Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information

A Solvent-Resistant Halogen Bond

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Contents

1. General Experimental

Chemicals and Spectroscopic Grade Solvents were purchased from Alfa Aeasar, Fisher Scientific UK Ltd., Sigma–Aldrich Company Ltd. or VWR International Ltd. and dried over molecular sieves before use. 1,1,2,2-Tetrachloroethane was de-acidified and dried by storing over $CaCl_2$ and molecular sieves overnight before filtering through basic alumina before use.

Automated UV/vis titrations were set up on Hellma 96-well quartz microplates purchased from Hellma Analytics and performed on a BMG Labtech POLARstar Omega or FLUOROstar microplate reader operated with software supplied by Omega.

^{1}H NMR spectra were recorded on a Bruker Avance II 400 (400.1 MHz) spectrometer using the deuterated solvent or a capillary insert with D_2O as the lock and the residual solvent or a reference in the capillary as the internal reference. In the assignment of ^{1}H NMR spectra, the chemical shift information (δH) for each resonance signal is given in units of parts per million (ppm) relative to trimethylsilane (TMS) where δH TMS = 0.00 ppm. Analysis was carried out using Topspin version 2.1.6 or iNMR version 5.2.1.

Measurement of solids was carried out on a Precisa 125A balance.

Measurement of liquids was handled by an internal syringe pump within the POLARStar or FLUOROStar during automated UV/vis titrations. In 12 tube NMR titrations, an Eppendorf Multipette Xstream was used to handle liquid measurements. In a 1-tube NMR titration, liquid measurements were handled with Hamilton Gastight syringes.

2. Procedure for automated UV/vis titrations

In a typical experiment, a 150 µL sample of host solution (0.1 mM 4-phenylazophenol for HB titrations, 0.01 mM tetramethylthiourea or 0.1 mM/ 1mM iodine for XB titrations) was added to the appropriate number of wells in a Hellma 96-well quartz microplate and placed in the microplate reader. An automated protocol script handled the addition of guest solution via internal syringe pump with additions of 8 × 3 µL followed by 8 × 6 µL and finally 8 × 10 µL. The [guest] was chosen to obtain a binding isotherm with >50% saturation. The specific [guest] used in each experiment can be seen in the binding isotherm for each titration shown below. Results were handled using Omega Mars software to extract absorbance values at three wavelengths (shown in figures below) and K_a data obtained by fitting the experimental results to a binding isotherm using 14Allmaster, a macro based excel fitting program written by Christopher A. Hunter (University of Sheffield).

3. Procedure for ^{1}H NMR titrations

i. **1-Tube Method:** 500 µl of host solution was added to a screw-cap Norell S-600 NMR tube and the initial spectrum recorded. To this solution, 4 × 10 µl, 4 × 20 µl and 4 × 50 µl aliquots of a guest (dissolved in host solution) were added, with a spectrum recorded after each addition.

ii. **12-Tube Method:** Alternatively, 12 NMR Norell S-400 tubes each with different concentrations of host and guest as measured out with a programmed Multipette XStream were set up and submitted to BACS automated sample recording.

In both cases, the [guest] was chosen to obtain a binding isotherm of >50% saturation. The specific [guest] used in each experiment can be seen in the binding isotherm for each titration.

4. Full Table of Association Constants

Table S1: Full table of solvent α and β values as well as association constants and errors*

			Hydrogen Bonding		Halogen Bonding	
	α_s	β_s	[1•3]	[1•4]	[2•3]	[2•4]
n-Octane	1.1	0.4	2400±1000	370±10	12±2	8,800±900
Carbon tetrachloride	1.4	0.6	410±120	24±1	6±1	7,300±600
Toluene	1	2.1	230±70	4±1	3±1	11,000±1,600
Diiodomethane	1.2	2.2	210±3	6±1	<1	37,000±14,000
Dibromomethane	1.9	1.5	110±10	<1	<1	34,000±4,500
Dichloromethane	1.9	2	90±7	9±5	2±1	58,000±10,000
Chloroform	2.2	0.8	52±2	2±1	1±1	20,000±1,000
Tetrachloroethane	2	1.3	35±9	6±1	<1	55,000±15,000
di-*n*-Octyl ether	0.9	5.3	<1	<1	<1	1600±350
Acetone	1.5	5.7	2±1	<1	<1	1900±300
Acetonitrile	1.8	5.1	3±1	<1	<1	2800±70
Nitromethane	1.7	3.7	5±1	<1	<1	2100±300
i-Propanol	2.7	5.5	<1	<1	<1	3600±70
Ethanol	2.7	5.8	–	–	–	3200±120
Methanol	2.7	5.8	–	–	–	2700±200

***Errors determined by 2 × standard deviation of multiple repeats of titrations**

5. Spectra and Binding isotherms of complexes of 4-phenylazophenol with tetramethylurea [1•3] in titled solvents

The HB donor 4-phenylazophenol is well known[S1] to offer a strong HB site (α = 4.2) and was also chosen as it has a characteristic UV/vis absorption band at 340 nm which is subjected to a bathochromic shift upon complexation to a HB acceptor.

n-Octane

Host: 4-phenylazophenol (**1**) 0.1 mM
Guest: Tetramethylurea (**3**)

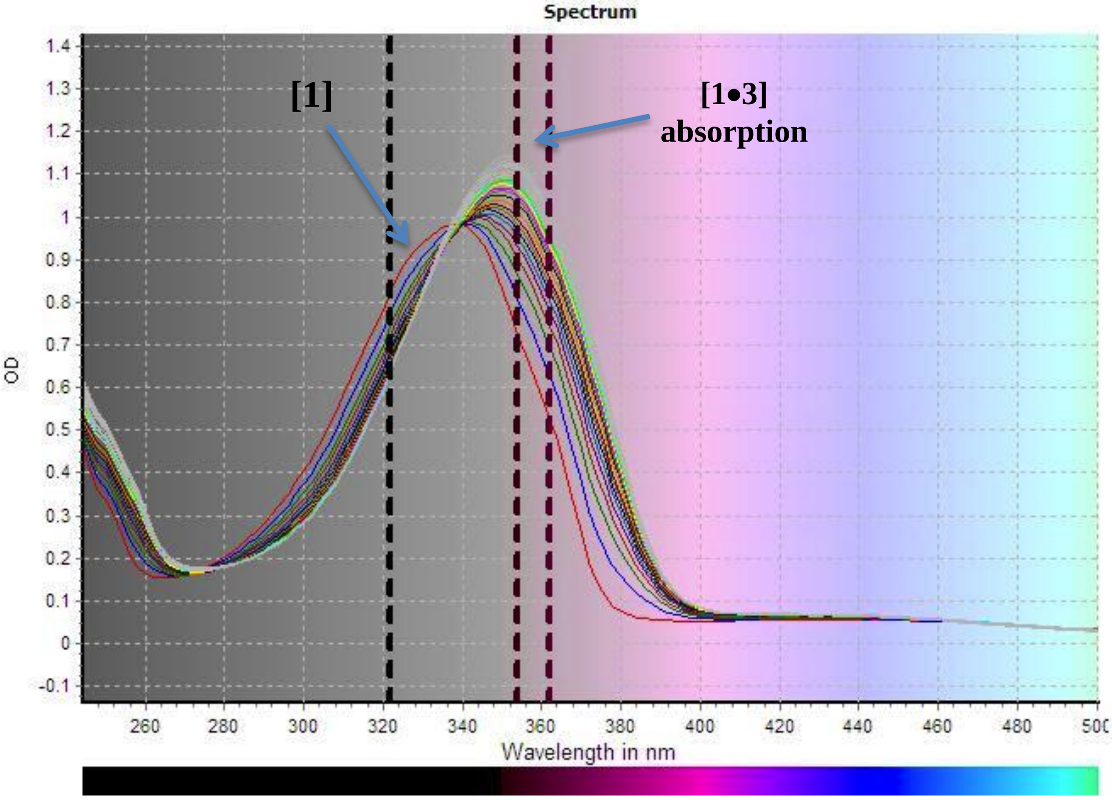


Figure S1: Annotated UV/vis spectra of titration of **1** with **3** in *n*-octane showing the change in absorption during the titration. Vertical dashed lines indicate wavelengths monitored for binding isotherm

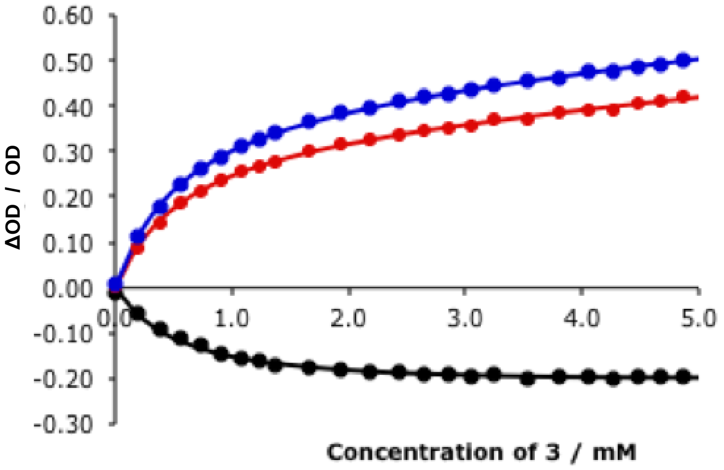


Figure S2: Binding isotherms for titration

$K_a = 2400 \pm 1000\ \mathrm{M}^{-1}$ 91% bound

Carbon Tetrachloride

Host: 4-phenylazophenol (**1**) 0.1 mM
Guest: Tetramethylurea (**3**)

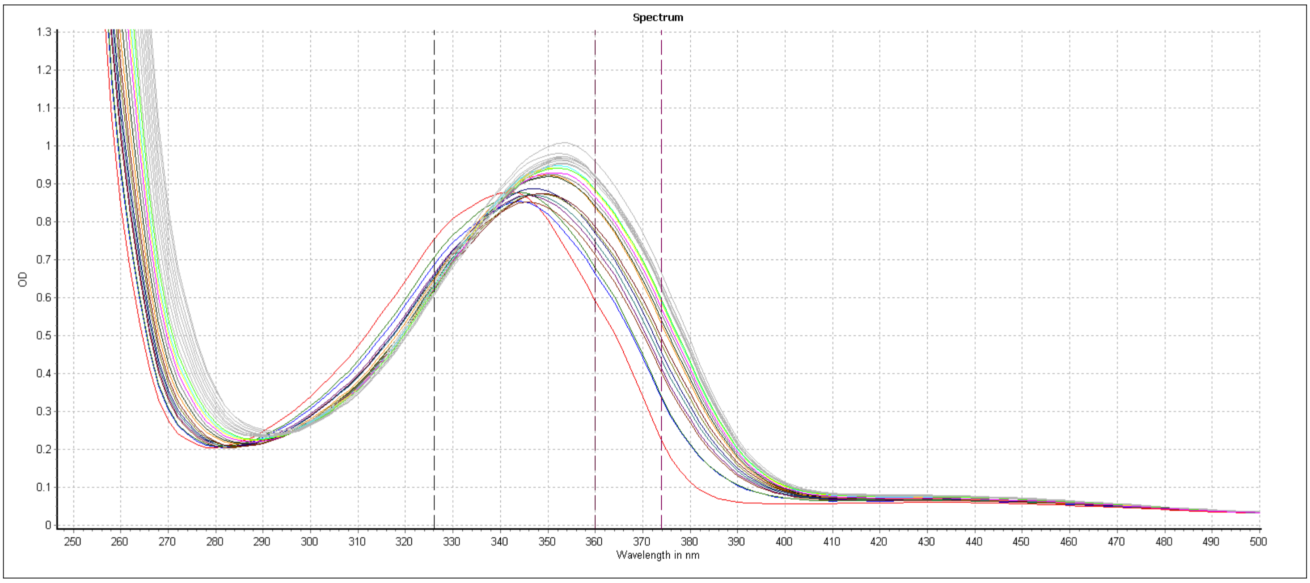


Figure S3: UV/vis spectra of titration of **1** with **3** in carbon tetrachloride. Vertical dashed lines indicate wavelengths monitored for binding isotherm.

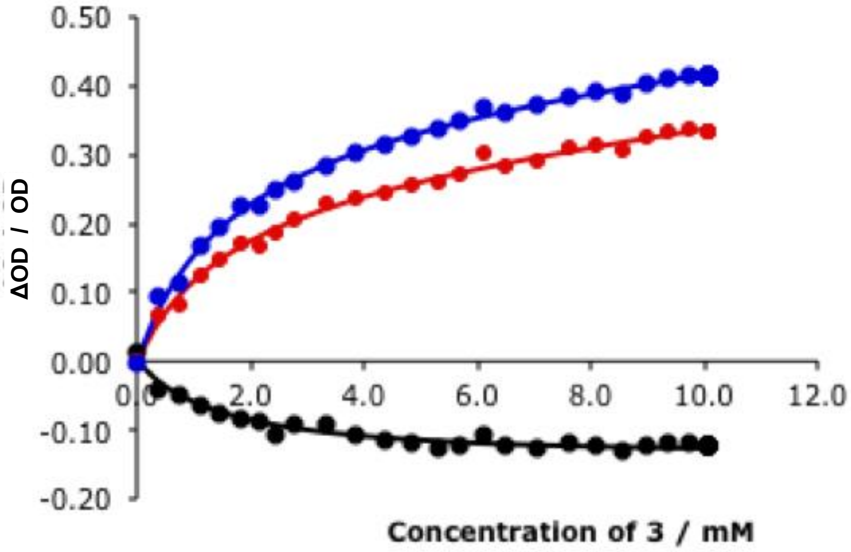


Figure S4: Binding isotherms for titration

K_a = 410±120 M^{-1} 86% bound

Toluene

Host: 4-phenylazophenol (**1**) 0.1 mM
Guest: Tetramethylurea (**3**)

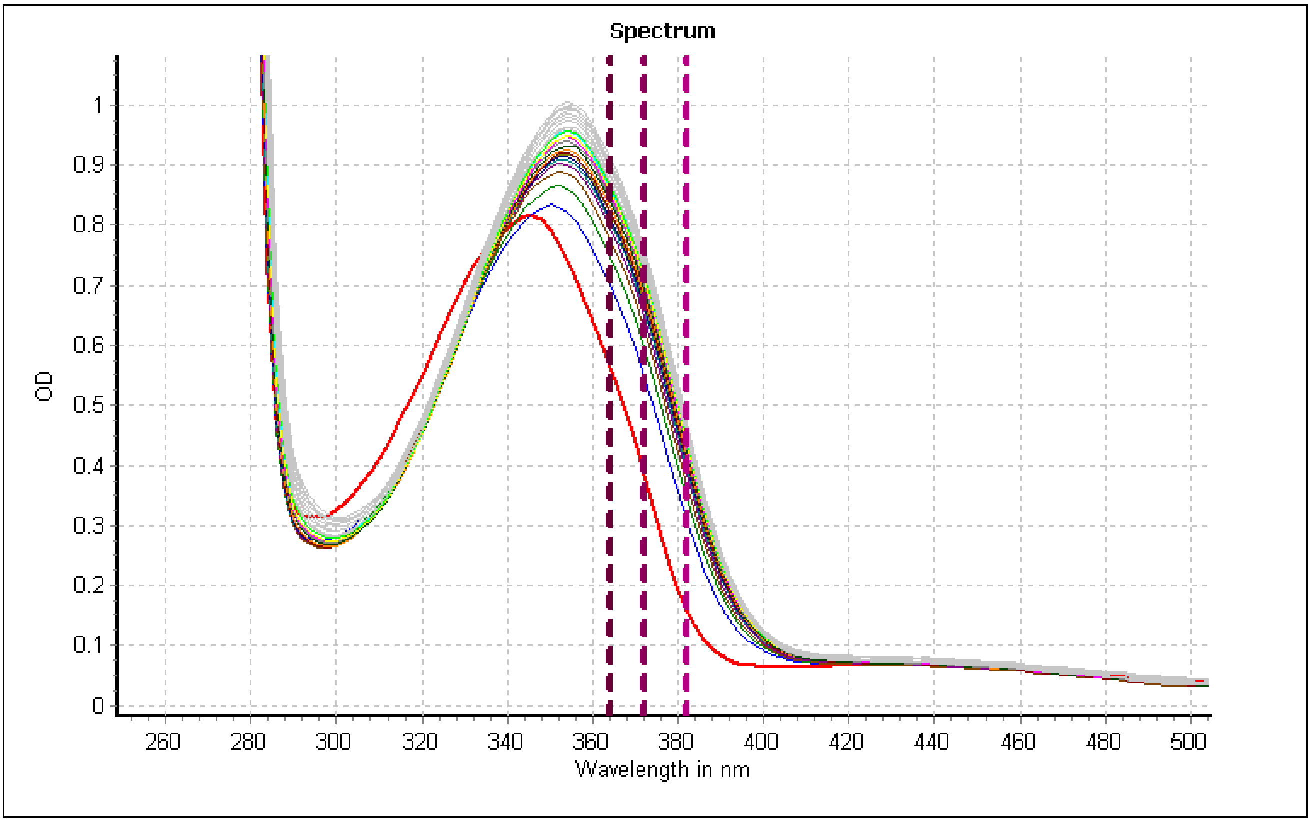


Figure S5: UV/vis spectra of titration of **1** with **3** in toluene. Vertical dashed lines indicate wavelengths monitored for binding isotherm.

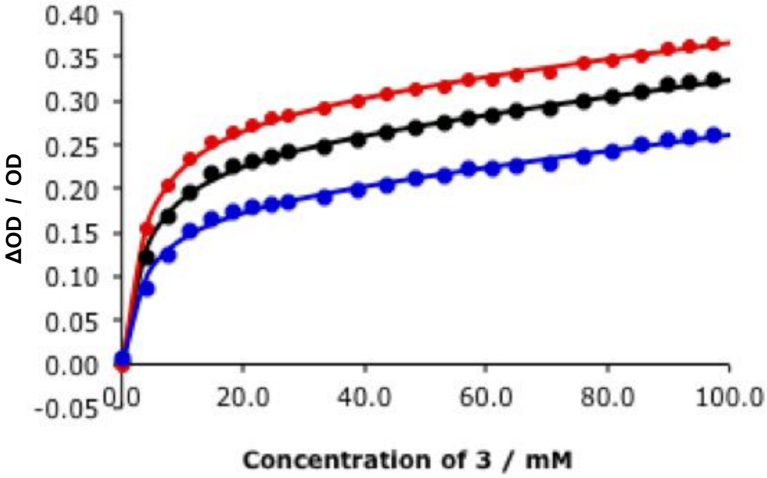


Figure S6: Binding isotherms for titration

$K_a = 230 \pm 70\ \mathrm{M}^{-1}$ 83% bound

CH_2I_2

Host: 4-phenylazophenol (**1**) 50 mM
Guest: Tetramethylurea (**3**)

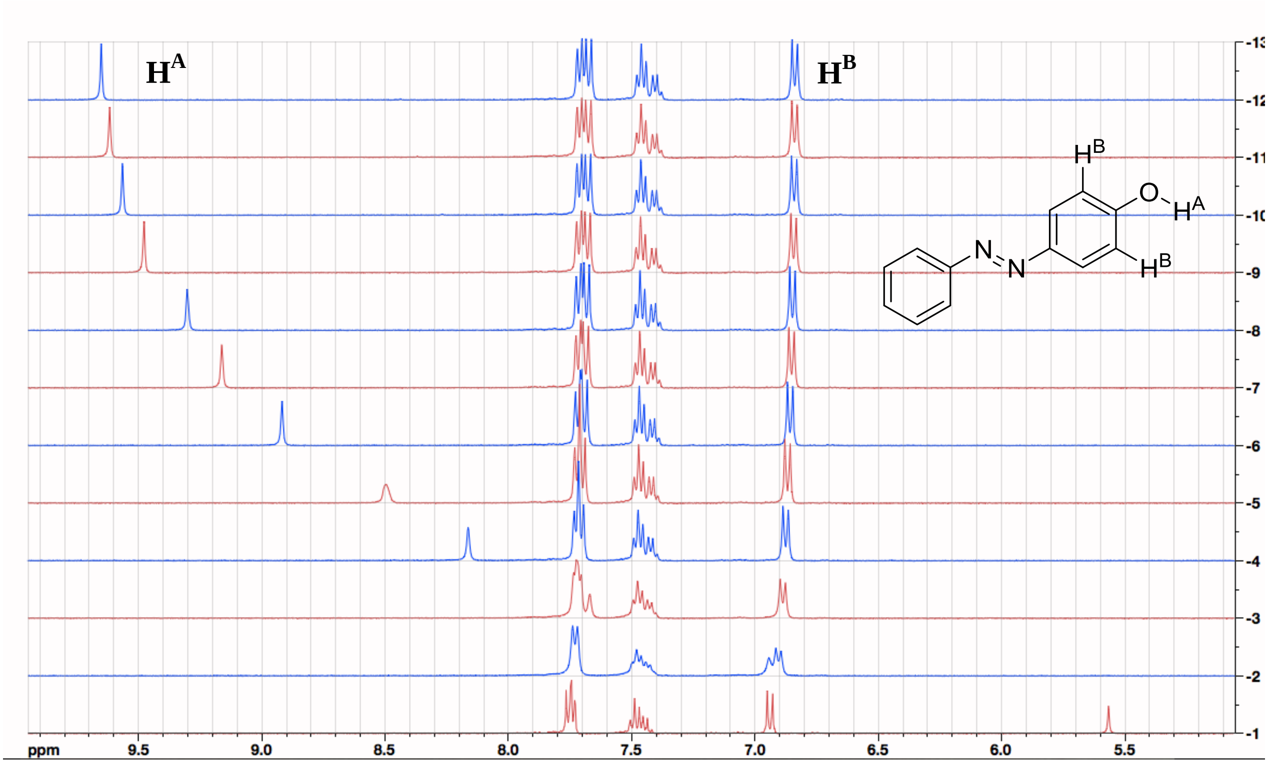
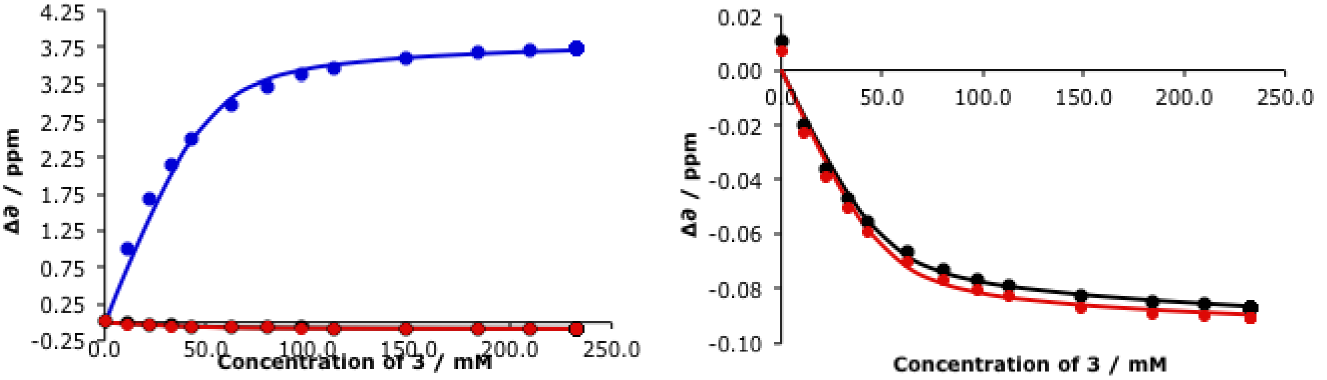


Figure S7: NMR spectra of the titration of 1 with 3 in diiodomethane



(a) Titration Curves for H^A and H^B

(b) Rescale to observe Titration Curve for H^B

Figure S8: Binding isotherms for titration: (a) shows all three curves fit, and (b) is rescaled to observe the fits for H^B.

$K_a = 210\pm3$ 96% bound

CH_2Br_2

Host: 4-phenylazophenol (**1**) 0.1 mM
Guest: Tetramethylurea (**3**)

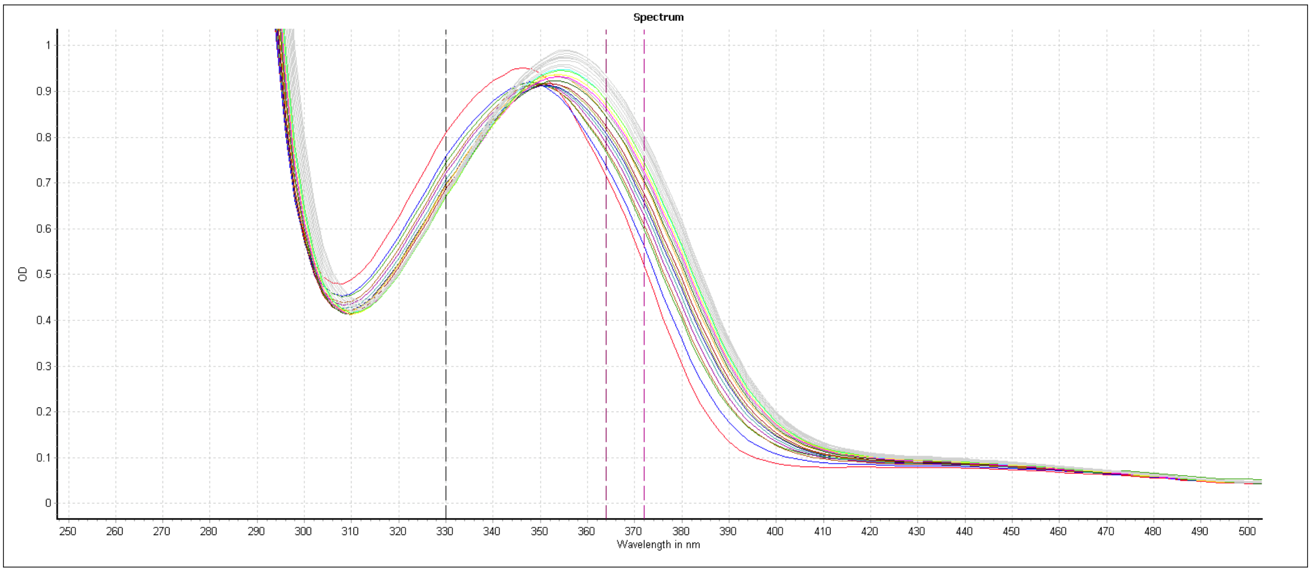


Figure S9: UV/vis spectra of titration of **1** with **3** in dibromomethane. Vertical dashed lines indicate wavelengths monitored for binding isotherm.

