Electronic Supplemental Information

Ir^{III} as a Strategy for Preorganization in H-bonded Motifs

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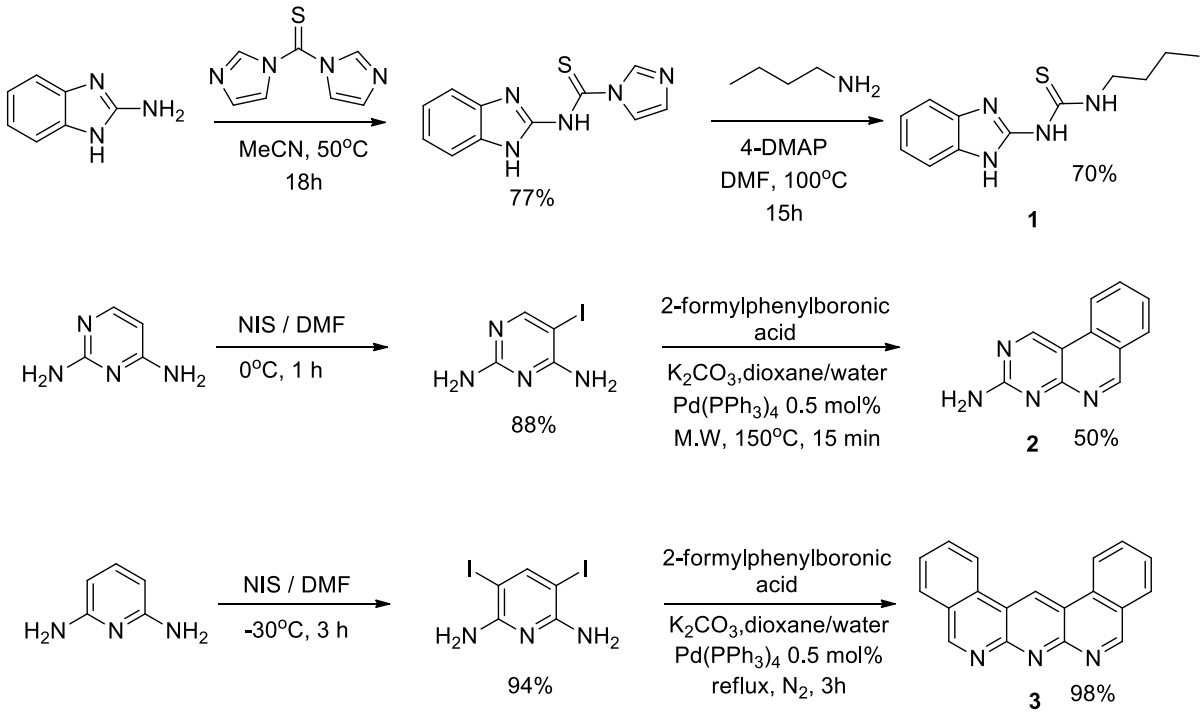
Table of Contents:

S1: Synthetic Schemes[1-4]

Scheme 1: Synthesis of H-bond donor **1** and acceptors **2, 3**



Compounds **1, 2, 3** were synthesised according to previously reported methods and their characterisation data are in agreement with literature.[1-4]

S2: Copies of NMR Spectra (^{1}H, ^{13}C)

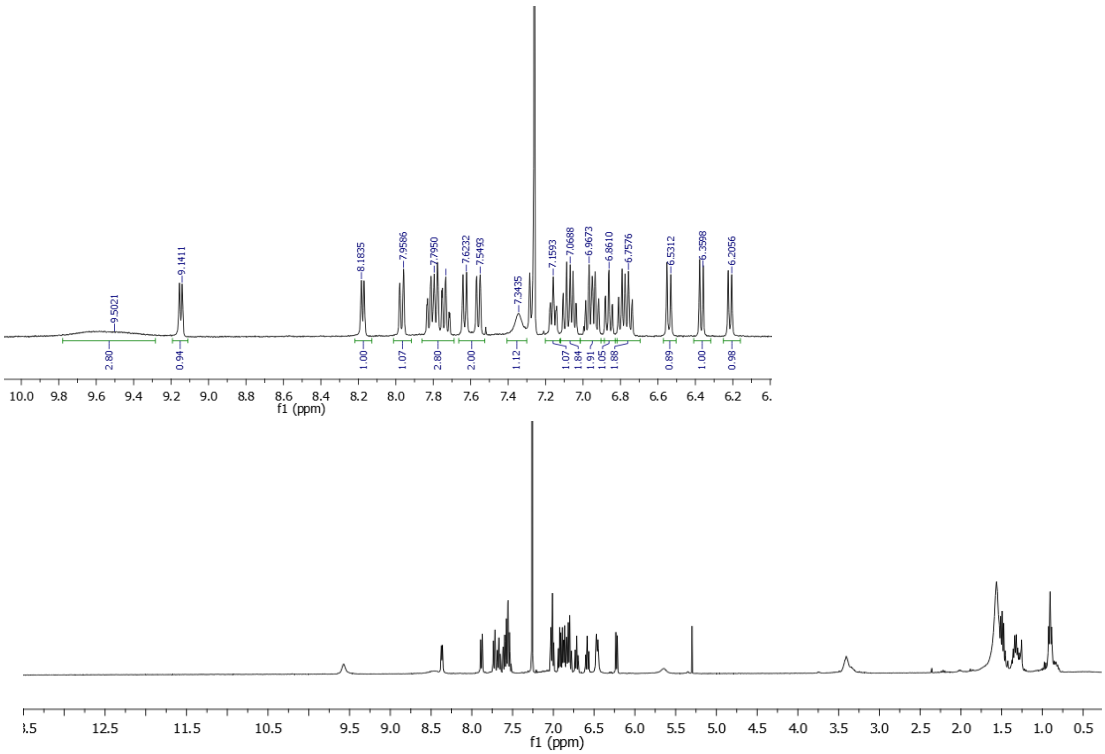


Figure S1 ^{1}H NMR (400 MHz) of complex **4** zoomed into the aromatic part (top), whole spectrum (bottom) measured in $CDCl_3$.

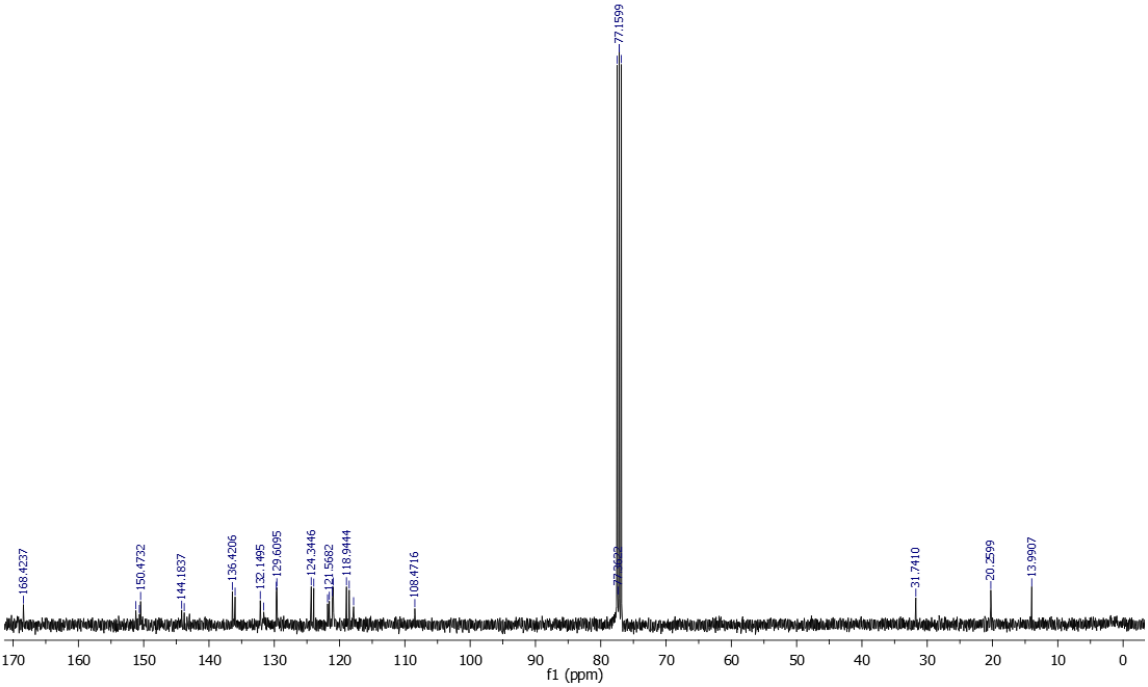


Figure S2 ^{13}C NMR (101 MHz) of complex **4** measured in $CDCl_3$.

