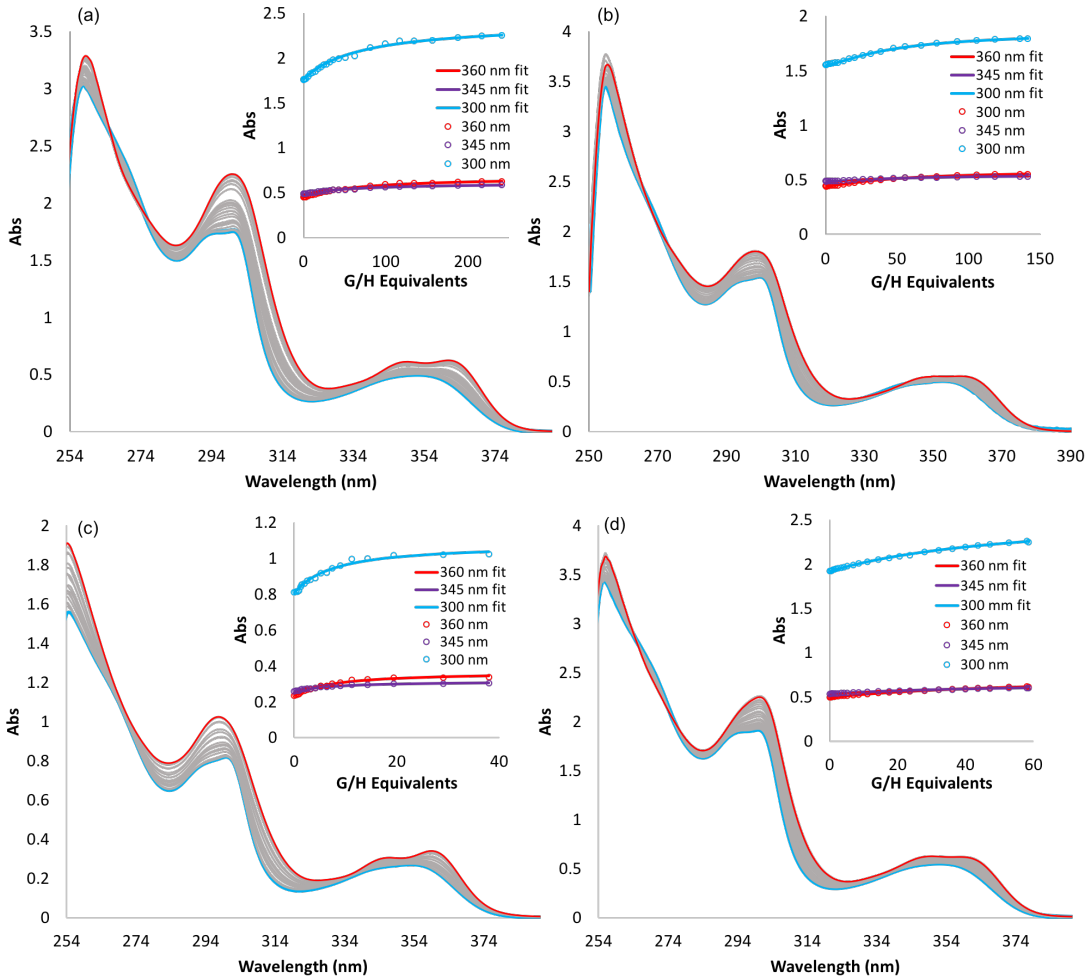

Figure S55: DMC analysis for **dt2** with TBA_2 Succinate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 Succinate, inset: global fitting analysis to 2:1 statistical model. (b) Titration of **dt2** with TBA Propionate, inset: global fitting analysis to 1:2 statistical model. (c) Titration of **dt2** with TBA_2 Succinate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Propionate, inset: global fitting analysis to 1:1 model.

Table S11: Summary of DMC Analysis for **dt2** with TBA_2 Succinate.

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt2·Suc	K_{11}	5770	10	2.9
mt3·Suc	K_{11}	550		
	K_{21}	140		
dt2·Pro	K_{11}	2300		
	K_{12}	1240		
mt3·Pro	K_{11}	600		

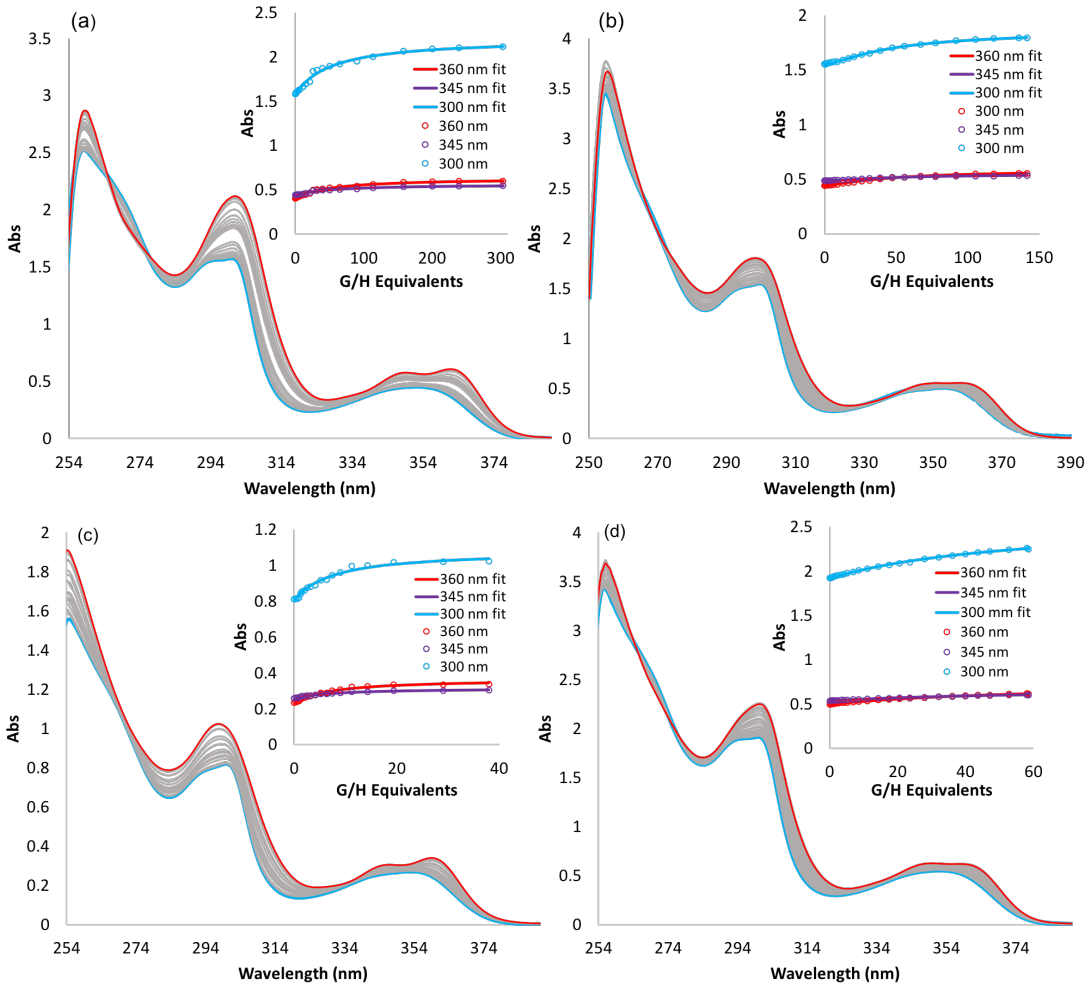

Figure S56: DMC analysis for **dt2** with TBA_2 Glutarate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 Glutarate, inset: global fitting analysis to 2:1 statistical model. (b) Titration of **dt2** with TBA Propionate, inset: global fitting analysis to 1:2 statistical model. (c) Titration of **dt2** with TBA_2 Glutarate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Propionate, inset: global fitting analysis to 1:1 model.