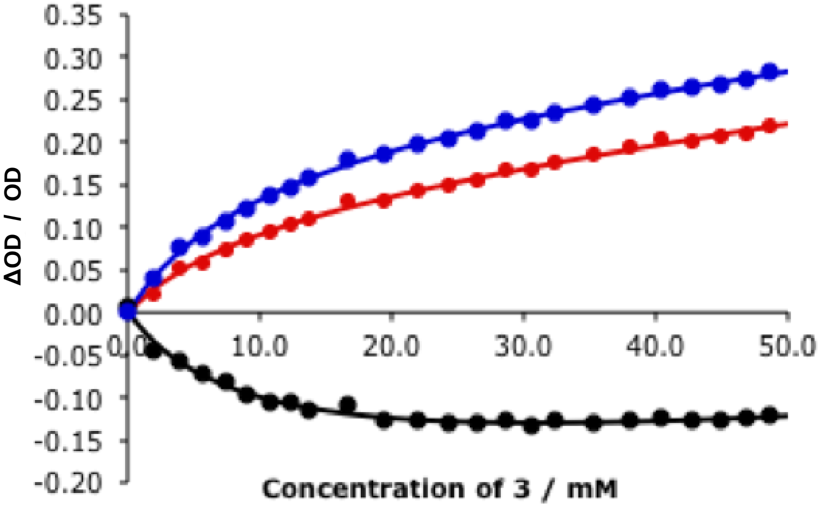


Figure S10: Binding isotherms for titration

K_a = 110±10 M^{-1} 83% bound

CH_2Cl_2

Host: 4-phenylazophenol (**1**) 0.1 mM
Guest: Tetramethylurea (**3**)

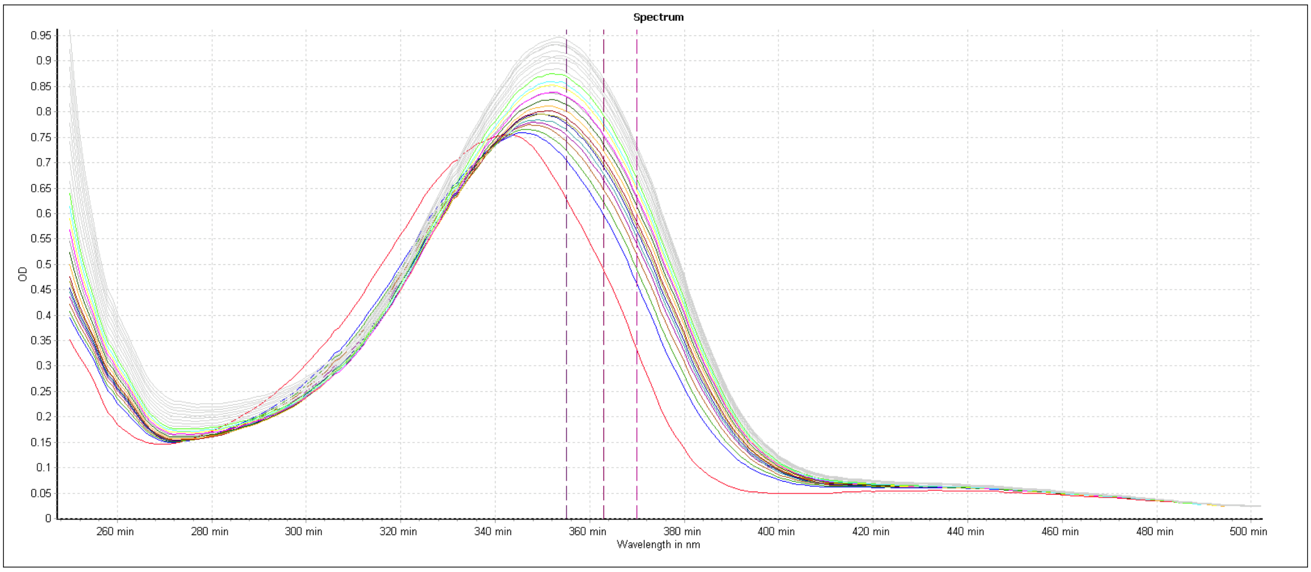


Figure S11: UV/vis spectra of titration of **1** with **3** in dichloromethane. Vertical dashed lines indicate wavelengths monitored for binding isotherm.

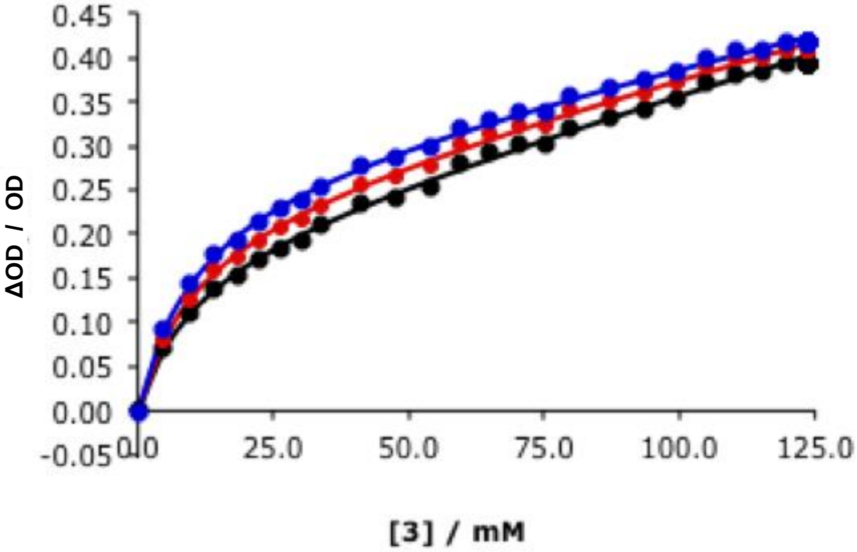


Figure S12: Binding isotherms for titration

$K_a = 90 \pm 7\ M^{-1}$ 83% bound

$CHCl_3$

Host: 4-phenylazophenol (**1**) 0.1 mM
Guest: Tetramethylurea (**3**)

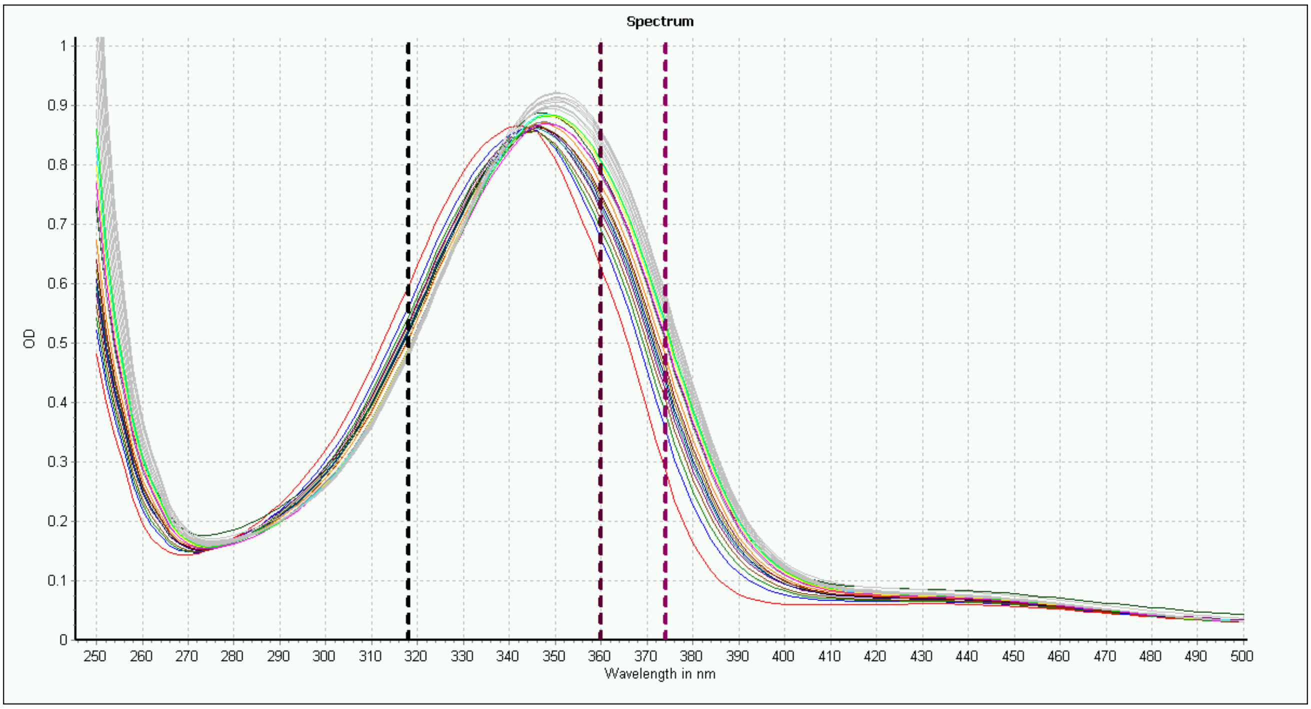


Figure S13: UV/vis spectra of titration of **1** with **3** in chloroform. Vertical dashed lines indicate wavelengths monitored for binding isotherm.

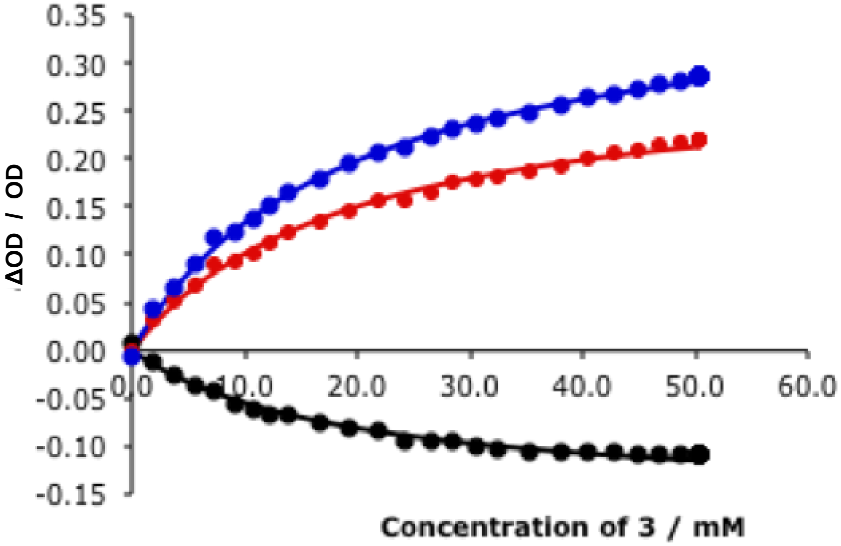


Figure S14: Binding isotherms for titration

$K_a = 52 \pm 2\ M^{-1}$ 73% bound

1,1,2,2-Tetrachloroethane

Host: 4-phenylazophenol (**1**) 0.1 mM
Guest: Tetramethylurea (**3**)

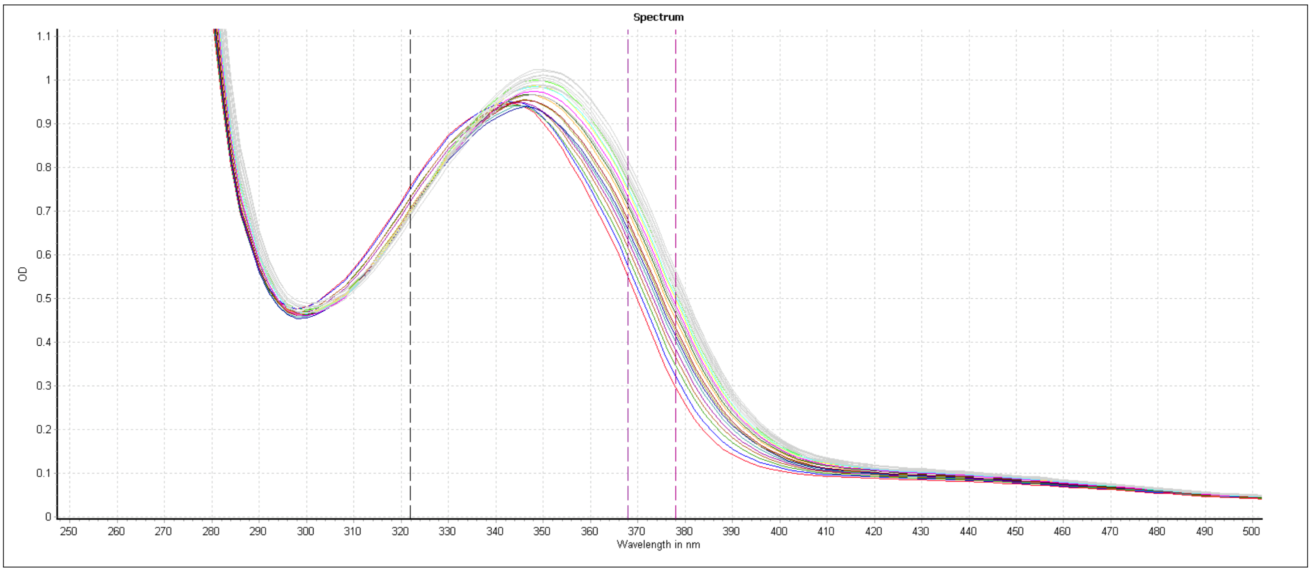


Figure S15: UV/vis spectra of titration of **1** with **3** in TCE. Vertical dashed lines indicate wavelengths monitored for binding isotherm.

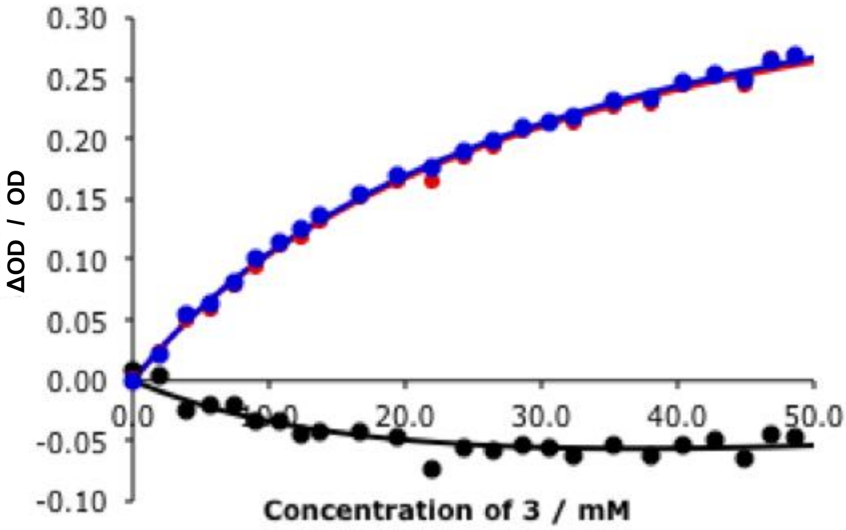


Figure S16: Binding isotherms for titration

$K_a = 35 \pm 9\ M^{-1}$ 63% bound

Acetone

Host: 4-phenylazophenol (**1**) 100 mM
Guest: Tetramethylurea (**3**)

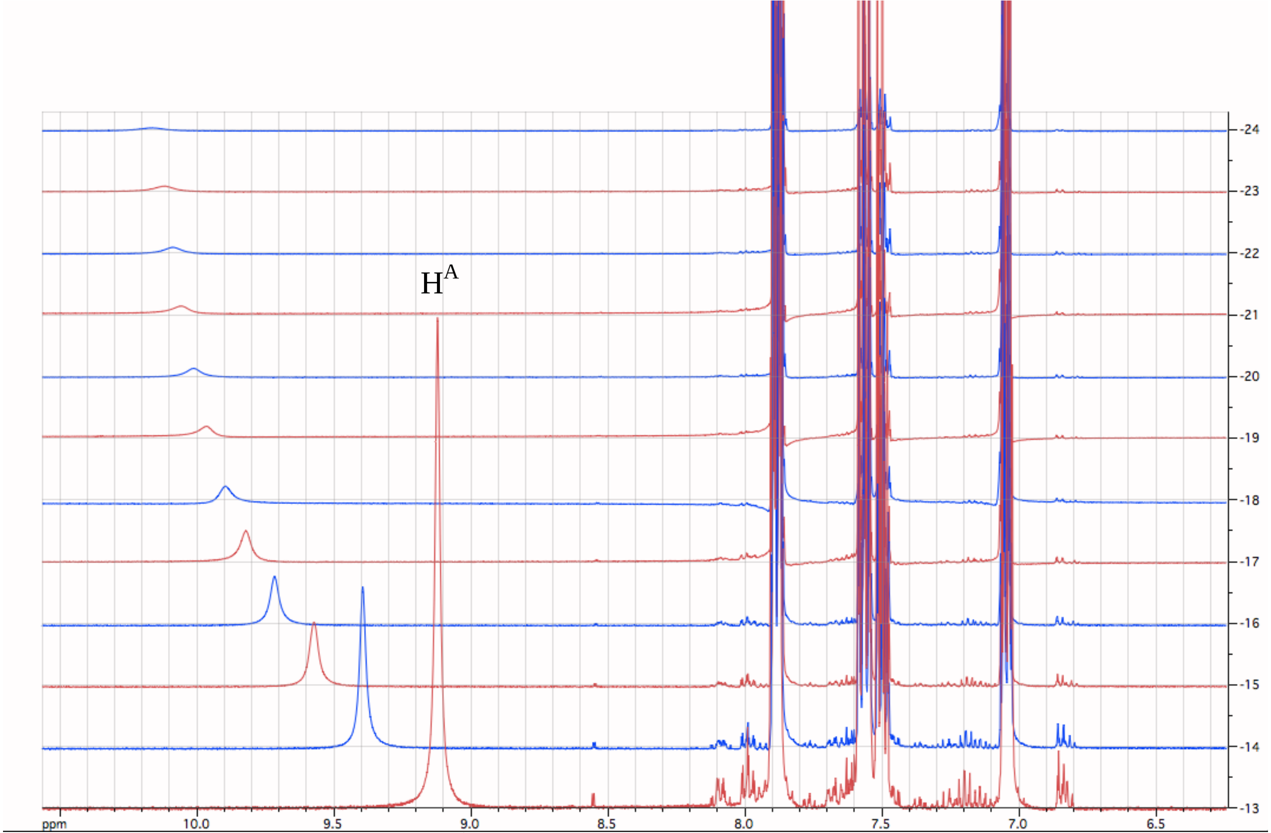
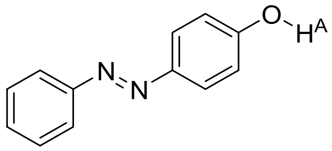


Figure S17: 400 MHz ^{1}H NMR spectra of titration of **1** with **3** in acetone



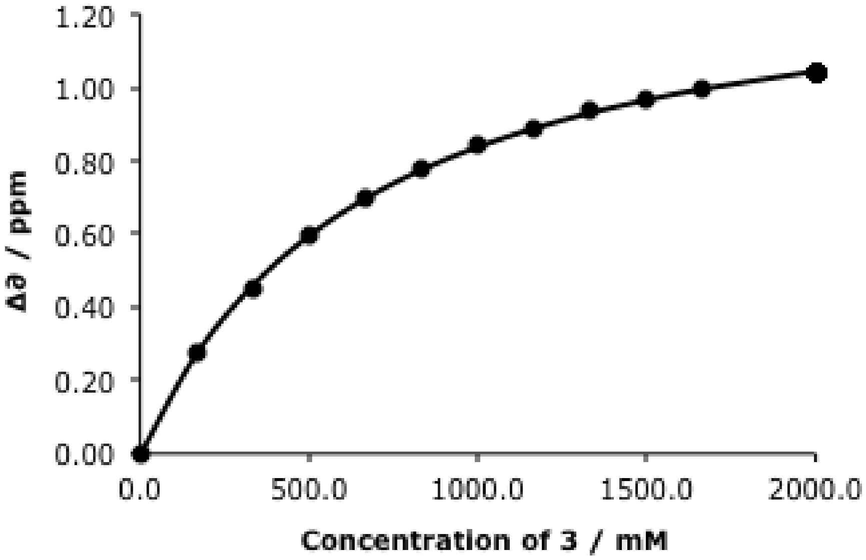


Figure S18: Binding isotherm for titration.

K_a = 2±1 M^{-1} 76% bound

Acetonitrile

Host: 4-phenylazophenol (**1**) 100 mM
Guest: Tetramethylurea (**3**)

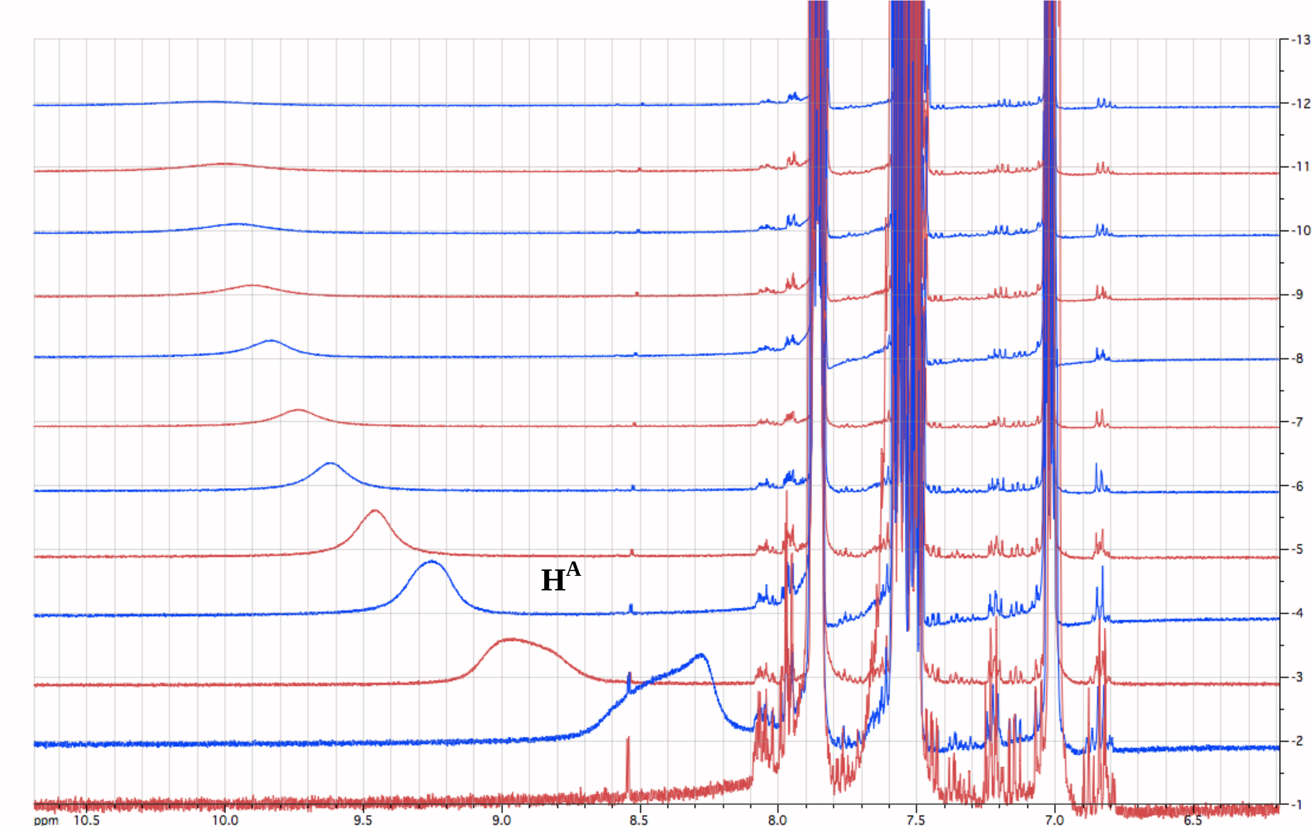
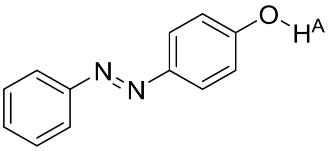


Figure S19: 400 MHz ^{1}H NMR spectra of titration of 1 with 3 in acetonitrile



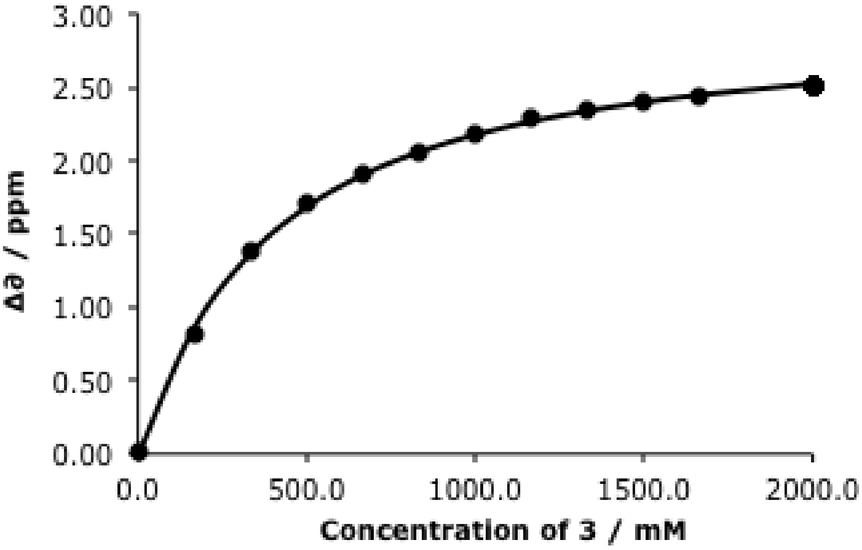


Figure S20: Binding isotherm for titration.

$K_a = 3\pm1\ M^{-1}$ 85% bound

CH_3NO_2

Host: 4-phenylazophenol (**1**) 100 mM
Guest: Tetramethylurea (**3**)

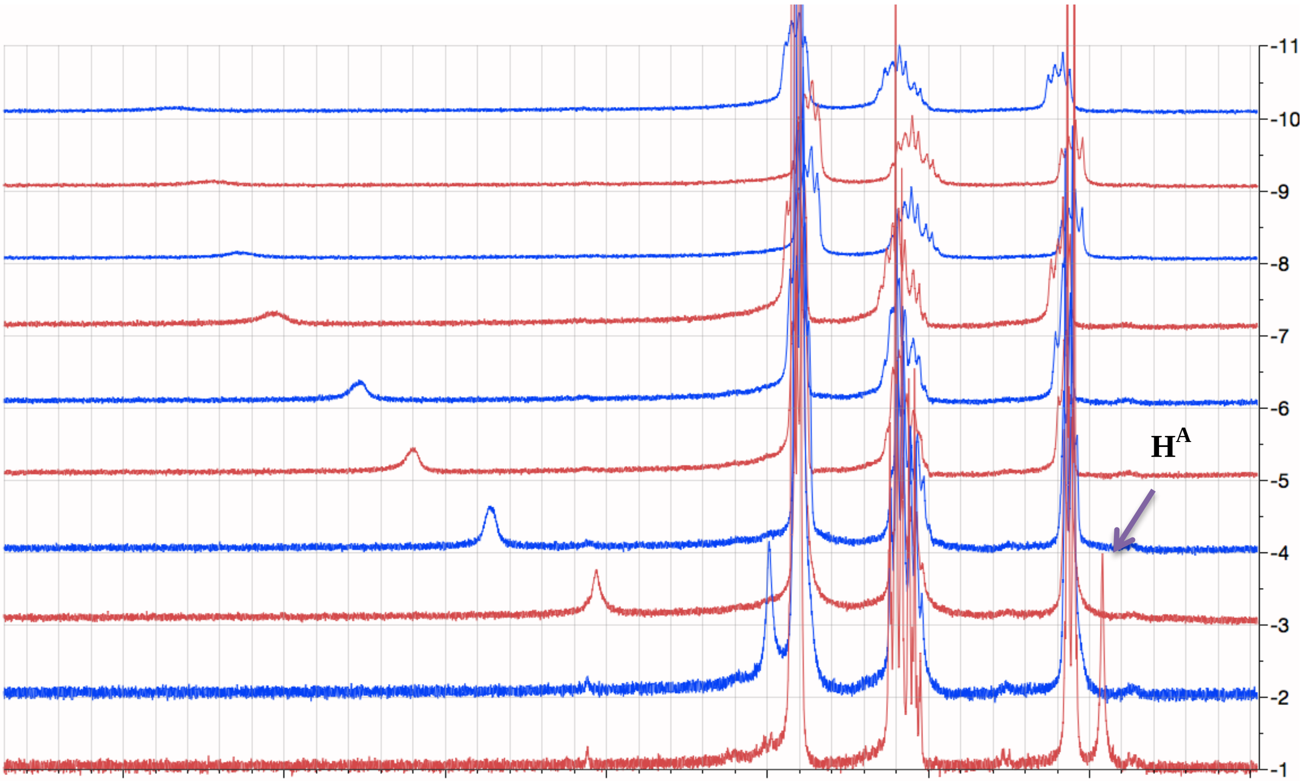
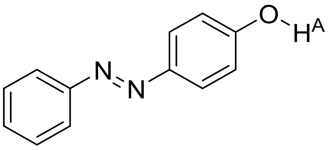


Figure S21: 400 MHz ^{1}H NMR spectra of titration of **1** with **3** in nitromethane



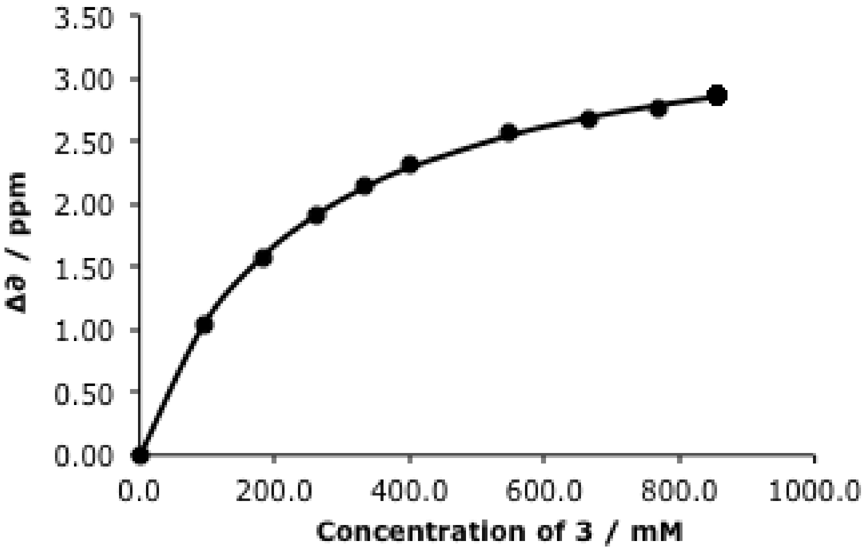


Figure S22: Binding isotherm for titration.