S3: ^{1}H NMR Binding and Dilution Studies

Data obtained from: http://app.supramolecular.org/bindfit

Compound **2**

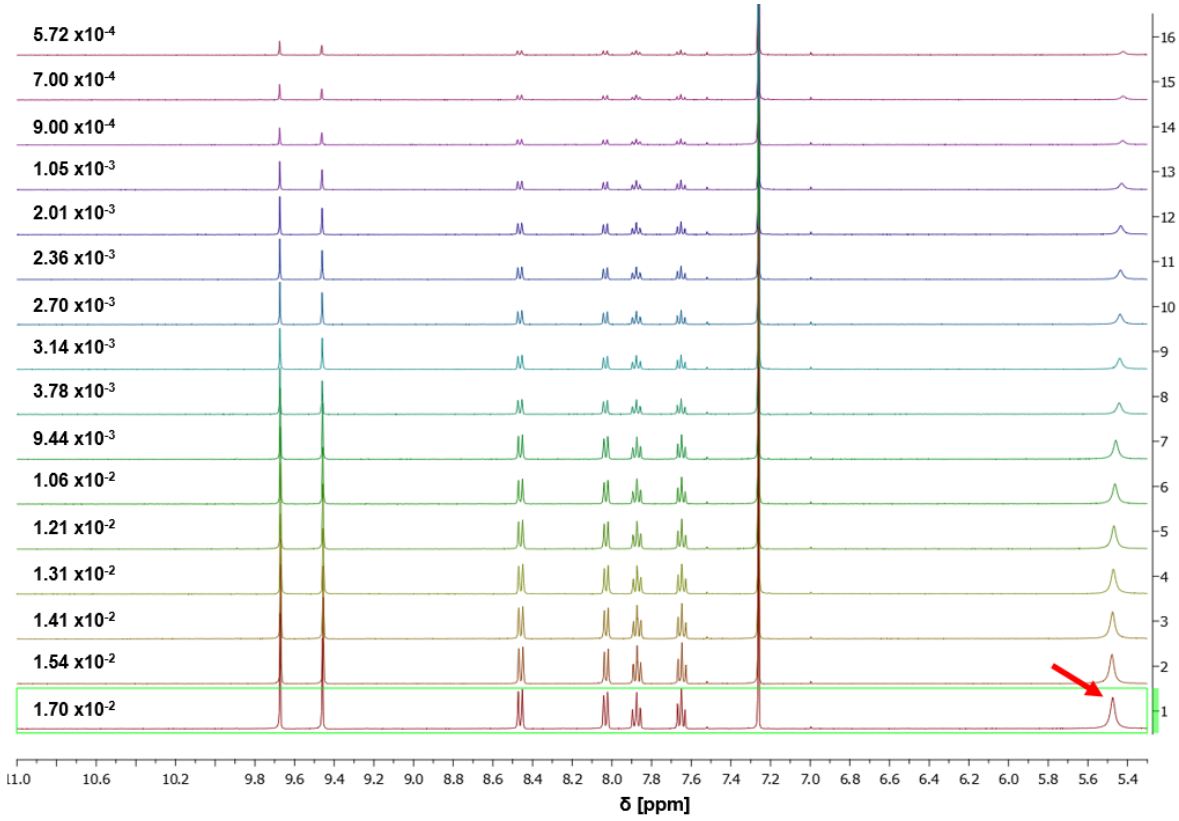


Figure S3 Stacked ^{1}H NMR (400 MHz) from dilution of **2** measured in $CDCl_3$.

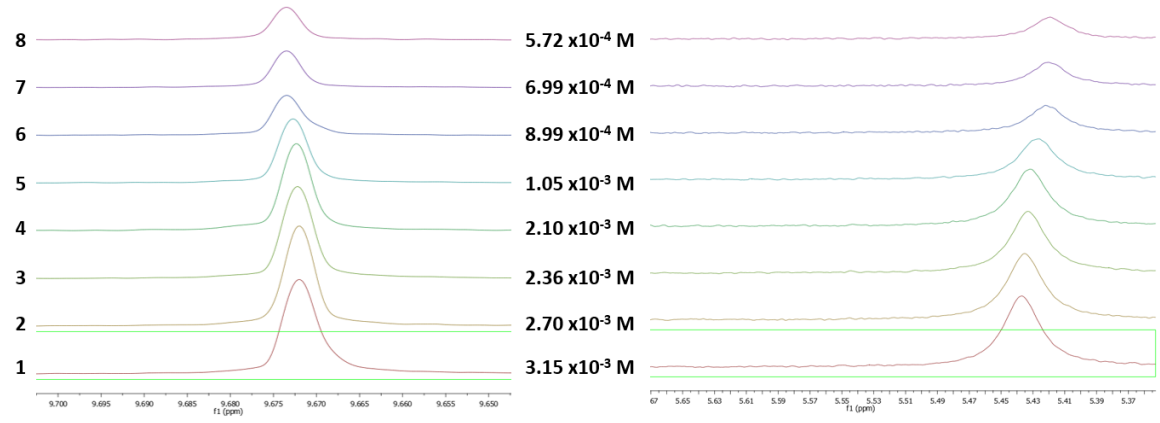


Figure S4 Stacked ^{1}H NMR (400 MHz), zoomed in, from dilution of **2** measured in $CDCl_3$.

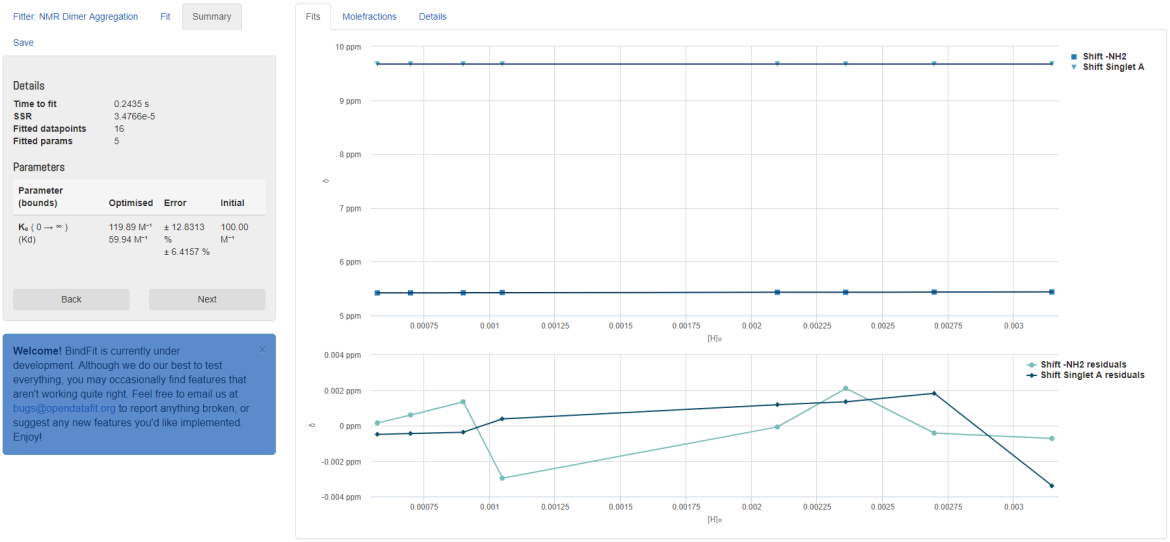


Figure S5 Data obtained for the dilution of compound **2** in $CDCl_3$.

Equal K/ Dimerization

$$K_e = 119.9\ M^{-1} \pm 13\% \quad K_d = 59.9\ M^{-1} \pm 6\%$$

Link to BindFit: http://app.supramolecular.org/bindfit/view/b6bffe0e-ba6f-49c6-bf08-e31e0dc4bd9c

Complex **4**

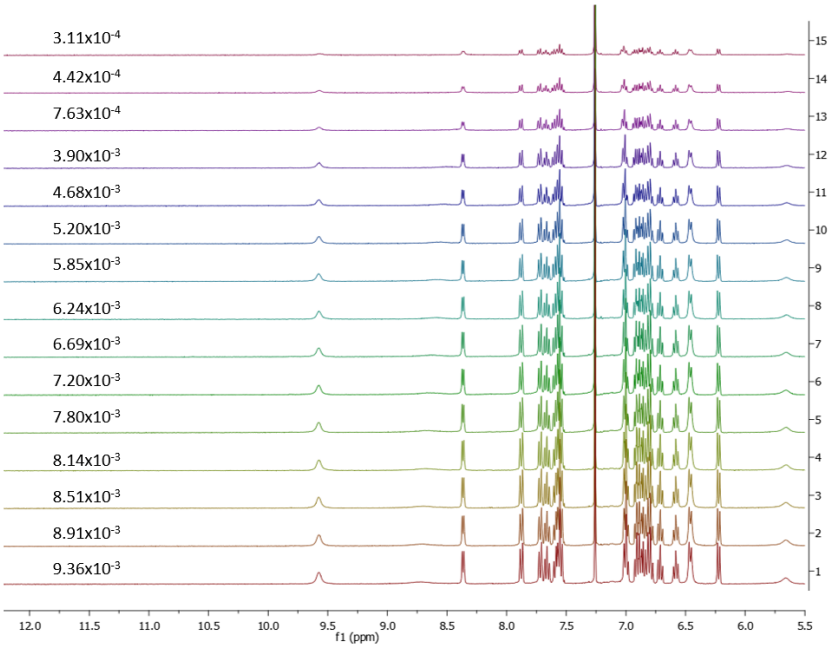


Figure S6 Stacked ^{1}H NMR (400 MHz), zoomed in, from dilution of **4** measured in $CDCl_3$.

Co-System **1•2**

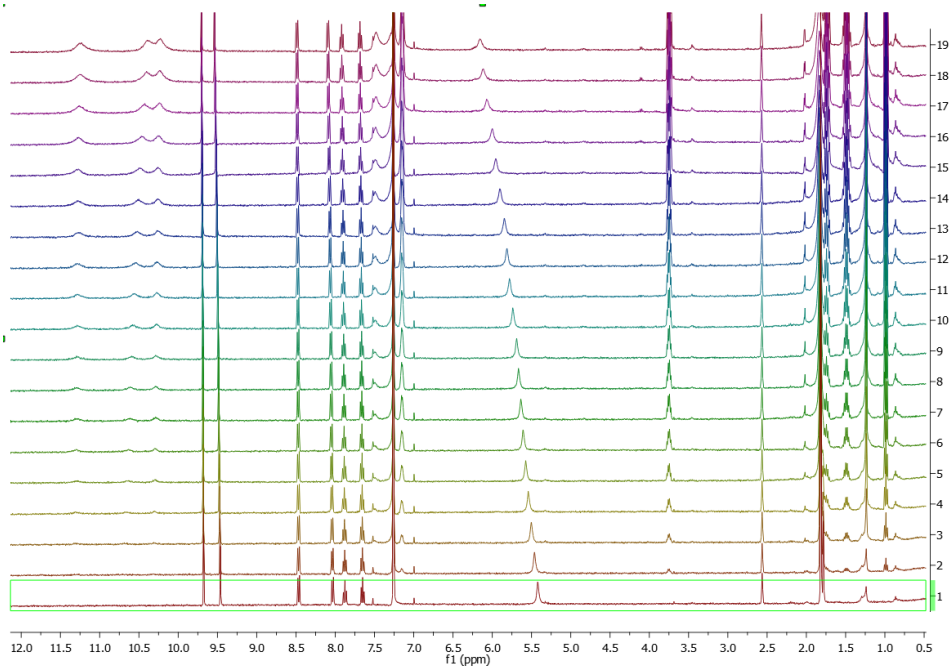


Figure S7 Stacked ^{1}H NMR (400 MHz) from titration experiment for co-system **1•2** measured in $CDCl_3$/ DMSO-d_6 (99:1).