Table S12: Summary of DMC Analysis for **dt2** with TBA_2 Glutarate.

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt2·Glu	K_{11}	51050	28	8.5
mt3·Glu	K_{11}	1000		
	K_{21}	250		
dt2·Pro	K_{11}	2300		
	K_{12}	1240		
mt3·Pro	K_{11}	600		

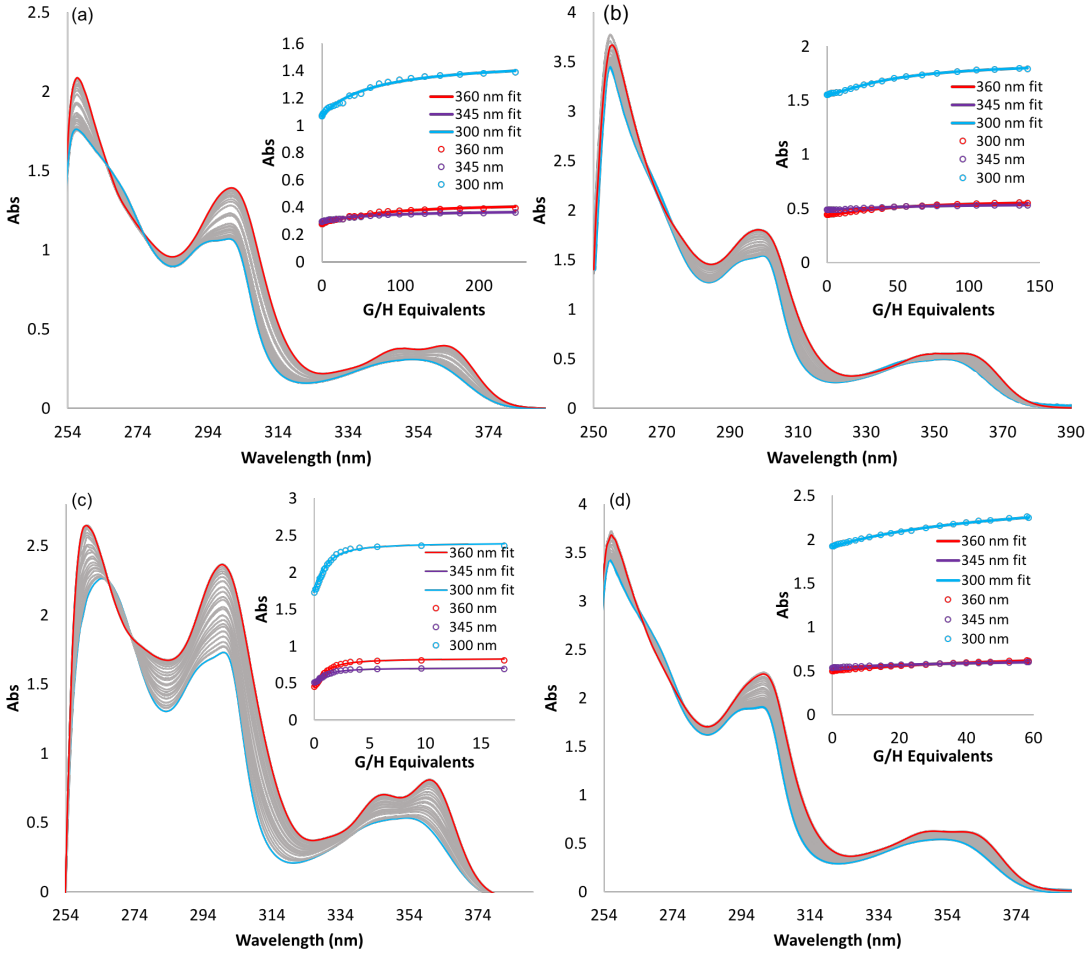

Figure S57: DMC analysis for **dt2** with TBA_2 Adipate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 Adipate, inset: global fitting analysis to 2:1 statistical model. (b) Titration of **dt2** with TBA Propionate, inset: global fitting analysis to 1:2 statistical model. (c) Titration of **dt2** with TBA_2 Adipate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Propionate, inset: global fitting analysis to 1:1 model.

Table S13: Summary of DMC Analysis for **dt2** with TBA_2 Adipate.

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt2·Adi	K_{11}	87190	102	30.7
mt3·Adi	K_{11}	660		
	K_{21}	165		
dt2·Pro	K_{11}	2300		
	K_{12}	1250		
mt3·Pro	K_{11}	600		