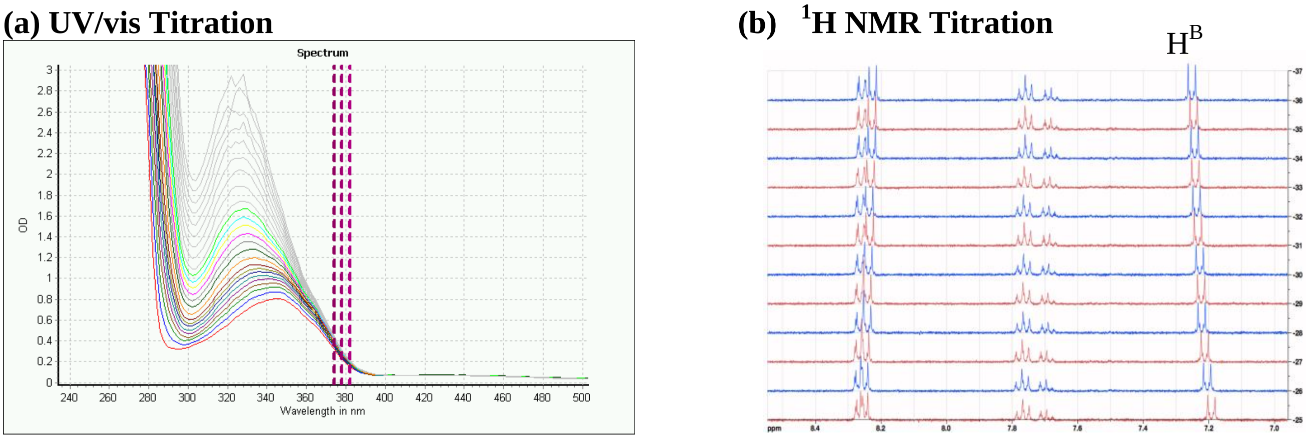
$K_a = 5 \pm 1\ M^{-1}$ 73% bound

6. Spectra and Binding isotherms of complexes of 4-phenylazophenol with tetramethylthiourea [1•4]

Note: Tetramethylthiourea has an absorption band which can overlap with the absorption band of 4-phenylazophenol. By monitoring longer wavelengths in the phenol band the binding isotherm can still be observed. To confirm the accuracy of monitoring these wavelengths, in some cases, NMR titrations were also run. These proved to be in good agreement with the K_a measured by UV/vis titrations. In some cases, especially when concentrated solutions of tetramethylthiourea were used as guest, the overlap was too great as to observe the binding isotherm. In these cases only NMR titrations were run to determine association constants.

n-Octane

Host: 4-phenylazophenol (**1**) 0.1 mM
Guest: Tetramethylthiourea (**4**)



(a) UV/vis Titration

(b) ^{1}H NMR Titration

Figure S23: (a) UV/vis spectra (dashed lines indicate wavelengths monitored for binding isotherms) and (b) 400 MHz ^{1}H NMR spectra of the titration of **1** with **4** in *n*-octane

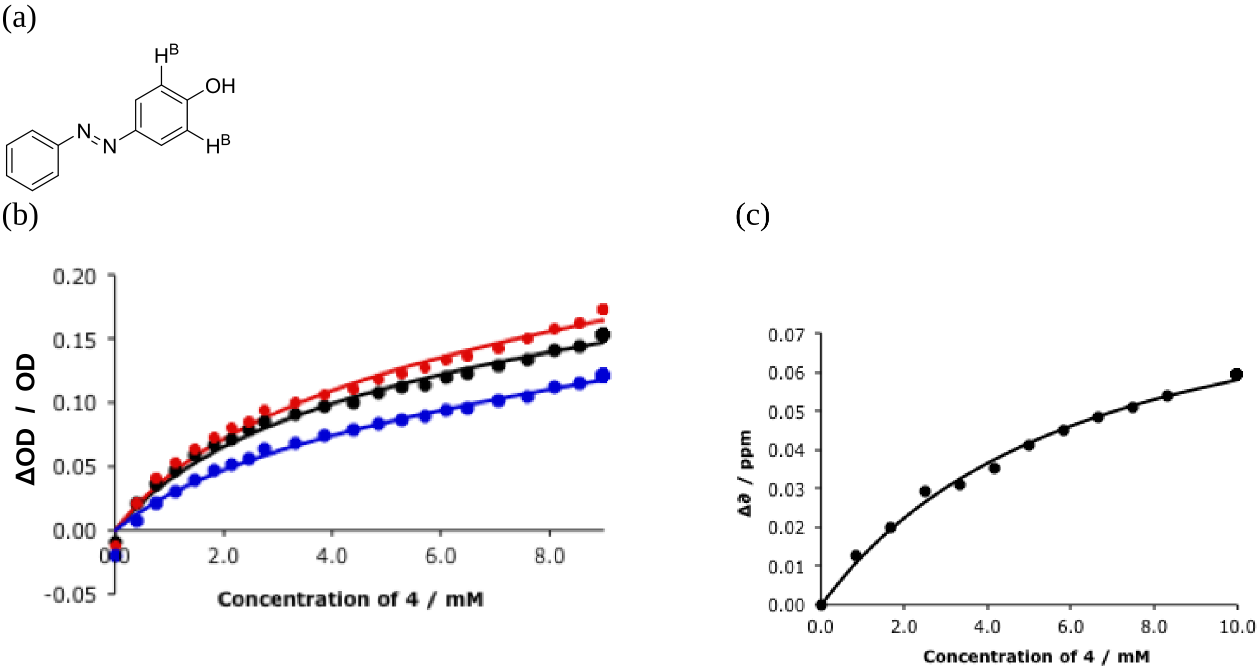


Figure S24: (a) Labeled molecular diagram showing the protons followed in (b) binding isotherm of UV/vis titration and (c) the NMR binding isotherm.

K_a = 370±10 M^{-1} 74% bound K_a = 200 M^{-1} 63% bound

Carbon tetrachloride

Host: 4-phenylazophenol (**1**) 10 mM
Guest: Tetramethylthiourea (**4**)

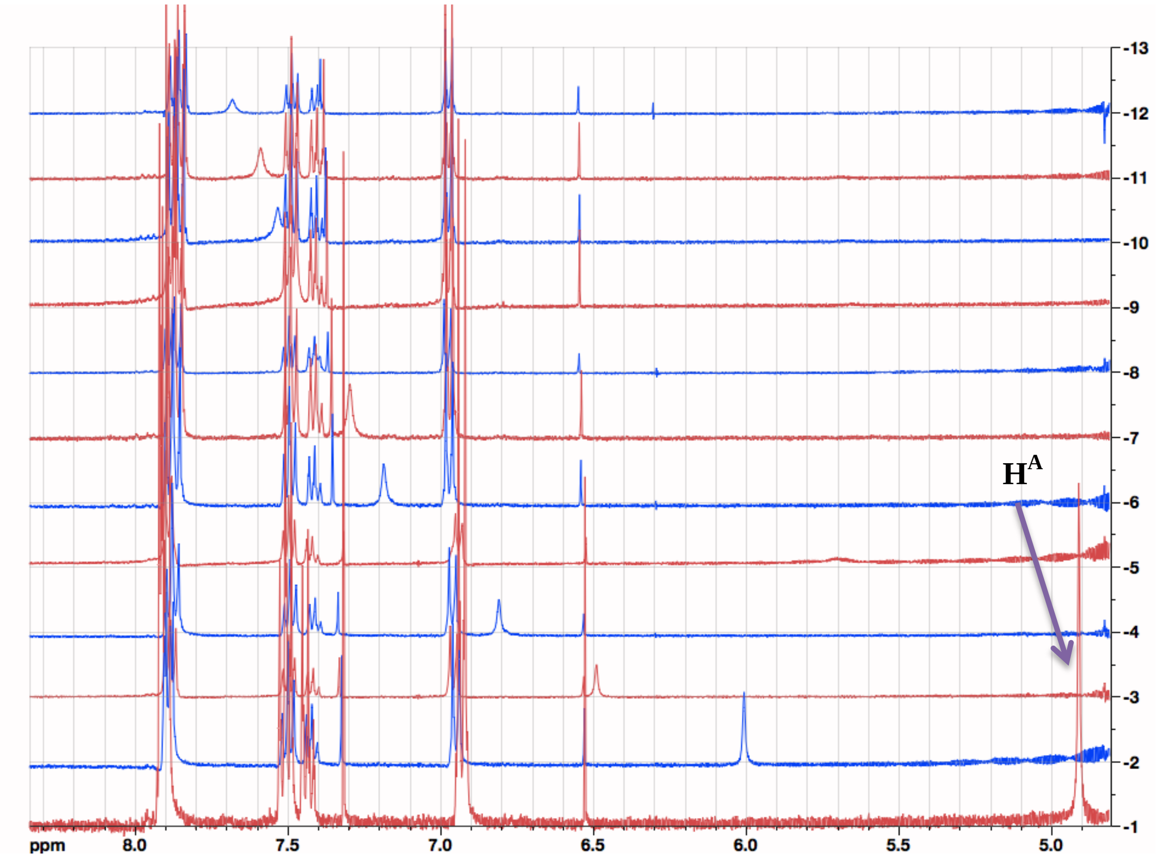
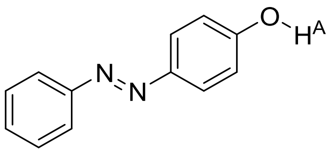


Figure S25: 400 MHz ^{1}H NMR spectra of the titration of **1** with **4** in carbon tetrachloride



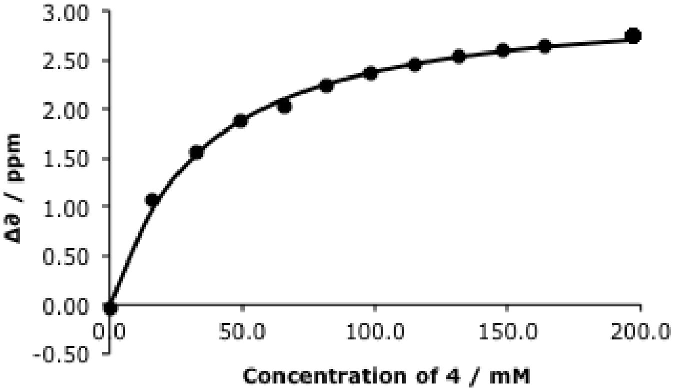


Figure S26: Binding isotherm for titration.

$$K_a = 24\pm1\ \mathrm{M}^{-1}\quad 87\%\ \text{bound}$$

Toluene

Host: 4-phenylazophenol (**1**) 0.25 mM
Guest: Tetramethylthiourea (**4**)

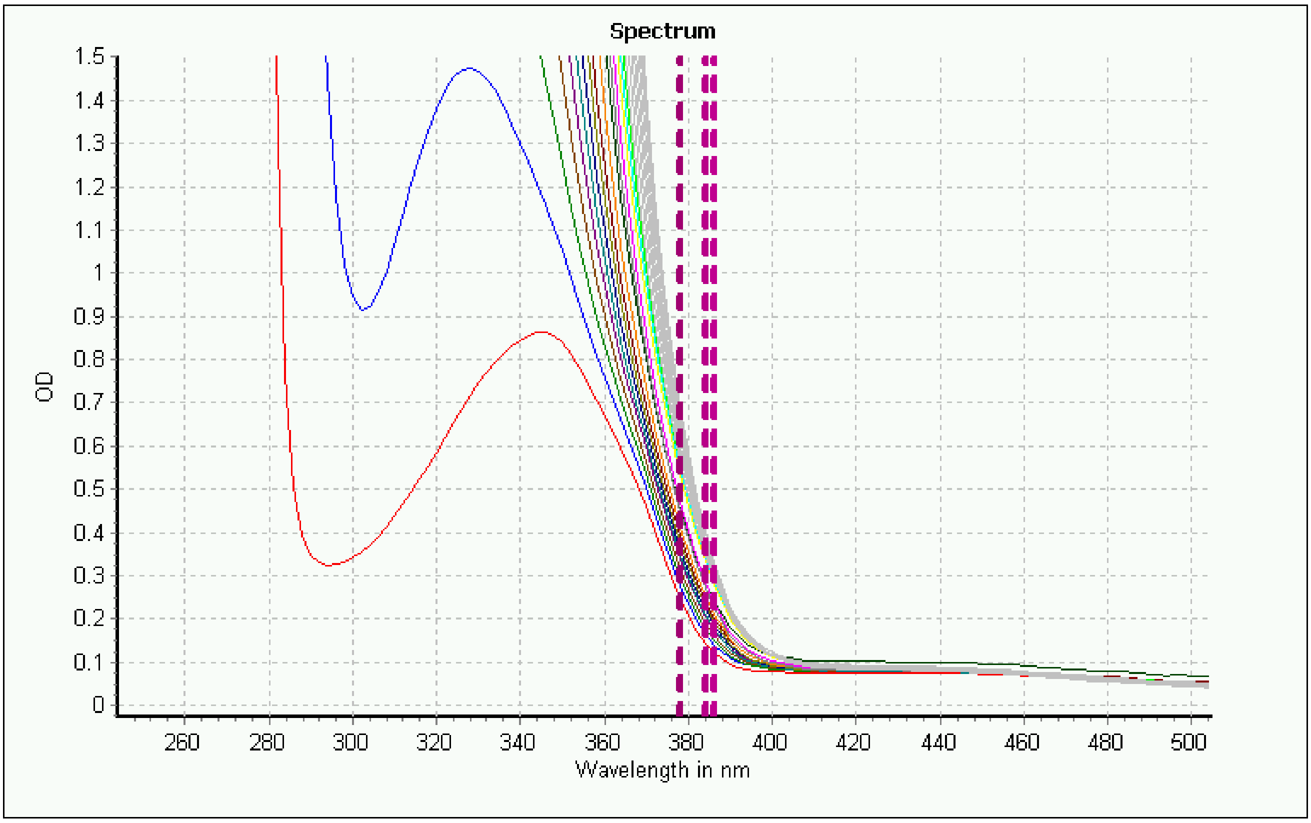


Figure S27: UV/vis spectra of the titration of **1** with **4** in toluene. Dashed lines indicate wavelengths monitored for binding isotherms.

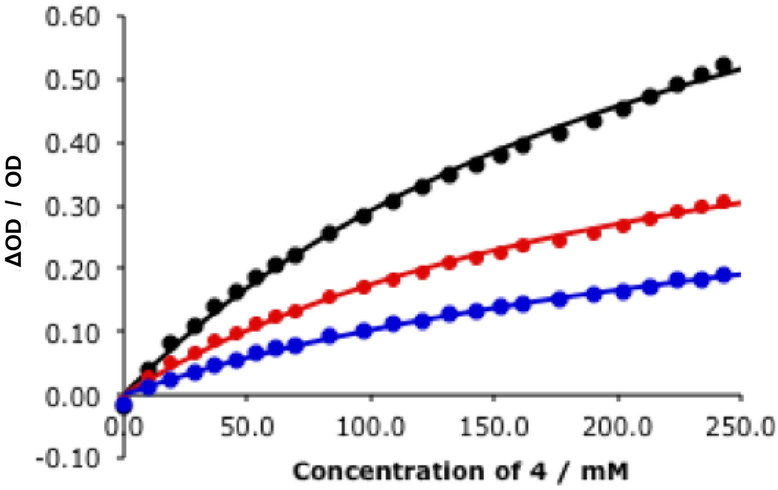


Figure S28: Binding isotherms for titration

$K_a = 4 \pm 1$ M^{-1} 51% bound

Diiodomethane

Host: 4-phenylazophenol (**1**) 100 mM
Guest: Tetramethylthiourea (**4**)

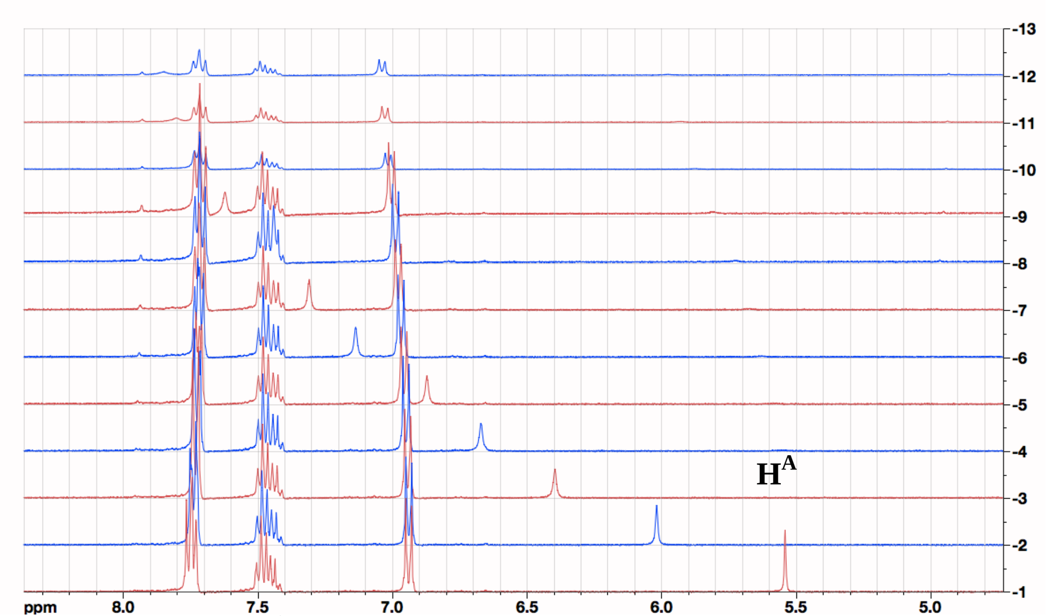
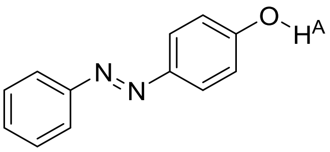


Figure S29: 400 MHz ^{1}H NMR spectra of the titration of **1** with **4** in diiodomethane



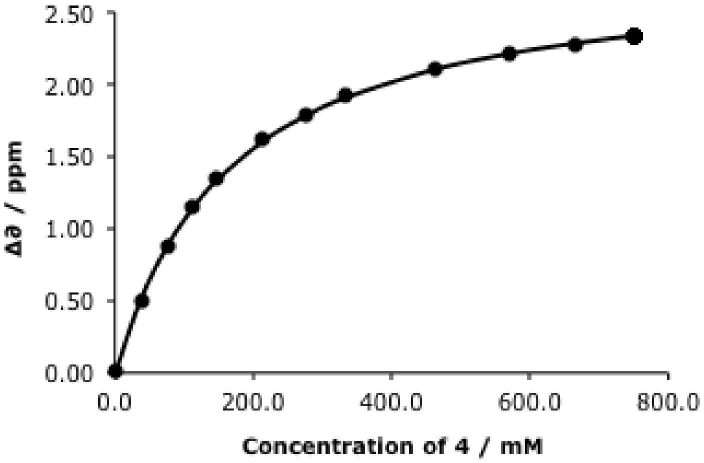


Figure S30: Binding isotherm for titration.

$$K_a = 6 \pm 1\ \mathrm{M}^{-1}\quad 83\%\ \text{bound}$$

Dichloromethane

Host: 4-phenylazophenol (**1**) 0.1 mM
Guest: Tetramethylthiourea (**4**)

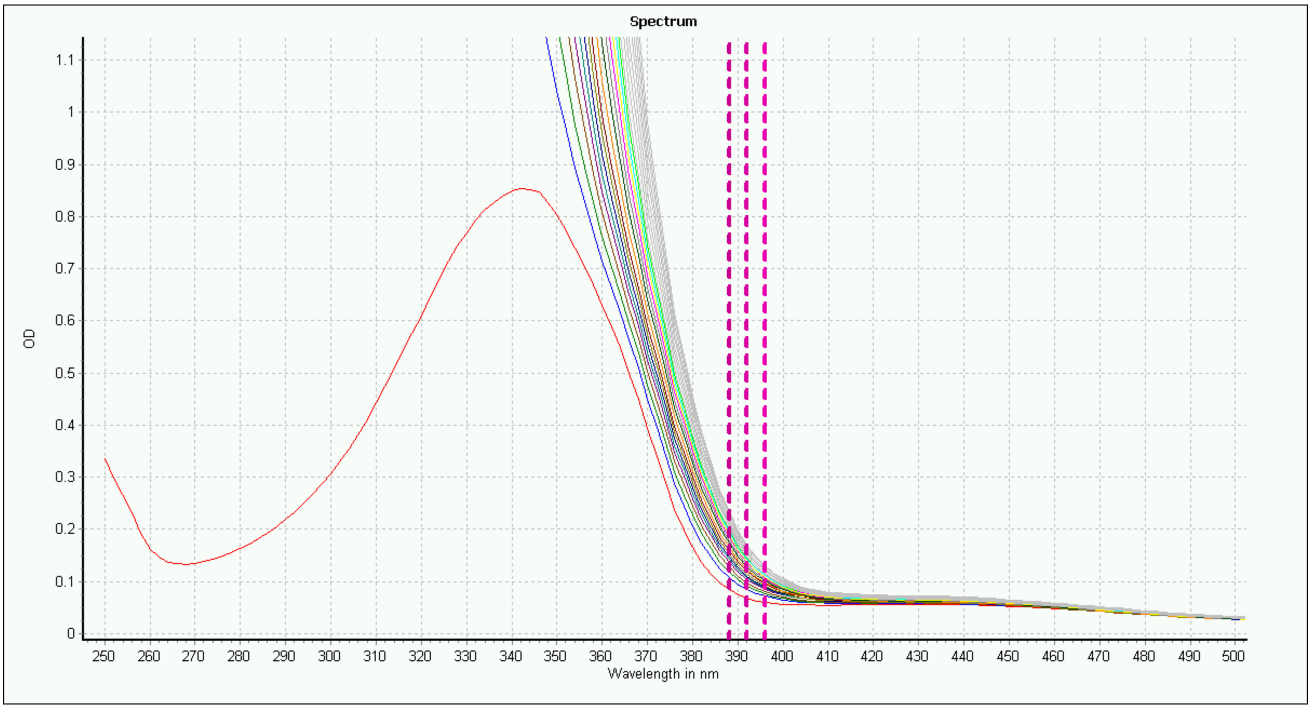


Figure S31: UV/vis spectra of the titration of **1** with **4** in dichloromethane. Dashed lines indicate wavelengths monitored for binding isotherms.