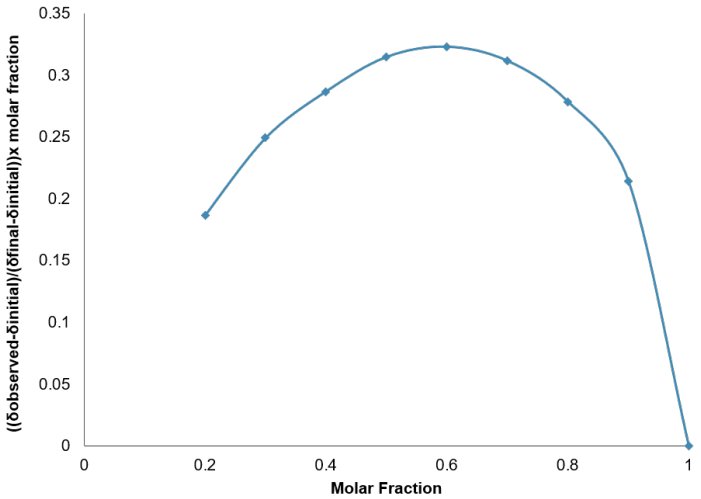


Figure S8 Job Plot for co-system **1•2** confirming 1:2 stoichiometry.

Figure S9 Results from the ^{1}H NMR binding studies of co-system **1•2** in $CDCl_3$/ DMSO-d_6 (99:1).

$$K_{11} = 2.7 \times 10^3\ M^{-1} \pm 5\% \quad K_{12} = 129\ M^{-1} \pm 1\%$$

Link to BindFit: http://app.supramolecular.org/bindfit/view/26de9cbb-4

Co-system **1•3**

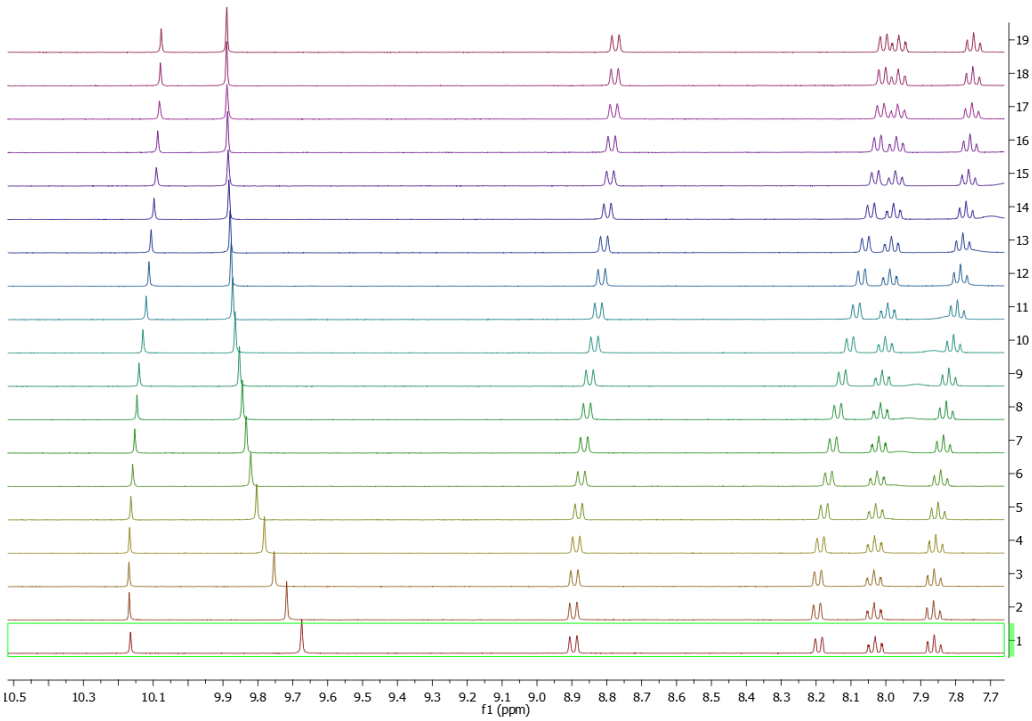


Figure S10 Stacked ^{1}H NMR (400 MHz) from titration experiment for co-system **1•3** measured in $CDCl_3$/ DMSO-d_6 (99:1).

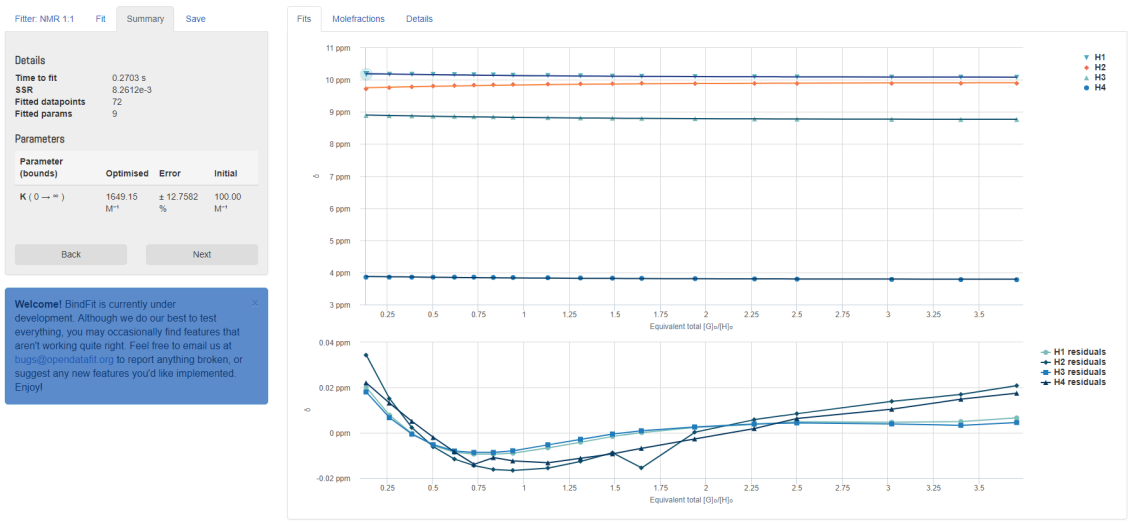


Figure S11 Results from the ^{1}H NMR binding studies of co-system **1•3** in $CDCl_3$/ DMSO-d_6 (99:1).

$$K = 1.6 \times 10^{3}\ M^{-1} \pm 13\%$$

Link to BindFit: http://app.supramolecular.org/bindfit/view/682fedf1-6aa2-42bd-a0b9-671e61b2af20

Co-system **4•2**

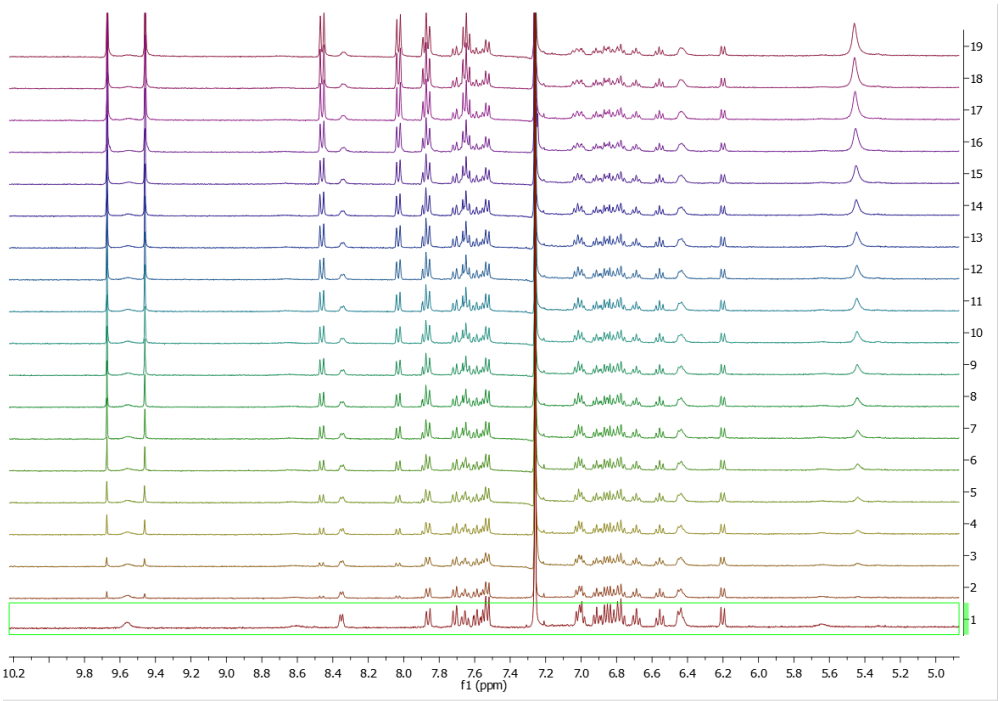


Figure S12 Stacked ^{1}H NMR (400 MHz), zoomed in, from titration experiment for co-system **4•2** in $CDCl_3$/ DMSO-d_6 (99:1).

Figure S13 Results from the ^{1}H NMR binding studies of co-system **4•2** in $CDCl_3$/ DMSO-d_6 (99:1).

$$K = 46\ M^{-1} \pm 5\%$$

Link to BindFit: http://app.supramolecular.org/bindfit/view/6fac1e49-5e9b-4d6f-b48e-a37e49458fa5

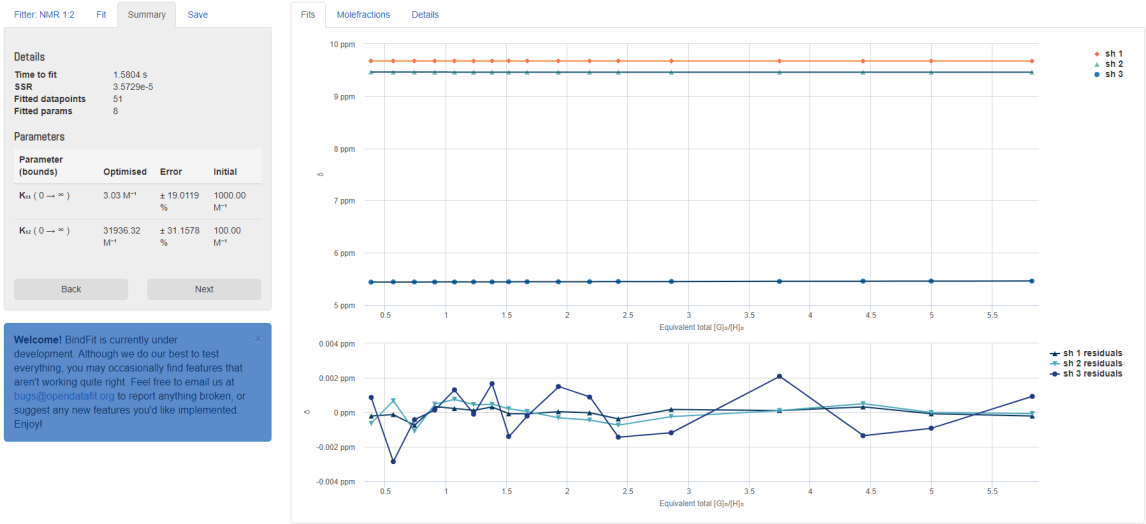


Figure S14 Results from the ^{1}H NMR binding studies of co-system **4•2** in $CDCl_3$/ DMSO-d_6 (99:1).