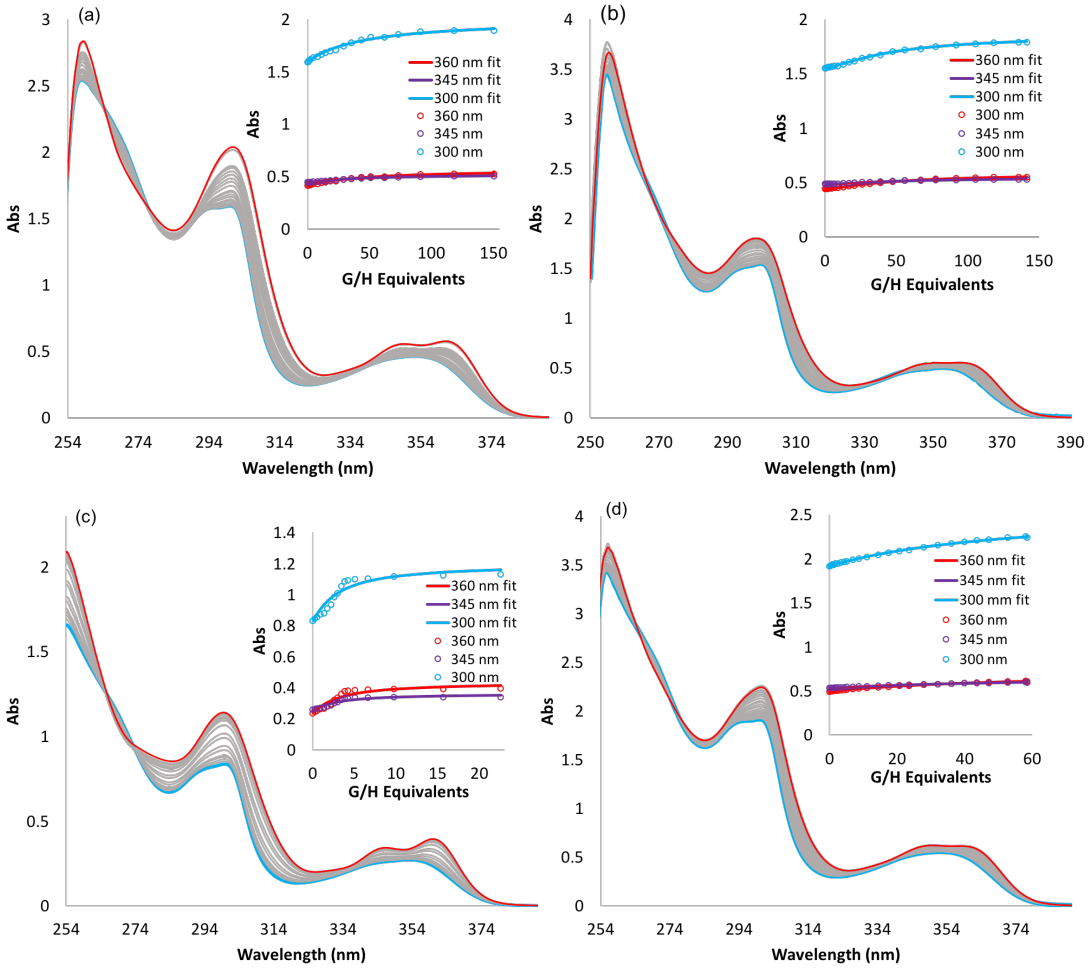

Figure S58: DMC analysis for **dt2** with TBA_2 Pimelate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 Pimelate, inset: global fitting analysis to 2:1 statistical model. (b) Titration of **dt2** with TBA Propionate, inset: global fitting analysis to 1:2 statistical model. (c) Titration of **dt2** with TBA_2 Pimelate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Propionate, inset: global fitting analysis to 1:1 model.

Table S14: Summary of DMC Analysis for **dt2** with TBA_2 Pimelate.

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt2·Pim	K_{11}	15600	7	2.1
mt3·Pim	K_{11}	1090		
	K_{21}	270		
dt2·Pro	K_{11}	2300		
	K_{12}	1240		
mt3·Pro	K_{11}	600		

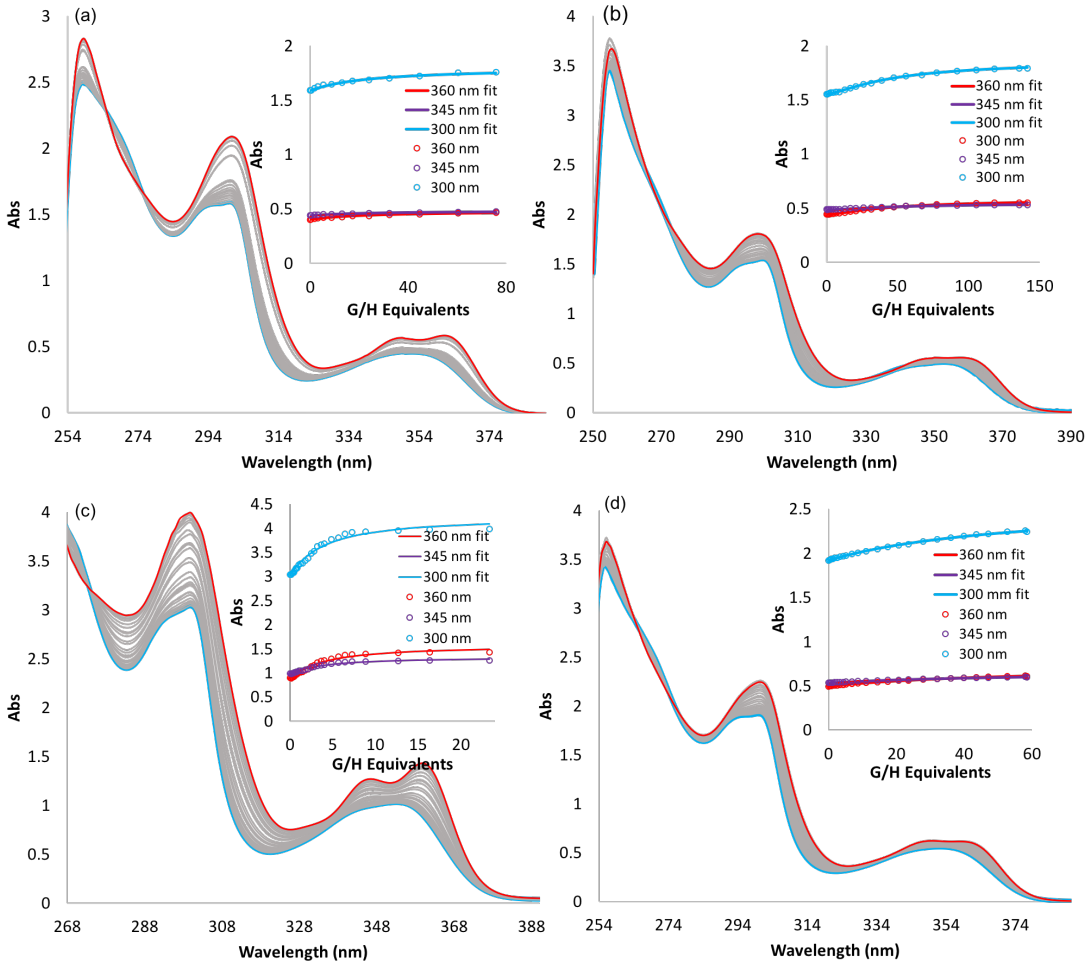

Figure S59: DMC analysis for **dt2** with TBA_2 Suberate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 Suberate, inset: global fitting analysis to 2:1 statistical model. (b) Titration of **dt2** with TBA Propionate, inset: global fitting analysis to 1:2 statistical model. (c) Titration of **dt2** with TBA_2 Suberate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Propionate, inset: global fitting analysis to 1:1 model.

Table S15: Summary of DMC Analysis for **dt2** with TBA_2 Suberate.