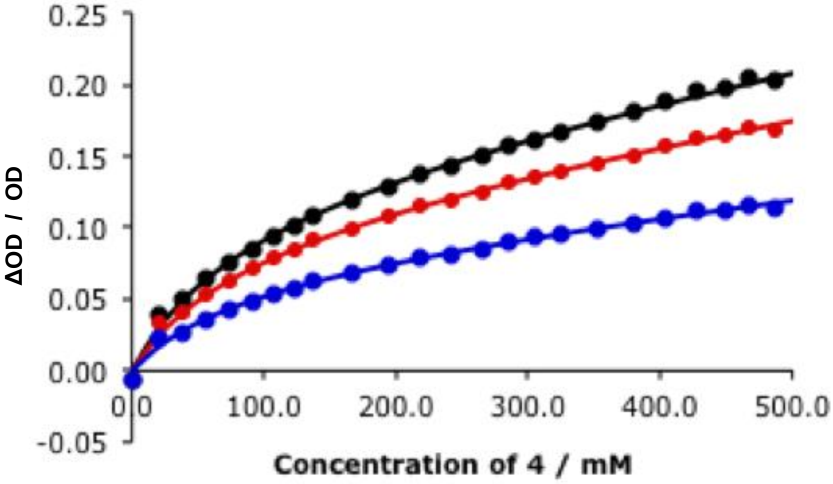


Figure S32: Binding isotherms for titration

$K_a = 9 \pm 5\ \mathrm{M}^{-1}$ 82% bound

Chloroform

Host: 4-phenylazophenol (**1**) 10 mM
Guest: Tetramethylthiourea (**4**)

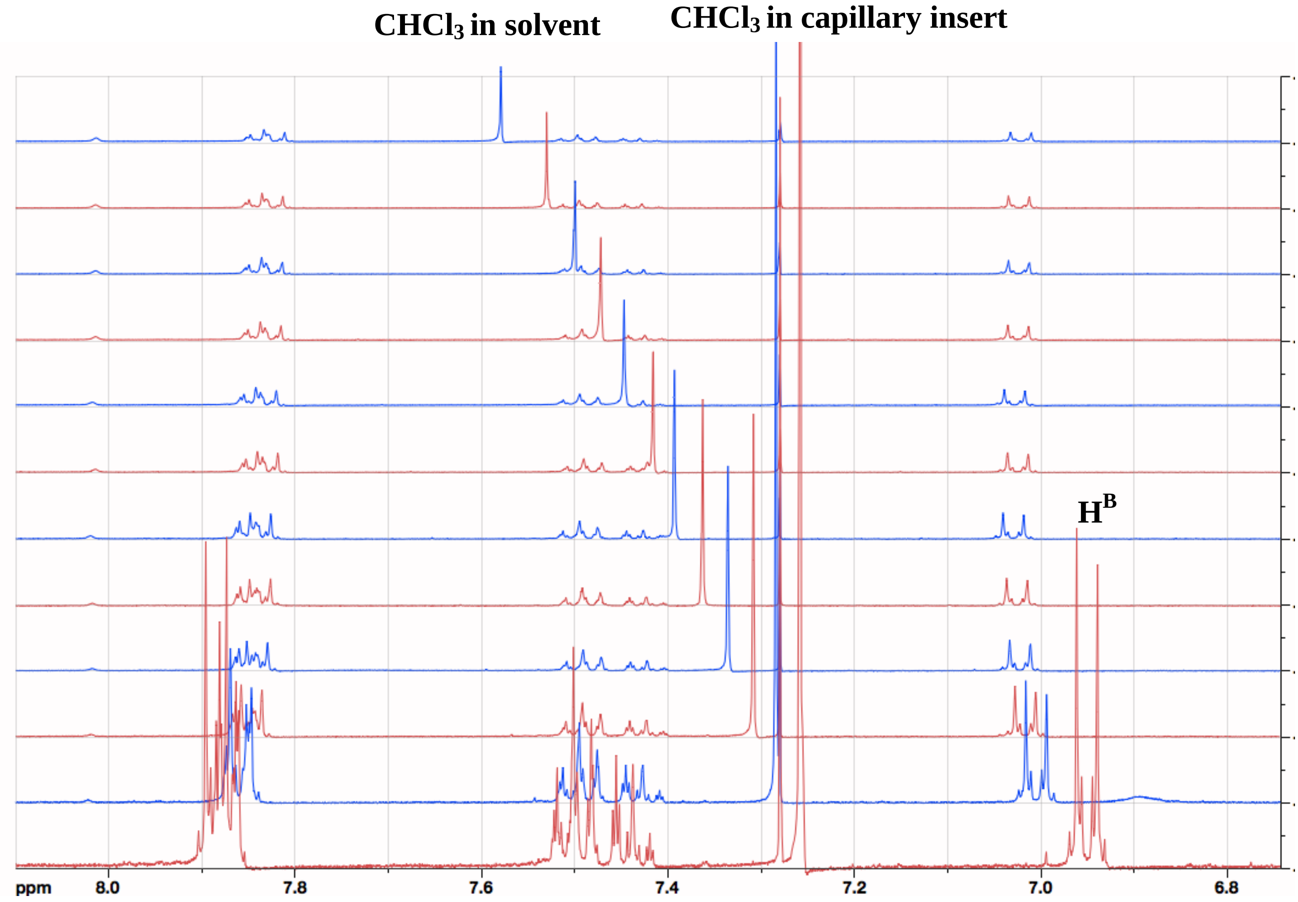
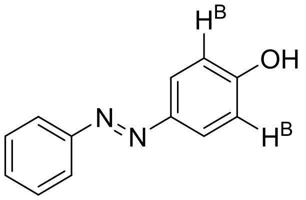


Figure S33: Annotated partial 400 MHz ^{1}H NMR spectra of the titration of **1** with **4** in chloroform



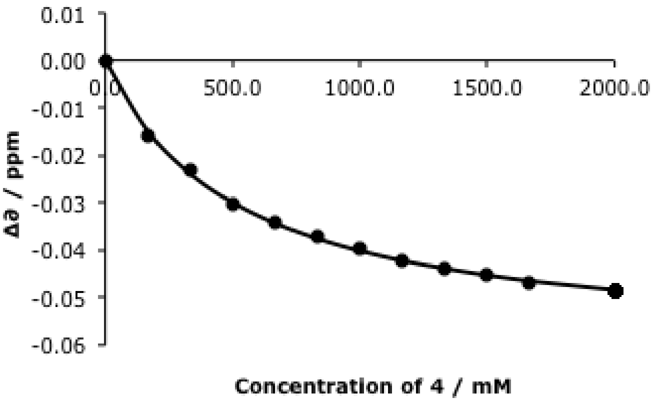


Figure S34: Binding isotherm for titration.

$K_a = 2 \pm 1\ M^{-1}$ 80% bound

1,1,2,2-Tetrachloroethane

Host: 4-phenylazophenol (**1**) 20 mM
Guest: Tetramethylthiourea (**4**)

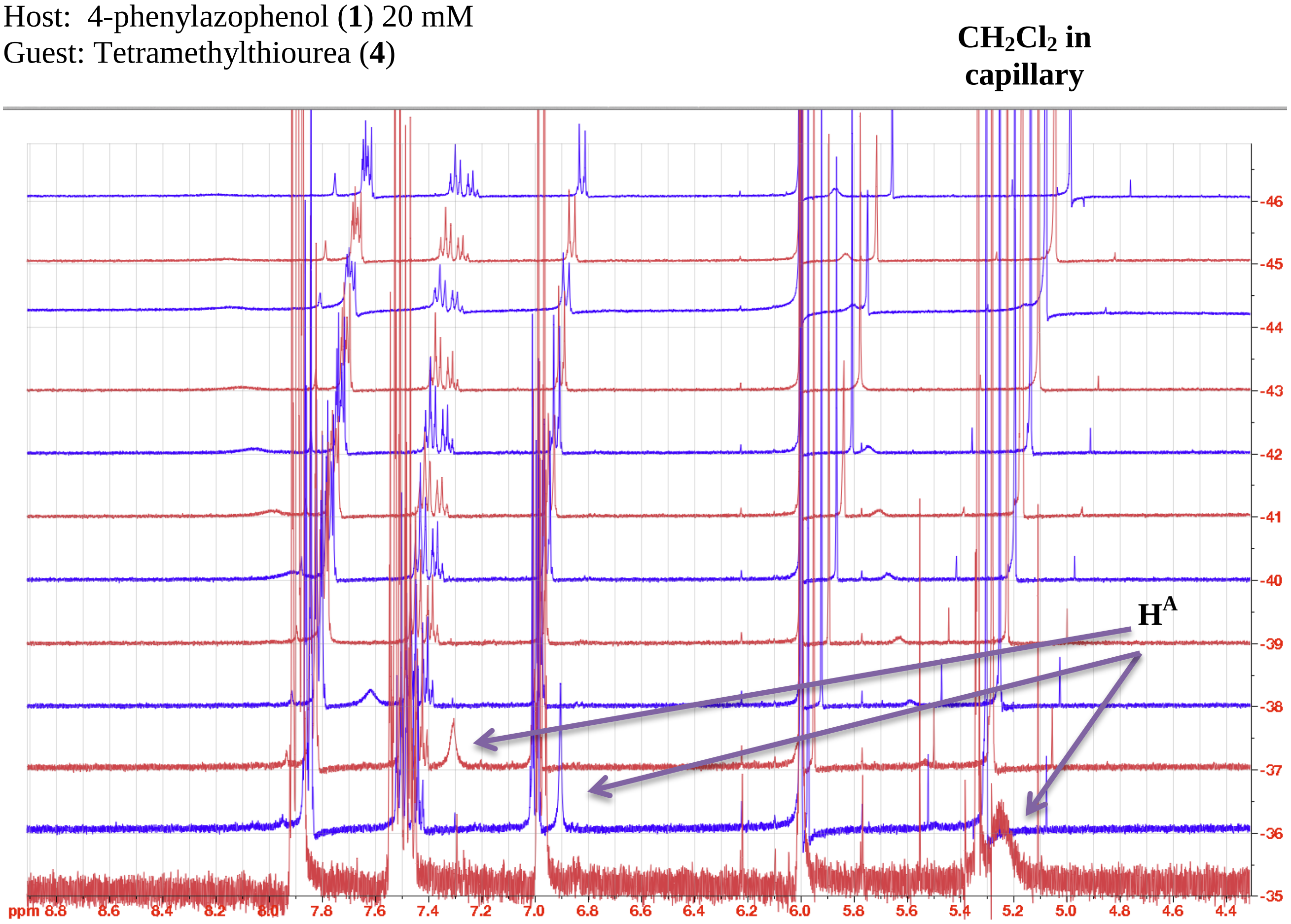
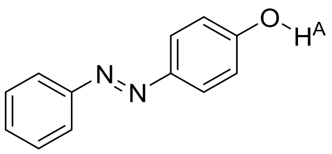


Figure S35: Annotated partial 400 MHz ^{1}H NMR spectra of the titration of **1** with **4** in TCE.



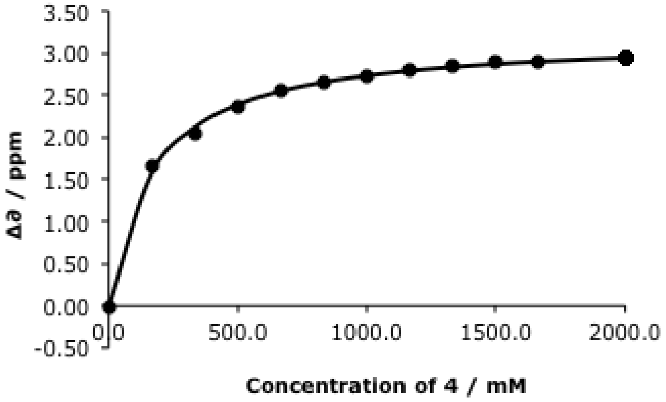


Figure S36: Binding isotherm for titration.

$K_a = 6 \pm 1\ M^{-1}$ 92% bound

7. Spectra and Binding isotherms of complexes of Iodine with tetramethylurea [2•3]

Iodine (**2**), chosen as the XB donor, has a characteristic UV/vis absorption at 530 nm in hexane which is affected by the formation of complexes with **3** or **4** where the absorption is subjected to a hypsochromic shift. Additionally formation of complexes also gives rise to a charge transfer band in the UV region. By using automated UV/vis titrations to monitor either of these two changes in absorption as a function of [G] binding isotherms can be observed. In the case of solvents with functional groups which could interact with iodine, binding isotherms for host-guest interactions were often obscured by charge transfer absorption bands arising from iodine•solvent interactions. In such cases, NMR titrations were carried out using the acceptor as the host and monitoring its chemical shift as a function of [iodine] to observe a binding isotherm

n-Octane

Host: Iodine (**2**) 1 mM
Guest: Tetramethylurea (**3**)

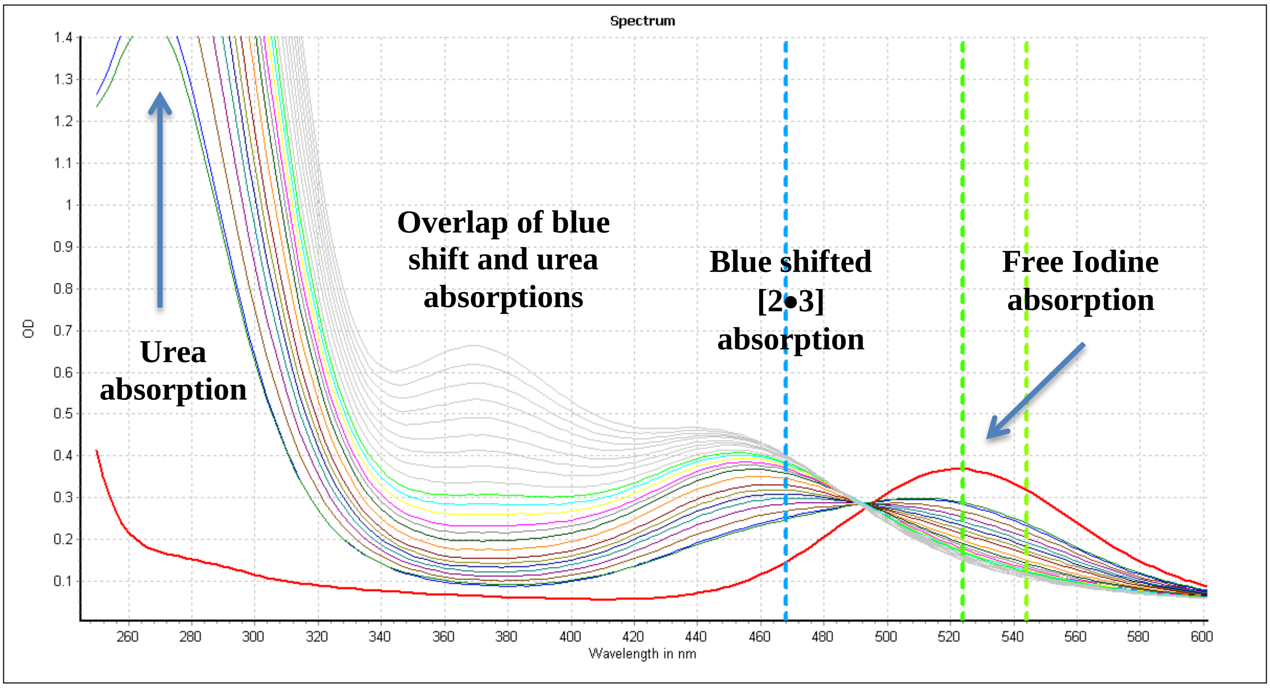


Figure S37: Annotated UV/vis spectra of the titration of **2** with **3** in *n*-octane to show the absorptions monitored

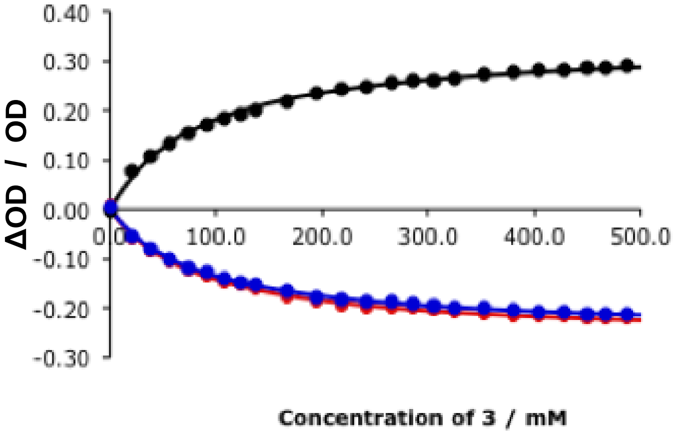


Figure S38: Binding isotherms for titration

$K_a = 12 \pm 2\ \mathrm{M}^{-1}$ 86% bound

Carbon tetrachloride

Host: Iodine (**2**) 0.5 mM
Guest: Tetramethylurea (**3**)

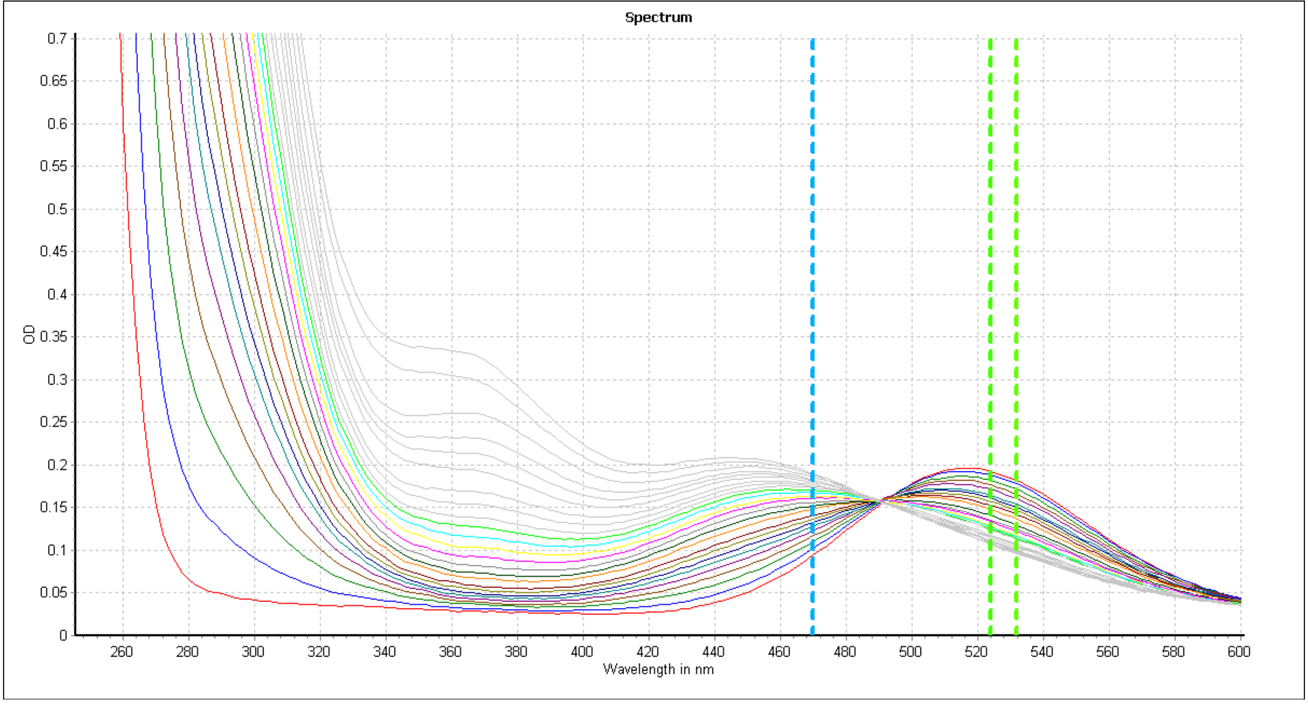


Figure S39: UV/vis spectra of the titration of **2** with **3** in carbon tetrachloride. Dashed lines indicate wavelengths monitored for binding isotherms.

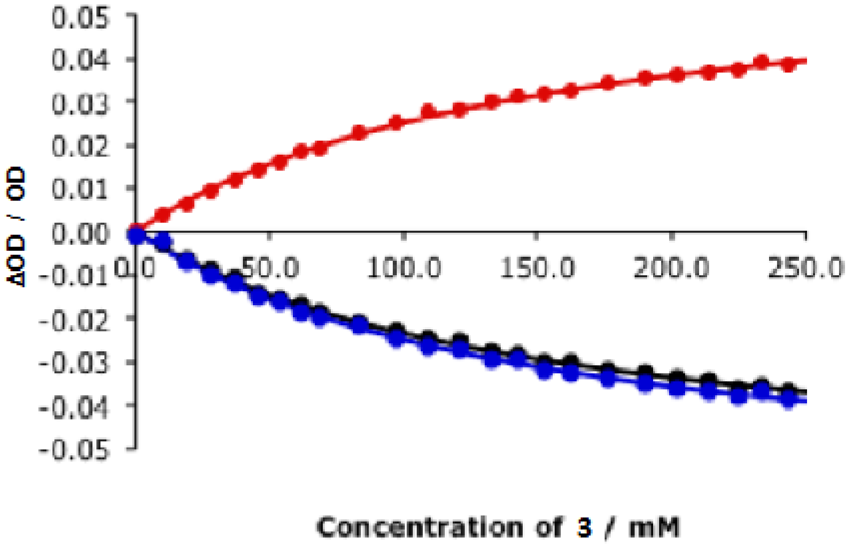


Figure S40: Binding isotherms for titration

$K_a = 6 \pm 1$ M^{-1} 62% bound

Toluene

Host: Iodine (**2**) 0.05 mM
Guest: Tetramethylurea (**3**)

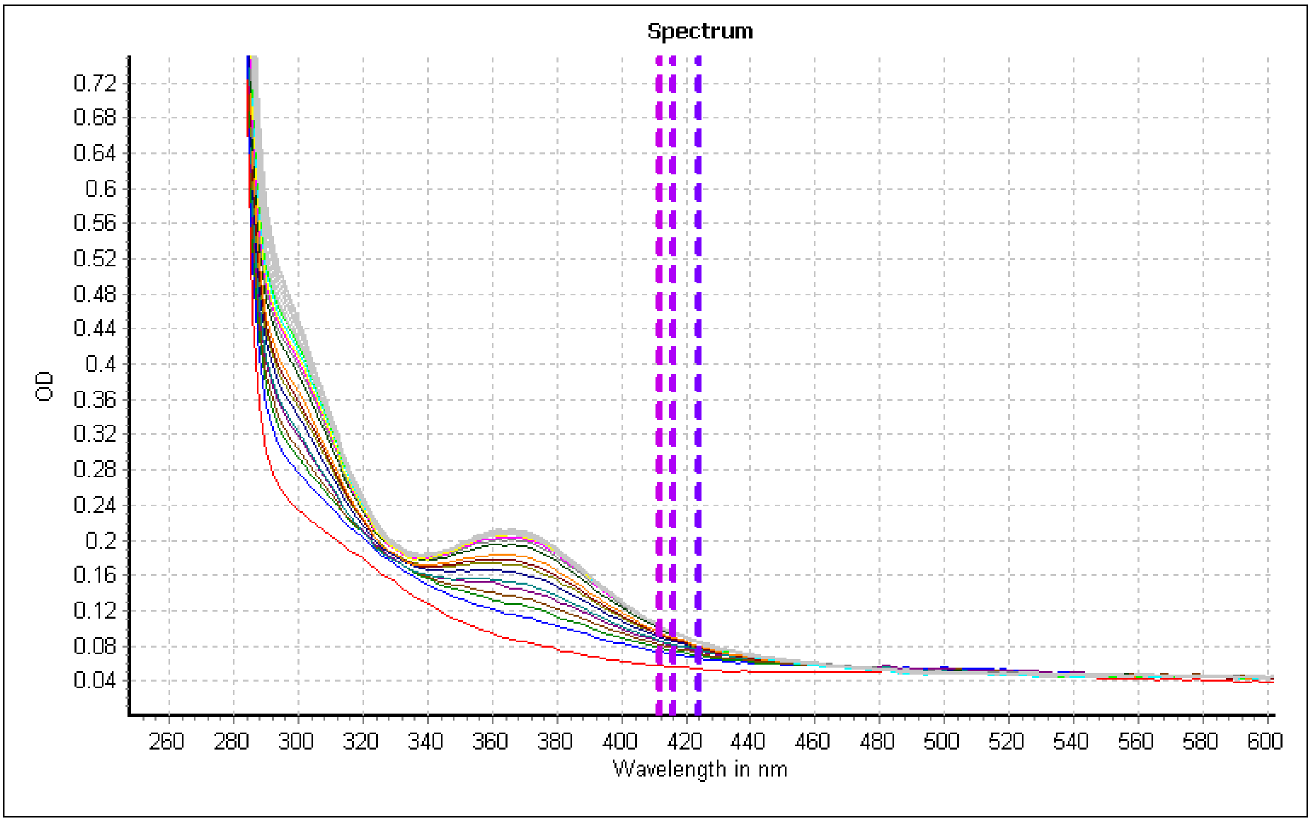


Figure S41: UV/vis spectra of the titration of **2** with **3** in toluene. Dashed lines indicate wavelengths monitored for binding isotherms.

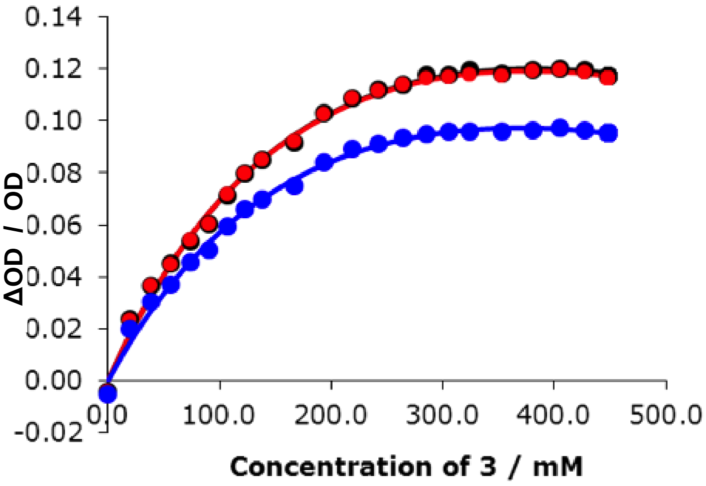


Figure S42: Binding isotherms for titration

$K_a = 3 \pm 1\ \text{M}^{-1}$ 62% bound

Dichloromethane

Host: Iodine (**2**) 1.2 mM
Guest: Tetramethylurea (**3**)

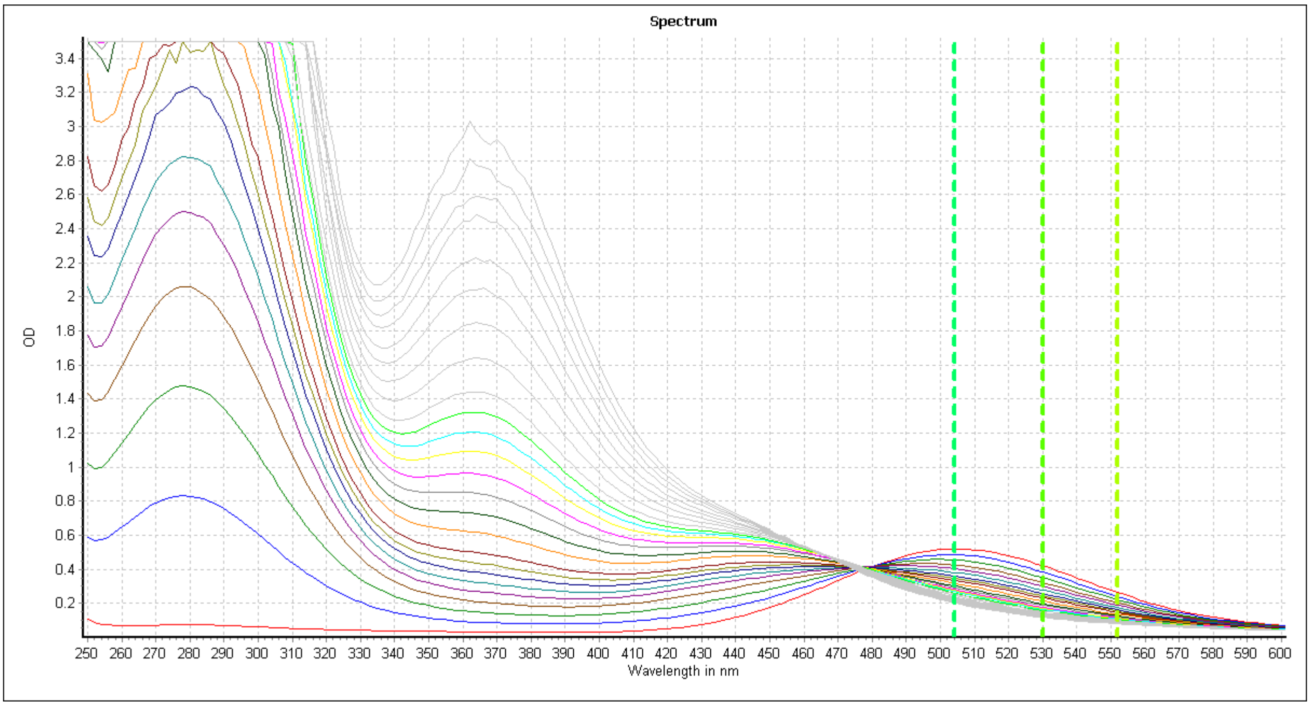


Figure S43: UV/vis spectra of the titration of **2** with **3** in dichloromethane. Dashed lines indicate wavelengths monitored for binding isotherms.

