Aromatic donor-acceptor interactions in non-polar environments

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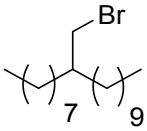
Contents

Experimental

All reagents were purchased from commercial suppliers: Acros Organics, Alfa Aesar, Sigma Aldrich, TCI Europe, Gross or Fluorochem. All reactions monitored using thin layer chromatography (TLC) using pre-coated MN Alugram Sil G/UV254 silica gel 60 aluminium backed plates. Plates were developed using standard techniques, UV light followed by a chemical dip, either $KMnO_4$ or bromocresol green. Flash Chromatography was performed on chromatography grade, silica 60 Å particle size 35-70 micron from Sigma Aldrich using the solvent system as stated.

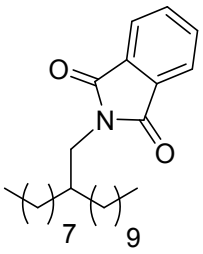
^1H, and ^{13}C was performed on Bruker Advance 250 (^1H 250 MHz), Bruker Advance 300 (^1H 300 MHz and ^{13}C 75 MHz), Bruker Advance 400 (^1H 400 MHz and ^{13}C 100 MHz) and Bruker Advance 500 (^1H 500 MHz and ^{13}C 125 MHz) as stated. Chemical shifts are reported in parts per million (ppm) relative to tetramethyl silane ($\delta = 0.00$). Coupling constants are reported in Hertz (Hz) and signal multiplicity is denoted as singlet (s), doublet (d), triplet (t), apparent triplet (apt), quartet (q), multiplet (m) and broad (b). HRMS recorded at ESPRC NMSF in Swansea on a LTQ Orbitrap XL.
Compounds **5,6** and **7** were synthesised according to the literature.[1,2]

Synthesis of **6**[1]



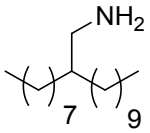
A mixture of 2-octyl-1-dodecanol (8.87 g, 29.7 mmol) and triphenylphosphine (11.7 g, 44.6 mmol) was dissolved in 300 mL THF under ambient conditions. Bromine (18.8 g, 118 mmol) was added slowly and the solution is stirred for 3 h. After this time 6 mL MeOH are added and the solvent is removed. The residue is suspended in hexane and the non-soluble part is removed by filtration. After evaporation of the solvent from the filtrate the obtained oil is purified by column chromatography (hexane) yielding the bromoalkane (7.72 g, 89%) as a colourless oil. ^1H NMR (300 MHz, $CDCl_3$, 298K): 3.44 (2H, d, J=4.8Hz), 1.58 (1H, m), 1.27 (32H, m), 0.88 (6H, t, J=6.7Hz); the ^1H NMR spectrum matches the literature data.[1]

Synthesis of **7**[2]



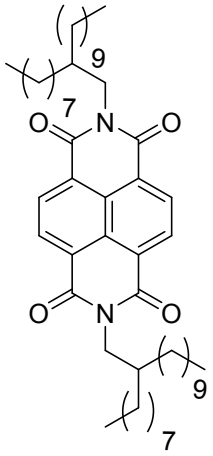
1-Bromo-2-octyldodecane (2.32 g, 6.42 mmol) and potassium phthalimide (1.31 g, 7.06 mmol) were dissolved in 10 ml of DMF and stirred for 10 h at 90 °C. After the mixture was cooled, it was poured to water (100 mL) and extracted with CH_2Cl_2. The combined organic layer was washed with 0.10 % KOH aq., water and saturated NH_4Cl aq. (150 mL). The solvent was then removed under reduced pressure and the residue suspended in hexane and the non-soluble part removed by filtration. The solvent was then removed under reduced pressure to yield a colourless oil (2.30 g, 84 %). ^{1}H NMR (300 MHz, $CDCl_3$, 298K): 7.84 (2H, m), 7.71 (2H, m), 3.56 (2H, d, J=7.3Hz), 1.87 (1H, m), 1.23 (32H, m), 0.86 (6H, m); the ^{1}H NMR spectrum matches the literature data.[2]

Synthesis of **8**[2]



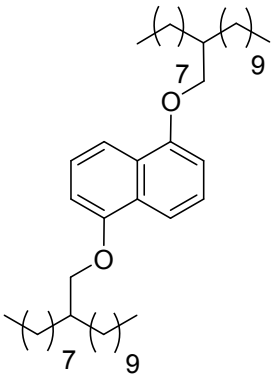
To a solution of *N*-(2-octyldodecyl)phthalimide (2.30 g, 5.38 mmol) in MeOH (30ml mL), hydrazine monohydride (0.809g, 16.4 mmol) was added. After the mixture was refluxed for 8 h, it was cool and then evaporated under vacuum. The residue was dissolved in dichloromethane and washed with 10 wt% KOH aq. (100 mL x2). The aqueous layer was extract with dichloromethane (50 mL × 3). The organic layer was combined and washed with the saturated NaCl aq. (100 mL x2), dried over anhydrous $MgSO_4$. The organic layer was concentrated to give a colorless oil (1.49 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$, 298K): 2.63 (2H, d, J=5.1Hz), 1.26 (33H, m), 0.88 (6H, t, J=6.8Hz) ; the ^{1}H NMR spectrum matches the literature data.[2]

Synthesis of **1**



1,4,5,8-napthalenetetracarboxylic dianhydride (150mg, 0.558mmol) and **7** (331mg 1.12mmol) were suspended in 6ml DMF in a pressure tight microwave tube. This was then sonicated until the mixture was homogenous. The reaction was heated under microwave irradiation at 140^{o}C for 20 minutes(Power Max 200W). The solvent was then removed under reduced pressure, then added to vigorously stirred 1M HCl for 30 minutes and extracted with chloroform the solvent removed under reduced pressure and dried under vacuo yielded brown solid (434mg, 94%) ^{1}H NMR (300 MHz, $CDCl_3$, 298K): 8.76 (4H, s), 4.12 (4H, d, J=7.3Hz), 1.98 (2H, m) 1.21 (64H, m), 0.86 (12H, m) ^{13}C NMR (125 MHz, $CDCl_3$, 298K): 163.24, 131.03, 126.76, 126.61, 44.98, 36.62, 31.92, 31.88, 31.66, 30.01, 29.62, 29.55, 29.33, 29.29, 26.43, 22.69, 22.66, 14.12 the ^{1}H NMR spectrum matches the literature data.[2]

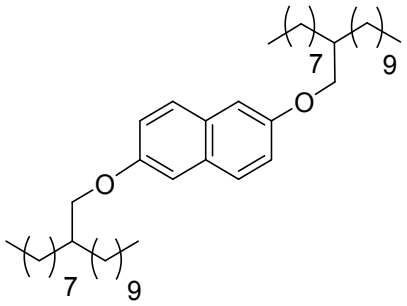
Synthesis of **2**



Potassium carbonate 1.55g (10.12mmol) was suspended in 50ml of acetonitrile and was sonicated for 30 mins then purged with N_2 for 30 minutes. To this mixture **5** 1.5g (4.15mmol) was added in one portion. After which 250mg (0.156mmol) of 1,5-

dihydroxynaphthalene, previously suspended *via* sonication in acetonitrile, was added using a dropping funnel. The reaction is then refluxed under N_2 for 24h. The reaction mixture is then filtered, the filtrate collected and solvent removed under reduced pressure. The residue is then dissolved in chloroform and washed with 1M HCl, brine, water. The organics are then dried over $MgSO_4$. The solvent is removed under reduced pressure and dried under vacuo to yield a brown residue. The residue was then dissolved in 20ml of DMF and stirred for 10h at 90 ^oC. After the mixture was cooled, it was poured into water (150 mL) and extracted with CH_2Cl_2. The combined organic layer was washed with 10% KOH aq., water and saturated NH_4Cl aq. The solvent was then removed under reduced pressure. The oil was then purified by flash column chromatography (hexane then to 4:1 hexane:CH_2Cl_2) to obtain a yellow oil (0.560g, 50%) ^1H NMR (300 MHz, $CDCl_3$, 298K): 7.83 (2H, d, J=8.5Hz), 7.34 (2H, ap t, J=5.9Hz), 6.82 (2H, d, J=7.6Hz), 4.00 (4H, d, J=5.4Hz), 1.99 (2H, m), 1.26 (64H, m), 0.87 (12H, m) ^{13}C NMR (125 MHz, $CDCl_3$, 298K): 154.89, 126.88, 125.03, 114.03, 108.31, 105.08, 70.84, 38.10, 36.10 31.93, 31.69, 30.05, 29.69, 29.66, 29.61, 29.48, 27.85, 26.96, 22.70, 14.13 HRMS calc M+H: ($C_{50}H_{88}O_2$): 721.6863 M+H found: 721.6857

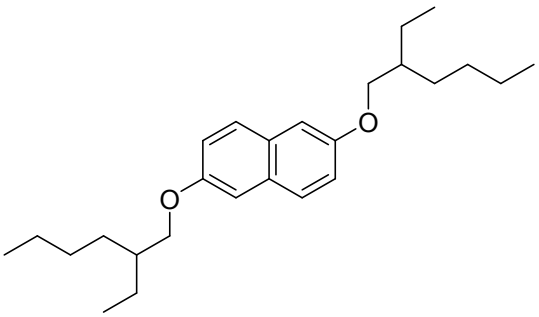
Synthesis of **3**



Potassium carbonate 1.12g (8.12mmol) was suspended in 50ml of acetonitrile and was sonicated for 30 mins then purged with N_2 for 30 minutes. **5** 2.7g (7.5mmol) was added in one portion. After which 200mg (0.125mmol) of 2,6-dihydroxynaphthalene, previously suspended *via* sonication in acetonitrile, was added using a dropping funnel. The reaction is then refluxed under N_2 for 24h. The reaction mixture is then filtered, the filtrate collected and solvent removed under reduced pressure. The residue is then dissolved in chloroform and washed with 1M HCl, brine, water. The organics are then dried over $MgSO_4$. The solvent is removed under reduced pressure

and dried under vacuo to yield a brown residue. The residue was then dissolved in 20ml of DMF and stirred for 10h at 90 ^{o}C. After the mixture was cooled, it was poured into water (150 mL) and extracted with CH_2Cl_2. The combined organic layer was washed with 10% KOH aq., water and saturated NH_4Cl aq. The solvent was then removed under reduced pressure. The oil was then purified by flash column chromatography (hexane then to 4:1 hexane:CH_2Cl_2) to obtain a yellow oil (0.428 g, 47%) ^{1}H NMR (300 MHz, $CDCl_3$, 298K): 7.60 (2H, d, J=8.7Hz), 7.10 (4H, m), 3.91 (4H, d, J=6.0Hz), 1.82 (2H, m), 1.27 (64H, m), 0.88 (12H, m) ^{13}C NMR (125 MHz, $CDCl_3$, 298K): 155.76, 129.66, 127.92, 119.28, 106.84, 70.95, 37.97, 31.95, 31.44, 30.07, 29.71, 29.68, 29.64, 29.38, 26.89, 22.73, 14.17
HRMS calc M+H: ($C_{50}H_{88}O_2$): 721.6863 M+H found: 721.6854

Synthesis of **4**



Potassium carbonate 1.55g (10.12mmol) was suspended in 50ml of acetonitrile and was sonicated for 30 mins then degassed using N_2 for 30 minutes. 1.8g (0.937mmol) of 2-ethylhexylbromide was then added. After which 300mg (0.187mmol) of 1,5-dihydroxynaphthalene suspended in sonicated acetonitrile and added via a dropping funnel. The reaction is then refluxed under N_2 for 24h. The reaction mixture is then filtered, the filtrate collected and solvent removed under reduced pressure. The residue is then dissolved in chloroform and washed with 1M HCl, water, Brine. The organics are then dried over $MgSO_4$. The solvent is removed under reduced pressure and dried under vacuo to yield a brown residue (0.551g, 77%). ^{1}H NMR (300 MHz, $CDCl_3$, 298K): 7.61 (2H,d, J=8.7Hz) 7.12 (4H,m), 3.94(4H,m) 1.78 (2H,m), 1.50 (6H,m), 1.35(10H,m), 0.94 (12H,m) ^{13}C NMR (125 MHz, $CDCl_3$, 298K): 155.8, 129.7, 127.9, 119.2, 106.9, 70.6, 39.4, 39.2, 30.6, 29.1, 24.0, 23.1, 22.9, 14.1, 11.2, 10.9