$$K_{11} = 3 \times 10^3\ M^{-1} \pm 19\% \quad K_{12} = 3.2 \times 10^4\ M^{-1} \pm 32\%$$

Link to BindFit: http://app.supramolecular.org/bindfit/view/b1520703-473c-4fbe-8d27-19b715bd17bb

Co-system **4•3**

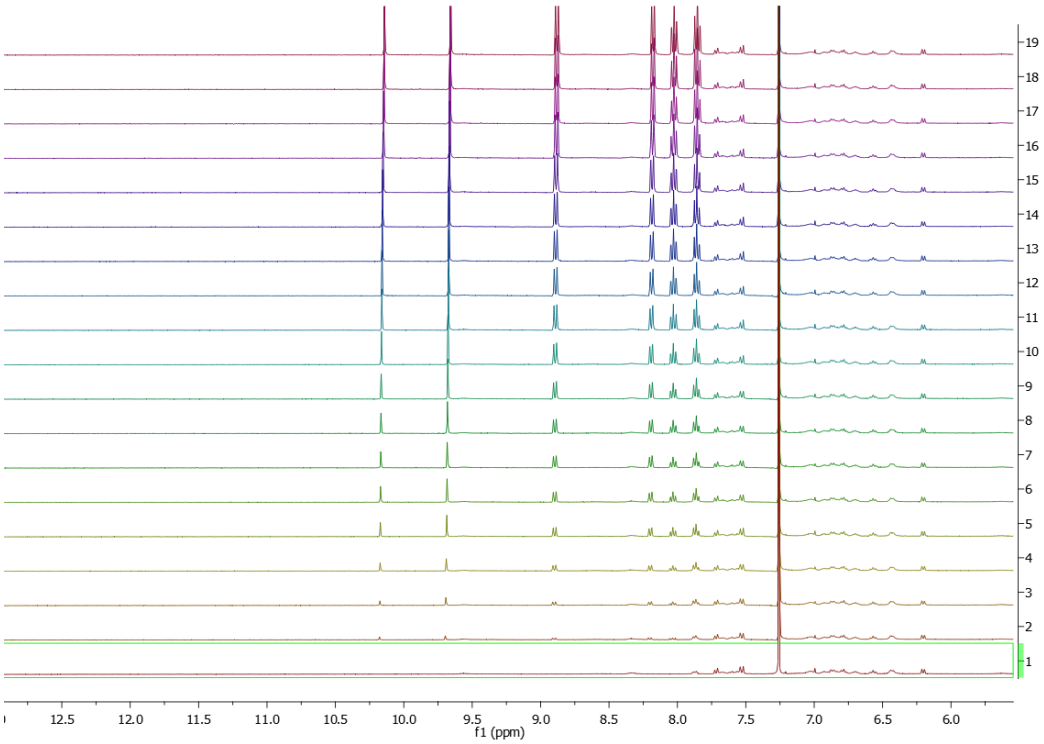


Figure S15 Stacked ^{1}H NMR (400 MHz), zoomed in, from titration experiment for co-system **4•3** in $CDCl_3$/ DMSO-d_6 (99:1).

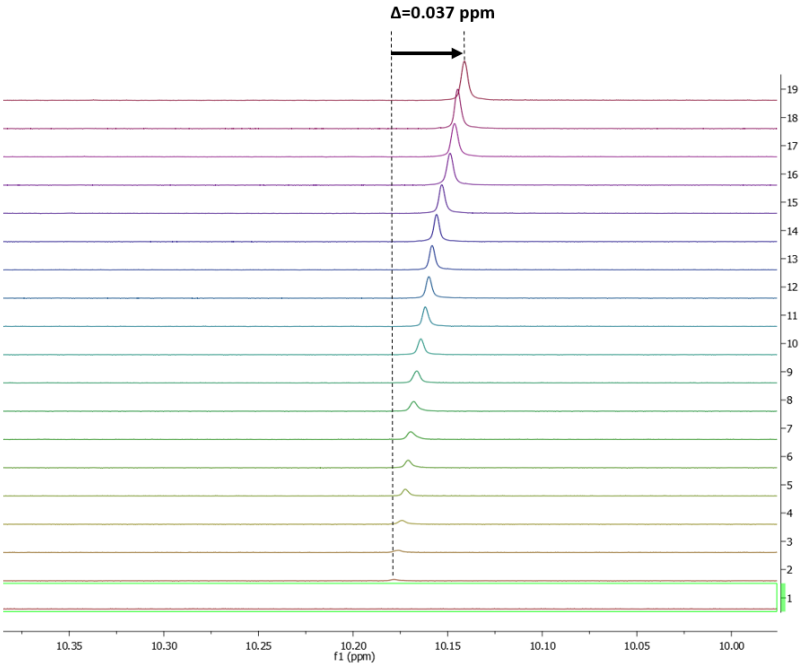


Figure S16 Stacked ^{1}H NMR (400 MHz), zoomed in to the region around 10.2 ppm, from titration experiment for co-system **4•3** in $CDCl_3$/ DMSO-d_6 (99:1).

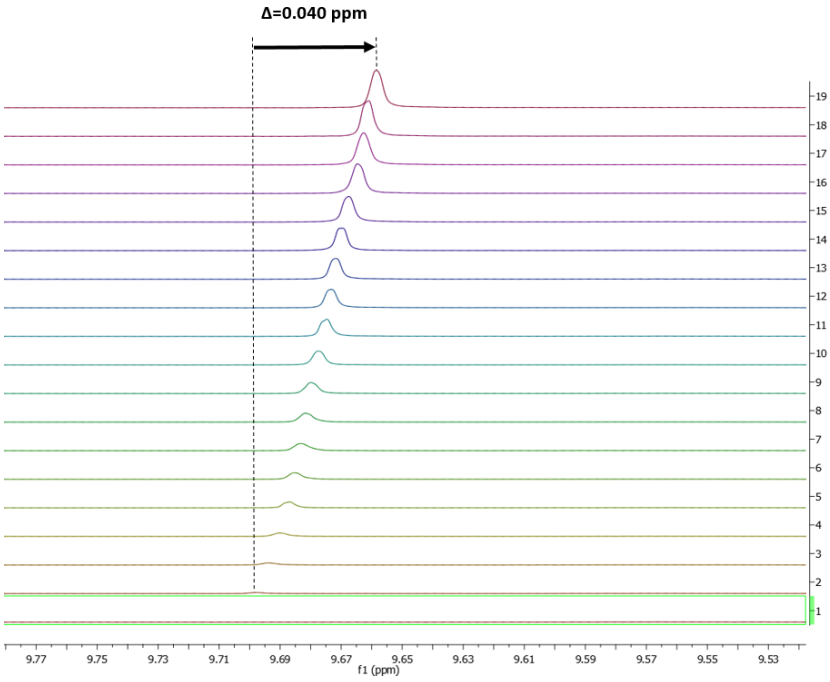


Figure S17 Stacked ^{1}H NMR (400 MHz), zoomed in to the region around 9.7 ppm, from titration experiment for co-system **4•3** in $CDCl_3$/ DMSO-d_6 (99:1).

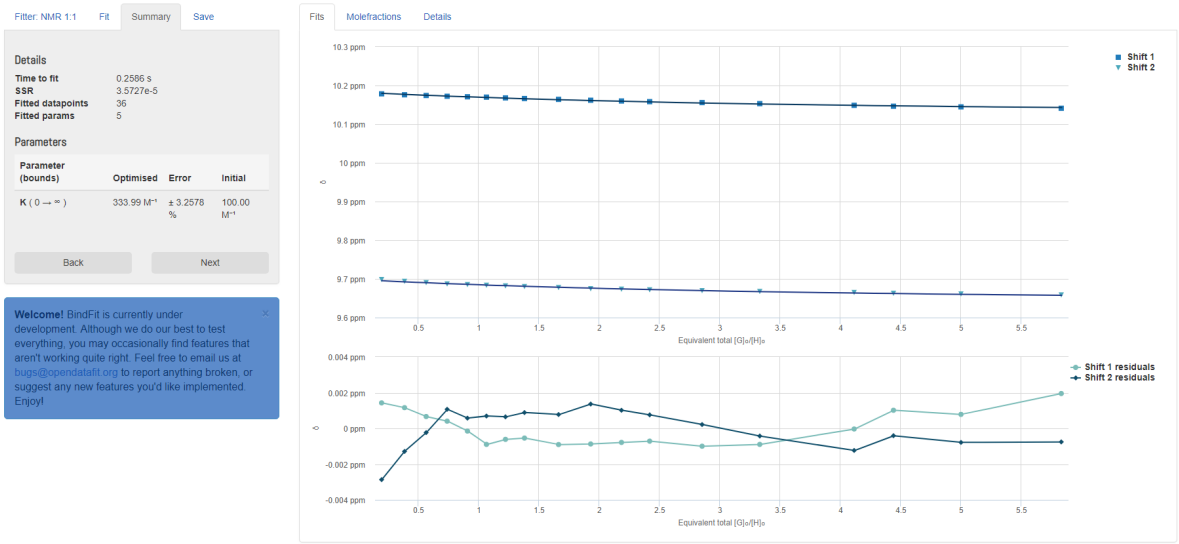


Figure S18 Results from the ^{1}H NMR binding studies for 1:1 stoichiometry of co-system **4•3** in $CDCl_3$/ DMSO-d_6 (99:1).

$$K = 334\ M^{-1} \pm 3\%$$

Link to BindFit: http://app.supramolecular.org/bindfit/view/1625e254-8506-4a5e-b634-f5dc738e4afa