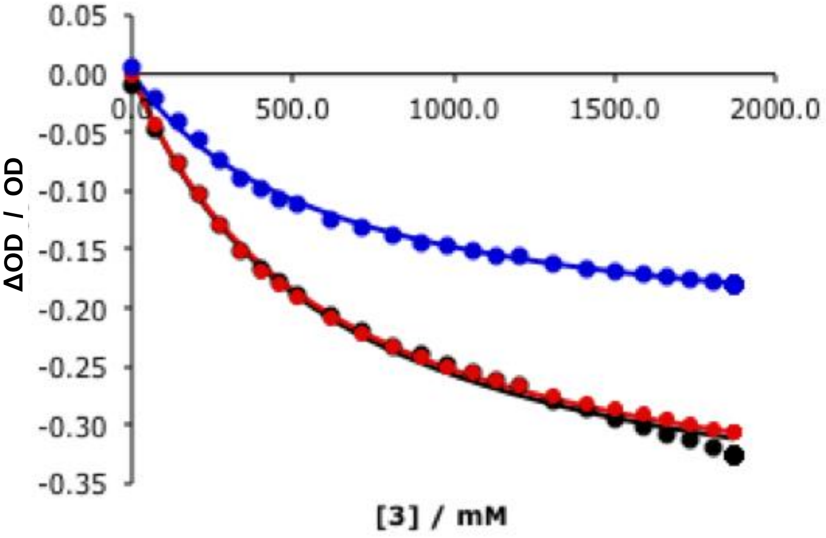


Figure S44: Binding isotherms for titration

$K_a = 2 \pm 1\ \text{M}^{-1}$ 75% bound

Chloroform

Host: Iodine (**2**) 1 mM
Guest: Tetramethylurea (**3**)

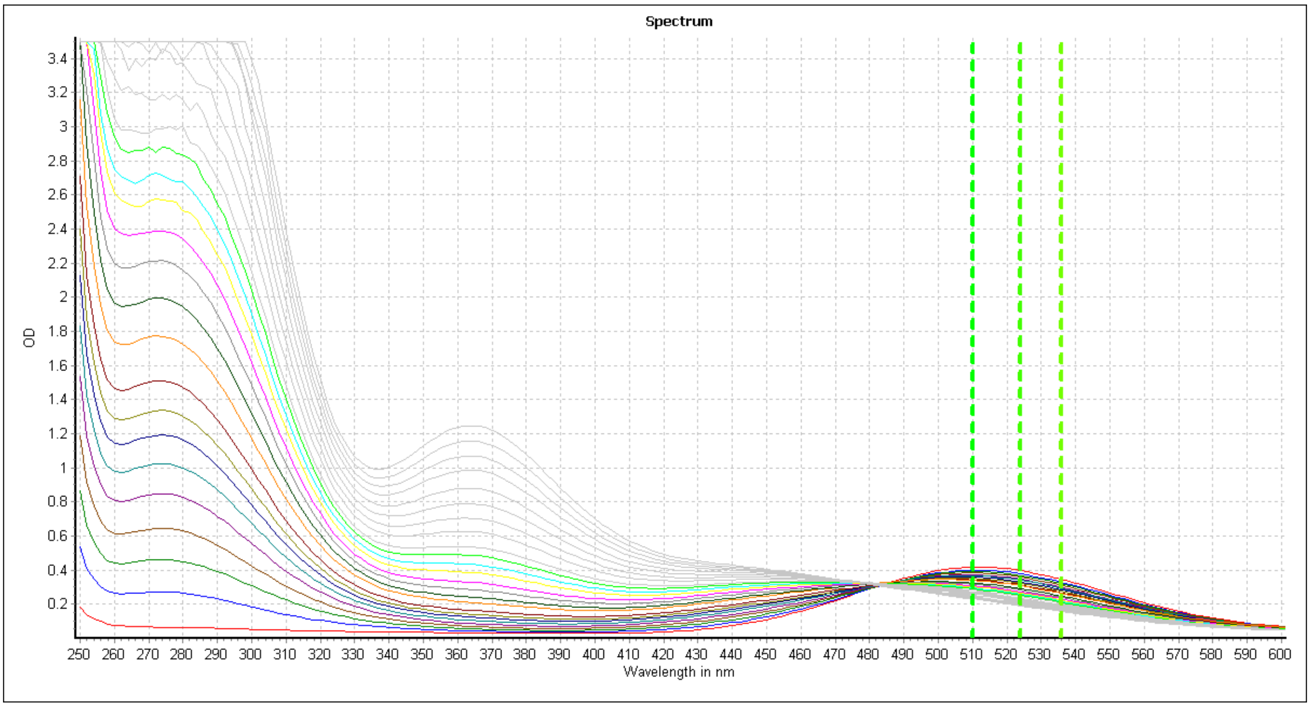


Figure S45: UV/vis spectra of the titration of **2** with **3** in chloroform. Dashed lines indicate wavelengths monitored for binding isotherms.

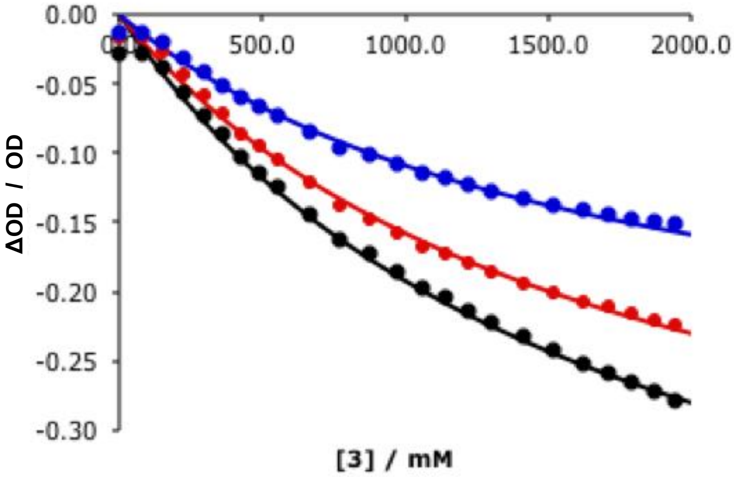


Figure S46: Binding isotherms for titration

$K_a = 1 \pm 1\ M^{-1}$ 54% bound

8. Spectra and Binding isotherms of complexes of Iodine with tetramethylthiourea [2•4]

n-Octane

Host: Tetramethylthiourea (**4**) 0.01 mM
Guest: Iodine (**2**)

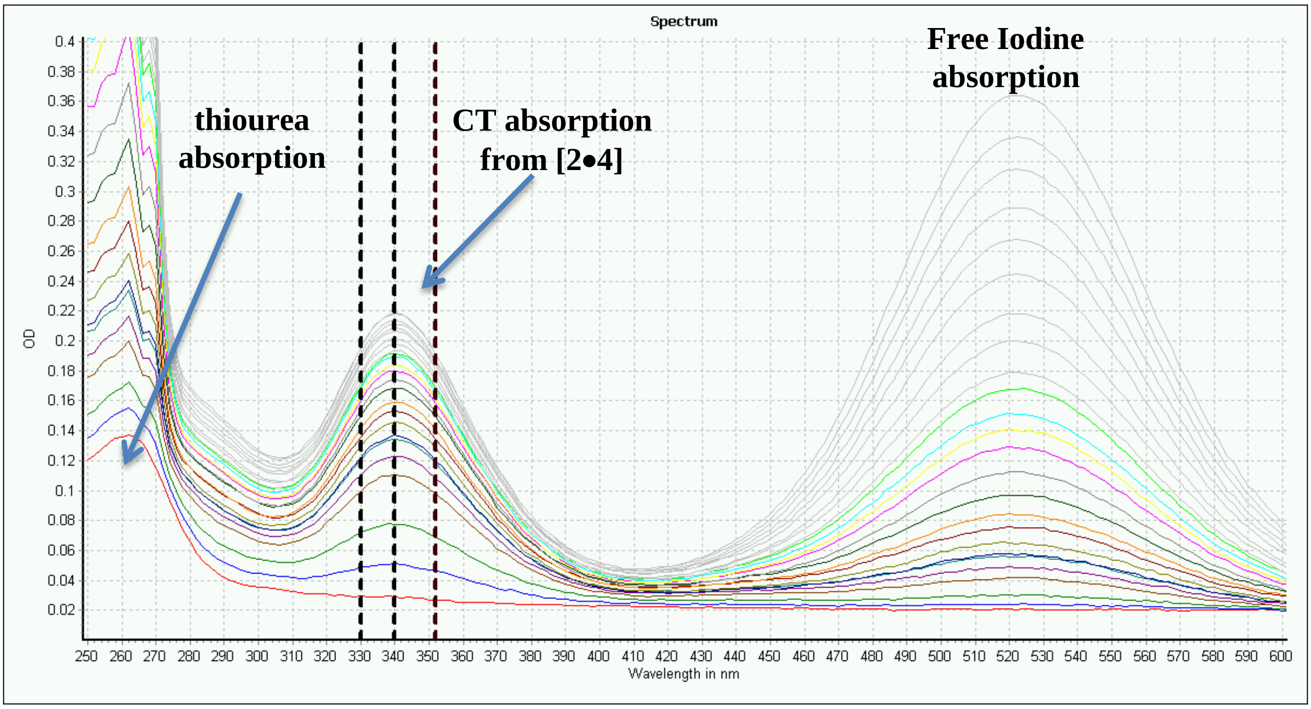


Figure S47: Annotated UV/vis spectra of the titration of **2** with **4** in *n*-octane. Dashed lines indicate wavelengths monitored for binding isotherms.

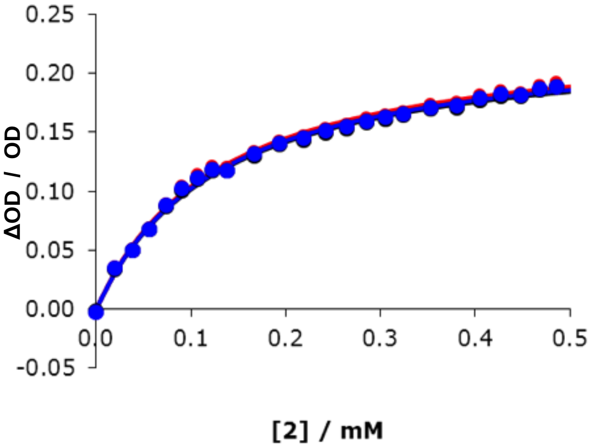


Figure S48: Binding isotherms for titration

K_a = 8,800 ± 900M^{-1} 81% bound

Carbon tetrachloride

Host: Tetramethylthiourea (**4**) 0.01 mM
Guest: Iodine (**2**)

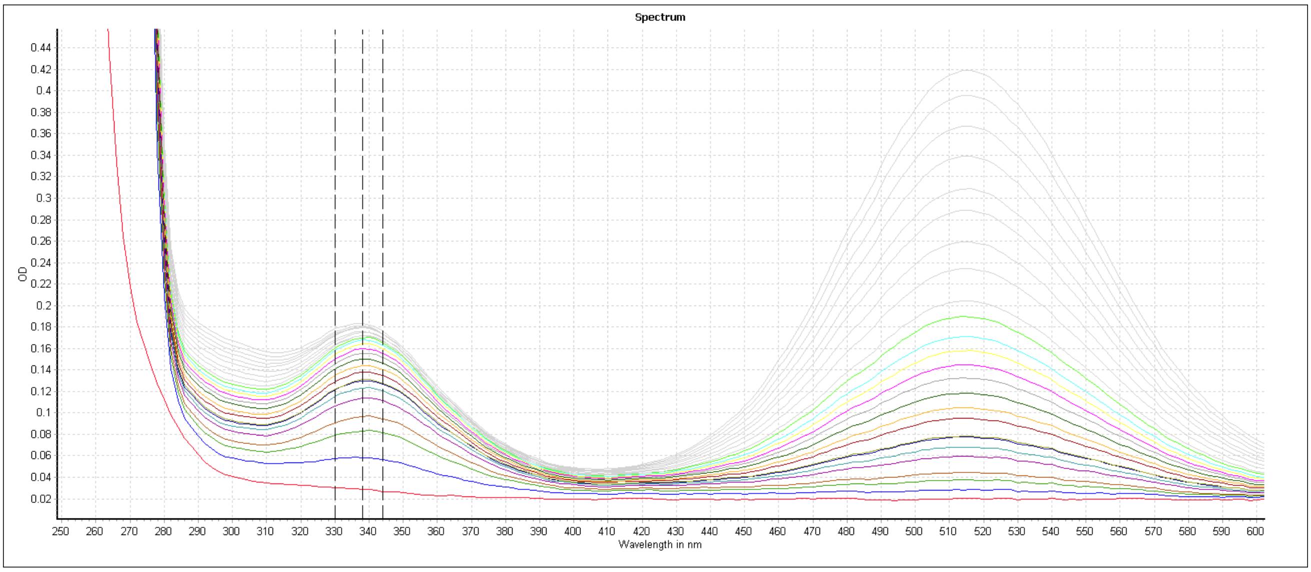


Figure S49: UV/vis spectra of the titration of **2** with **4** in carbon tetrachloride. Dashed lines indicate wavelengths monitored for binding isotherms.

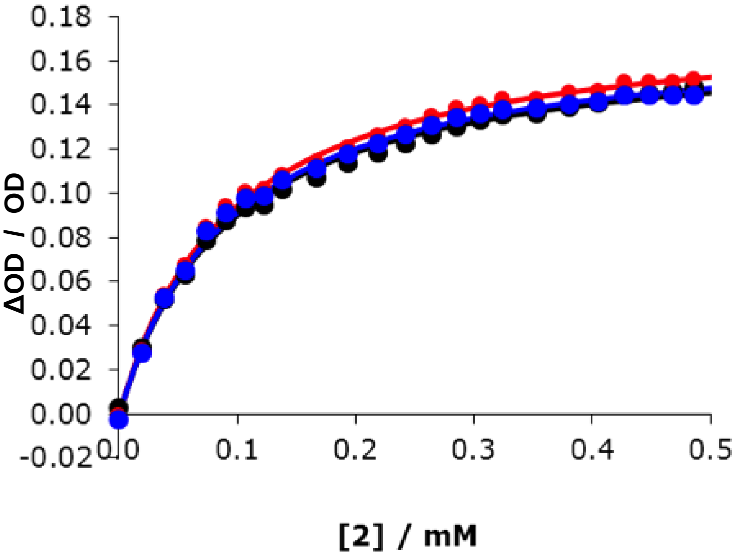


Figure S50: Binding isotherms for titration

K_a = 7,300 ± 600M^{-1} 87% bound

Toluene

Host: Iodine (**2**) 0.1 mM
Guest: Tetramethylthiourea (**4**)

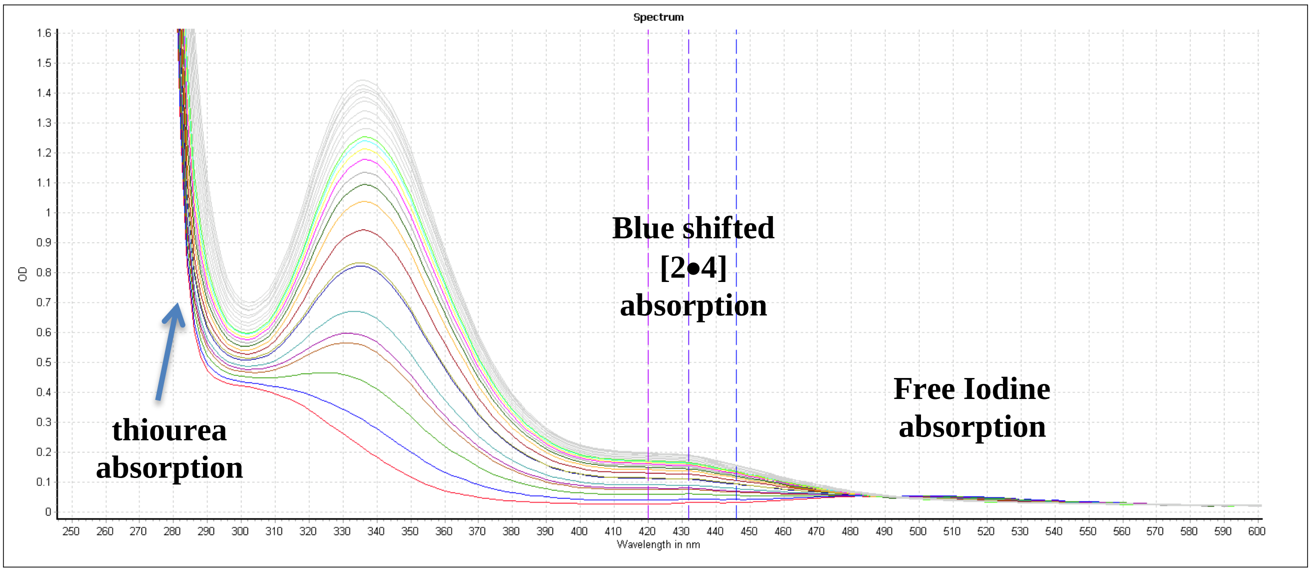


Figure S51: Annotated UV/vis spectra of the titration of **2** with **4** in toluene. Dashed lines indicate wavelengths monitored for binding isotherms.

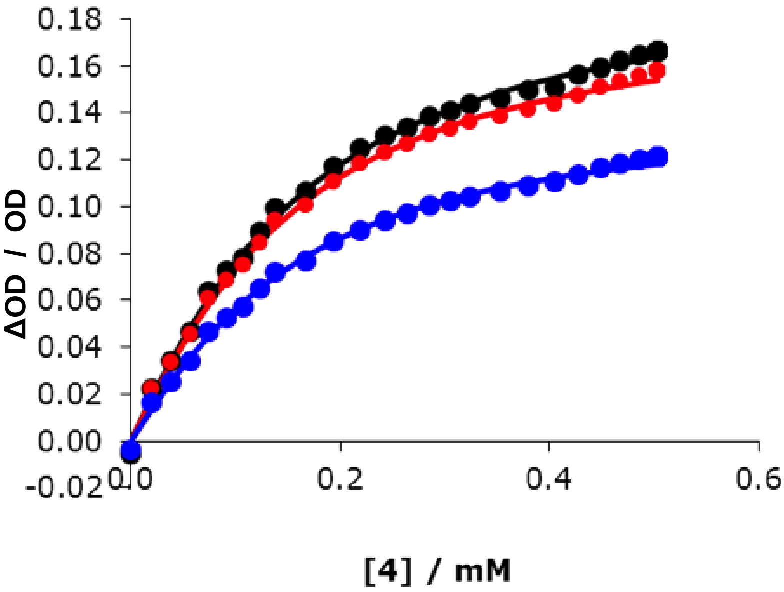


Figure S52: Binding isotherms for titration

$K_a = 11{,}000 \pm 1600\text{M}^{-1}$ 82% bound

Diiodomethane

Host: Iodine (**2**) 1 mM
Guest: Tetramethylthiourea (**4**)

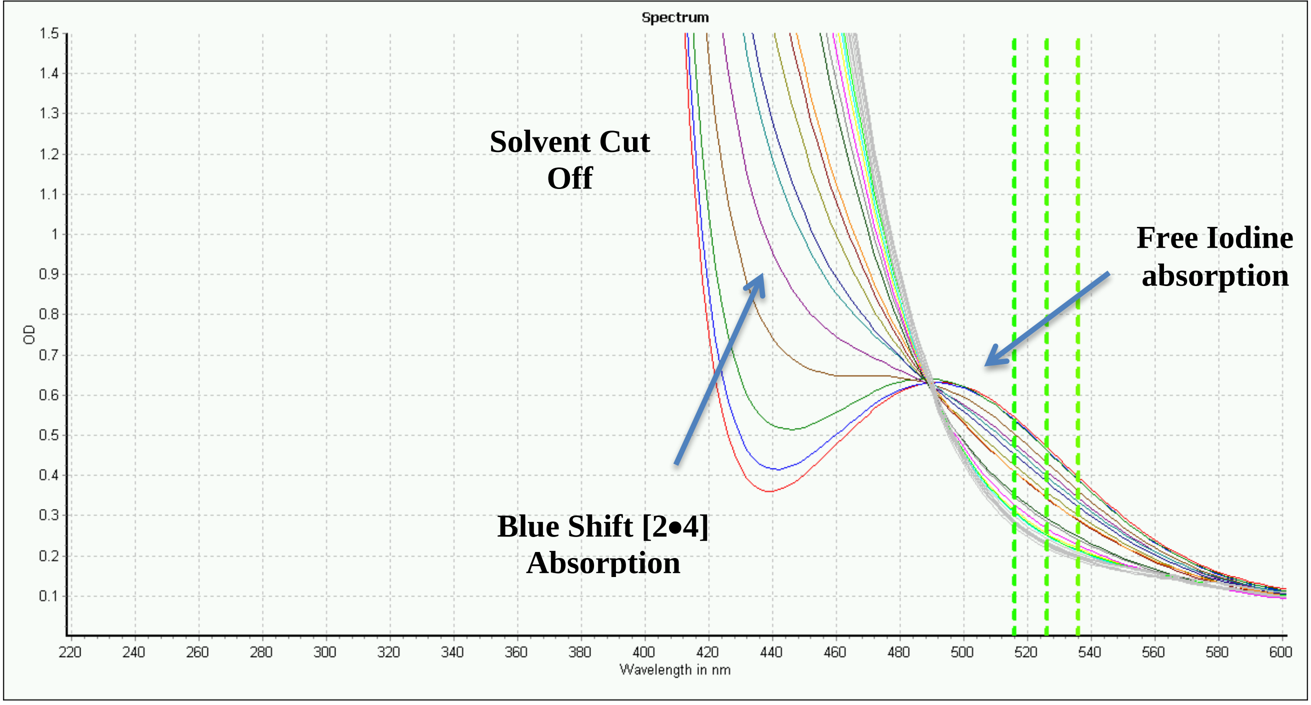


Figure S53: Annotated UV/vis spectra of the titration of **2** with **4** in diiodomethane. Dashed lines indicate wavelengths monitored for binding isotherms.

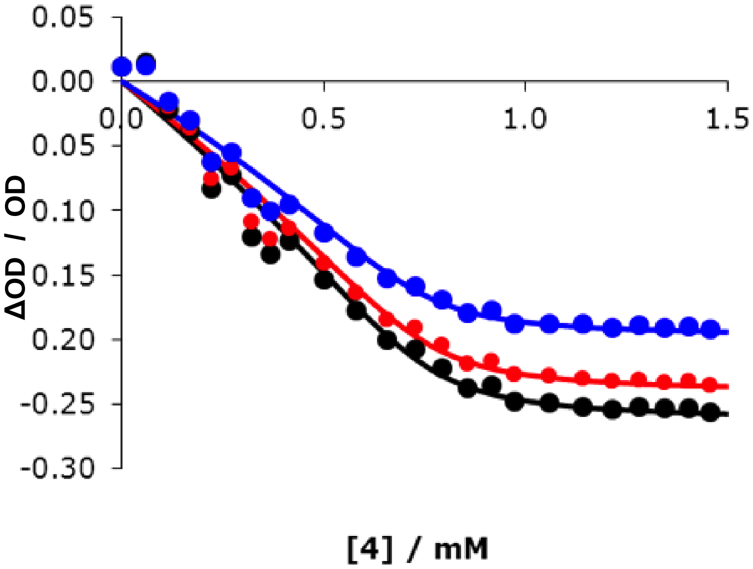


Figure S54: Binding isotherms for titration

K_a = 37,000 ± 14,000M^{-1} 97% bound

Dibromomethane

Host: Tetramethylthiourea (**4**) 0.01 mM
Guest: Iodine (**2**)

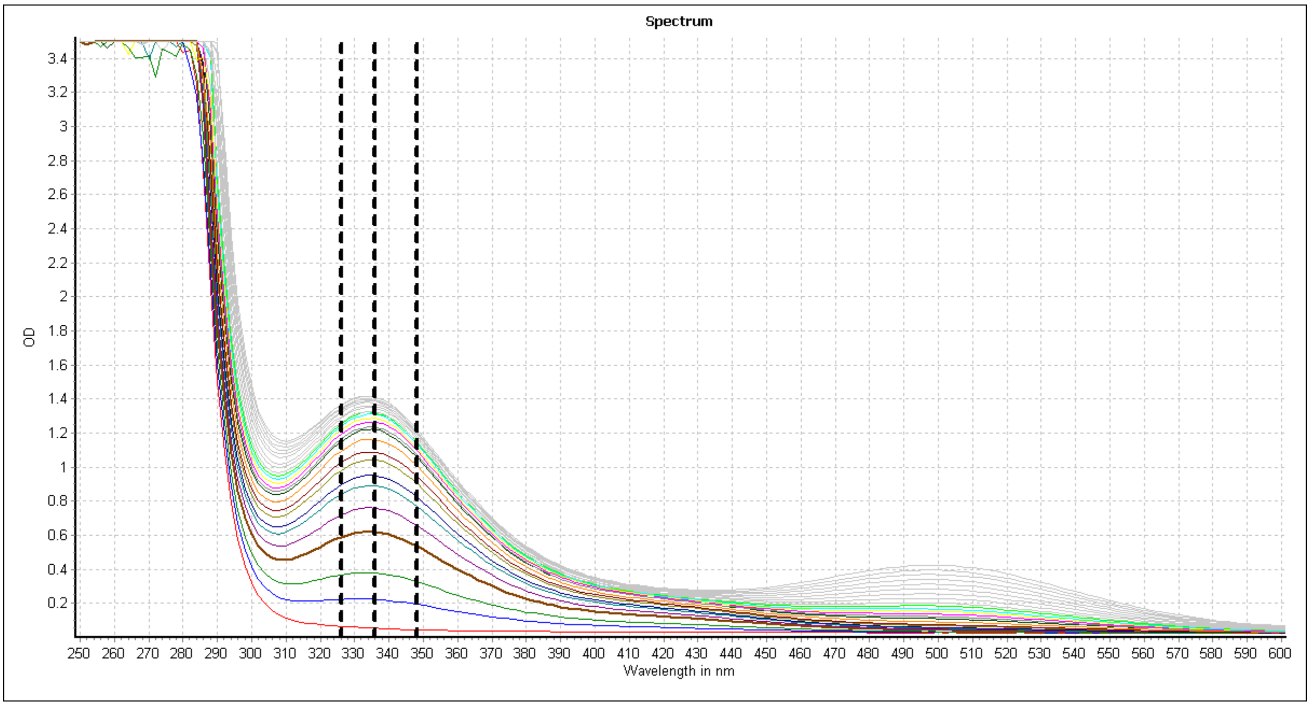


Figure S55: UV/vis spectra of the titration of **2** with **4** in dibromomethane. Dashed lines indicate wavelengths monitored for binding isotherms.