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt2·Sub	K_{11}	2120	1.5	0.4
mt3·Sub	K_{11}	2050		
	K_{21}	510		
dt2·Pro	K_{11}	2300		
	K_{12}	1240		
mt3·Pro	K_{11}	600		

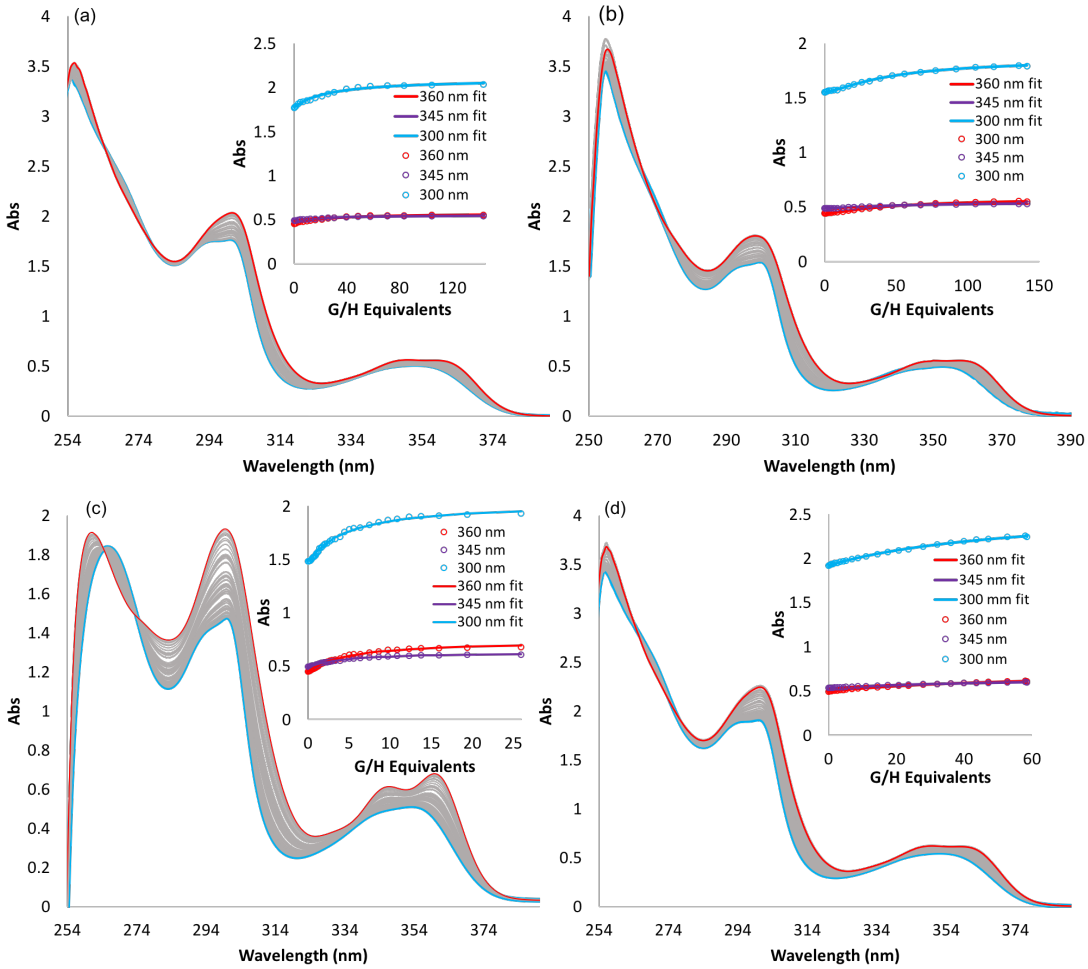

Figure S60: DMC analysis for **dt2** with TBA_2 Azelate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 Azelate, inset: global fitting analysis to 2:1 statistical model. (b) Titration of **dt2** with TBA Propionate, inset: global fitting analysis to 1:2 statistical model. (c) Titration of **dt2** with TBA_2 Azelate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Propionate, inset: global fitting analysis to 1:1 model.

Table S16: Summary of DMC Analysis for **dt2** with TBA_2 Azelate.

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt2·Aze	K_{11}	9840	2.6	0.8
mt3·Aze	K_{11}	1400		
	K_{21}	350		
dt2·Pro	K_{11}	2300		
	K_{12}	1240		
mt3·Pro	K_{11}	600		

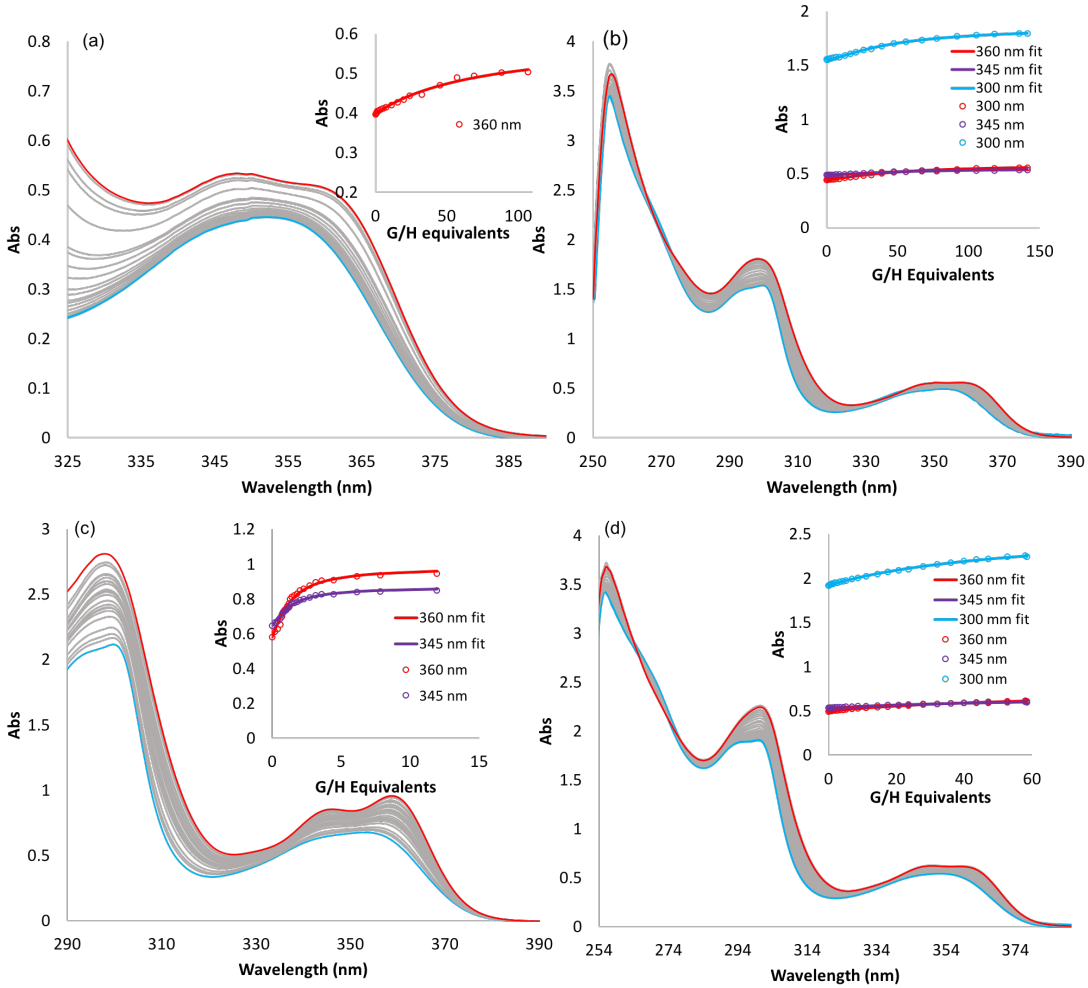

Figure S61: DMC analysis for **dt2** with TBA_2 *trans,trans*-Muconate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 *trans,trans*-Muconate, inset: peak at 360 nm fit to 2:1 statistical model. (b) Titration of **dt2** with TBA Propionate, inset: global fitting analysis to 1:2 statistical model. (c) Titration of **dt2** with TBA_2 *trans,trans*-Muconate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Propionate, inset: global fitting analysis to 1:1 model. For (a) and (c), spectra are only shown to 320 nm due to interference arising from the added *trans,trans*-Muconate anion.