NMR Dilutions

Dilution Data for **1**		Dilution Data for **2**		Dilution data for **3**	
Concentration	Shift	Concentration	Shift	Concentration	Shift
0.02500	8.6717	0.02500	7.9826	0.02500	7.6323
0.02400	8.6752	0.02400	7.9821	0.02400	7.6311
0.02308	8.6781	0.02307	7.9814	0.02307	7.6306
0.02222	8.6820	0.02222	7.9808	0.02222	7.6304
0.02069	8.6880	0.02142	7.9801	0.02142	7.6300
0.02000	8.6915	0.02069	7.9794	0.02069	7.6295
0.01936	8.6944	0.02000	7.9787	0.02000	7.6293
0.01875	8.6969	0.01923	7.9782	0.01923	7.6291
0.01818	8.6995	0.01851	7.9775	0.01851	7.6286
0.01766	8.7021	0.01785	7.9767	0.01785	7.6284
0.01704	8.7040	0.01666	7.9754	0.01666	7.6276
0.01648	8.7069	0.01530	7.9741	0.01530	7.6270
0.01596	8.7092	0.01388	7.9727	0.01388	7.6266
0.01500	8.7144	0.01250	7.9714	0.01250	7.6258
0.01402	8.7191	0.01071	7.9696	0.01071	7.6248
0.01304	8.7250	0.00937	7.9684	0.00937	7.6242
0.01210	8.7302	0.00810	7.9670	0.00810	7.6238
0.01119	8.7354	0.00714	7.9665	0.00576	7.6227
0.01035	8.7405	0.00638	7.9659	0.00526	7.6227
0.00955	8.7454	0.00576	7.9657	0.00483	7.6224
0.00877	8.7494	0.00447	7.9652	0.00447	7.6221
0.00785	8.7538	0.00416	7.9650	0.00365	7.6218
0.00694	8.7587	0.00365	7.9644		
0.00622	8.7615				
0.00564	8.7640				
0.00516	8.7657				
0.00475	8.7678				
0.00439	8.7691				
0.00410	8.7706				
0.00384	8.7714				
0.00361	8.7724				

Table S1 Dilution Data

T = 25 °C; concentrations are M and chemical shifts are ppm (relative to TMS). DN compounds most downfield peak monitored. All studied in heptane : octane-d_{18} : 1,1,2,2-tetrachloroethane 95.2 : 4.8 : 0.1

A dimerization model was fit to the dilution data as per Bogdan *et al.*[3] using SciDavis.

$$K_{dim} = ((sqrt(1+4*K*x)-1)/(2*K*x)*dm)+(1+(1-sqrt(1+4*K*x))/(2*K*x))*di$$

All fits are shown below:

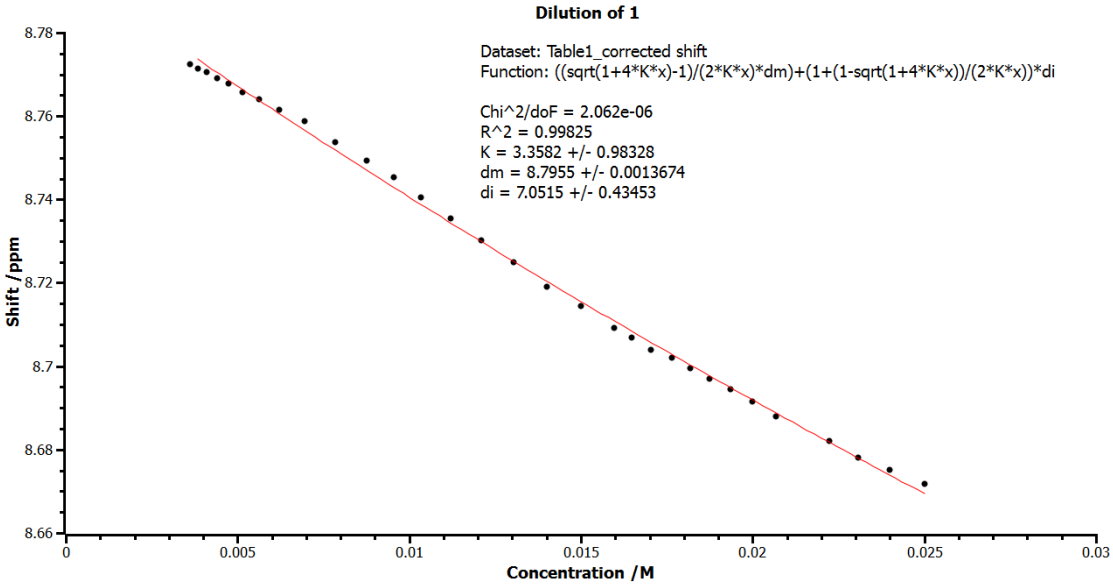


Figure S1 Dilution Data and Fit of **1**

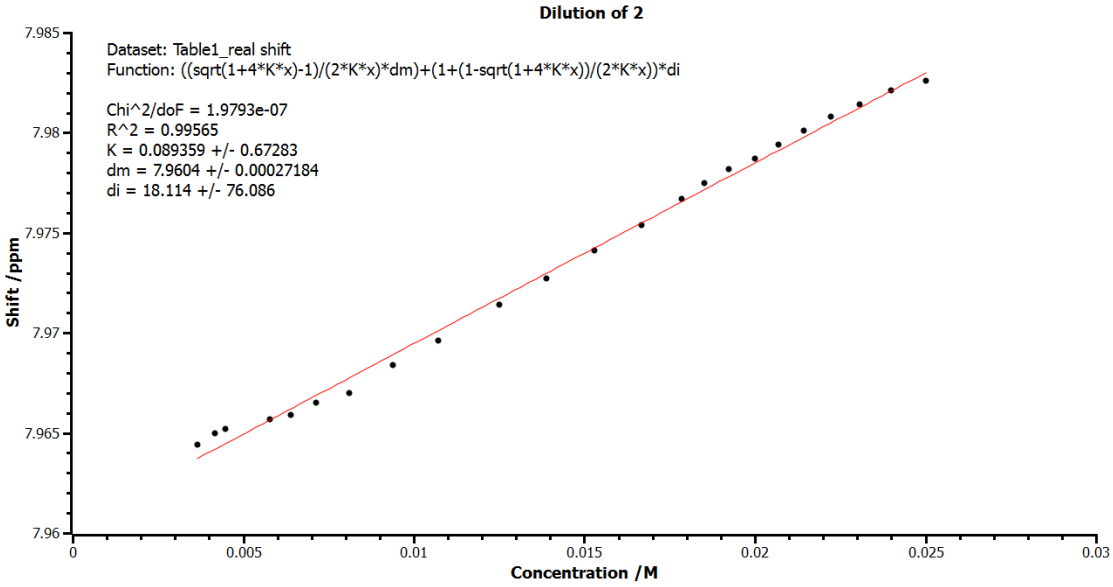


Figure S2 Dilution Data and Fit of **2**

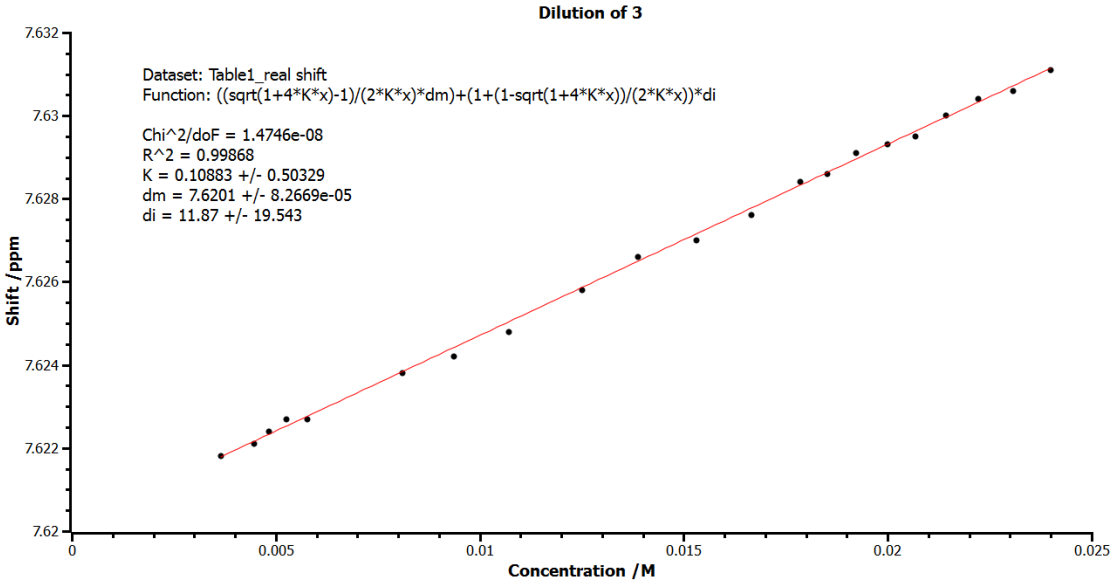


Figure S3 Dilution Data and Fit of **3**

NMR Titrations

^{1}H NMR titration data 24.96mM **1** and increasing concentration of **2**

Conc. of **2**	Shift of **1**
0.00000	8.6761
0.00250	8.6680
0.00495	8.6602
0.00971	8.6446
0.01202	8.6389
0.01429	8.6331
0.01870	8.6209
0.02084	8.6164
0.02295	8.6116
0.02501	8.6052
0.02704	8.6003
0.03010	8.5916
0.03292	8.5883
0.03481	8.5837
0.03850	8.5757
0.04207	8.5697
0.04552	8.5635
0.04885	8.5571
0.05208	8.5535
0.05521	8.5473

Table S2 1·2 Titration Data

T = 25 °C; concentrations are M and chemical shifts are ppm (relative to TMS). 0.6ml of 24.96mM **1** in a dry NMR tube with increasing amounts of a solution containing 252.4mM **2** and 24.96mM **1**. Studied in heptane : octane-d_{18} : 1,1,2,2-tetrachloroethane 95.2 : 4.8 : 0.1

^{1}H NMR titration data 24.96mM **1** and increasing concentration of **3**

Conc of **3**	Shift of **1**
0.00000	8.6705
0.00247	8.6672
0.00489	8.6643
0.00959	8.6591
0.01188	8.6540
0.01412	8.6540
0.01847	8.6496
0.02059	8.6479
0.02267	8.6452
0.02672	8.6417
0.03063	8.6381
0.03440	8.6348
0.03804	8.6309
0.04157	8.6281
0.04497	8.6260
0.05146	8.6197
0.05755	8.6151
0.06328	8.6115
0.06868	8.6081
0.07377	8.6056
0.07859	8.6028
0.08313	8.6000
0.08745	8.5979

Table S3 1·3 Titration Data

T = 25 °C; concentrations are M and chemical shifts are ppm (relative to TMS). 0.6ml of 24.96mM **1** in a dry NMR tube with increasing amounts of a solution containing 249.4mM **3** and 24.96mM **1**. Studied in heptane : octane-d_{18} : 1,1,2,2-tetrachloroethane 95.2 : 4.8 : 0.1

^{1}H NMR titration data 24.90mM **1** and increasing concentration of **4**

Conc of **4**	Shift of **1**
0.00000	8.6863
0.00250	8.6816
0.00495	8.6776
0.00971	8.6689
0.01202	8.6668
0.01429	8.6641
0.01870	8.6569
0.02085	8.6547
0.02296	8.6523
0.02502	8.6492
0.02705	8.6461
0.03101	8.6404
0.03294	8.6389
0.03483	8.6362
0.03852	8.6331
0.04032	8.6316
0.04208	8.6249
0.04553	8.6206
0.04887	8.6217
0.05210	8.6188
0.05523	8.6163
0.05827	8.6140

T = 25 °C; concentrations are M and chemical shifts are ppm (relative to TMS). 0.6ml of 24.90mM **1** in a dry NMR tube with increasing amounts of a solution containing 252.2mM **4** and 24.90mM **1**. Studied in heptane : octane-d_{18} : 1,1,2,2-tetrachloroethane 95.2 : 4.8 : 0.1

A 1:1 binding model[4] was fit to the ^{1}H NMR titration data. The fit was performed in SciDavis the equation is show below:

$$K_a = (b*K*x)/(1+K*x)$$

All fits are shown below:

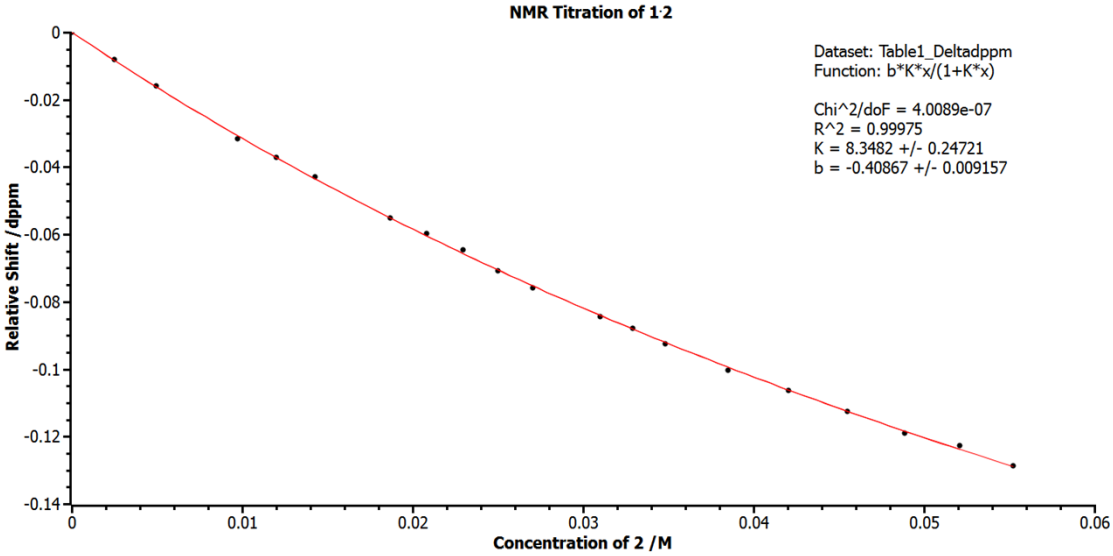


Figure S4 ^{1}H NMR Titration and Fit of **1·2**

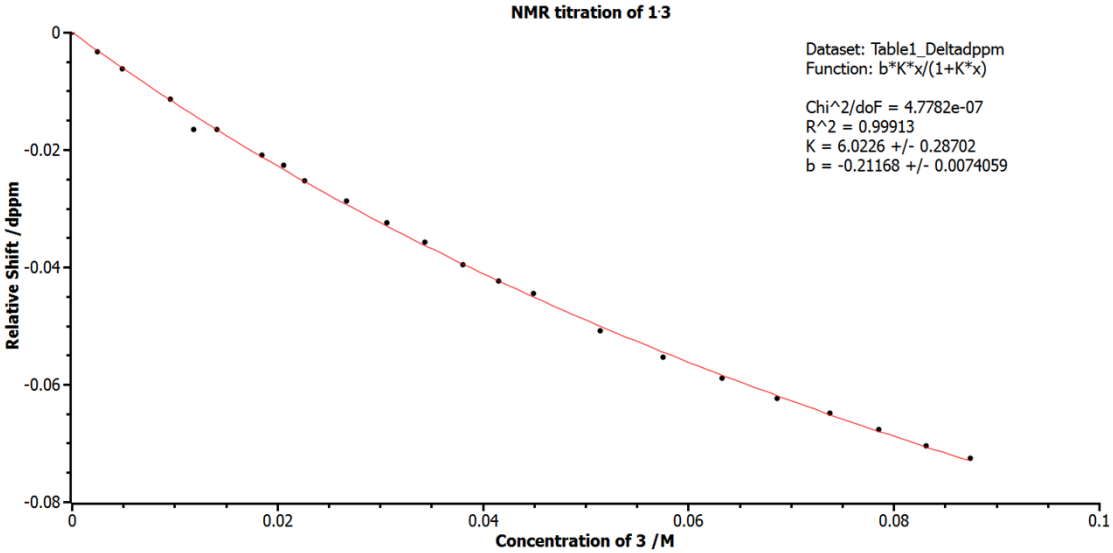


Figure S5 ^{1}H NMR Titration and Fit of **1·3**

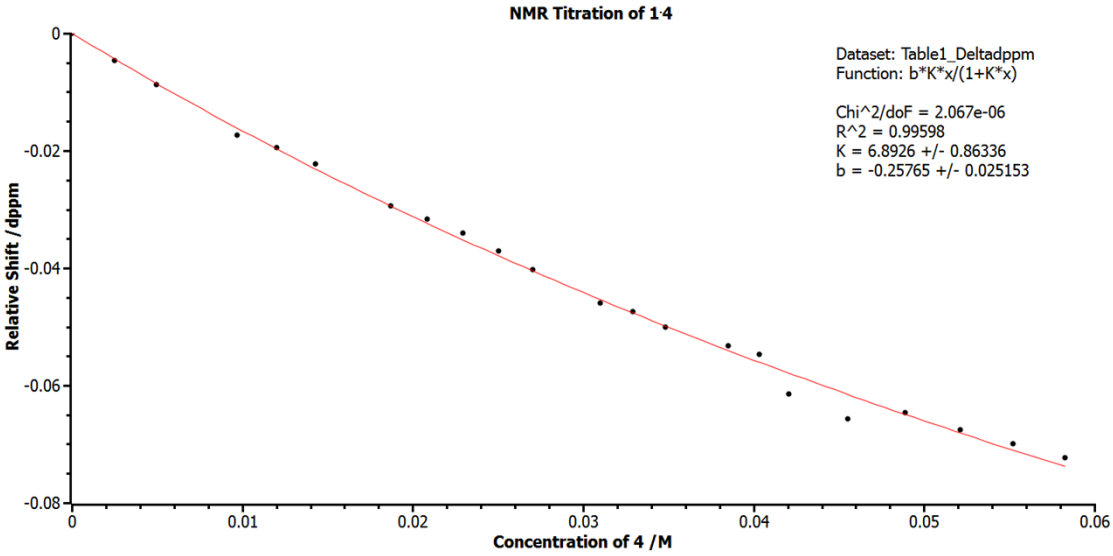


Figure S6 ^{1}H NMR Titration and Fit of **1·4**

UV-vis Titrations

UV titrations were performed on a Chirascan CD spectrometer or a Perkin Elmer lambda 650.. T = 25 °C, carried out in heptane initial 0.5ml of 25mM of with increasing amounts of a solution containing 250mM **2,3** or **4** and 25mM **1**. The same binding model as per **1**·**2** and **1**·**3** was used.[4] Spectra and Fitted traces obtained are shown below (Blue: 0 Equiv. of DN; Green: 1 Equiv. of DN, Red: 3 Equiv. of DN):

UV-Vis titration data 25.04mM **1** and increasing concentration of **2**

Conc of **2**	A at λ Max
0.00000	0.07749
0.00248	0.12002
0.00490	0.16439
0.00962	0.24769
0.01191	0.28191
0.01415	0.31783
0.01852	0.37744
0.02064	0.40469
0.02273	0.43172
0.02478	0.45919
0.02679	0.48728
0.03070	0.53729
0.03261	0.55933
0.03448	0.58902
0.03814	0.63673
0.03992	0.66324
0.04167	0.68471
0.04508	0.73230
0.04839	0.76744
0.05159	0.80753
0.05469	0.84207
0.05769	0.87987

0.5ml of 25.04mM of **1** in heptane with increasing amounts of a solution containing 250.0mM **2** and 25.04mM **1**

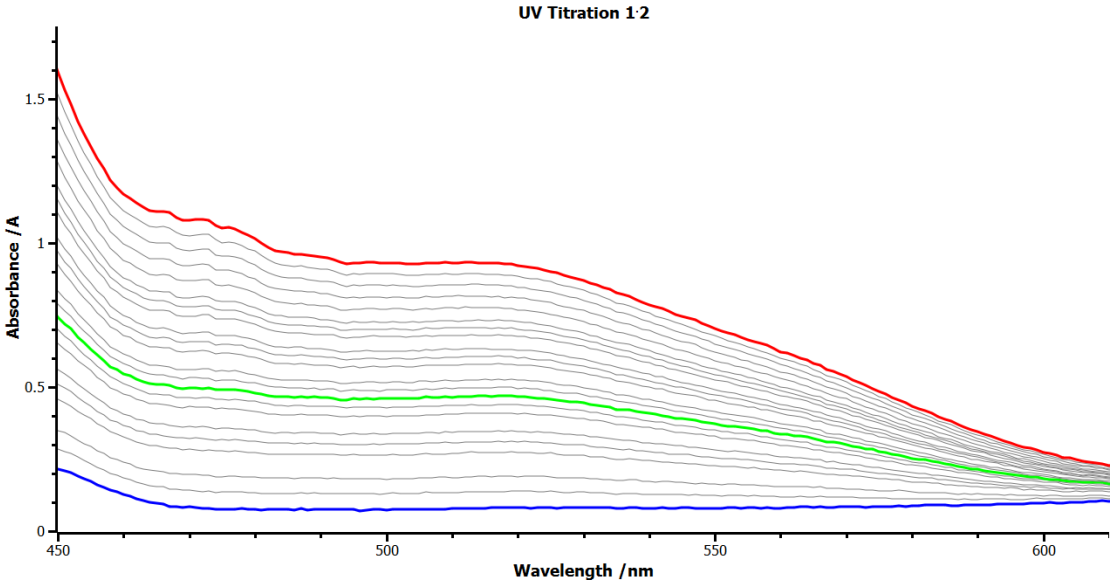


Figure S7 UV-vis Titration Spectra of **1·2**

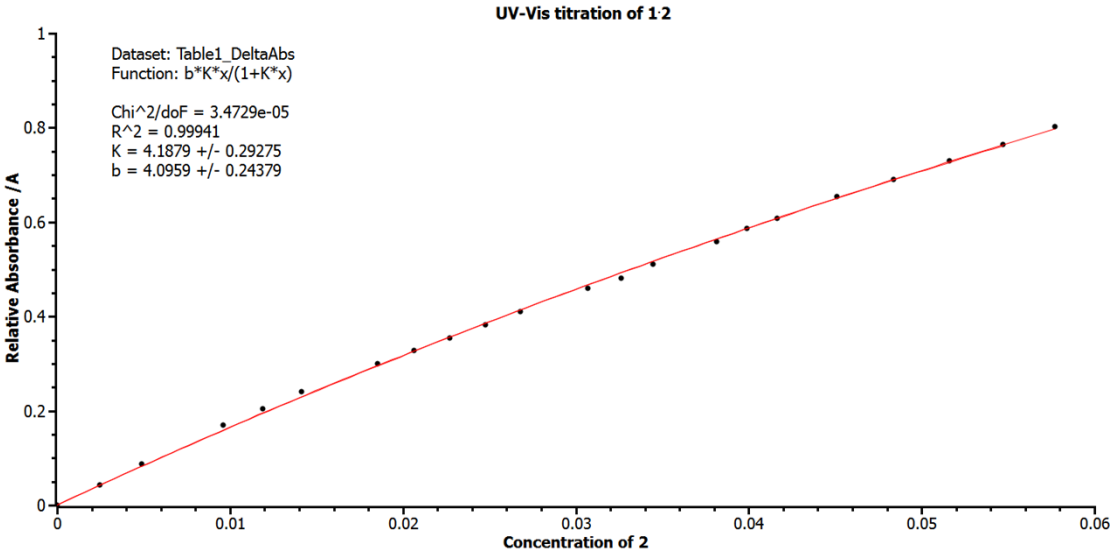


Figure S8 UV-vis Titration Data and Fit of **1·2**

UV-Vis titration data 25.06mM **1** and increasing concentration of **3**

Conc of **3**	A at λ Max
0.00000	0.05422
0.00248	0.06950
0.00492	0.08487
0.00965	0.11690
0.01194	0.13829
0.01419	0.15096
0.01858	0.18106
0.02071	0.19101
0.02280	0.20363
0.02485	0.22110
0.02687	0.22704
0.03080	0.25080
0.03271	0.26065
0.03459	0.27431
0.03826	0.28849
0.04004	0.29793
0.04180	0.30438
0.04523	0.32060
0.04854	0.34000
0.05175	0.35462
0.05486	0.37474
0.05788	0.38372

0.5ml of 25.06mM of **1** in heptane with increasing amounts of a solution containing 250.8mM **3** and 25.06mM **1**