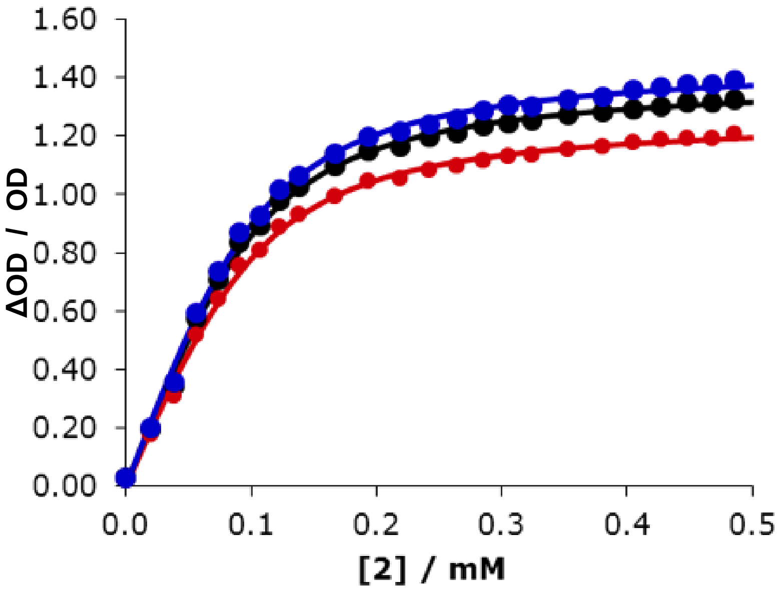


Figure S56: Binding isotherms for titration

K_a = 34,000 ± 4,500M^{-1} 94% bound

Dichloromethane

Host: Tetramethylthiourea (**4**) 0.05 mM
Guest: Iodine (**2**)

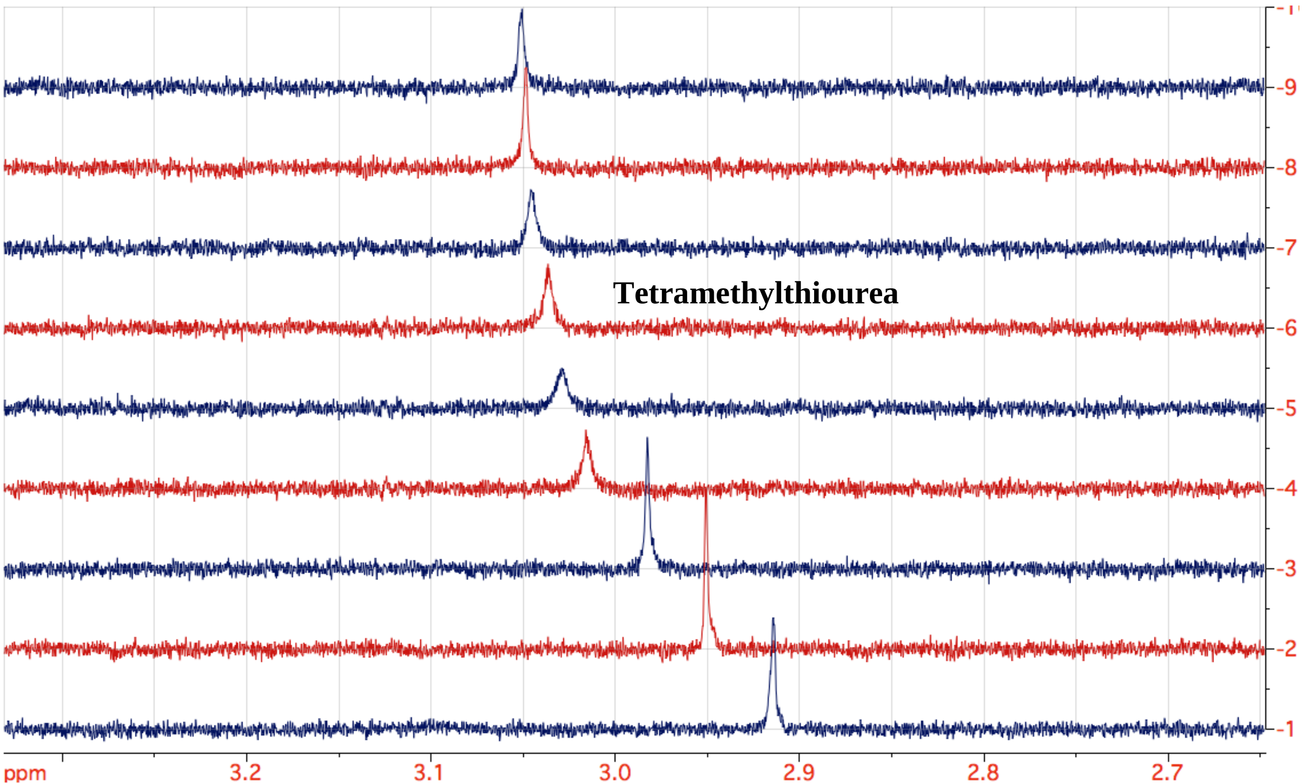


Figure S57: 400 MHz ^{1}H NMR spectra of the titration of **2** with **4** in dichloromethane

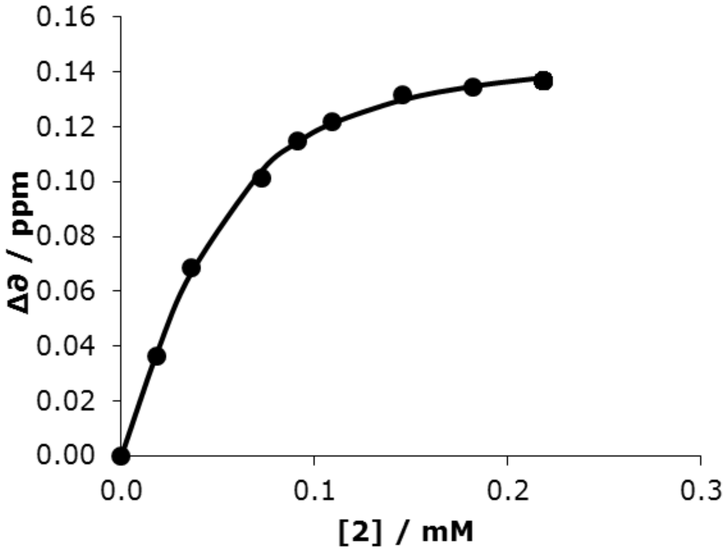


Figure S58: Binding isotherm for titration

K_a = 58,000 ± 10,000M^{-1} 91% bound

Chloroform

Host: Tetramethylthiourea (**4**) 0.01 mM
Guest: Iodine (**2**)

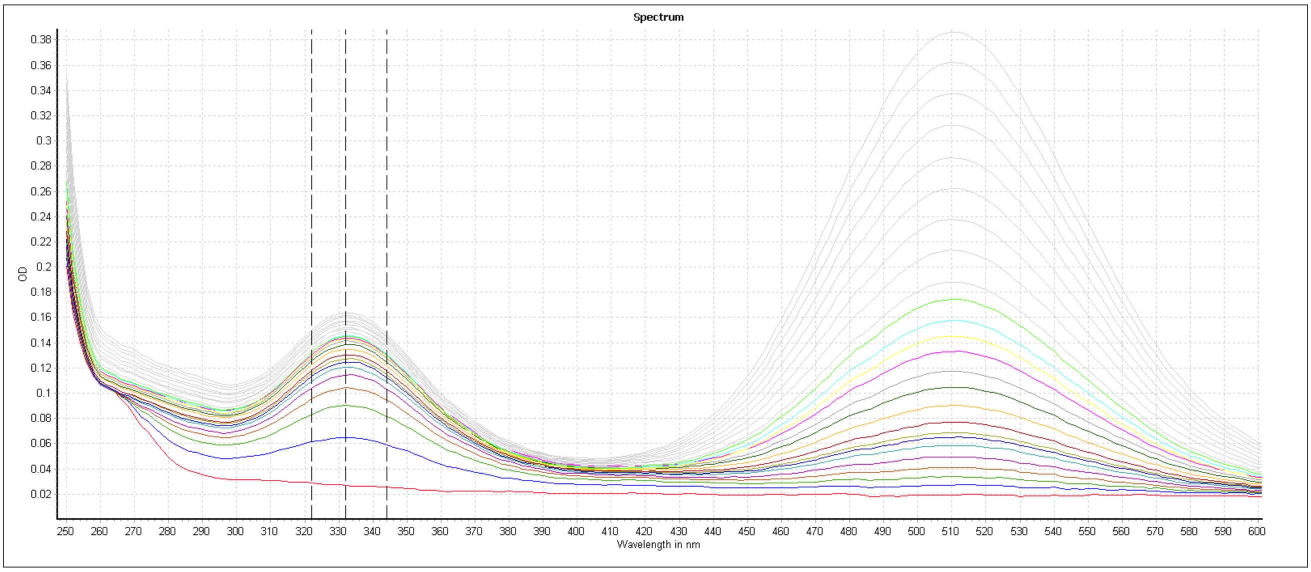


Figure S59: UV/vis spectra of the titration of **2** with **4** in chloroform. Dashed lines indicate wavelengths monitored for binding isotherms.

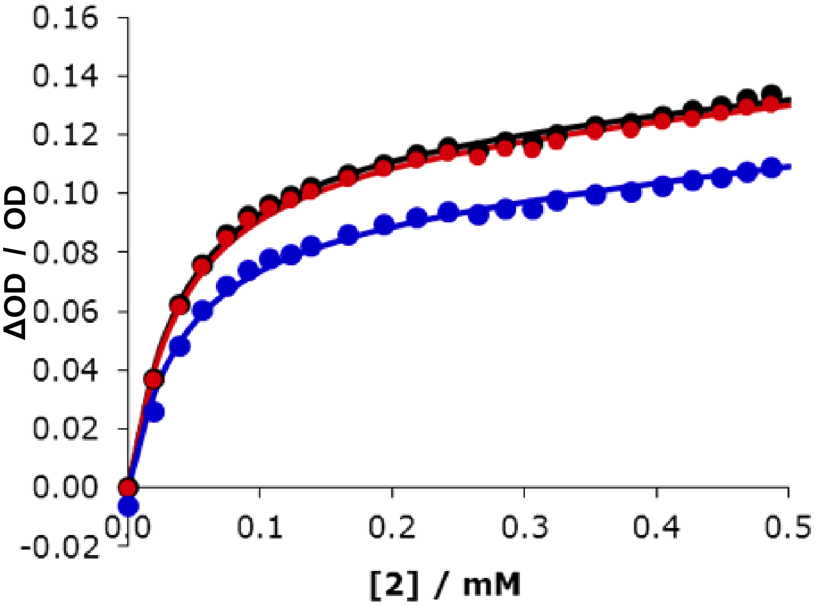


Figure S60: Binding isotherms for titration

K_a = 20,000 ± 1,000M^{-1} 94% bound

1,1,2,2-tetrachloroethane

Host: Tetramethylthiourea (**4**) 0.2 mM
Guest: Iodine (**2**)

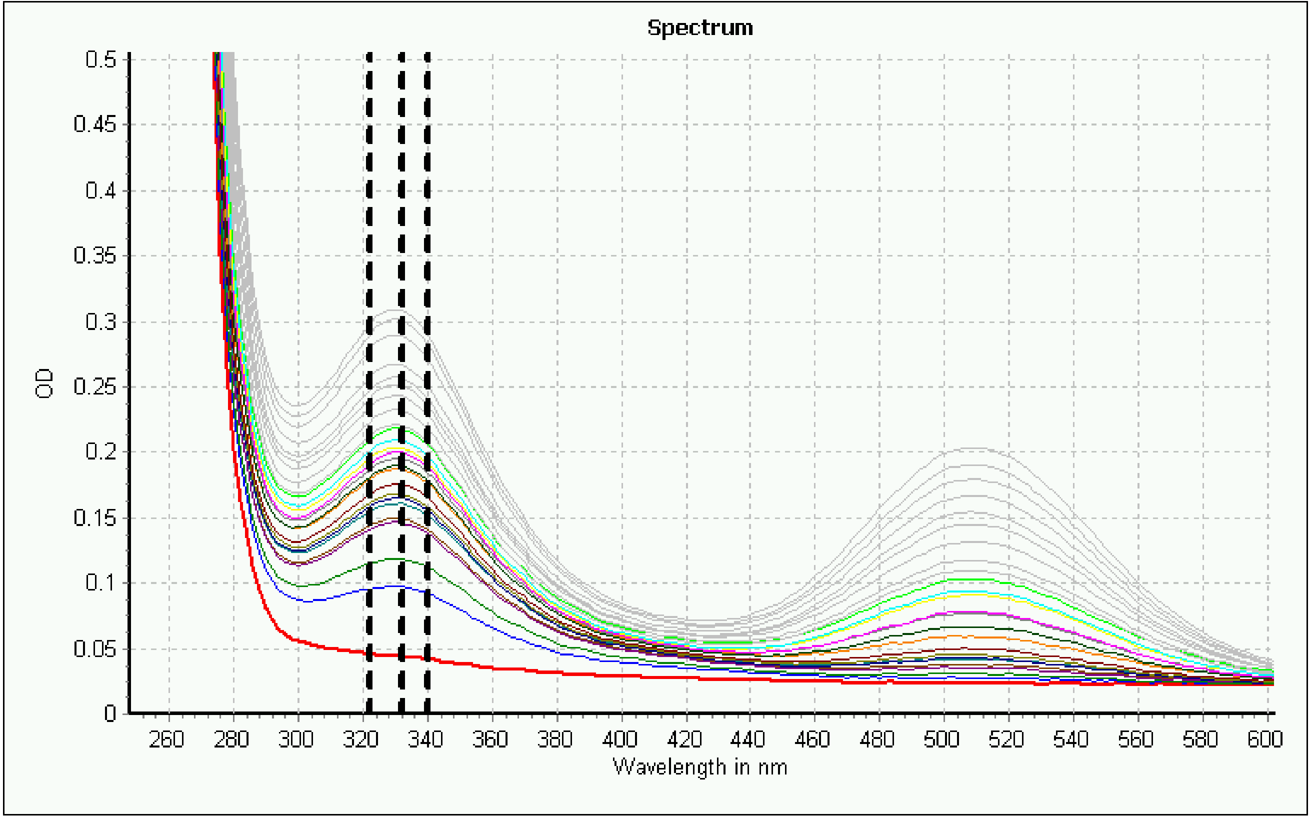


Figure S61: UV/vis spectra of the titration of **2** with **4** in 1,1,2,2-tetrachloroethane (TCE). Dashed lines indicate wavelengths monitored for binding isotherms.

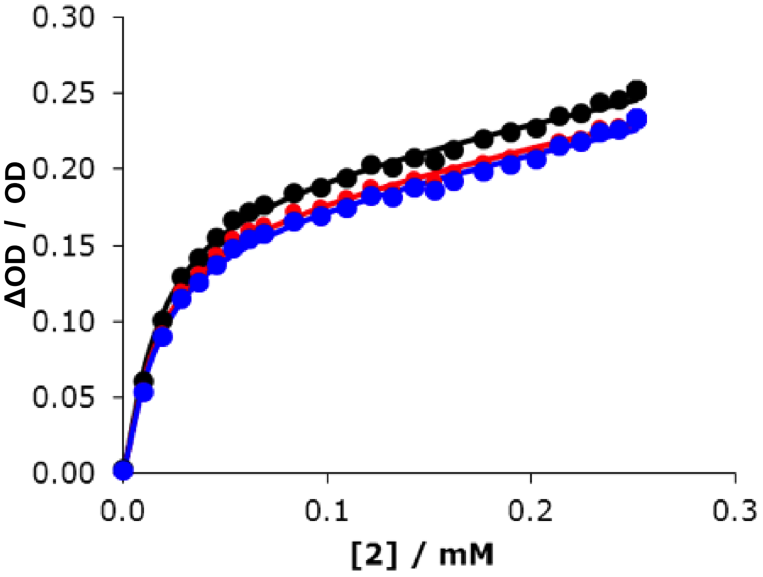


Figure S62: Binding isotherms for titration

K_a = 55,000 ± 15,000M^{-1} 95% bound

Di-*n*-octyl ether

Host: Iodine (**2**) 1 mM
Guest: Tetramethylthiourea (**4**)

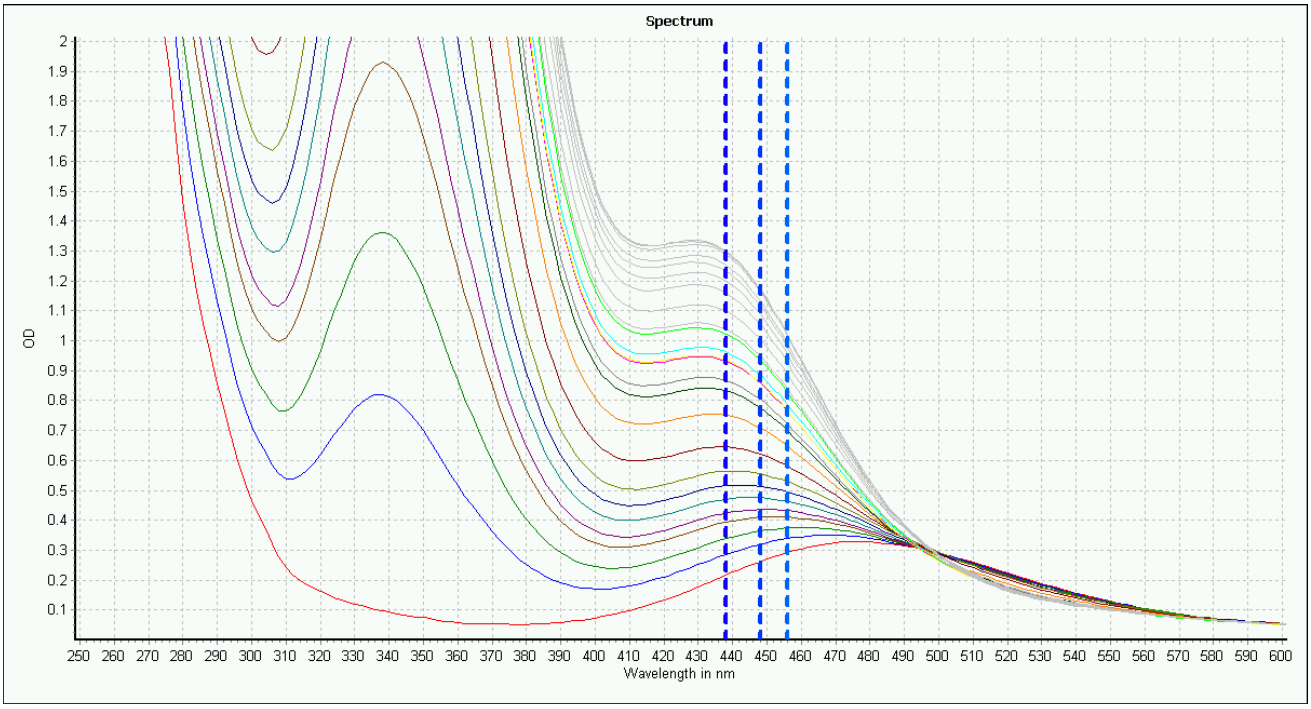


Figure S63: UV/vis spectra of the titration of **2** with **4** in di-*n*-octyl ether. Dashed lines indicate wavelengths monitored for binding isotherms.

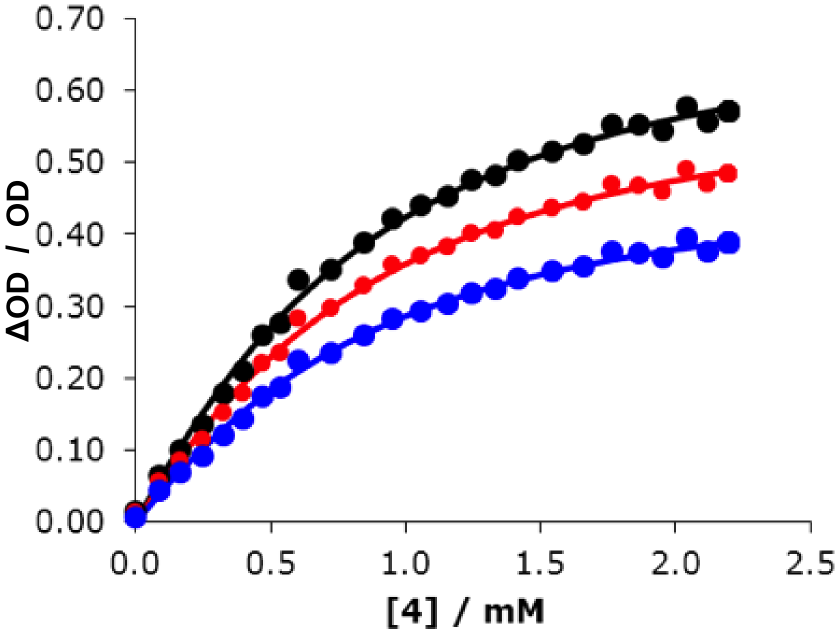


Figure S64: Binding isotherms for titration

K_a = 1,600 ± 350M^{-1} 77% bound

Acetone

Host: Tetramethylthiourea (**4**) 1 mM
Guest: Iodine (**2**)

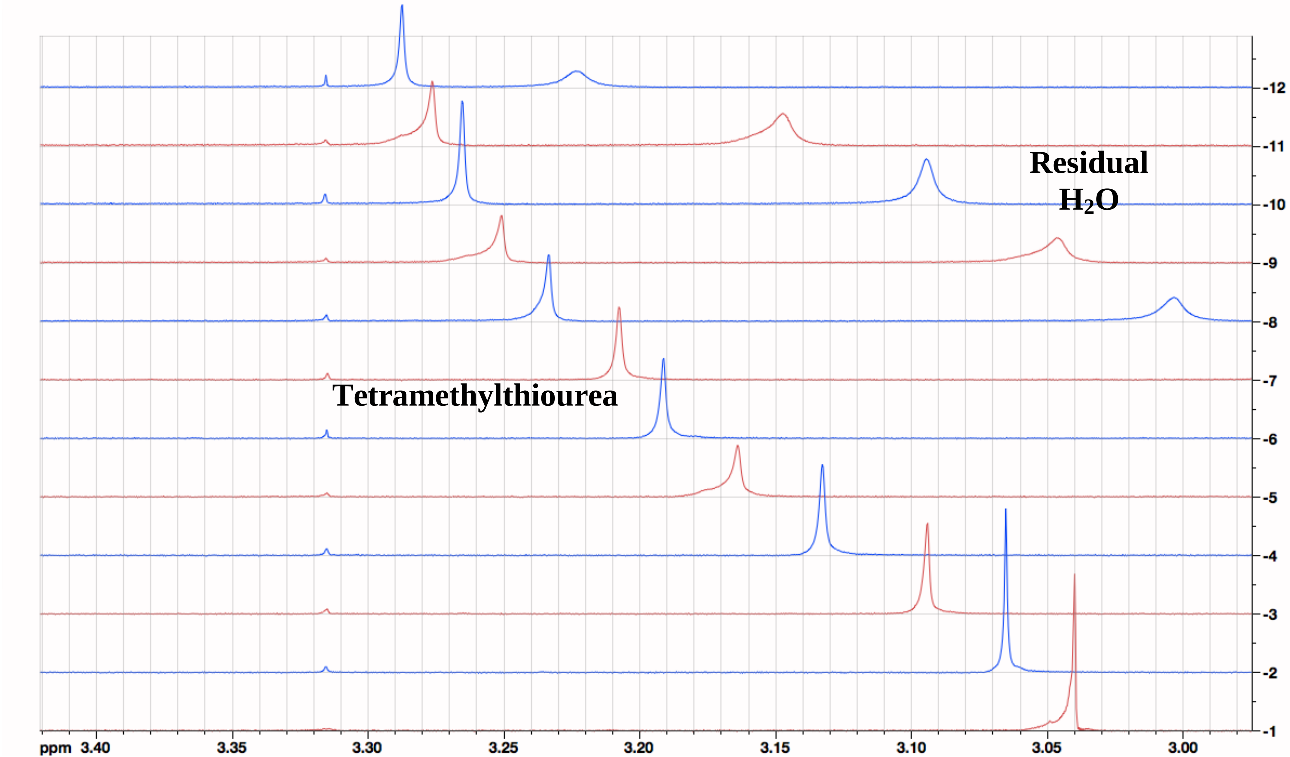


Figure S65: Annotated partial 400 MHz ^{1}H NMR spectra of the titration of **2** with **4** in acetone

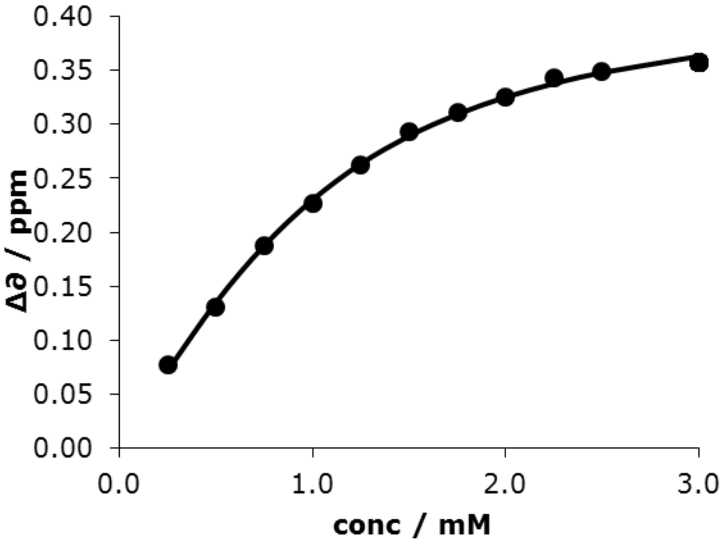


Figure S66: Binding isotherm for titration

K_a = 1,900 ± 300 M^{-1} 78% bound

Acetonitrile

Host: Tetramethylthiourea (**4**) 1 mM
Guest: Iodine (**2**)

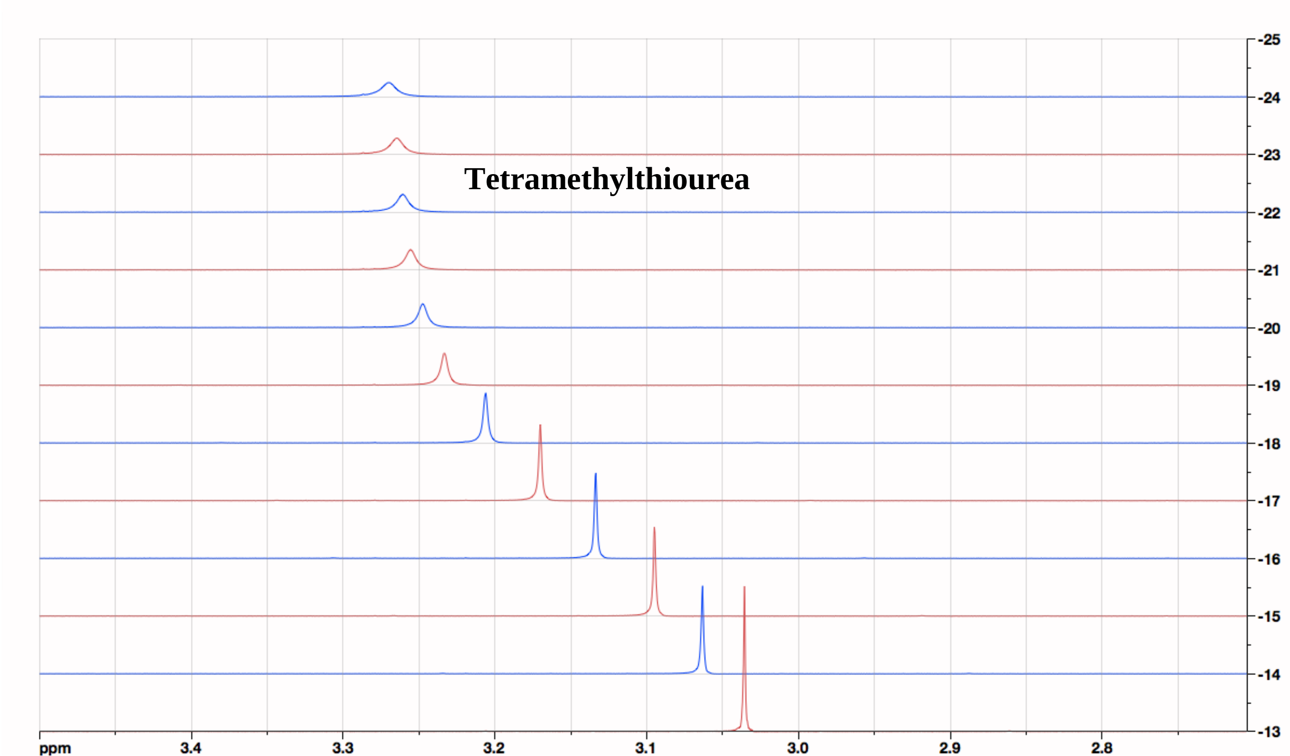


Figure S67: Partial 400 MHz ^{1}H NMR spectra of the titration of **2** with **4** in acetonitrile