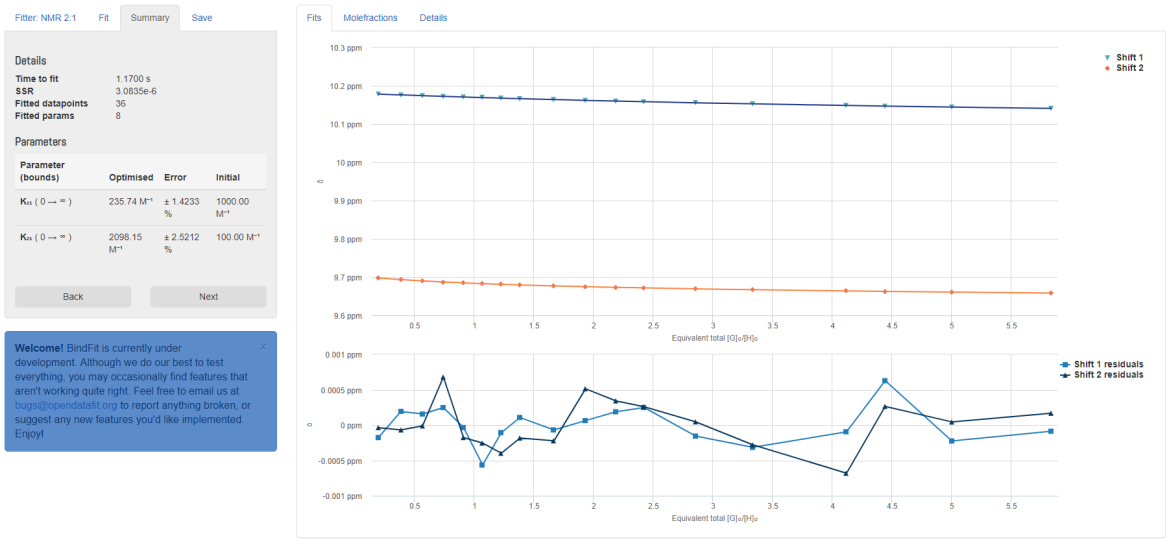


Figure S19 Results from the ^{1}H NMR binding studies for 2:1 stoichiometry of co-system **4•3** in $CDCl_3$/ DMSO-d_6 (99:1).

$$K_{11} = 236\ M^{-1} \pm 1\% \quad K_{21} = 2.1 \times 10^3\ M^{-1} \pm 3\%$$

Link to Bindfit: http://app.supramolecular.org/bindfit/view/ba6a1ac1-8e2e-4fa7-ad4d-ae115574319f

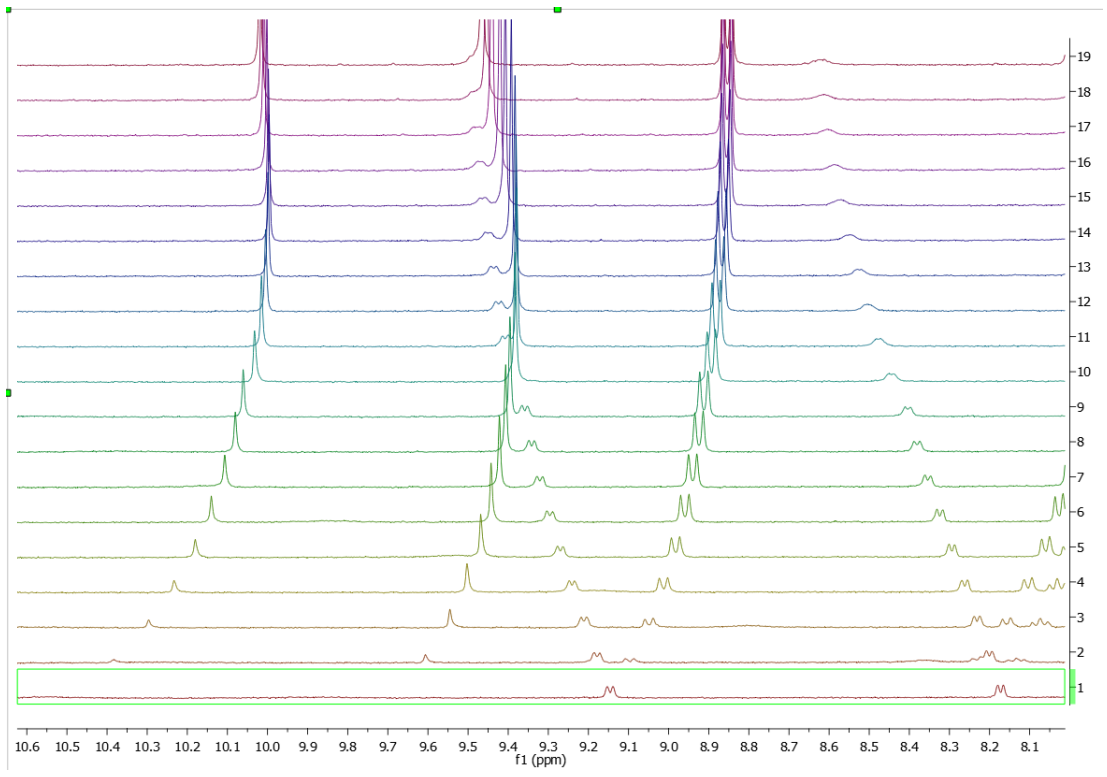


Figure S20 Stacked ^{1}H NMR (400 MHz), zoomed in (10.5 -8.0 ppm), from titration experiment for co-system **4•3** in $CDCl_3$/ DMSO-d_6 (99:1).

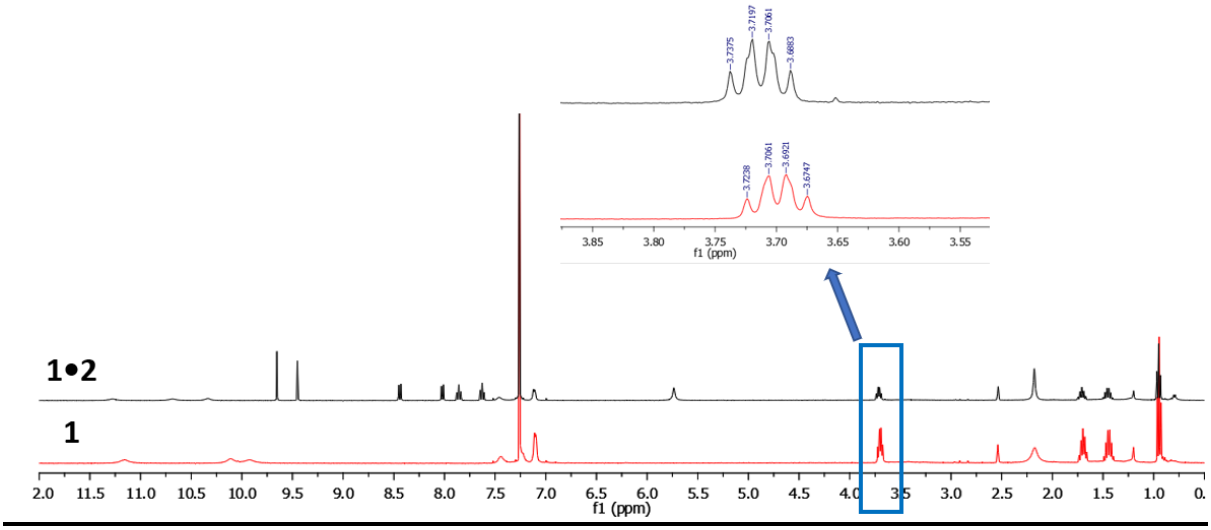


Figure S21 Stacked ^{1}H NMR (400 MHz), **of compound 1 (red) and 1:1 system 1•2 (black), zoomed into -CH_2- adjacent to NHc)** in $CDCl_3$/ DMSO-d_6 (99:1).

S4: UV-vis Binding and Dilution Studies

Compound **2**

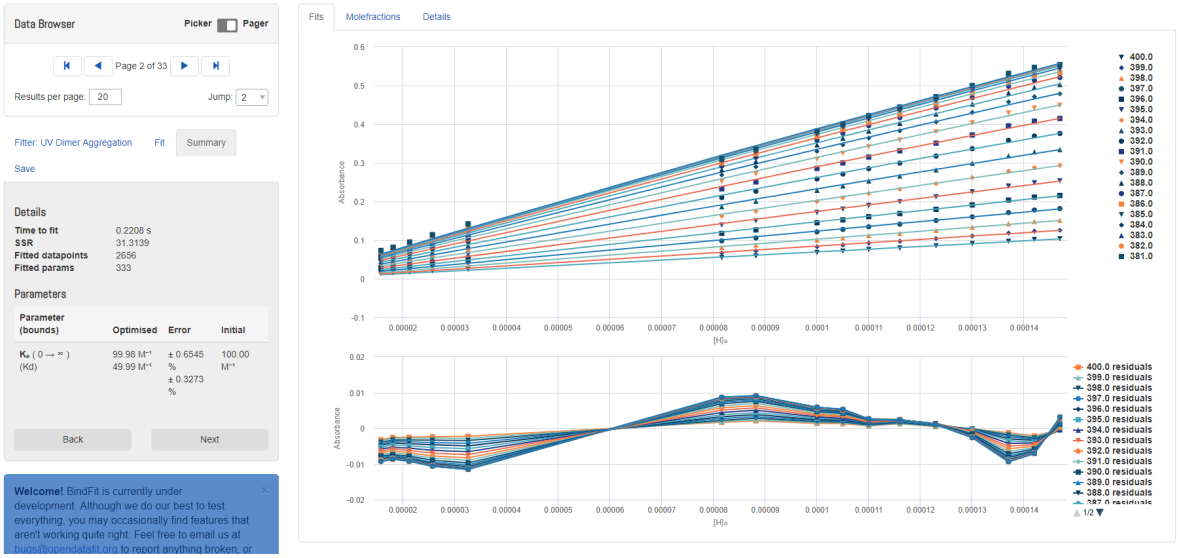


Figure S22 Results from the UV-vis dilution studies for the compound **2** in $CHCl_3$.

$$K_e = 100\ M^{-1} \pm 0.7\% \quad K_d = 50\ M^{-1} \pm 0.3\%$$

Link to BindFit: http://app.supramolecular.org/bindfit/view/13ce7d0c-511c-4286-ad06-7ad705e0f687