Table S17: Summary of DMC Analysis for **dt2** with TBA_2 *trans,trans*-Muconate.

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt2·ttM	K_{11}	57550	64	19.2
mt3·ttM	K_{11}	680		
	K_{21}	170		
dt2·Pro	K_{11}	2300		
	K_{12}	1240		
mt3·Pro	K_{11}	600		

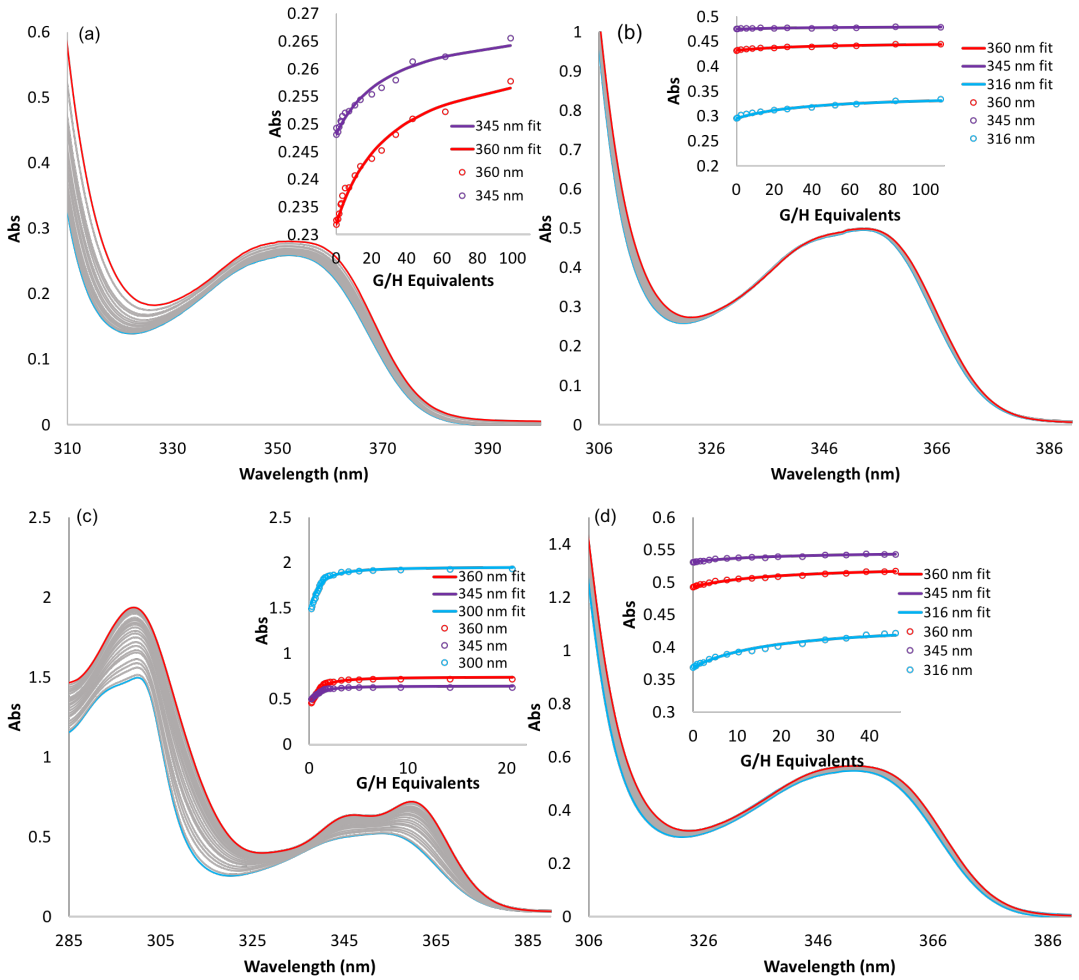

Figure S62: DMC analysis for **dt2** with TBA_2 Terephthalate. All UV-Vis titrations were performed in aqueous DMSO solution (1:9 *v/v*) at 298 K. (a) Titration of **mt3** with TBA_2 Terephthalate, inset: global fitting analysis to 2:1 statistical model. (b) Titration of **dt2** with TBA Benzoate, inset: global fitting analysis to 1:2 full. (c) Titration of **dt2** with TBA_2 Terephthalate, inset: global fitting analysis to 1:1 model. (d) Titration of **mt3** with TBA Benzoate, inset: global fitting analysis to 1:1 model.

Table S18: Summary of DMC Analysis for **dt2** with TBA_2 Terephthalate

		K_a (M^{-1})	*EM* (mM)	K_{intra} (M^{-1})
dt2·Ter	K_{11}	86900	210	191
mt3·Ter	K_{11}	1240		
	K_{21}	310		
dt2·Bnz	K_{11}	18900		
	K_{12}	200		
mt3·Bnz	K_{11}	1840		

6 – Fluorescence Screening Data

Fluorescence ion screening was performed as follows: 1 mM stock solutions of relevant anion were prepared in H_2O/DMSO (*1:9 v/v*) and added to a solution of macrocycle **dt1** or **dt2** such that the final receptor concentration was 25 μM and the final anion concentration was 250 μM. Anions were all added as tetrabutylammonium (TBA) salts with the exception of HCO_3^- which was added as the tetraethylammonium (TEA) salt. Fluorescence spectra were obtained on a Cary Eclipse fluorimeter with the following parameters: λ_{ex} = 300 nm, λ_{em} = 330-500 nm. Fluorescent screening confirmed selective interactions for **dt1** and **dt2** with dicarboxylates over other anions tested.