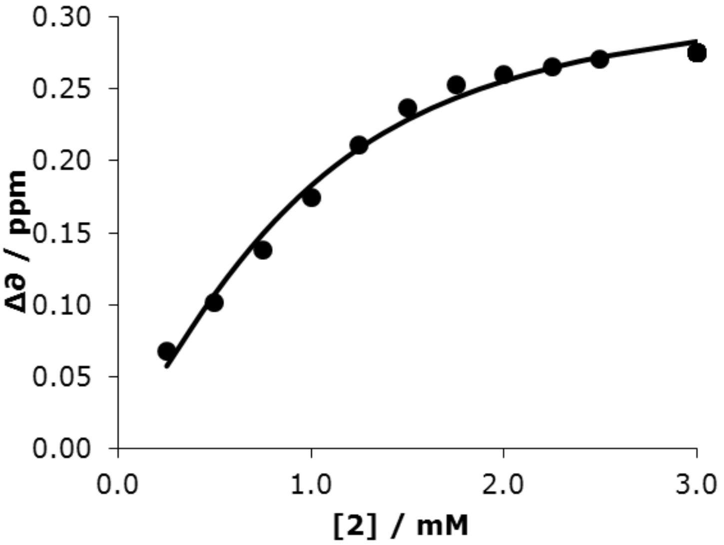


Figure S68: Binding isotherm for titration

K_a = 2,800 ± 70 M^{-1} 79% bound

Nitromethane

Host: Tetramethylthiourea (**4**) 10 mM
Guest: Iodine (**2**)

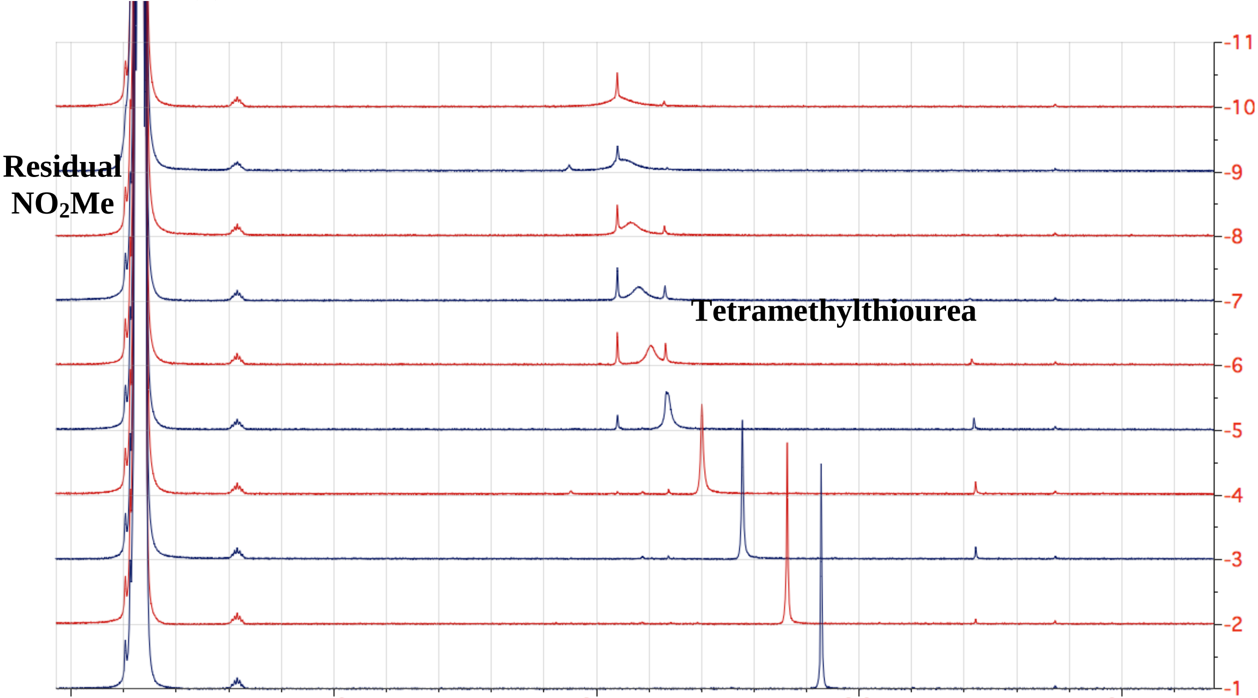


Figure S69: Partial 400 MHz ^{1}H NMR spectra of the titration of **2** with **4** in nitromethane

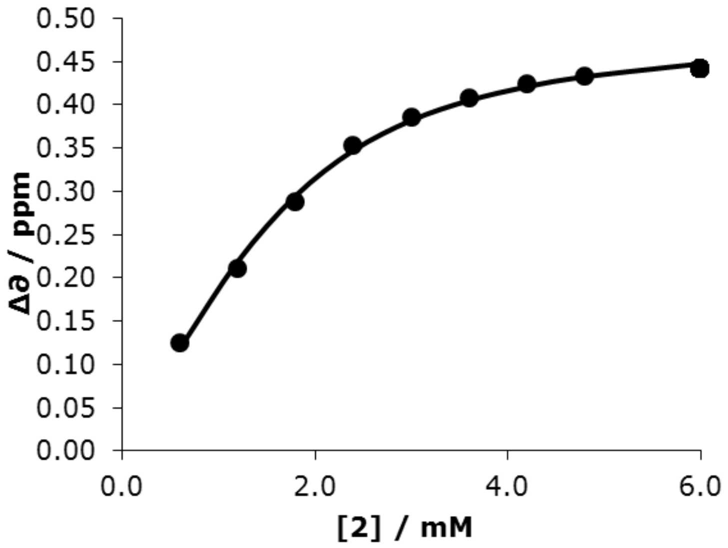


Figure S70: Binding isotherm for titration

K_a = 2100 ± 300 M^{-1} 86% bound

i-Propanol

Host: Tetramethylthiourea (**4**) 1 mM
Guest: Iodine (**2**)

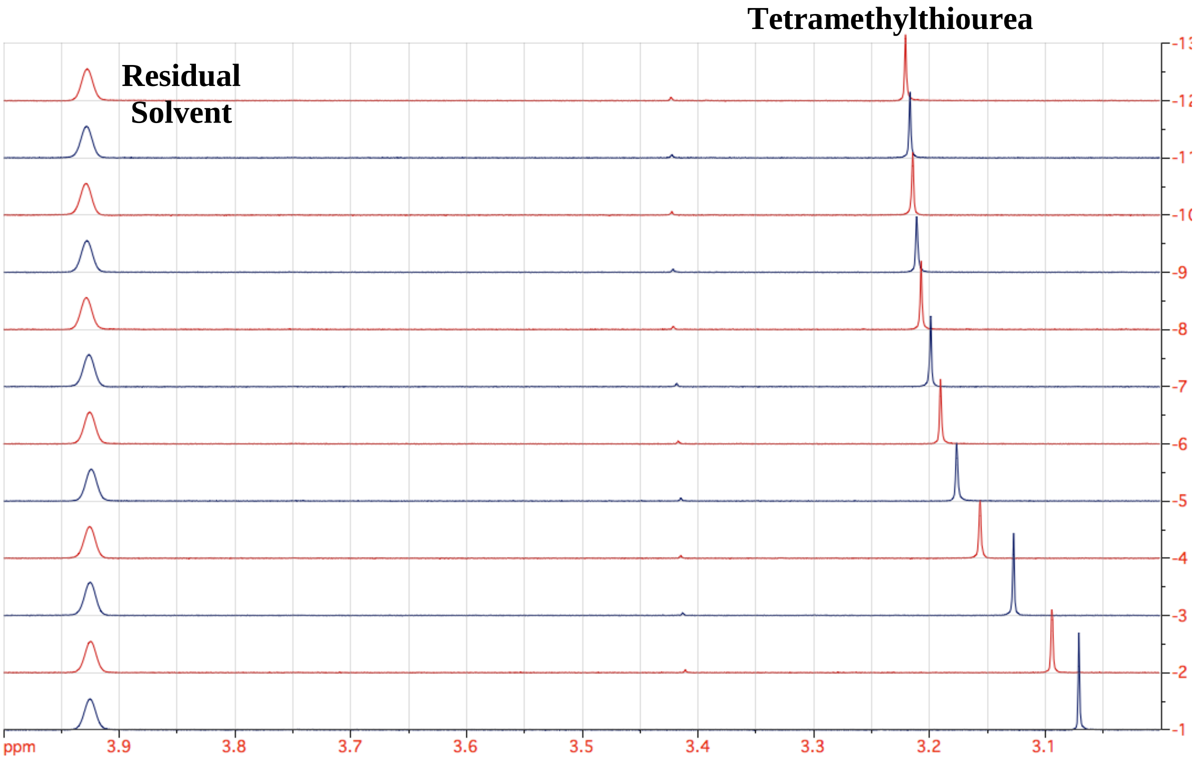


Figure S71: Partial 400 MHz ^{1}H NMR spectra of the titration of **2** with **4** in *i*-propanol.

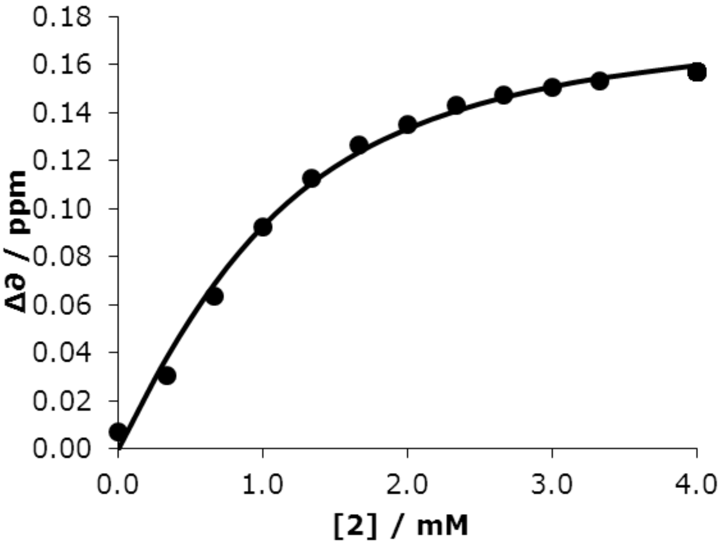


Figure S72: Binding isotherm for titration

$K_a = 3600 \pm 70\ M^{-1}$ 86% bound

Ethanol

Host: Tetramethylthiourea (**4**) 1 mM
Guest: Iodine (**2**)

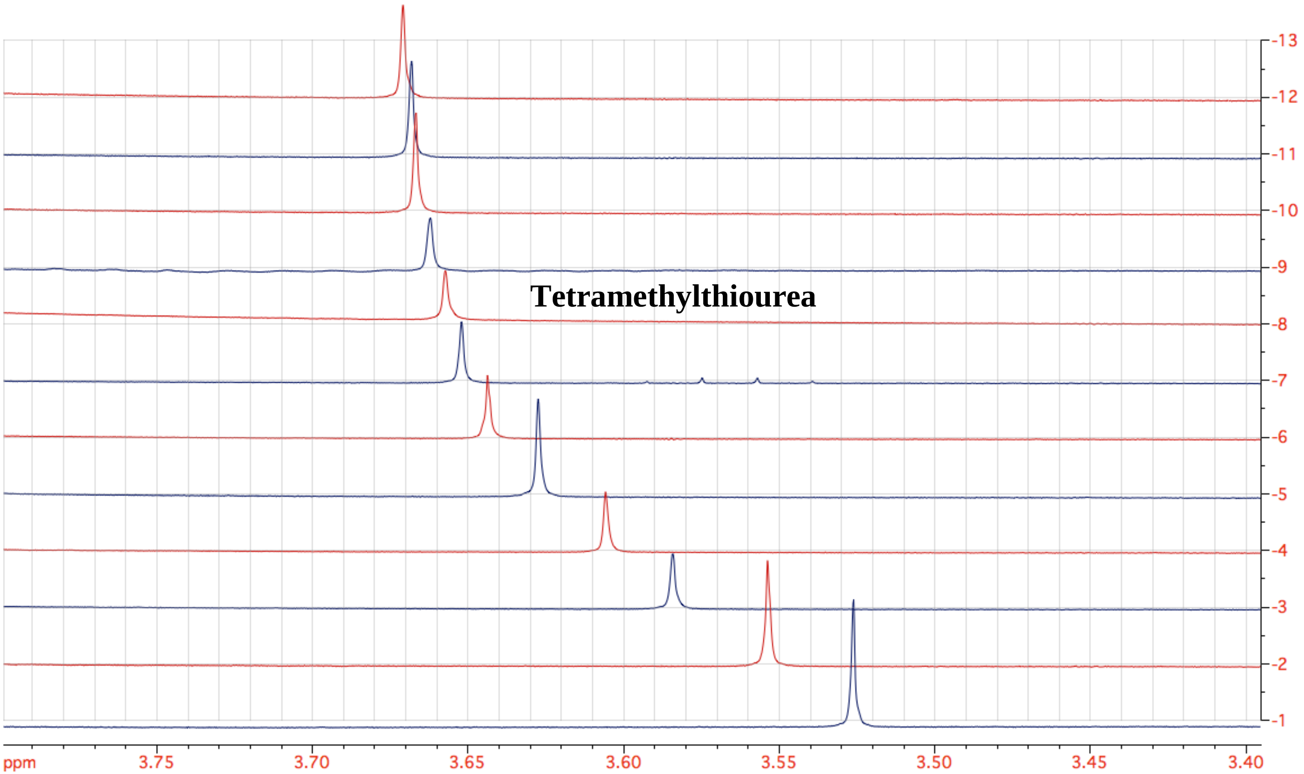


Figure S75: Partial 400 MHz ^{1}H NMR spectra of the titration of **2** with **4** in ethanol.

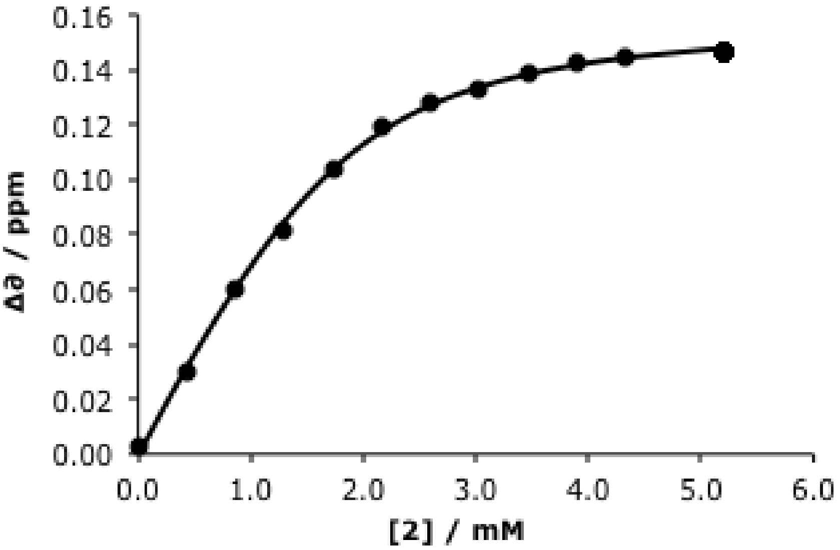


Figure S76: Binding isotherm for titration

K_a = 3200 ± 120 M^{-1} 94% bound

Methanol

Host: Tetramethylthiourea (**4**) 1 mM
Guest: Iodine (**2**)

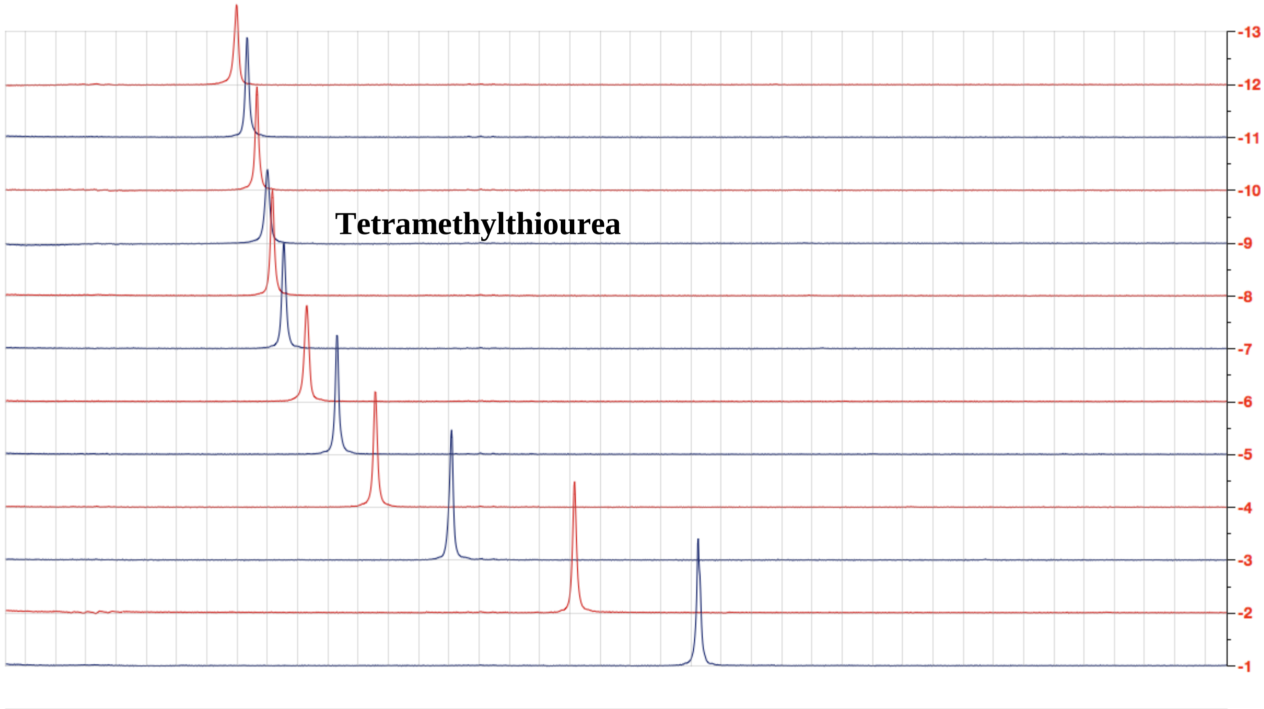


Figure S73: Partial 400 MHz ^{1}H NMR spectra of the titration of **2** with **4** in methanol.

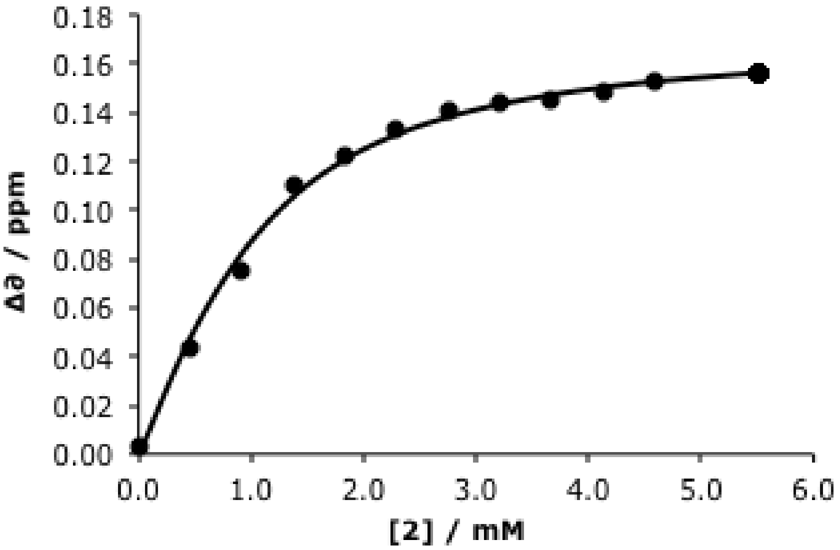


Figure S74: Binding isotherm for titration

$K_a = 2700 \pm 200\ \text{M}^{-1}$ 94% bound

9. Solvent Mixing Experiment Result

In these solvent mixing experiments, a stock solution of each of thiourea [**4**] = 0.1 mM and iodine [**2**] = 0.5 mM were made in the following solvent mixtures; 100/0 95/5, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80 & 0/100% octane/TCE respectively. The 11 titrations of tetramethylthiourea **4** with iodine **2** were then carried out in the same manner as described above using the automated UV/vis spectroscopy plate reader procedure.

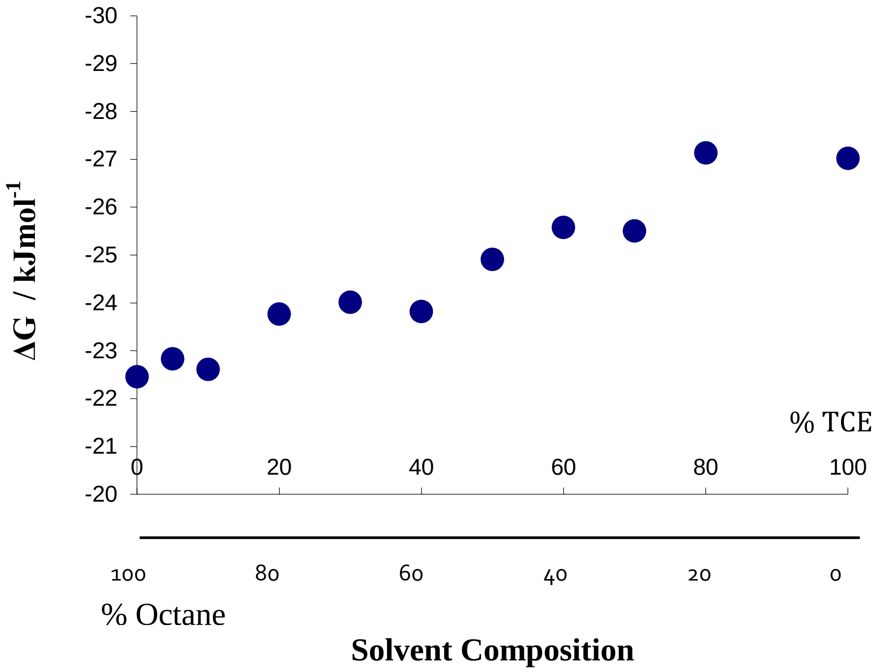


Figure S77: Plot of the complex stability, ΔG, vs solvent composition

10. Table of Association Constants of Molecular Iodine•Solvent Complexes

The association constant of the 2•solvent complexes in *n*-octane were all determined by UV/vis spectroscopy titrations using the automated procedure as described above. In all cases, 1 mM [**2**] was used as the host and neat solvent the guest. In all cases, the decrease in absorption of free iodine and concurrent increase of blue shifted **2**•guest complex absorption was monitored with respect to the [guest] to obtain a binding isotherm (as in S37).

Table S2: Association constants of 2•solvent complexes in *n*-octane

Guest Solvent	K_a (M^{-1})
carbon tetrachloride	0.3 ±1
toluene	0.2 ±1
diiodomethane	immiscible
dibromomethane	0.3 ±1
dichloromethane	0.1 ±1
chloroform	0.5 ±1
1,1,2,2-tetrachloroethane	0.2 ±1
di-*n*-octyl ether	0.5 ±1
acetone	1 ±1
valeronitrile*	0.5 ±1
nitromethane	2 ±1
i-propanol	0.6 ±1

* as acetonitrile and octane were immiscible, valeronitrile was chosen as a appropriate alternative

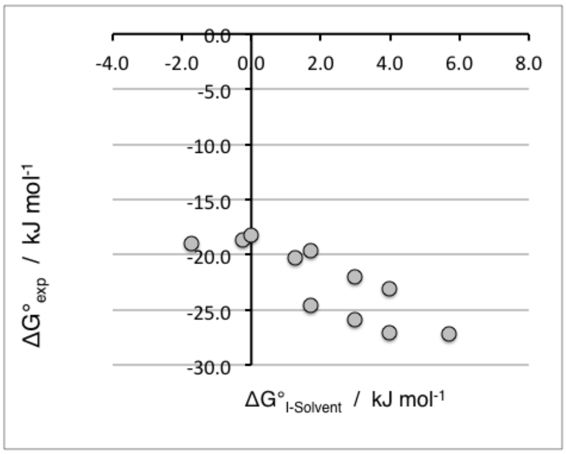
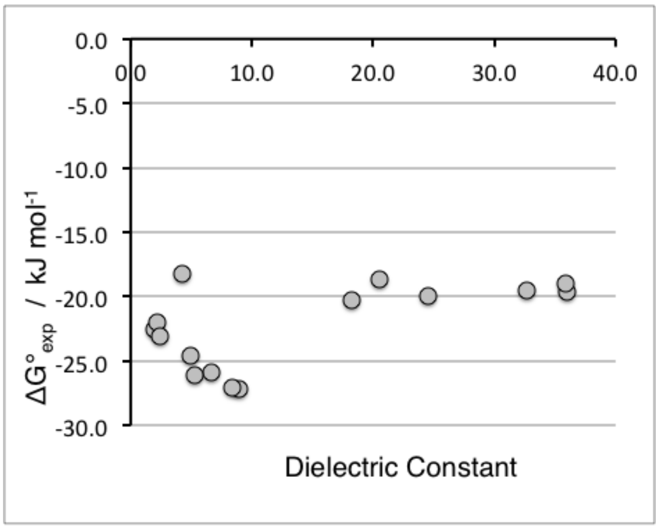
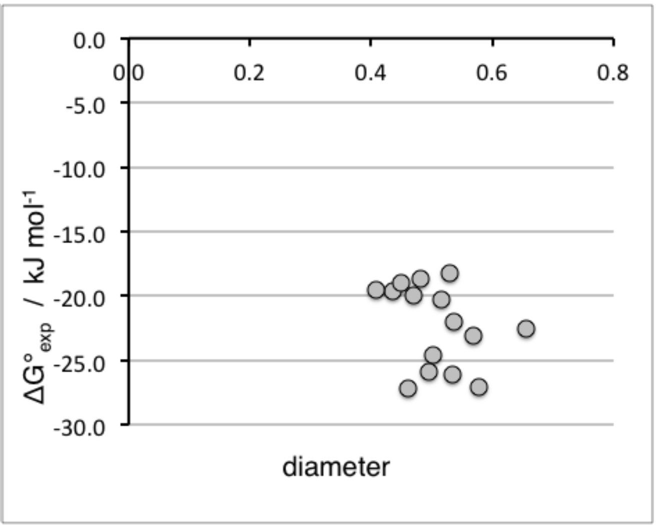


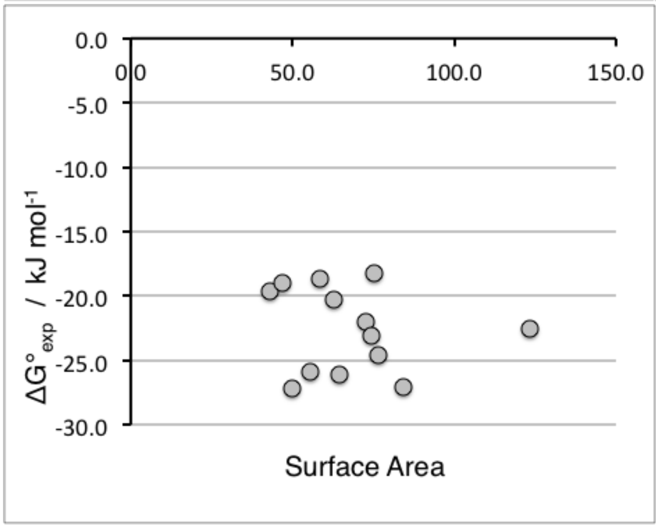
Figure S78: Plot of ΔG° of 2•4 vs the ΔG° of 2•Guest Solvent

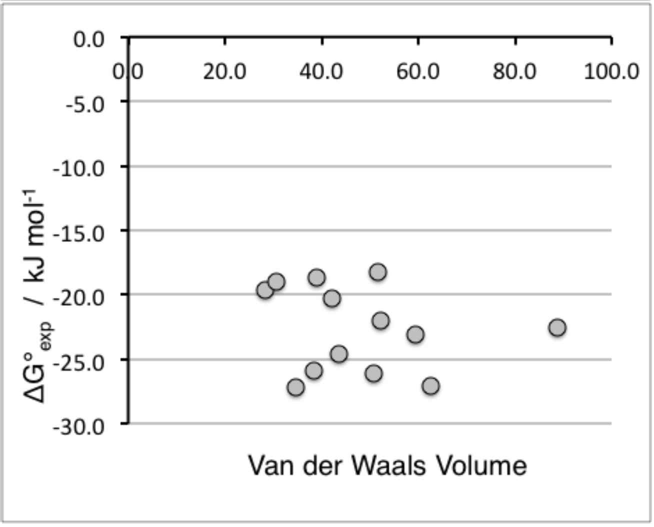
11. Plots of [2•4] Complex Stability vs. Thermophysical Solvent Properties

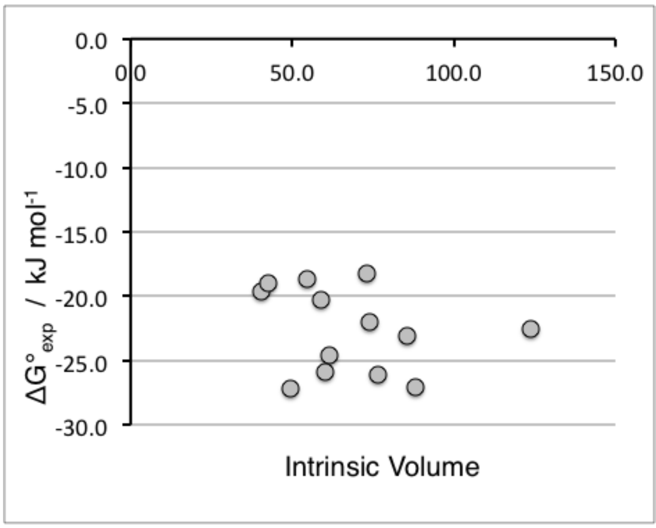
The following are plots of the complex stability vs. a thermophysical property of the solvent as collected by Marcus.[S2] Solvent diameter is the size to describe a solvent as if its molecules were spherical, van der Waals Surface area and Volume are estimations of size based on calculations, intrinsic volume is the volume of a mole of solvent, T(m.p), T(b.p) & T(critical point) are the temperatures of melting, boiling and the critical point respectively, d is the solvent density, V is the molar volume, αp is the isobaric expansibility κ_T is the isothermal compressibility, p vapor pressure at 25 ˚C, ΔH_v is the enthalpy of vaporization, δ is the (Kamlet–Taft) polarizability parameter, Cp is the constant pressure heat capacity. $E_T(30)$ is Dimroth and Reichardt's solvachromic parameter with E_T^N a normalized cognate quantity. SB is a a solvatochromic scale described by Catalan. π^* is Kamlet and Taft's solvachromic parameter. Units for each plot are shown in the caption below.