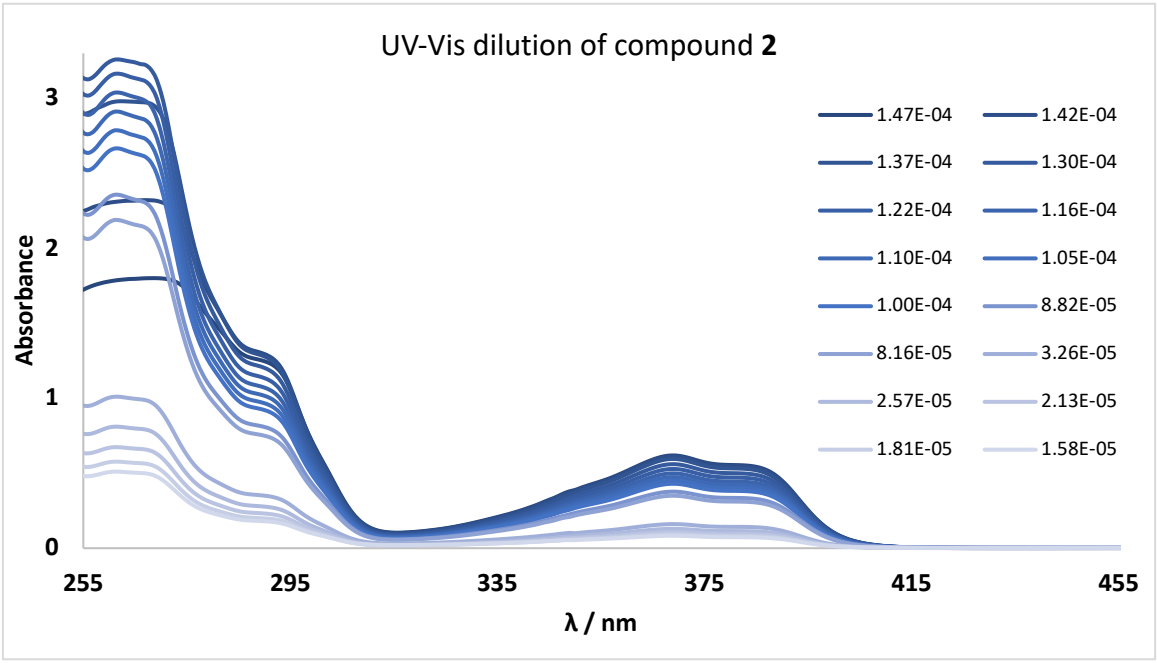


Figure S23 Absorbance spectra from UV-vis dilution studies for the compound **2** in $CHCl_3$.

Compound **3**

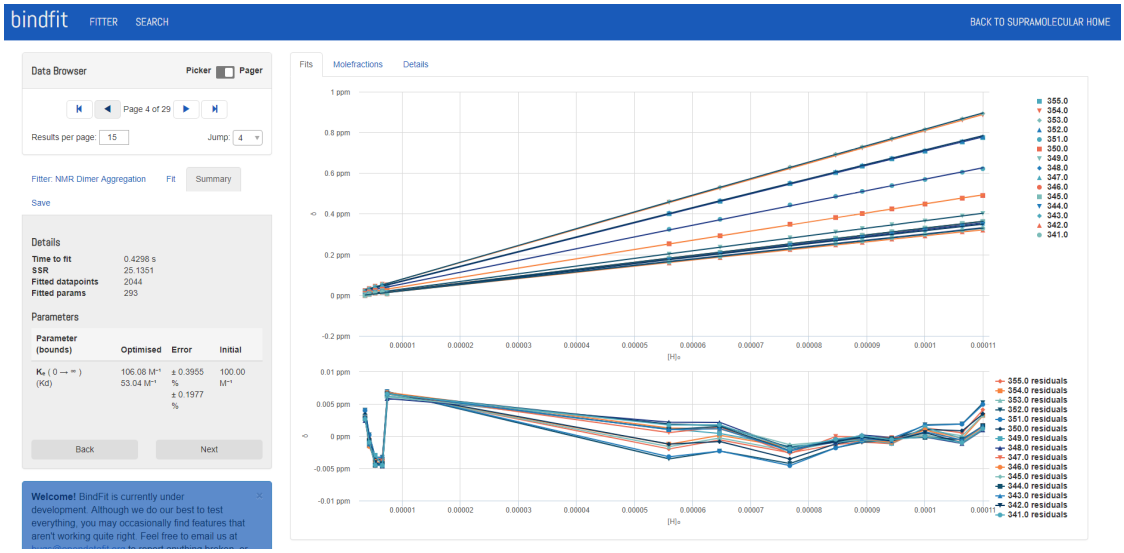


Figure S24 Results from the UV-vis dilution studies for the compound **3** in $CHCl_3$.

$$K_e = 106.1\ M^{-1} \pm 0.4\% \quad K_d = 53.04\ M^{-1} \pm 0.2\%$$

Link to BindFit: *http://app.supramolecular.org/bindfit/view/0bc49803-7*

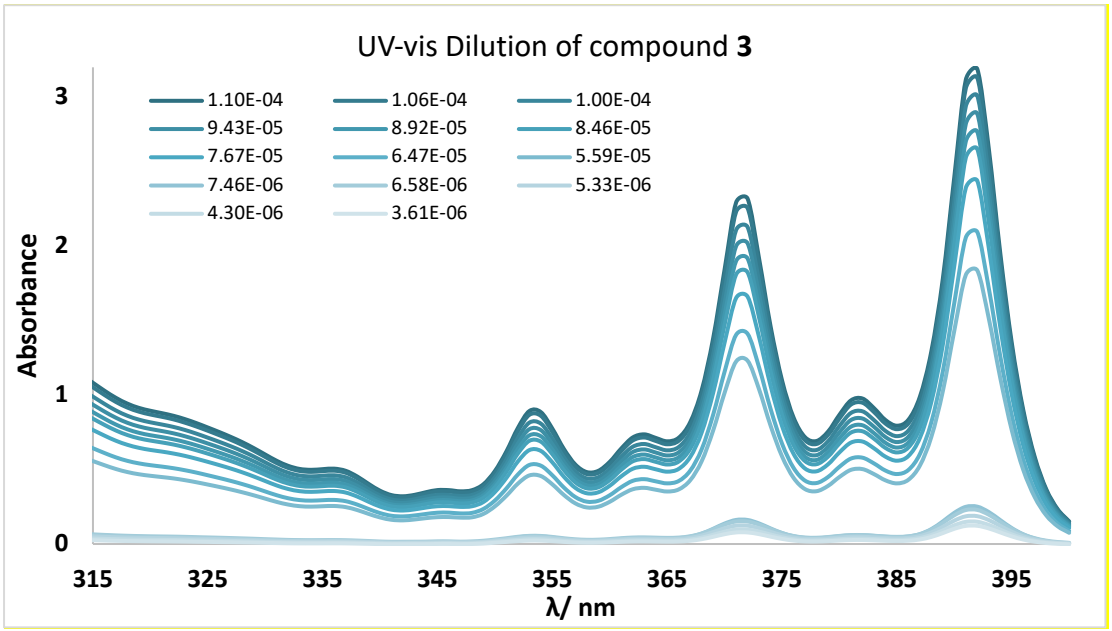


Figure S25 Absorbance spectra from UV-vis dilution studies of compound **3** in $CHCl_3$.

Co-System **1•2**

*no back concentration

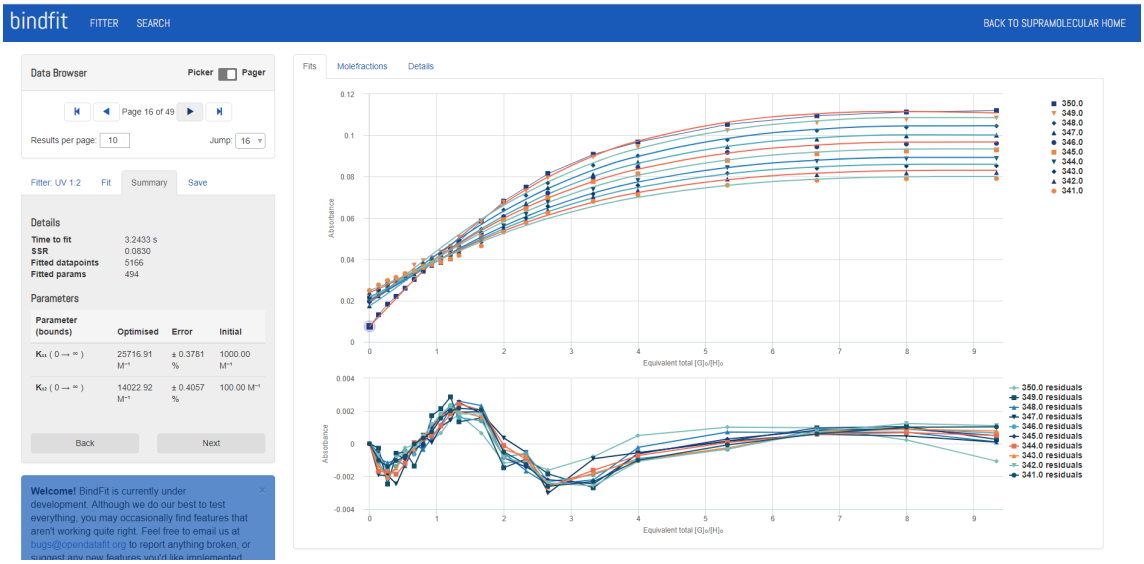


Figure S26 Results from the UV-vis titration studies (without the back concentration of the host) for the co-system **1•2** in $CHCl_3$/ DMSO (99:1).

$$K_{11} = 2.6 \times 10^4\ M^{-1} \pm 0.4\% \quad K_{12} = 1.4 \times 10^4\ M^{-1} \pm 0.4\%$$

Link to BindFit: http://app.supramolecular.org/bindfit/view/928218d4-0168-4da0-bc14-7072259deb38