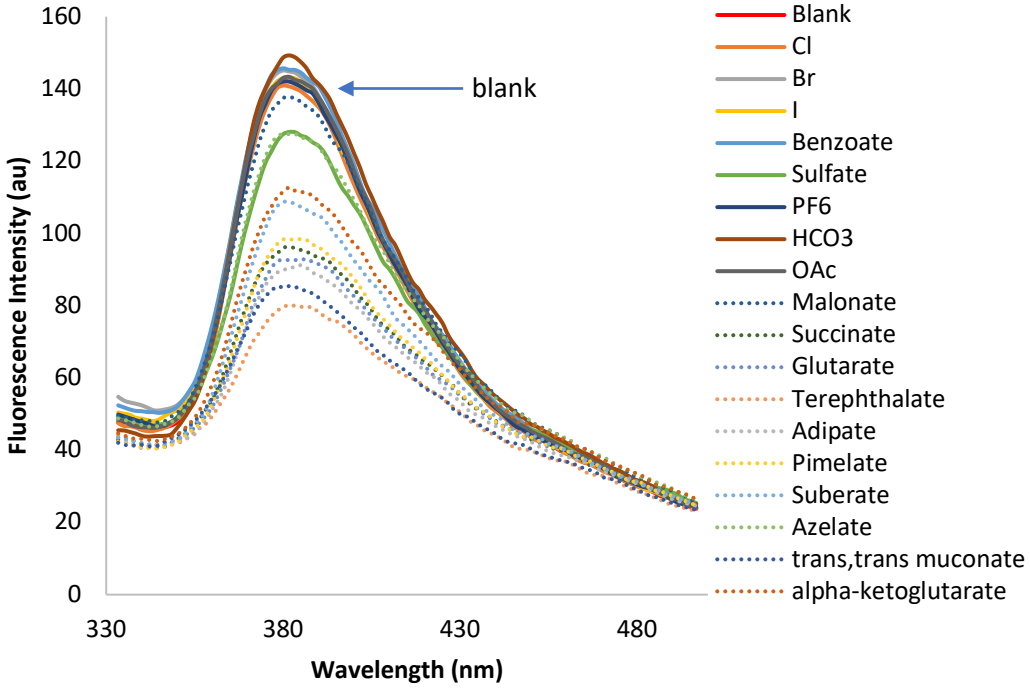

Figure S63: Fluorescence spectra of **dt1** (25 uM) in H_2O/DMSO (*1:9 v/v*) in presence of 10 equivalents of anion. Dicarboxylates are shown as dotted lines. λ_{ex} = 300 nm, λ_{em} = 330-500 nm.

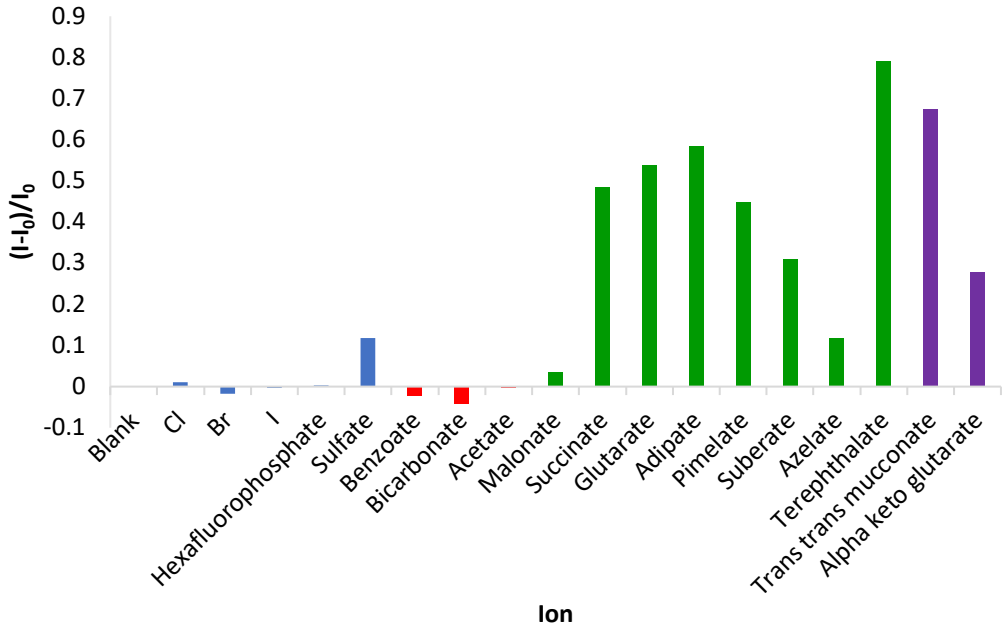

Figure S64: Changes in fluorescence intensity from fluorescent screening of **dt2**. $I-I_0/I_0$ of peak maxima at 380 nm. Halides, sulfate and hexafluorophosphate shown in blue, mono carboxylates shown in red, linear dicarboxylates in green and non-linear dicarboxylates in purple.

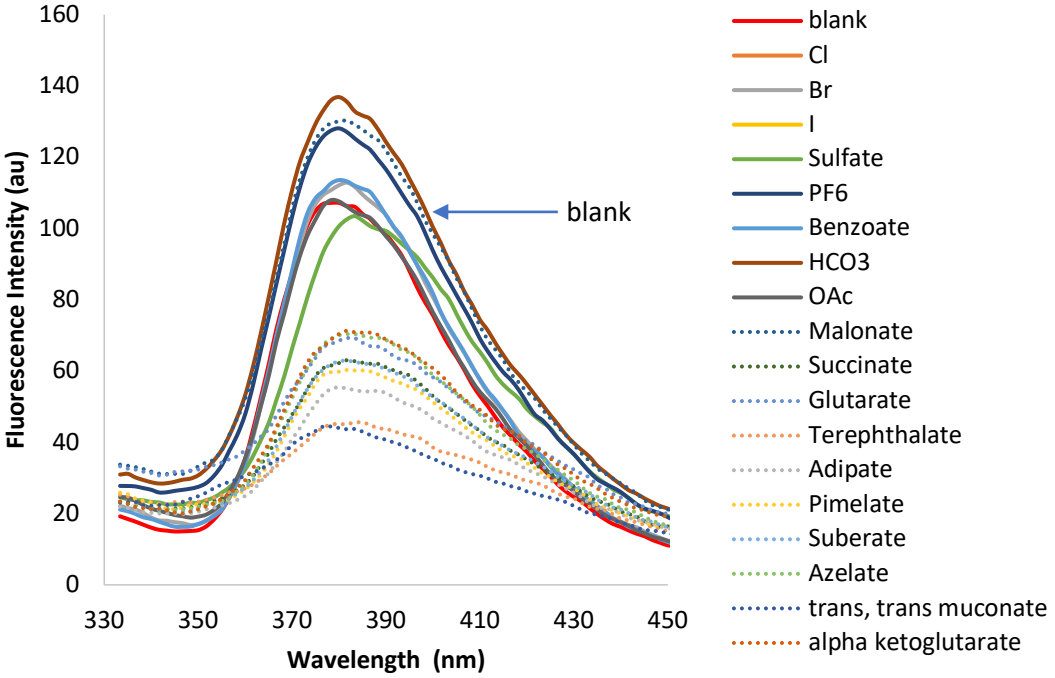

Figure S65: Fluorescence spectra of **2** (25 μM) in H_2O/DMSO (*1:9 v/v*) in presence of 10 equivalents of anion. Dicarboxylates are shown as dotted lines. λ_{ex} = 300 nm, λ_{em} = 330-500 nm.