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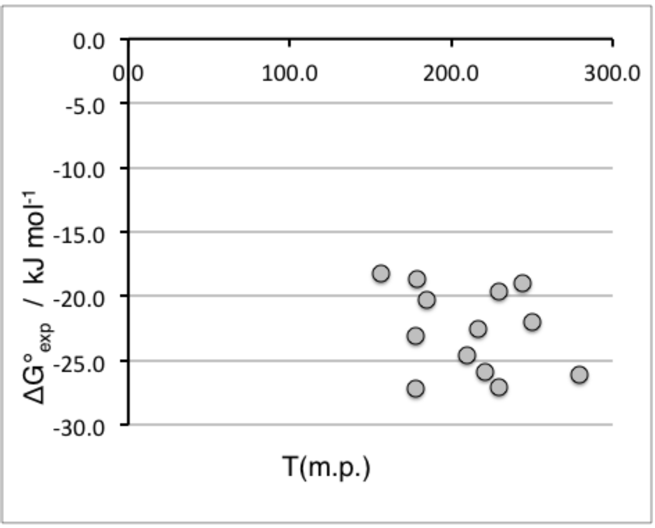
Intrinsic Volume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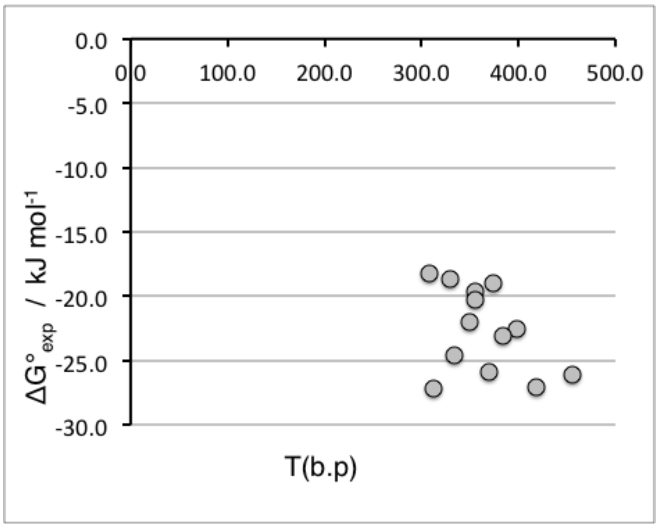
T(m.p.)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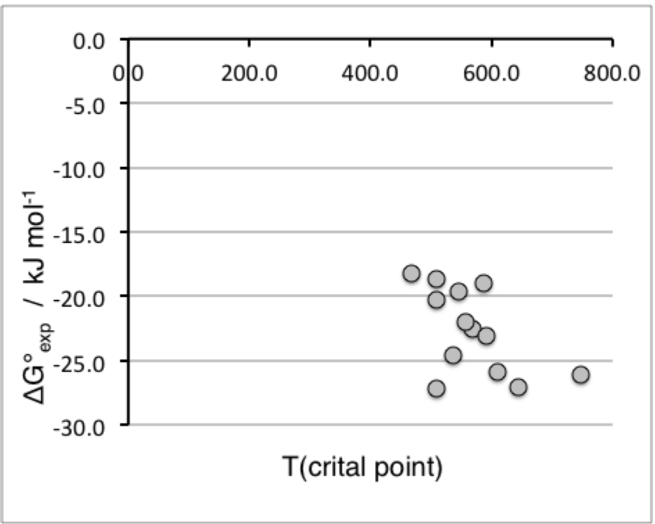
ΔG°exp / kJ mol-1
T(b.p)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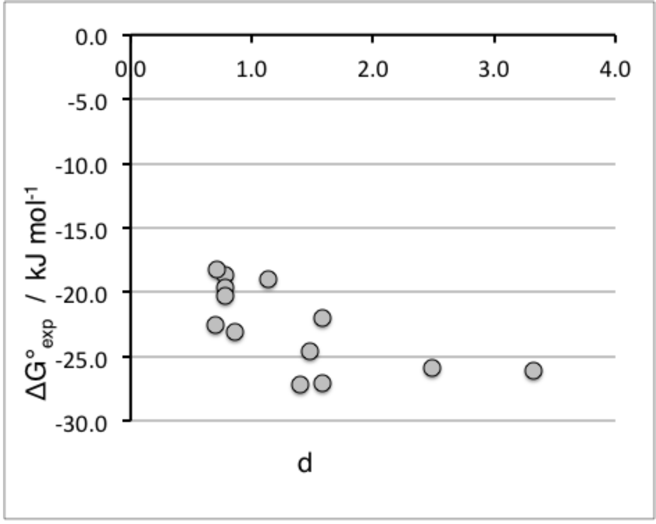
T(crital point)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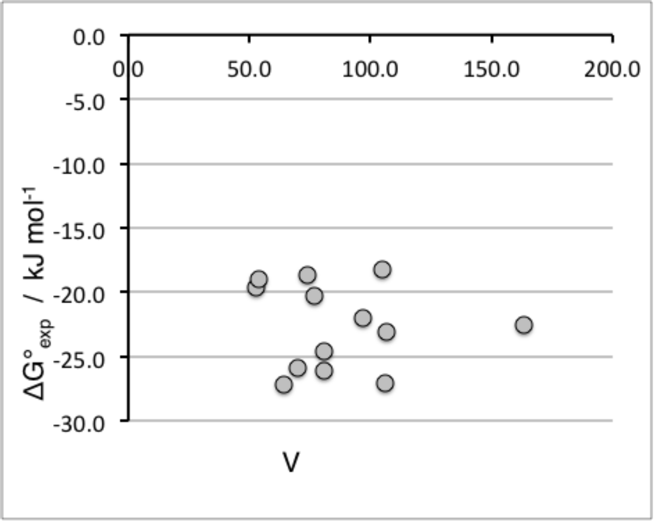
ΔG°exp / kJ mol-1
d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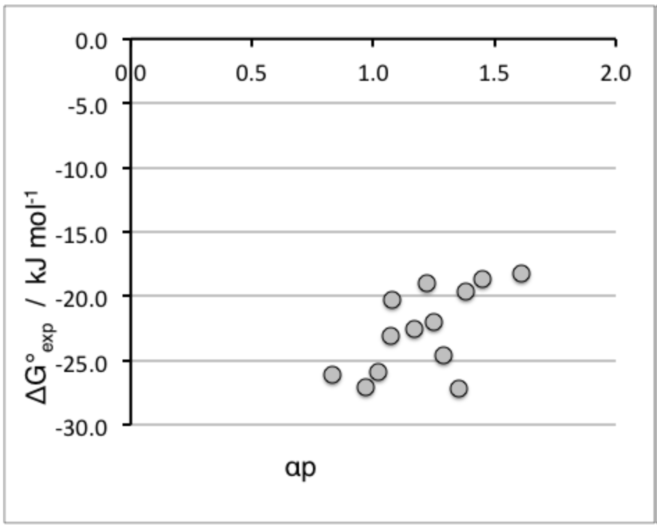
ΔG°exp / kJ mol-1
V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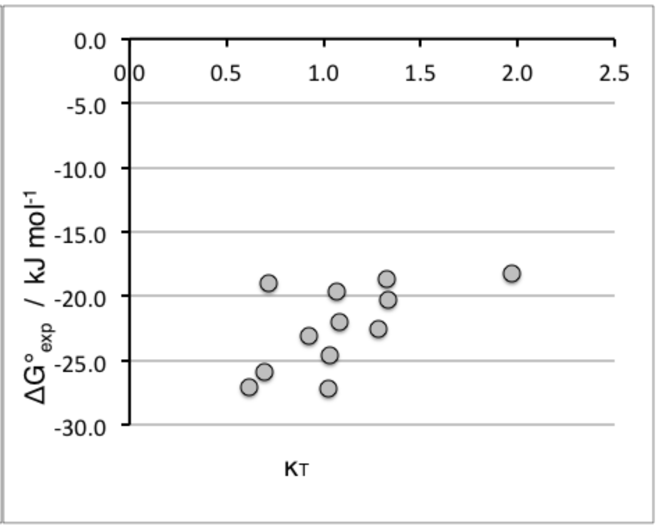
ΔG°exp / kJ mol-1
αp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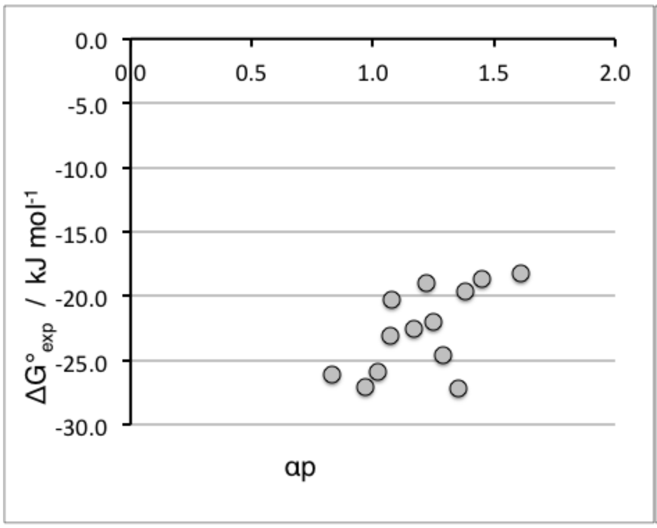
ΔG°exp / kJ mol-1
κT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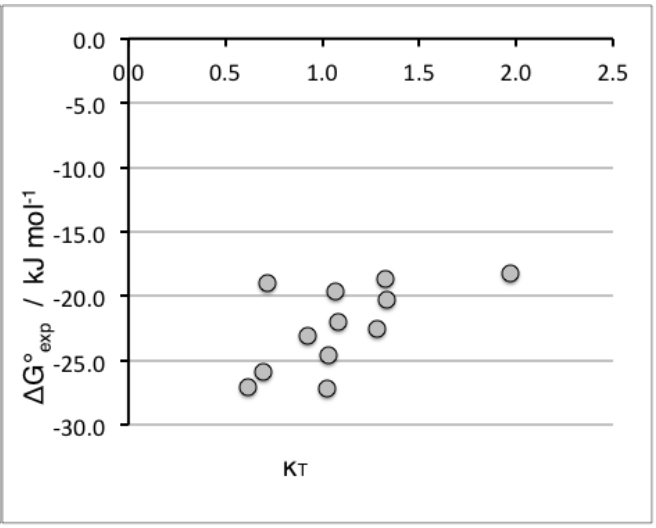
ΔG°exp / kJ mol-1
αp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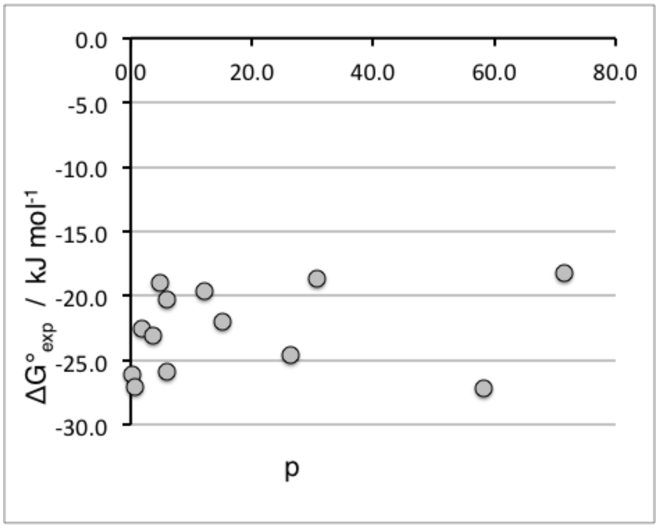
2.0
2.5
ΔG°exp / kJ mol-1
κT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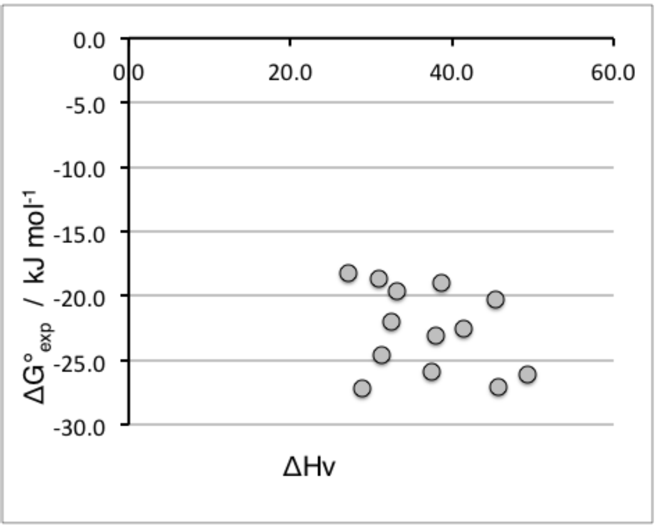
ΔG°exp / kJ mol-1
p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60.0
ΔG°exp / kJ mol-1
ΔHv

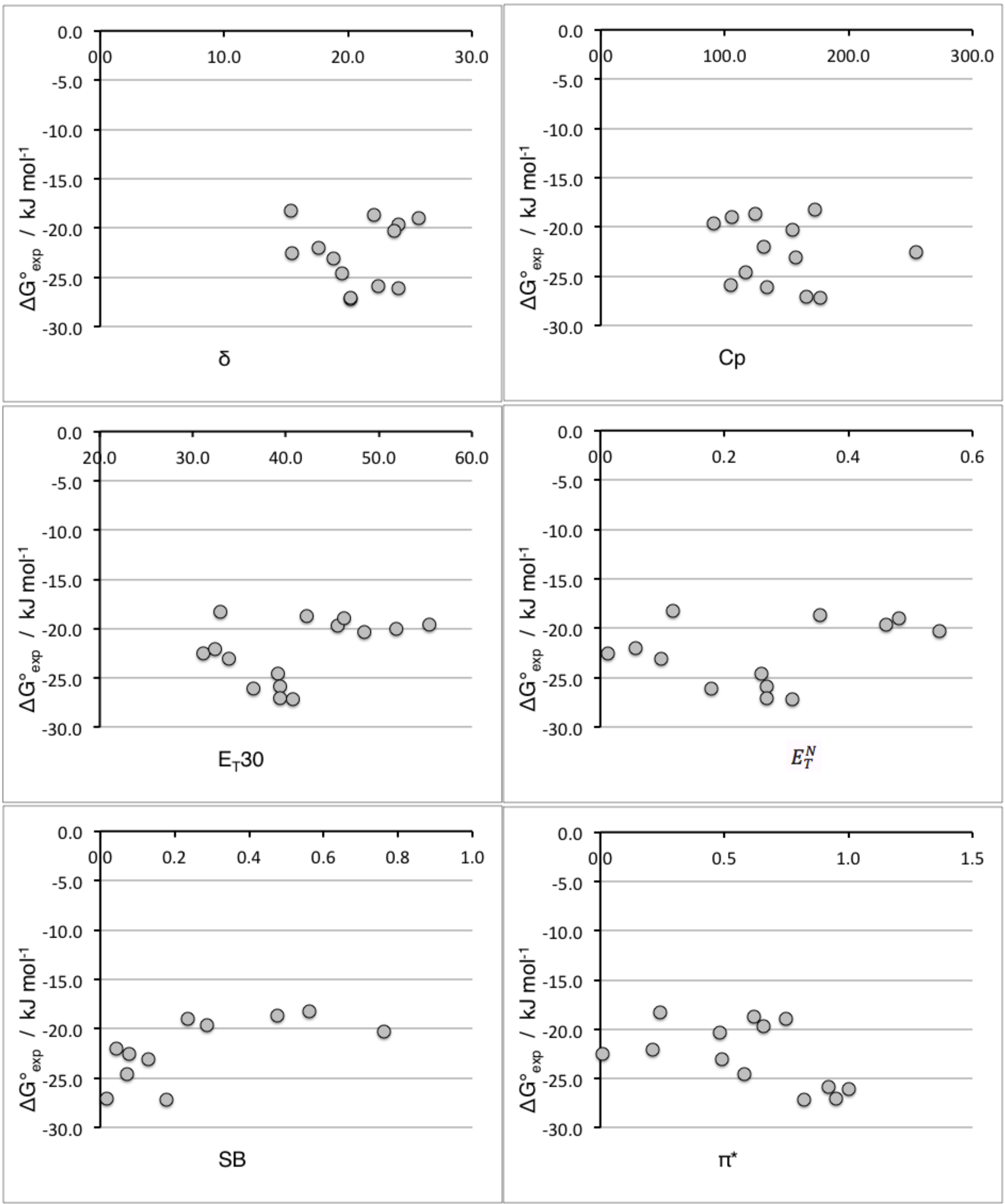
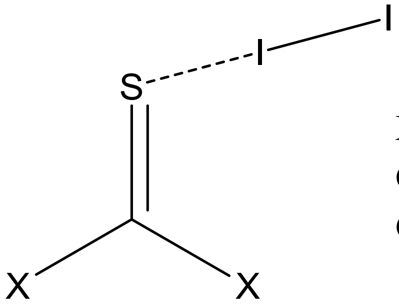


Figure S79: Units: diameter in nm, VdW surface area in 10^4 m^2 mol^{-1}, VdW volume in cm^3 mol^{-1} intrinsic volume in cm^3 mol^{-1}, $T_{m.p}$, $T_{b.p}$, $T_{critical}$ point in K; d in g cm^3; V in cm^3 mol^{-1}, α_p 10^{-3} K^{-1}; κ_T GPa^{-1}; p in kPa; ΔHv in kJ mol^{-1}; δ in J$^{1/2}$ cm$^{-3/2}$; C_p in J K^{-1} mol^{-1}.E_T30 in kcal mol^{-1}, E_T^N, SB and π* are dimensionless.

12. Crystal Structures of iodine-thiocarbonyl adducts

Table S3. Geometries of thiocarbonyl-iodine adducts

REFCODE[S3]	S···I (Å)	C=S···I (°)	I–I (Å)	I–I···S (°)	C=S (Å)	type of C=S group
BIMMEP[S5]	2.716	101.9	2.808	177.5	1.666	$S_2C=S$
BZHTIC10 [S6]	2.663	95.5	2.917	178.5	1.749	$N_2C=S$
CAYXUX [S7]	2.635	105.7	2.873	177.5	1.675	$S_2C=S$
CEWMIA [S6]	2.487	102.7	3.148	177.9	1.735	$N_2C=S$
CEWMOG [S6]	2.580	102.7	2.984	177.6	1.693	$N_2C=S$
CEWNAT [S6]	2.588	101.2	2.986	178.2	1.705	$N_2C=S$
DAYCIP [S8]	2.805	102.7	2.812	175.4	1.663	$S_2C=S$
GIDYOH [S9]	2.874	98.2	2.811	179.6	1.740	$N_2C=S$
HAFLAC [S10]	2.780	96.1	2.826	175.9	1.696	$N_2C=S$
ICUXAG [S11]	2.733	105.4	2.819	175.7	1.670	$S_2C=S$
KUWDEL [S12]	2.748	103.6	2.817	176.9	1.678	$N_2C=S$
KUWDIP [S12]	2.738	100.2	2.849	177.9	1.675	$N_2C=S$
KUWDIP [S12]	2.843	105.7	2.767	173.7	1.646	N(C)C=S
KUWDOV [S12]	2.773	104.5	2.802	176.1	1.673	$N_2C=S$
LOPQEM [S13]	2.503	104.7	3.054	176.0	1.734	$N_2C=S$
LOPQIQ [S13]	2.507	104.9	3.056	173.7	1.707	$N_2C=S$
MSNROD [S14]	3.099	99.6	2.751	178.5	1.629	N(S)C=S
OBIWOM [S15]	3.098	93.3	2.790	176.3	1.674	$N_2C=S$
TCAPLI [S16]	2.687	110.0	2.879	176.2	1.716	N(C)C=S
TIJMAB [S17]	2.668	100.0	2.863	176.1	1.686	$S_2C=S$
TURMEY [S18]	2.824	97.4	2.815	177.5	1.678	$N_2C=S$
TURMIC [S18]	2.849	90.1	2.790	178.8	1.677	$N_2C=S$
UJEVOU [S11]	2.912	102.3	2.790	177.9	1.666	$S_2C=S$
VARCIA [S19]	2.711	99.5	2.832	176.6	1.699	$S_2C=S$
WURHAT [S20]	3.129	99.5	2.761	172.4	1.683	$N_2C=S$
ZEBQOM [S21]	2.873	101.5	2.769	178.4	1.690	N(O)C=S



X = NR_2 (R= alkyl, aryl, H);
OR (R = aryl), SR (R = aryl);
CR_3 (R = alkyl, H)

13. Reactivity of tetramethylthiourea with iodine

In polar solvents, the **2•4** complex was observed to react slowly to give new signals in the ^{1}H NMR spectrum. These signals were observed in samples which were prepared for titration and left for prolonged time. The titration of **2** with **4**, shown in Figure S79, was left for 10 hr before recording the spectra and shows the resonance signals of 4 which shift upon addition of guest. In addition to this, the intensity of these signals is seen to decrease with concurrent increasing intensity of a new resonance signal corresponding to the reacted species. As a result to minimize any reaction titrations were carried out without delay upon making the host and guest solutions. For UV/vis measurements, collection of titration data was complete within 15 minutes. For NMR titrations, collection of data for a titration was complete within an hour.

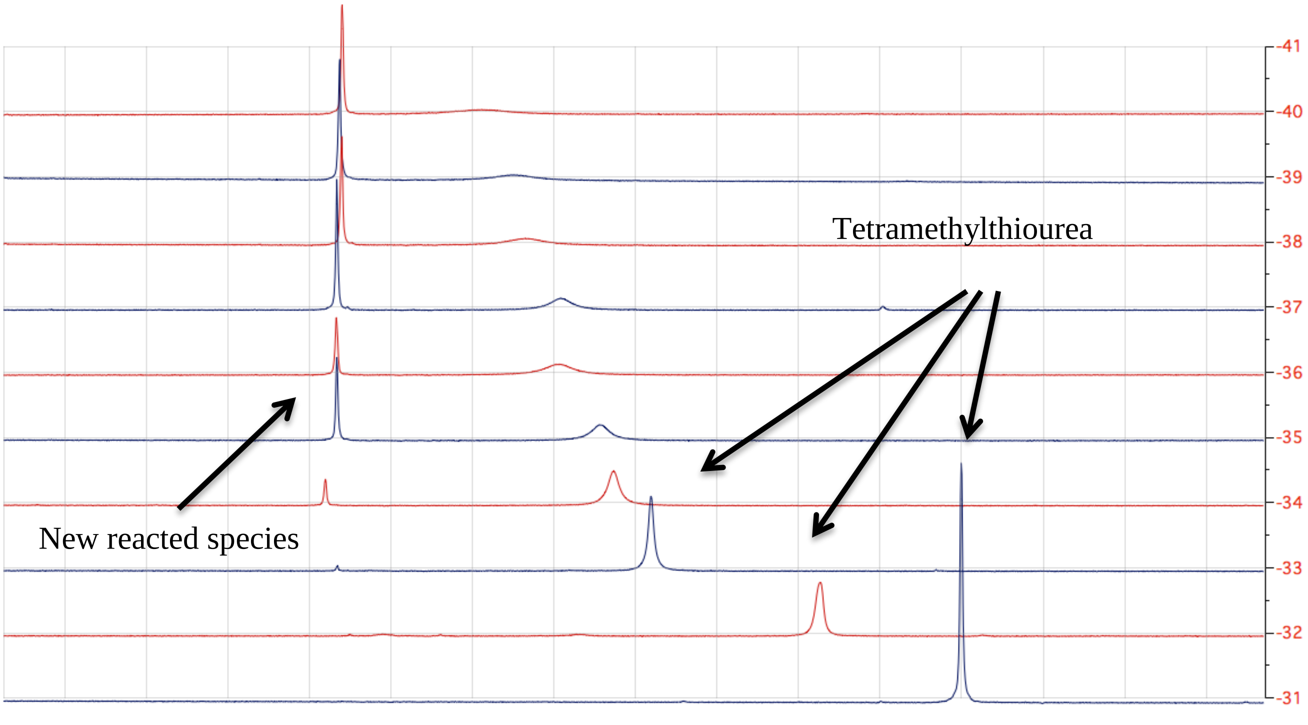


Figure S80: Partial 400 MHz ^{1}H NMR spectra of the titration of **2** with **4** in nitropropane after 10 h

14. References

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