**With back concentration:

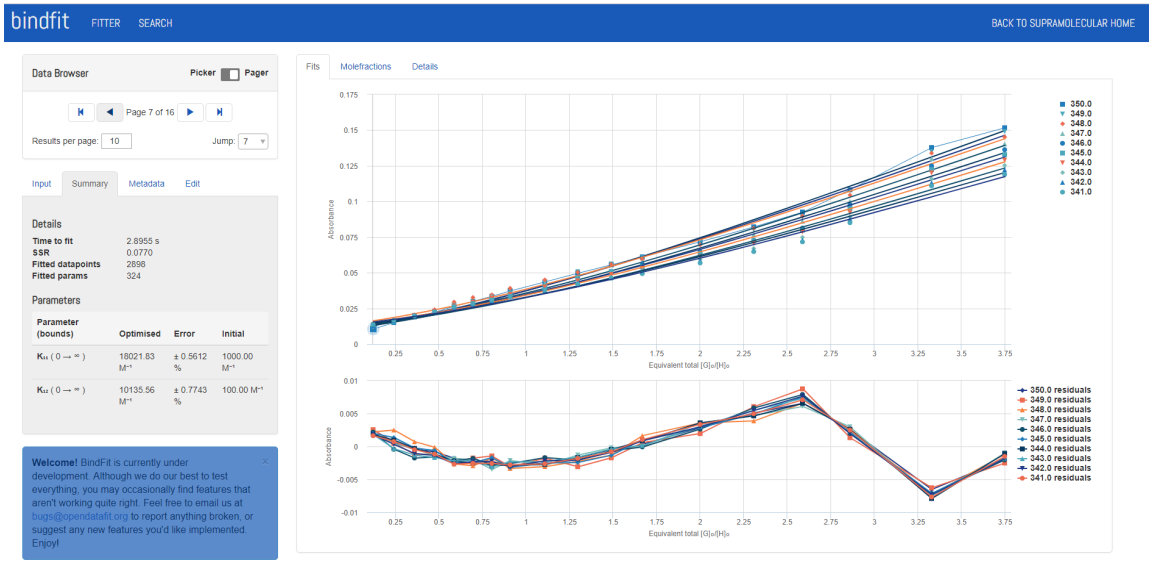


Figure S27 Results from the UV-vis titration studies (with the back concentration of the host) for the co-system **1•2** in $CHCl_3$/ DMSO (99:1).

$$K_{11} = 1.8 \times 10^4\ M^{-1} \pm 0.6\% \quad K_{12} = 1.0 \times 10^4\ M^{-1} \pm 0.8\%$$

Link to BindFit: http://app.supramolecular.org/bindfit/view/815d41ba-f622-4b75-a2d7-723b33face3d

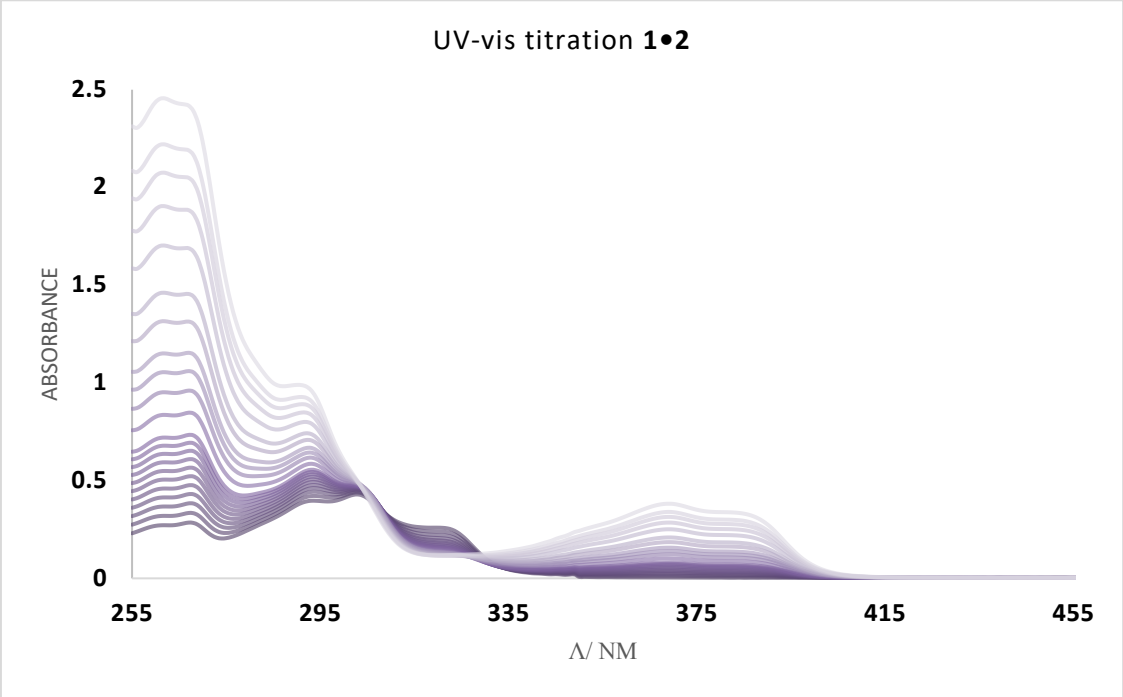


Figure S28 Absorbance spectra from UV-vis titration studies (with the back concentration of the host) for the co-system **1•2** in $CHCl_3$/ DMSO (99:1).

Co-System **1•3**

**no back concentration*

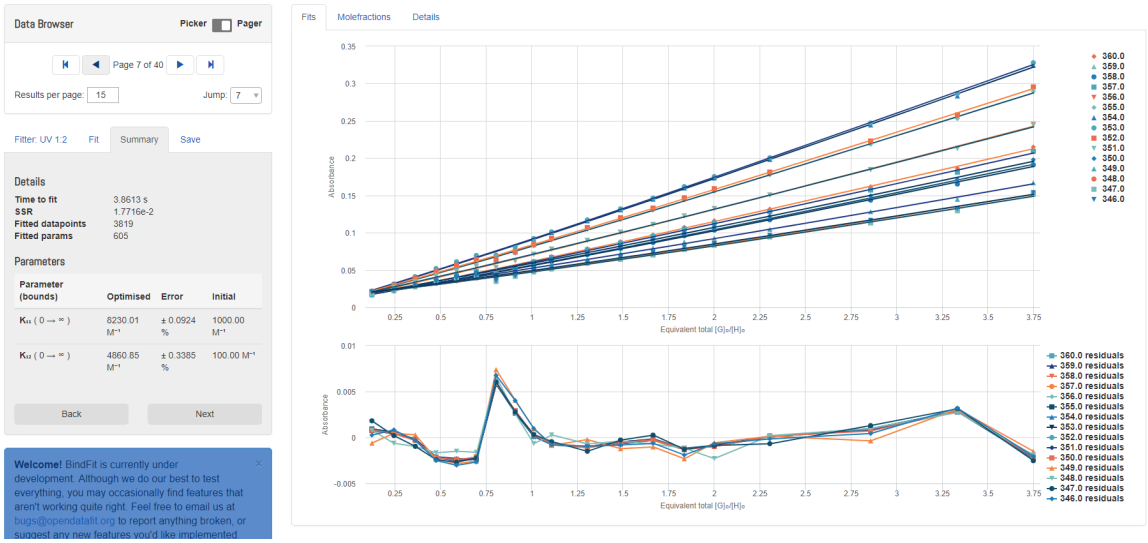


Figure S29 Results from the UV-vis titration studies (without the back concentration of the host) for the co-system **1•3** in $CHCl_3$/ DMSO (99:1).

$$K_{11} = 8.2 \times 10^3\ M^{-1} \pm 0.1\% \quad K_{12} = 4.8 \times 10^4\ M^{-1} \pm 0.3\%$$

Link to BindFit: http://app.supramolecular.org/bindfit/view/33f5a4a1-7006-4173-9bd4-16aa2af531e6

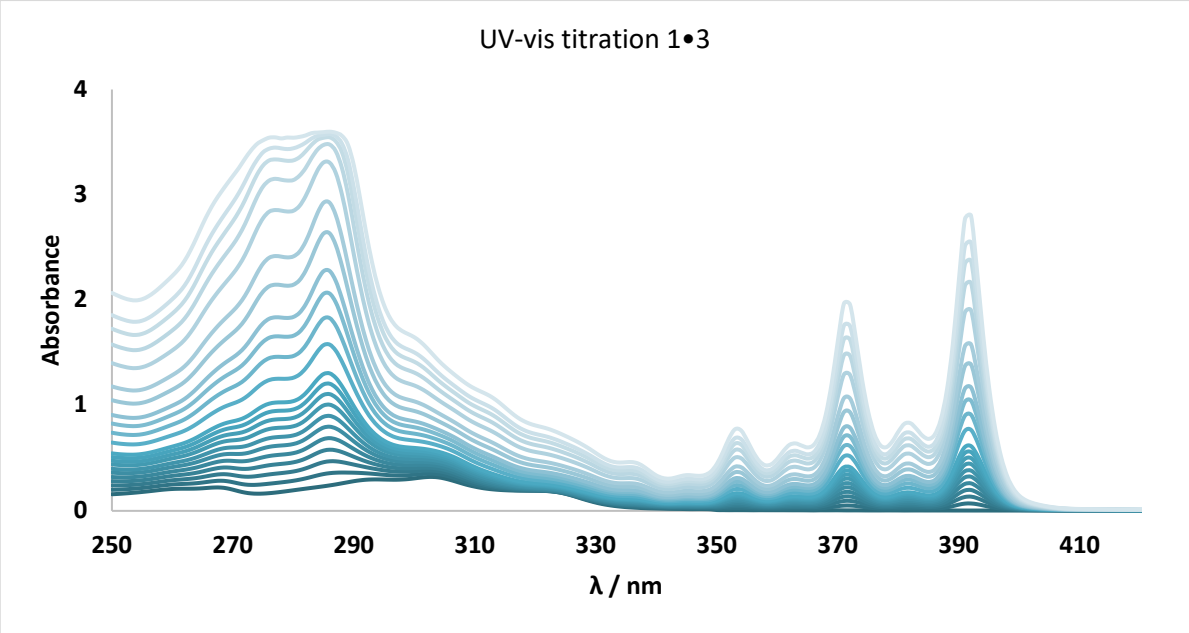


Figure S30 Results from the UV-vis titration studies (without the back concentration of the host) for the co-system **1•3** in $CHCl_3$/ DMSO (99:1).