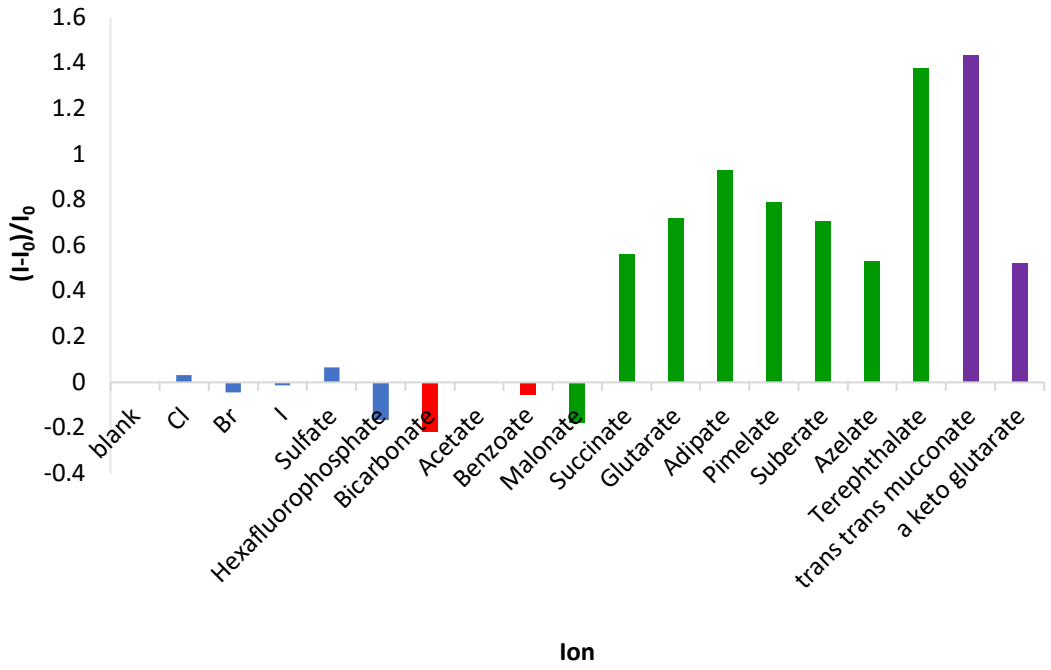

Figure S66: Changes in fluorescence intensity from fluorescent screening of **2**. $I-I_0/I_0$ of peak maxima at 380 nm. Halides, sulfate and hexafluorophosphate shown in blue, mono carboxylates shown in red, linear dicarboxylates in green and non-linear dicarboxylates in purple.

7 – NMR Studies

NMR titrations studies were carried out as follows: a stock solution (2.5 mM, 1500 μL) of **dt1** or **dt2** was prepared in DMSO-d_6/0.5% H_2O. From this, 500 μL was transferred to an NMR tube and the remaining 1000 μL stock solution used to dissolve a solution of dicarboxylate guest (as TBA salt) to a concentration of 37.5 mM. Sequential ^1H NMRs were taken at 298 K with addition of small aliquots of anion guest (typically 1-50 μL) between each spectra acquisition. For each titration experiment, approximately 20 aliquots of anion were added. Stack plots provided are representative of the whole titration experiment.

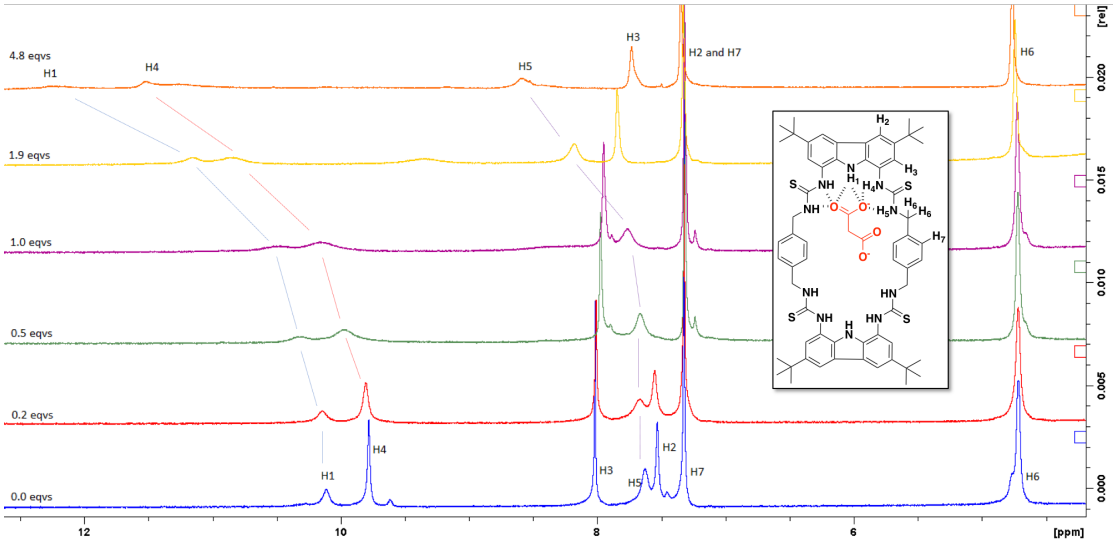

Figure S67: Aromatic region from the ^{1}H NMR titration of **dt2** with TBA_2Malonate in DMSO/0.5% H_2O at 298 K displaying intermediate exchange.

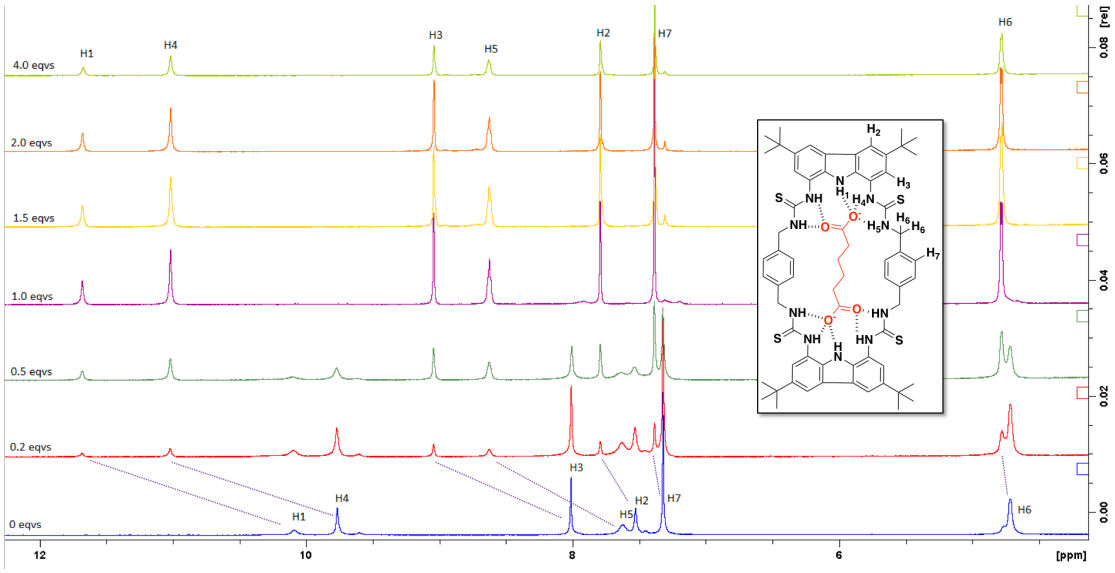

Figure S68: Aromatic region from the ^{1}H NMR titration of **dt2** with TBA_2Adipate in DMSO/0.5% H_2O at 298 K displaying slow exchange, indicative of strong 1:1 binding.