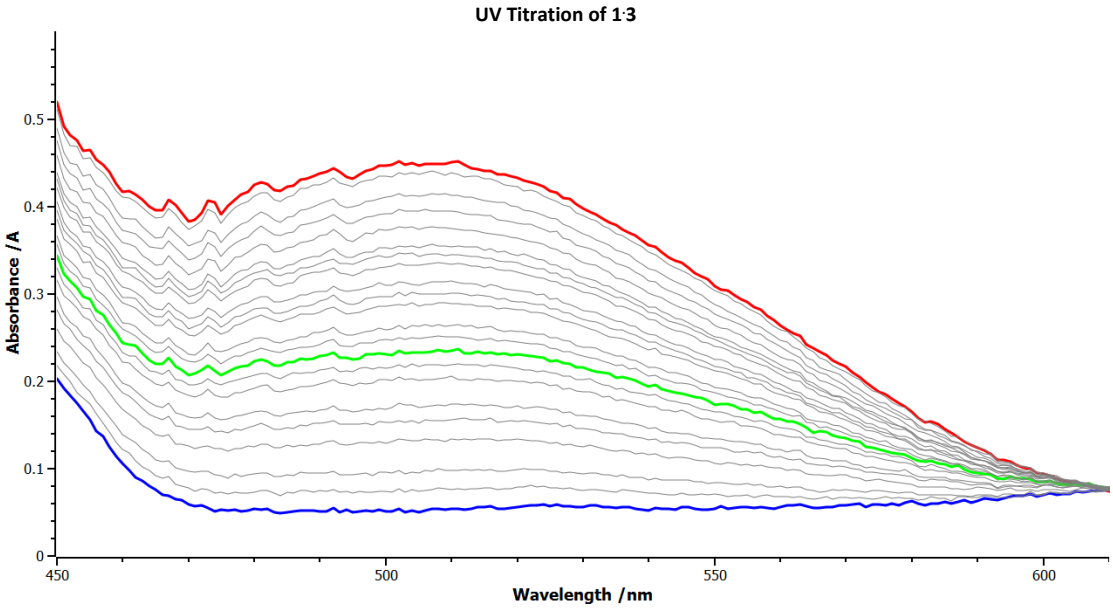


Figure S9 UV-vis Titration Spectra of **1·3**

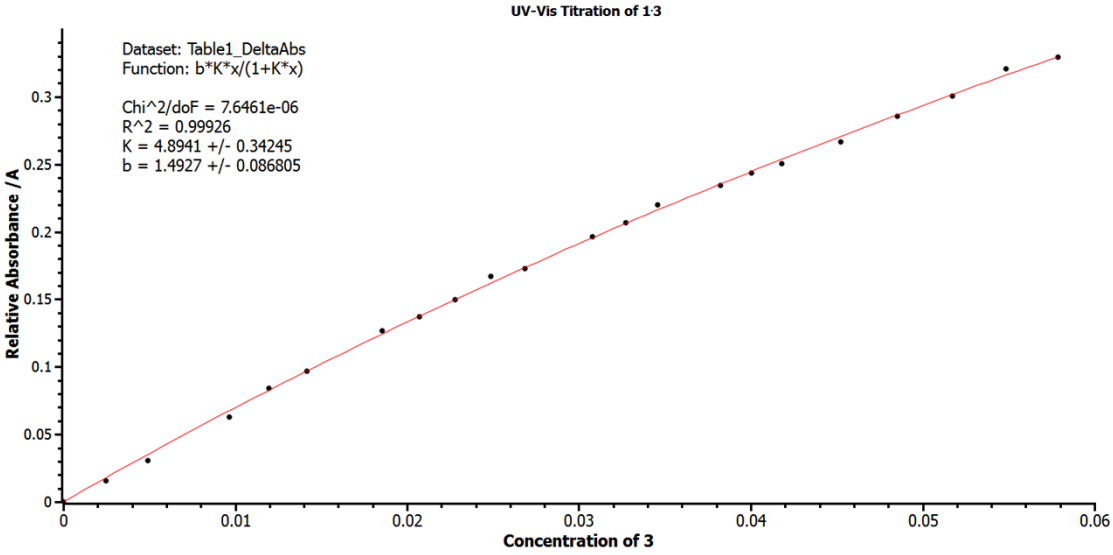


Figure S10 UV-vis Titration Data and Fit of **1·3**

UV-Vis titration data 24.93mM **1** and increasing concentration of **4**

Conc of **4**	A at λ Max
0.00000	0.16597
0.00246	0.18904
0.00486	0.20970
0.00954	0.24759
0.01181	0.26670
0.01622	0.29942
0.01834	0.32008
0.02048	0.33822
0.02255	0.35398
0.02458	0.37030
0.02657	0.38716
0.03046	0.41739
0.03235	0.43353
0.03421	0.44812
0.03783	0.47539
0.03959	0.48873
0.04133	0.50317
0.04472	0.52919
0.04800	0.55250
0.05118	0.57453
0.05425	0.59654
0.05723	0.59910

0.5ml of 24.93mM of **1** in heptane with increasing amounts of a solution containing 248.0mM **3** and 24.93mM **1**

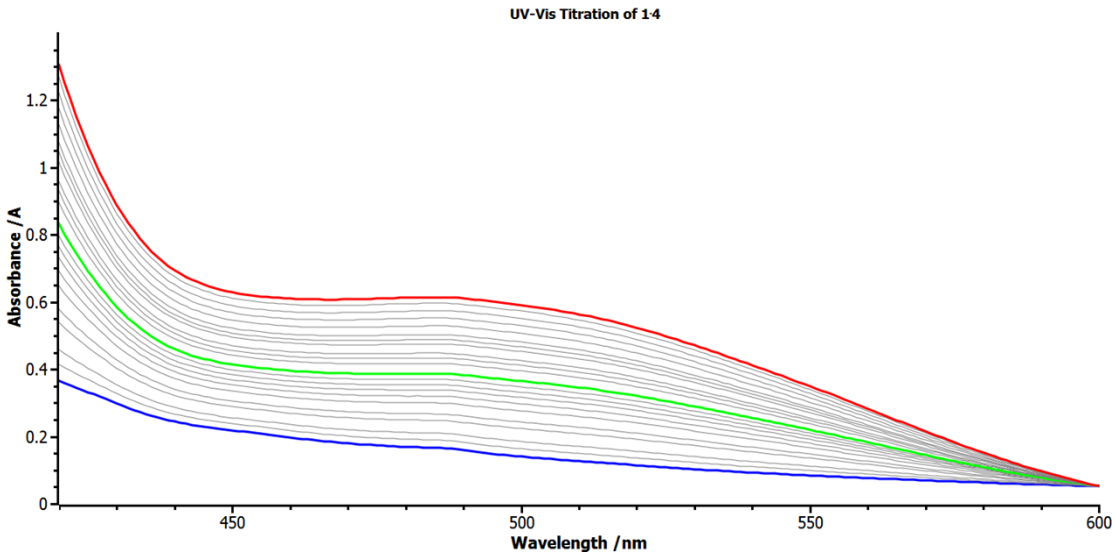


Figure S11 UV-vis Titration Spectra of **1·4**

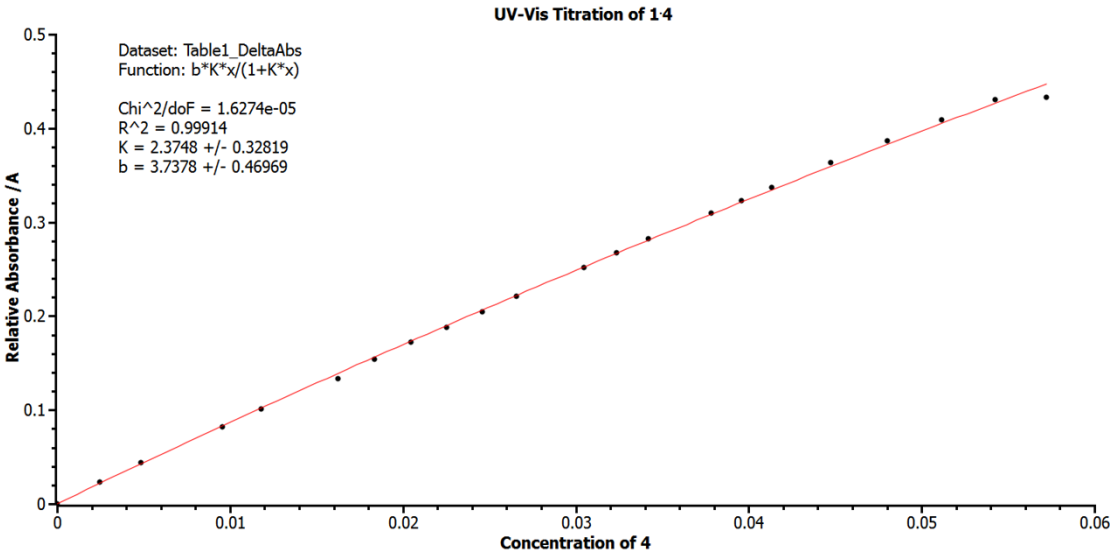


Figure S12 UV-vis Titration Data and Fit of **1·4**

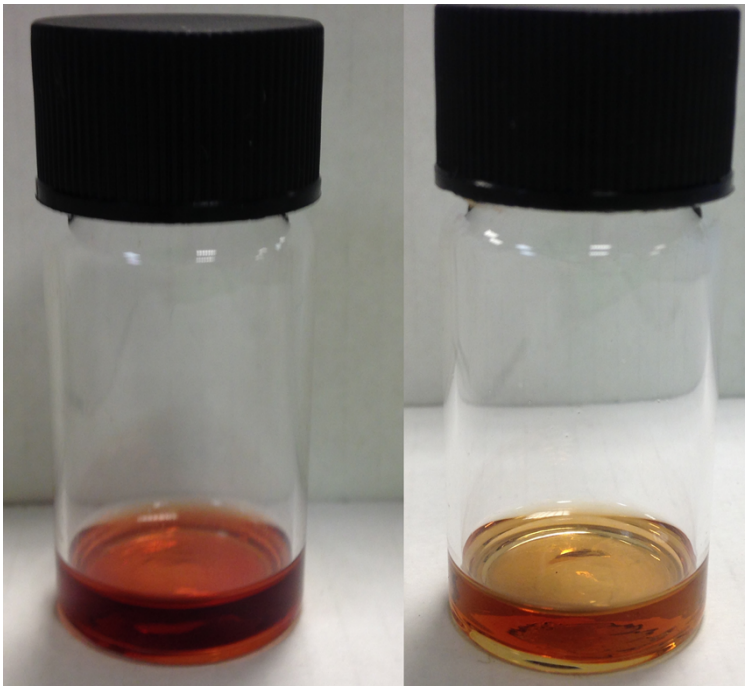


Figure S13 1·4 after UV Titration in hexane (left) **1·4** at the same concentration in chloroform (right)

VT-NMR Isodesmic Model[5]

The self-assembly of the DN and NDI aggregates was studied using temperature dependent ^{1}H NMR. The temperature-dependant data was fitted to the isodesmic model using the Boltzmann equation[6]:

$$y = A_2 + \frac{A_1 - A_2}{1 + \exp\left[\frac{x - x_0}{dx}\right]}$$

Where A_1 = minimum value of the physical parameter monitored
A_2 = maximum value of the physical parameter monitored
x_0 = melting temperature (T_m when $Ø_{agg} = 0.5$)
dx = characteristic temperature that is related to the slope of the function at the melting temperature (T*).
This slope is related to ΔH via:

$$T* = \frac{-RT_m^2}{0.908\Delta H}$$

The degree of aggregation, Ø, as a function of temperature, T is given by:

$$\emptyset(T) \cong \frac{1}{1 + \exp\left[-0.908\Delta H \frac{T - T_m}{RT_m^2}\right]}$$

From the degree of aggregation, the number-averaged degree of polymerisation DP_N can be calculated directly, via:

$$DP_N(T) = \frac{1}{\sqrt{1 - \emptyset(T)}}$$

The DP_N can then be related to the total concentration of molecules C_T, and the association constant K, via[7]:

$$DP_N(T) = \frac{1}{2} + \frac{1}{2}\sqrt{4KC_T + 1}$$

From this equation the distribution of material was calculated using the following equations.

$$C_1 = \frac{2KC_T + 1 - \sqrt{4KC_T + 1}}{2K^2C_T}$$

$$C_n = K^{n-1}C_1^n$$

The number average aggregate size or the mean number of monomers per π-stack (*N*mers) can be calculated, via[6,8–11]:

$$N = \frac{C_T}{C_N} = \frac{C_1 + 2C_2 + 3C_3 + \ldots + nC_n}{C_1 + C_2 + C_3 + \ldots + C_n}$$

VT-NMR was performed on a Bruker Advance 500 (^{1}H 500 MHz). On a 0.6ml solution in a dry NMR tube of 5.5mM **1** or 1:1 **1**·**2** 26.9mM solution. Studied in heptane : octane-d_{18} : 1,1,2,2-tetrachloroethane 95.2 : 4.8 : 0.1. Boltzmann fits and aggregation graphs are shown below:

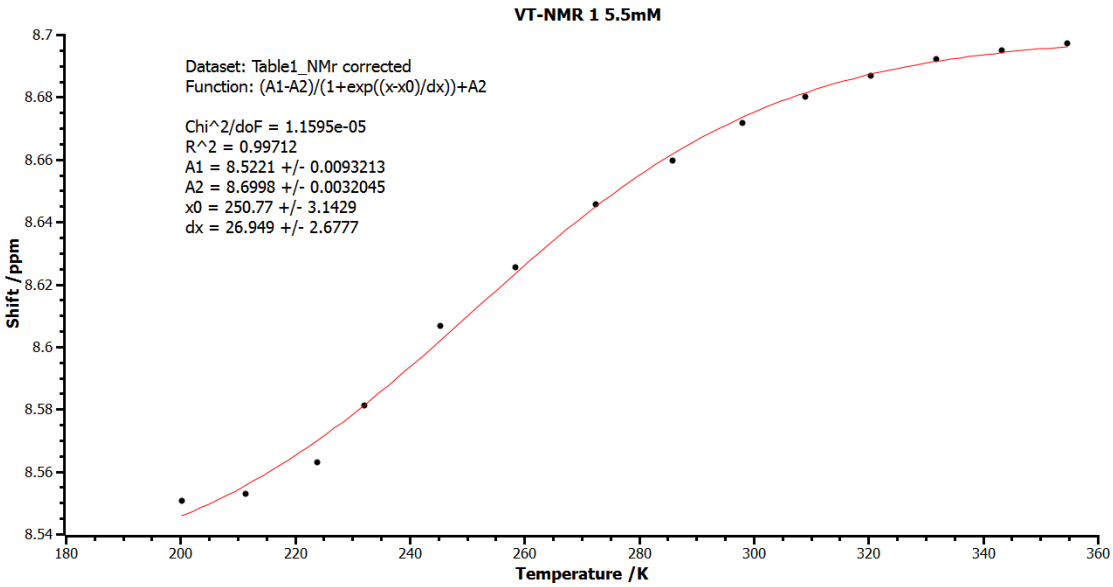


Figure S14 VT NMR data and Fit of **1**

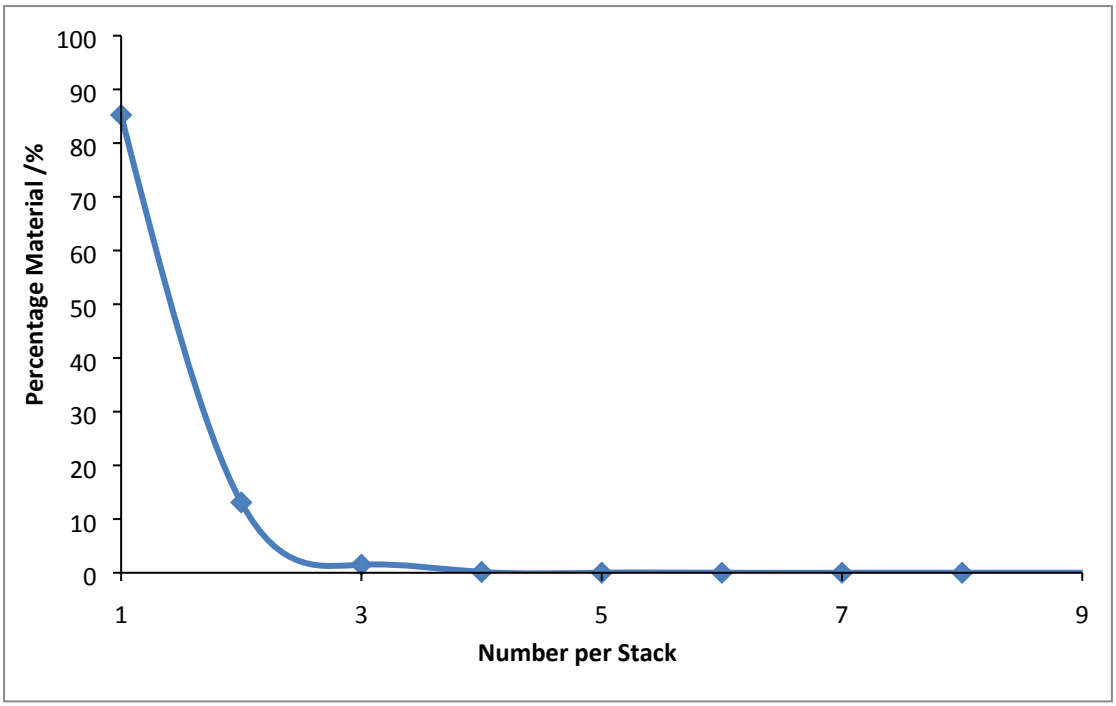


Figure S15 Distribution of species of **1**

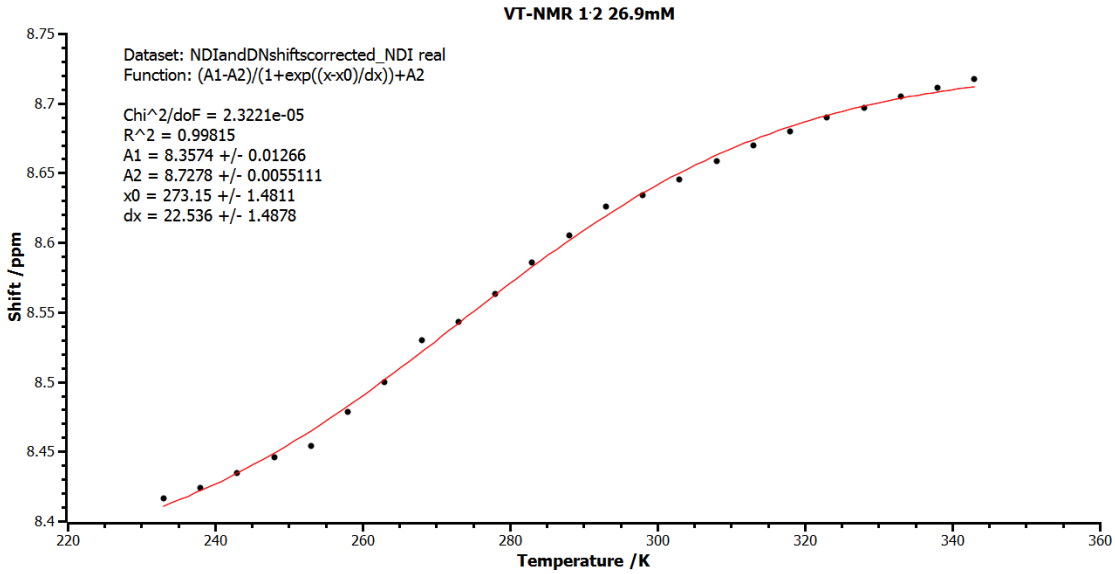


Figure S16 VT NMR data and Fit of **1·2**

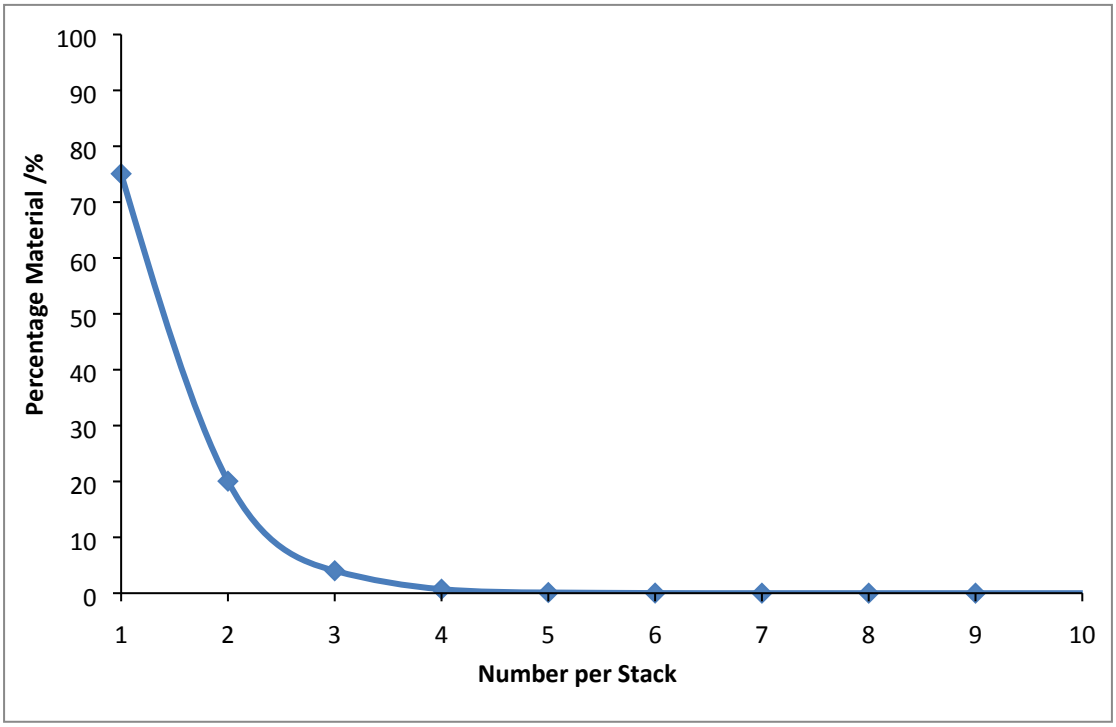


Figure S17 Distribution of species of **1·2**

ITC Data

ITC was performed on a Microcal Inc. MCS-ITC Micro Calorimetry unit. Data was then analysed using IC2ITC software using a dimerization model or aggregation model.[12,13]

In the case of single compound dilution of **1** a stock 110mM solution was programmed to be titrated into heptane (1.8mL) in 7.50uL injections of 9.43 second duration at 480 second intervals.(Actual injection of 7.50044 as reported by MCS-ITC) Raw ITC data, Experimental and calculated heat exchanges and St.dev^2/ Dof vs K_{dim} graphs shown below:

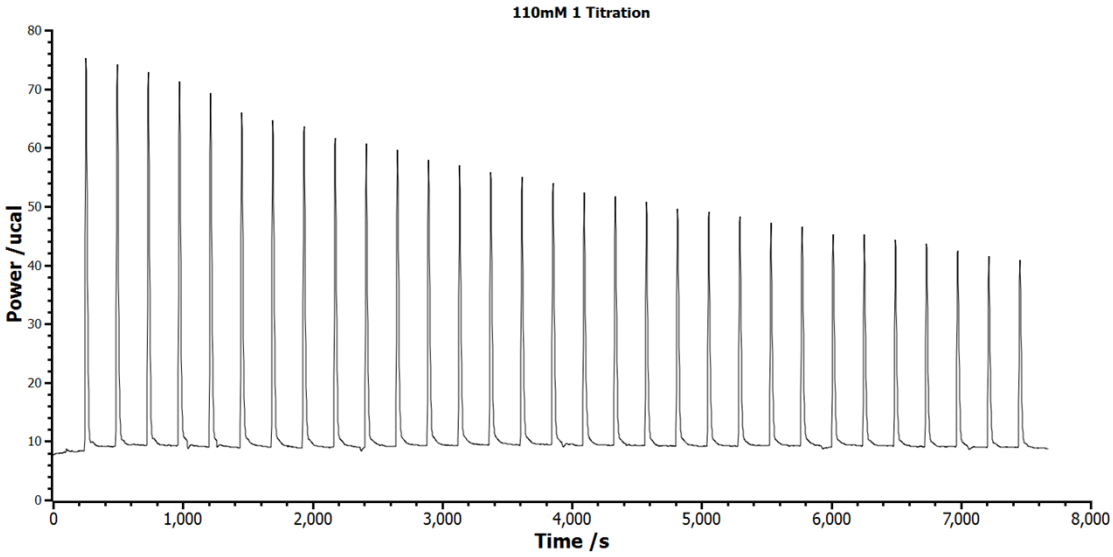


Figure S18 Raw ITC 110mM **1**

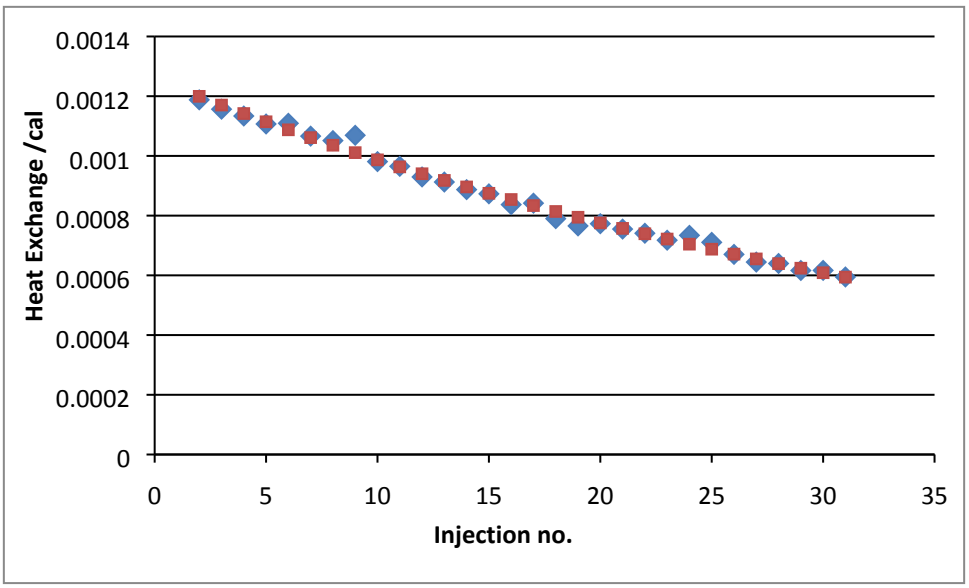


Figure S19 Experimental (blue) and calculated (red) heat exchanges of **1**

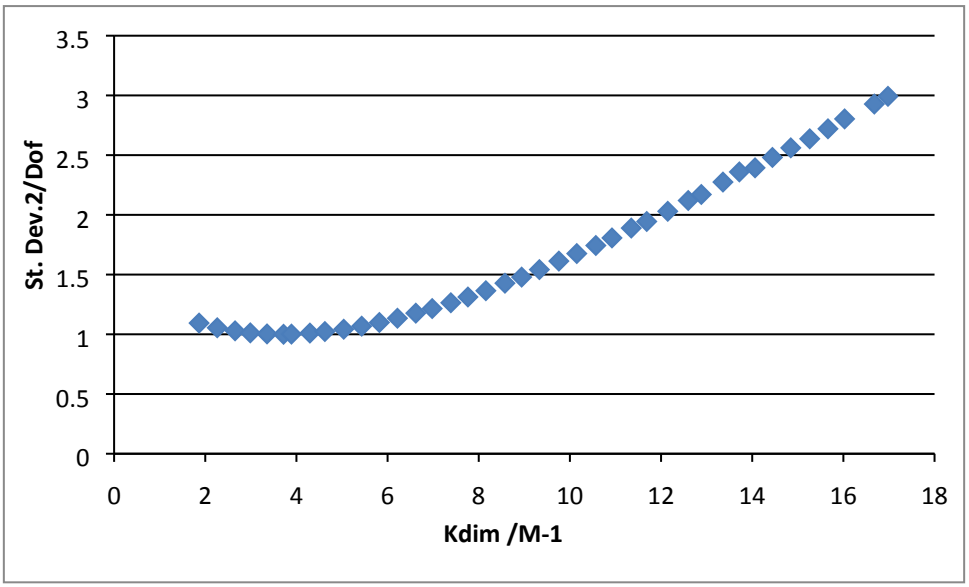


Figure S20 K_{dim} of **1**

In the case of single compound dilutions of **2** and **3** a stock 150mM solution was programmed to be titrated into heptane (1.8 mL) in 15.00 uL injections of 9.43 seconds injection time at 480 second intervals.(Actual injection of 14.99959uL as reported by MCS-ITC) Raw ITC data (initial 2.004 uL injection omitted from raw data), Experimental and calculated heat exchanges St.dev^2/ Dof vs K_{dim} graphs shown below:

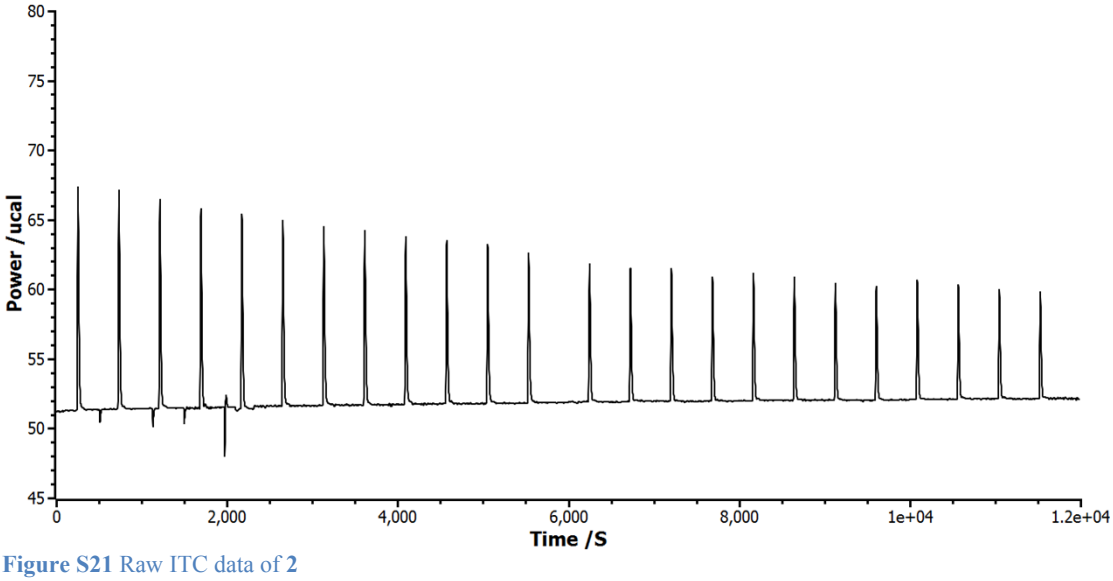


Figure S21 Raw ITC data of **2**

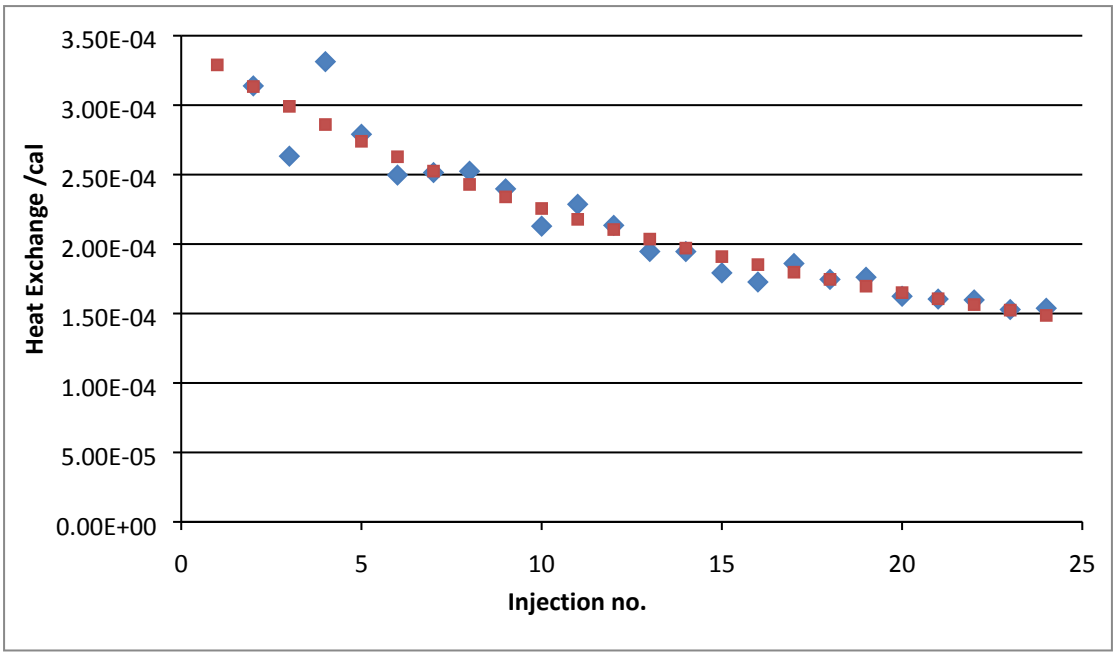


Figure S22 Experimental (blue) and calculated (red) heat exchanges of **2**

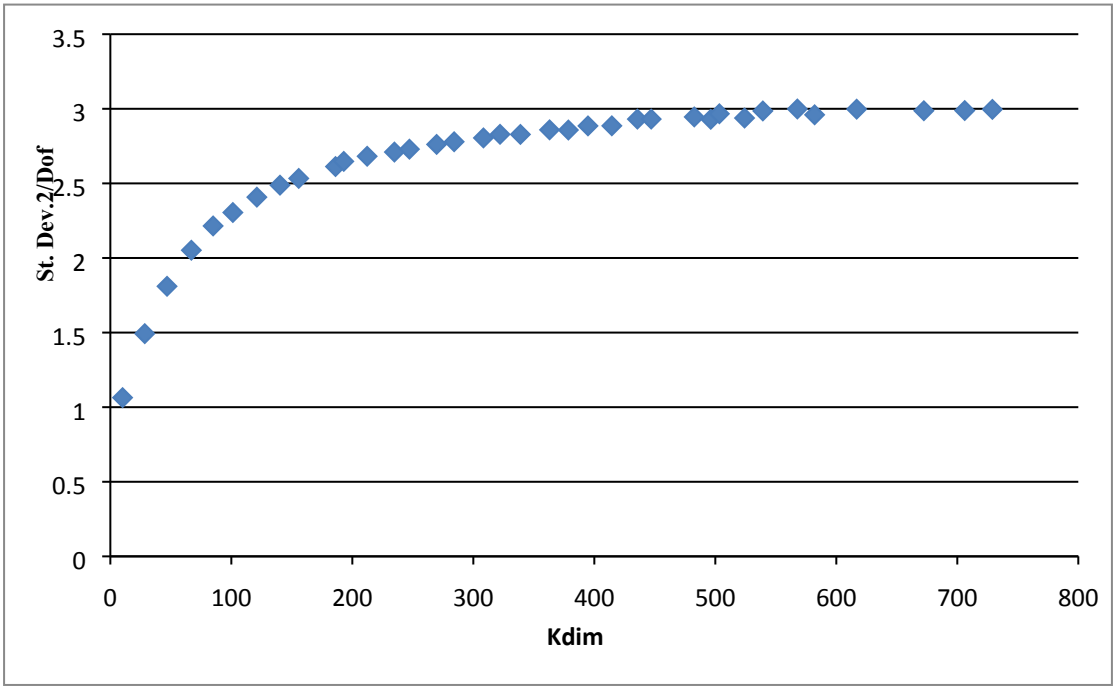


Figure S23 K_{dim} of **2**

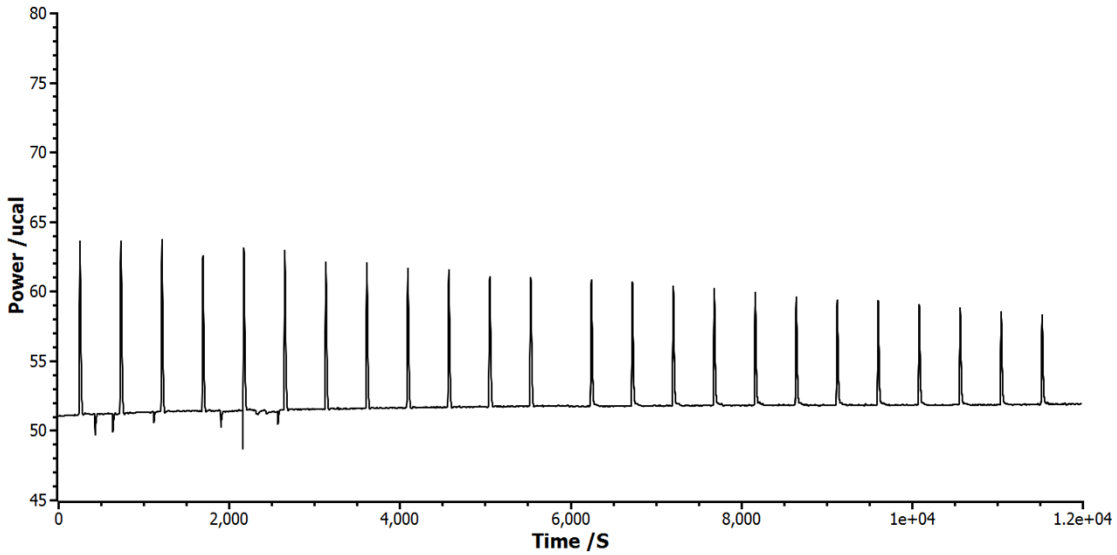


Figure S24 Raw ITC data of **3**

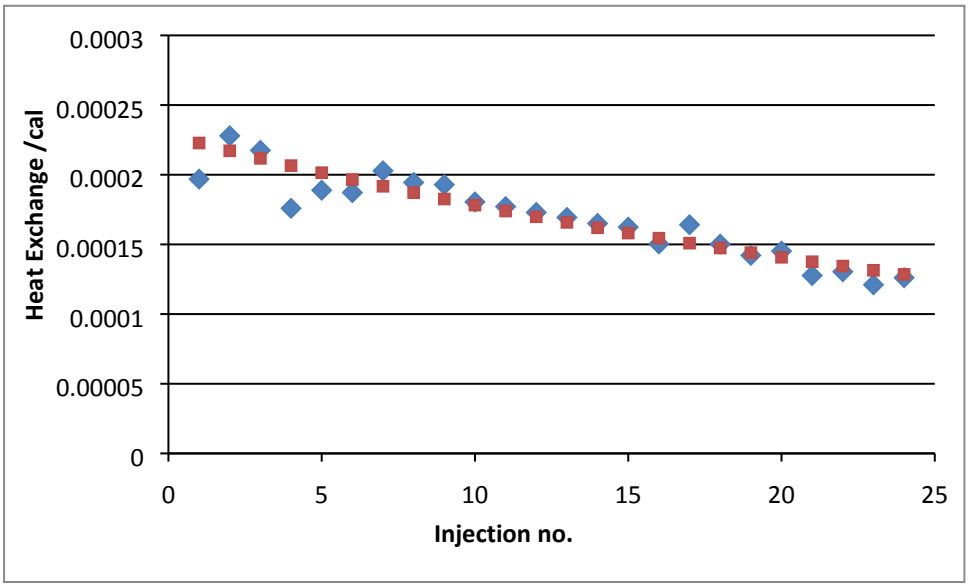


Figure S25 Experimental (blue) and calculated (red) heat exchanges of **3**

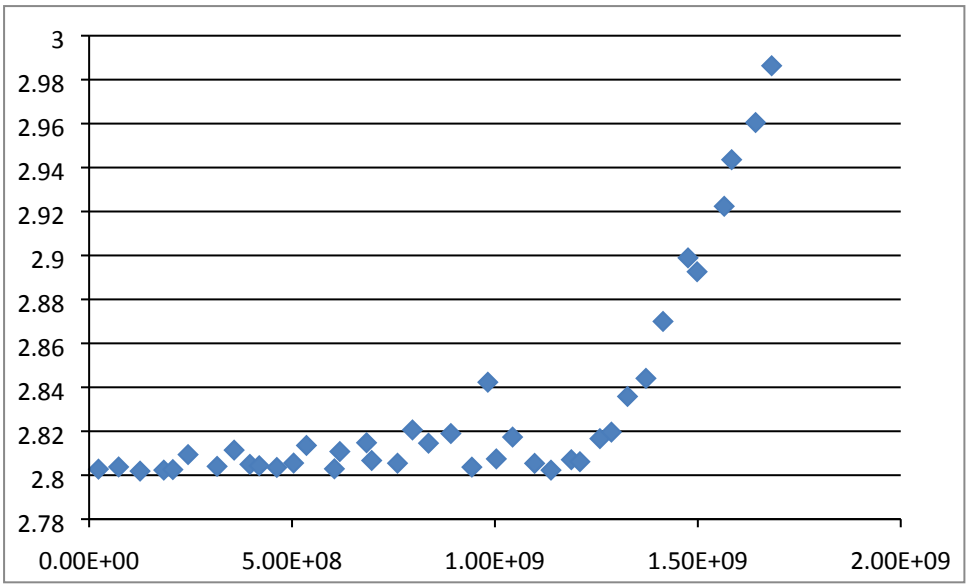


Figure S26 K_{dim} **of 3**

The titration the cell was filled with 1ml of 24.92mM **1** in heptane and 0.376M of **2** in heptane were programmed to be titrated into at 5.00 uL injections of a duration of 6.29 seconds at 440 second intervals (initial 2.004 uL injections shown in raw data omitted from calculations, actual injection of 4.99456 uL as reported by MCS-ITC)) . Raw ITC data, Experimental and calculated heat exchanges and St.dev^2/ Dof vs K_{dim} graphs shown below:

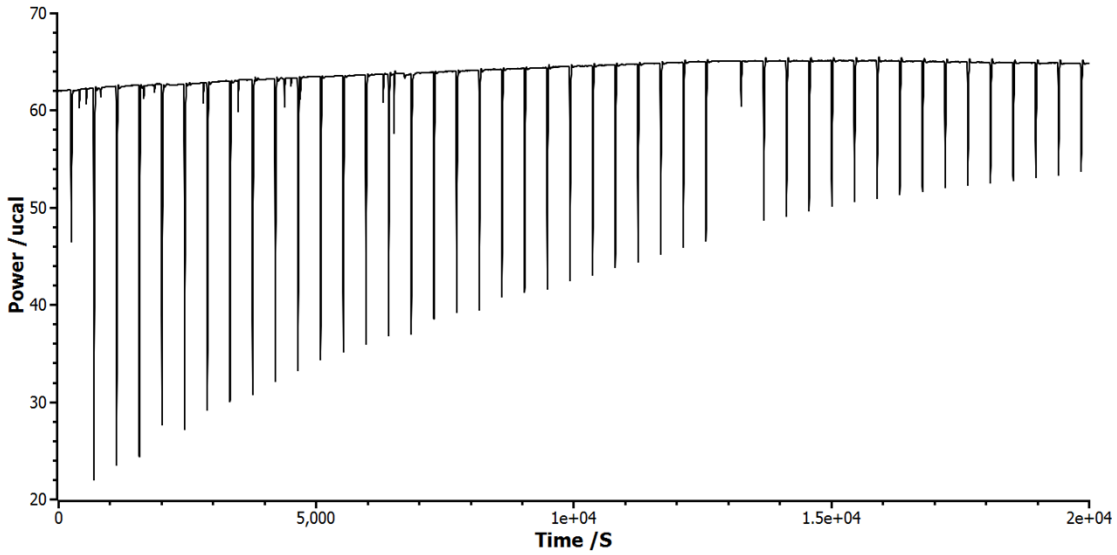


Figure S27 Raw ITC of **1**·**2**

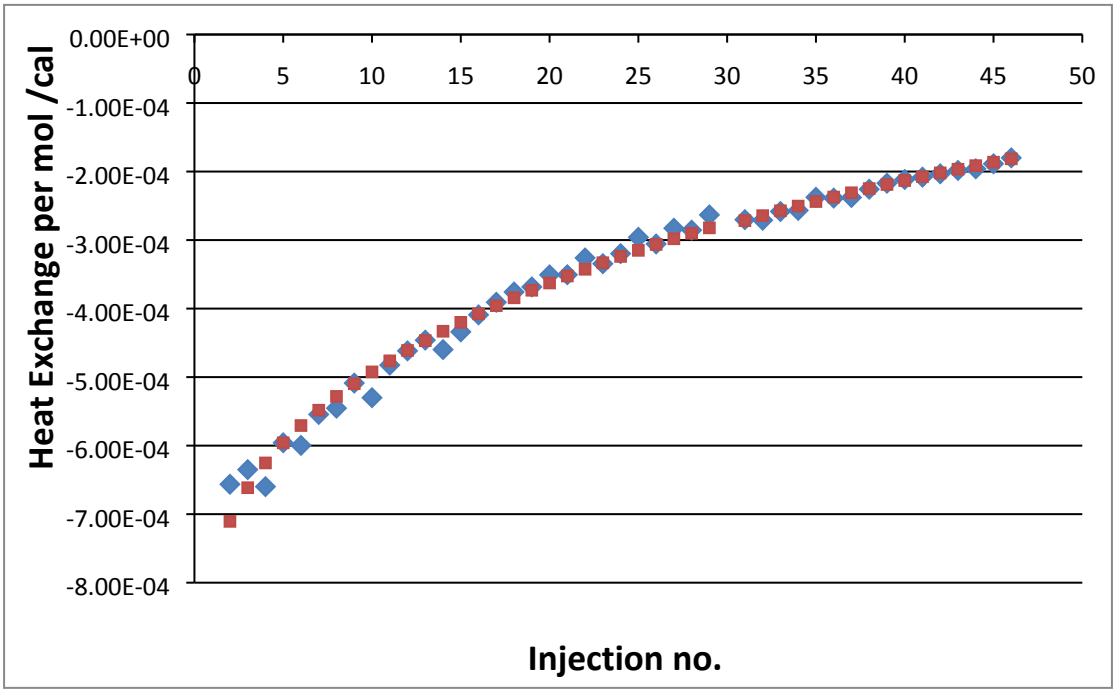


Figure S28 Experimental (blue) and calculated (red) heat exchanges of **1**·**2**

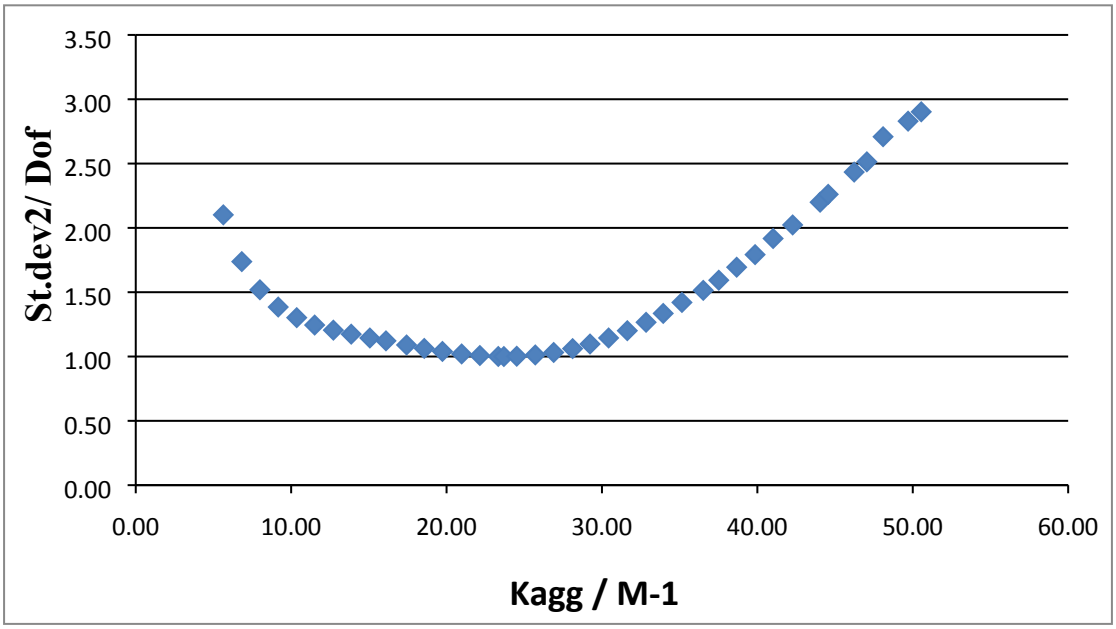


Figure S29 Kagg of 1·2

The titration the cell was filled with 1ml of 24.94 mM **1** in heptane and 0.375mM of **3** in heptane were programmed to be titrated into it at 5.00 uL injections of a duration of 6.29 seconds at 440s intervals x15 and 2.00 uL injections at duration of 5.04 secs at 440 second intervals, ((initial 2.004 uL injections shown in raw data omitted from calculations and Injection 13 omitted from calculations, actual injections were 4.99456 uL and 2.004 uL as reported by MCS ITC) . Raw ITC data, Experimental and calculated heat exchanges and St.dev^2/ Dof vs K_{agg} graphs shown below:

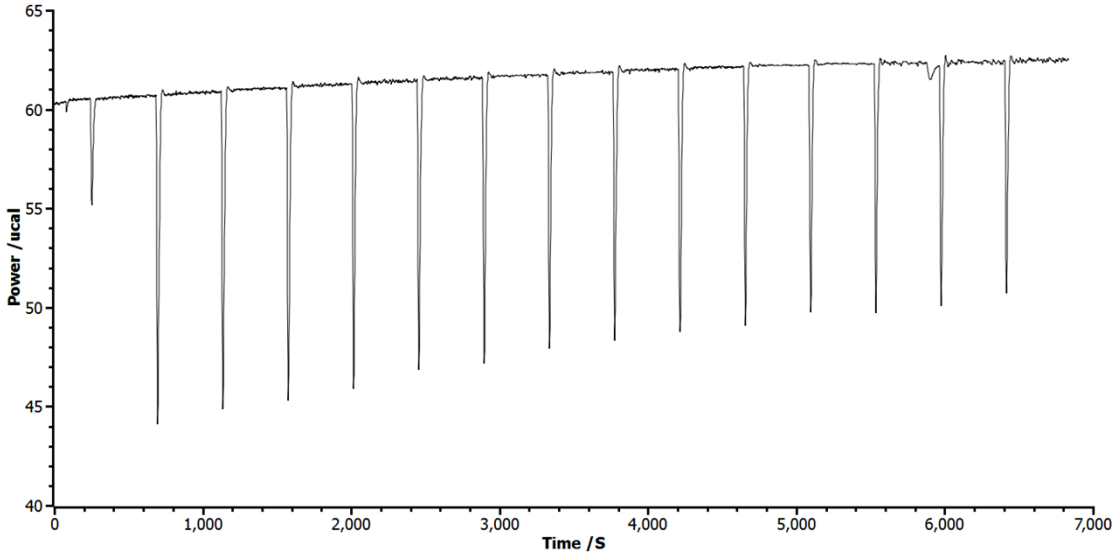


Figure S30 Raw ITC data of **1·3**

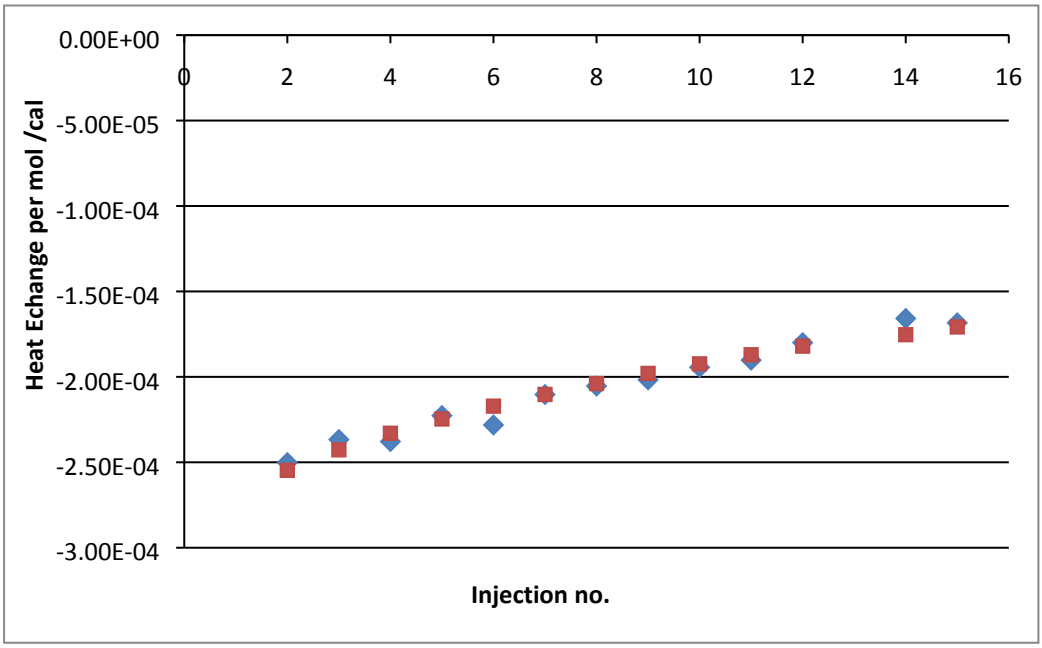


Figure S31 Experimental (blue) and calculated (red) heat exchanges of **1·3**

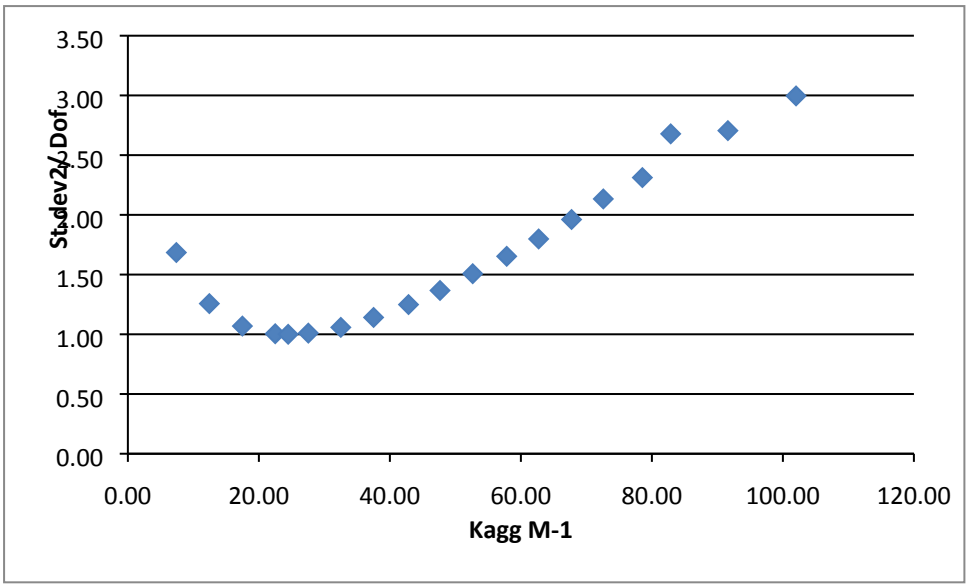


Figure S32 Kagg of **1**·**3**

The titration the cell was filled with 1ml of 25.02 mM **1** in heptane and 0.375mM of **4** in heptane were programmed to be titrated into it at 5.00 uL injections of a duration of 6.29 seconds at 480s intervals x23, (initial 2.004 uL injections shown in raw data omitted from calculations, actual injections were 4.99456 uL and 2.004 uL as reported by MCS ITC) . Raw ITC data, Experimental and calculated heat exchanges and St.dev^2/ Dof vs K_{agg} graphs shown below:

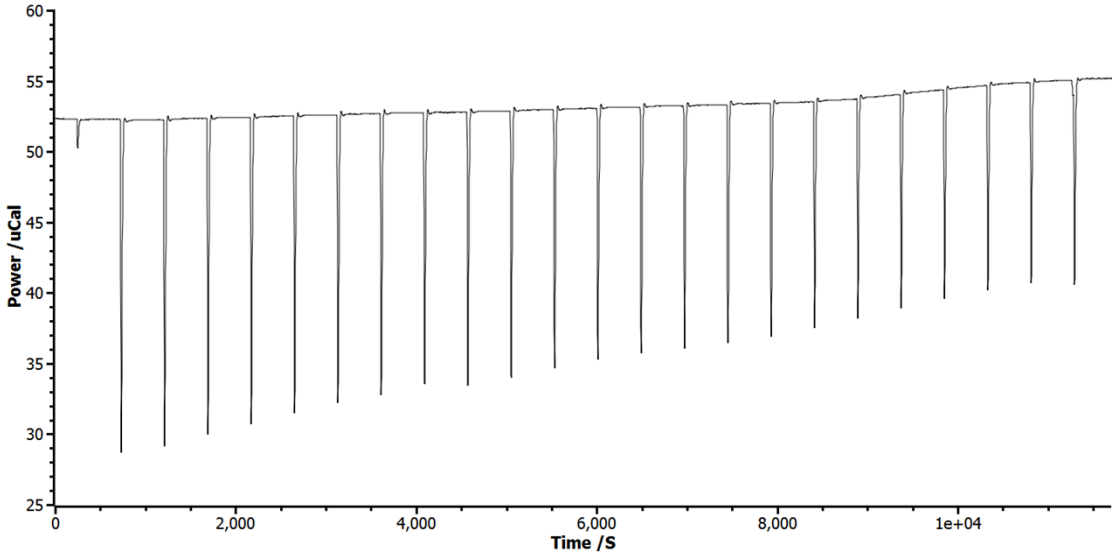


Figure S33 Raw ITC of 1·4

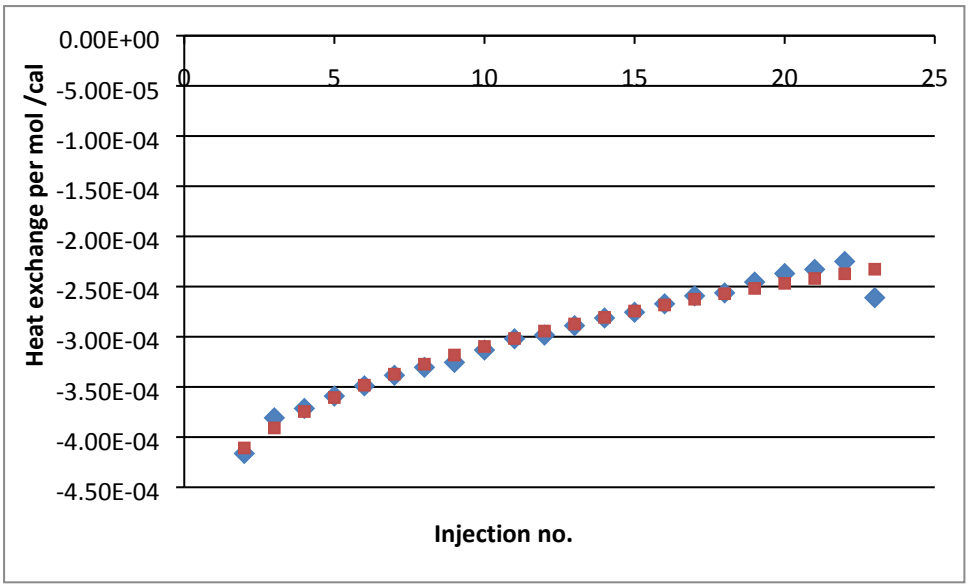


Figure S34 Experimental (blue) and calculated (red) heat exchanges of **1**·**4**

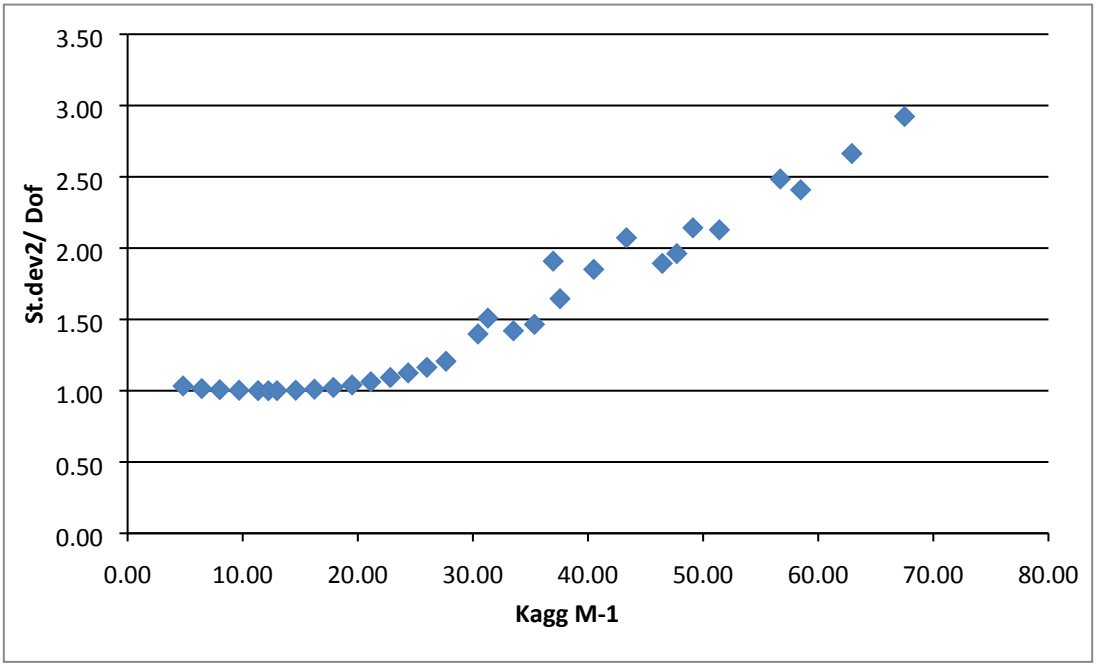


Figure S35 Kagg of **1**·**4**

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