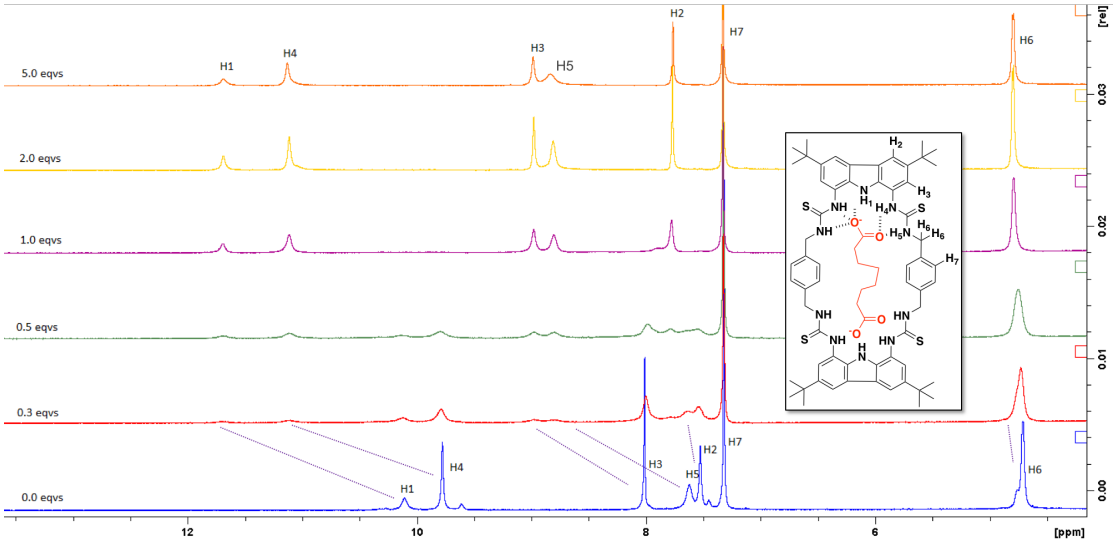

Figure S69: ^{1}H NMR titration of **dt2** with TBA_2Azelate in DMSO/0.5% H_2O at 298 K displaying slow exchange.

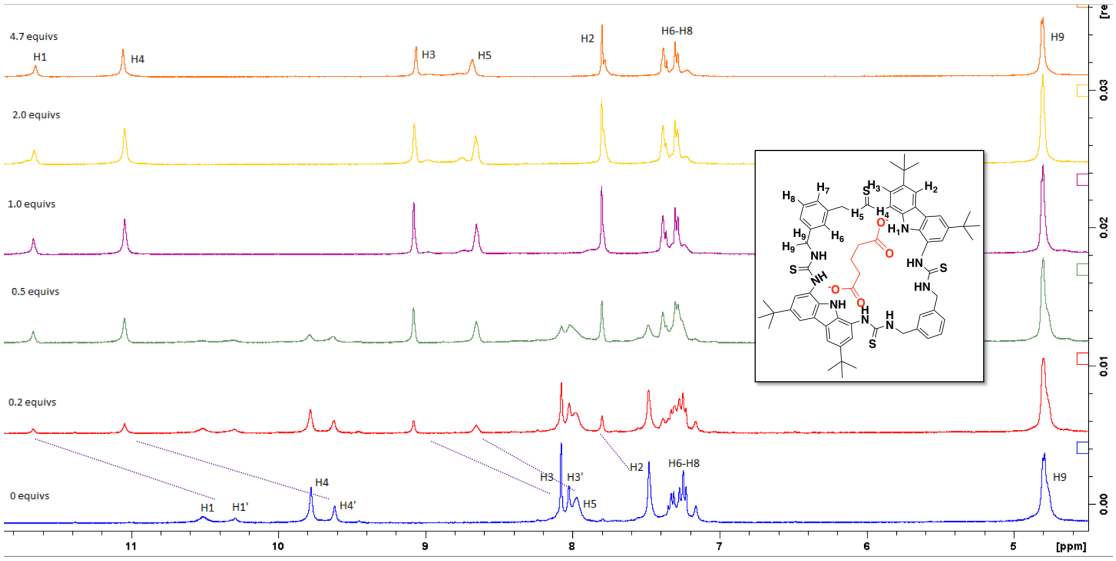

Figure S70: ^{1}H NMR titration of **dt1** with TBA_2Adipate in DMSO/0.5% H_2O at 298 K displaying slow exchange. Slow exchange is displayed and also clear loss of conformational isomer peaks, which suggests a strong 1:1 complex is formed.

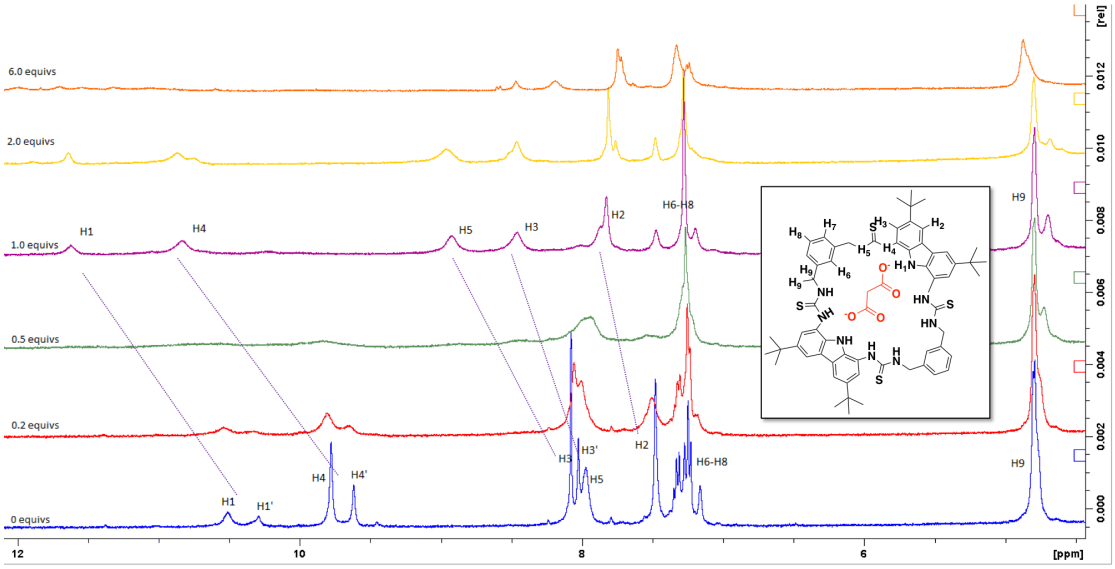

Figure S71: ^{1}H NMR titration of **dt1** with TBA_2Malonate in DMSO/0.5% H_2O at 298 K displaying slow exchange. Intermediate exchange is observed as well as loss of conformational isomerism up to 1 equivalents of guest. Above 1 equivalents of guest, peak splitting is observed, which could indicate higher order complex formation.

8 – References

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