Co-System **4•2**

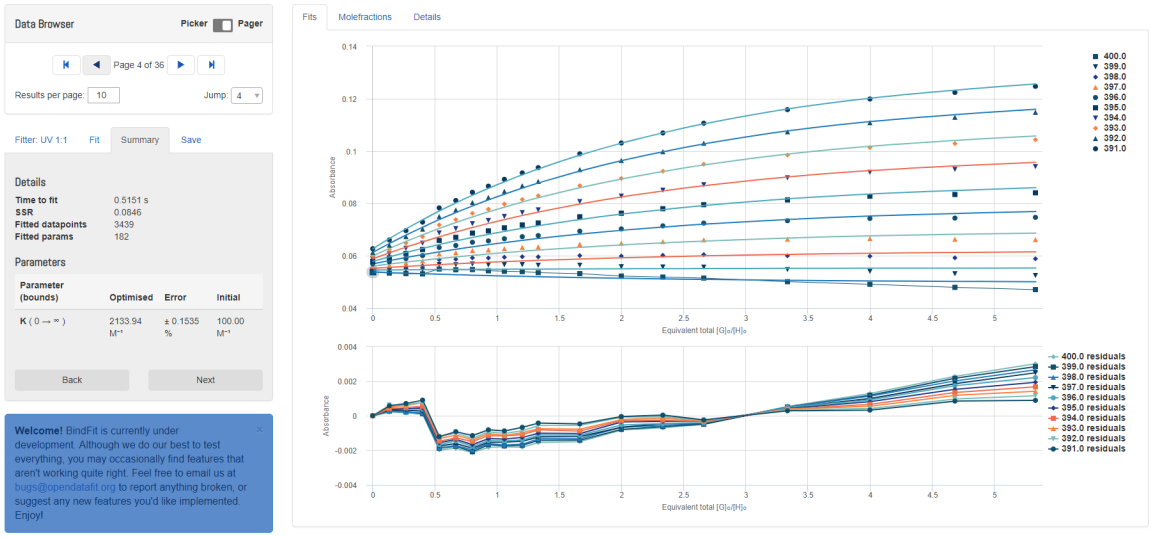


Figure S31 Results from the UV-vis titration studies for the co-system **4•2** in $CHCl_3$/ DMSO (99:1).

$$K=2.1 \times 10^3\ M^{-1} \pm 0.2\%$$

Link to BindFit: http://app.supramolecular.org/bindfit/view/c9af70a6-f8db-4e99-a912-32998e91387b

Co-System **4•3**

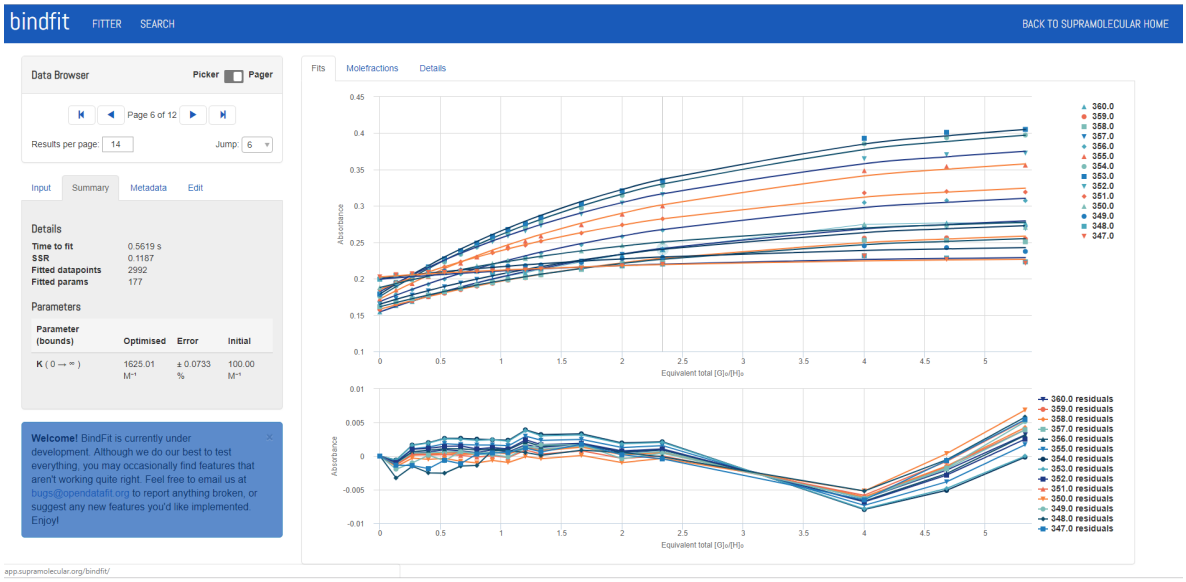


Figure S32 Results from the UV-vis titration studies for the co-system **4•3** in $CHCl_3$/ DMSO (99:1).

$$K = 1.6 \times 10^3\ M^{-1} \pm 0.1\%$$

Link to BindFit: http://app.supramolecular.org/bindfit/view/15caade0-df8b-4d57-bd65-e398f5acc89c

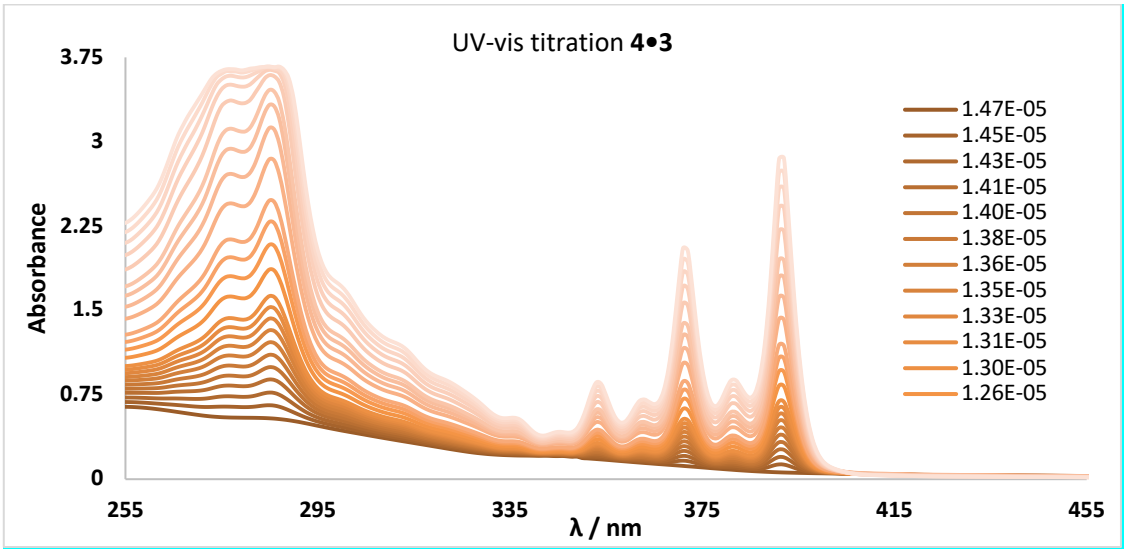
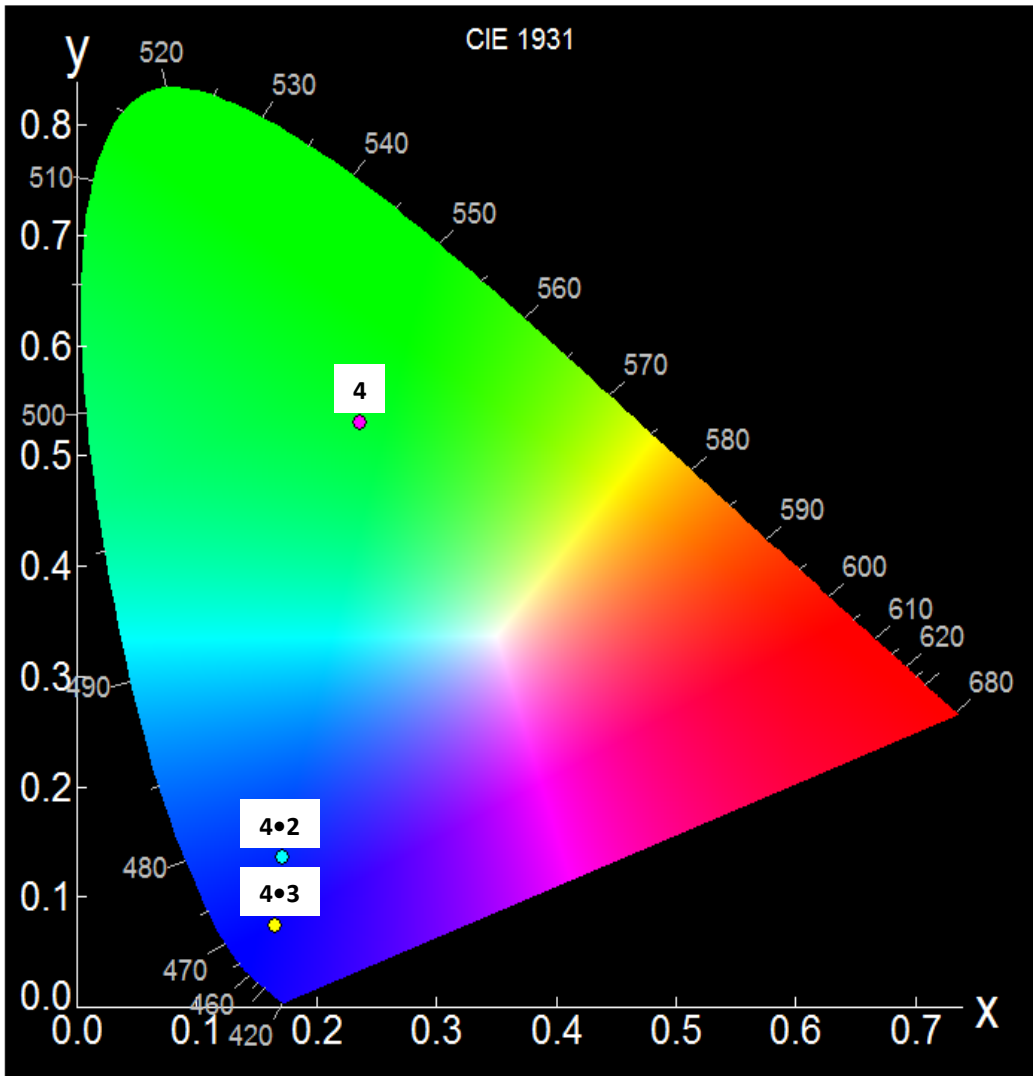


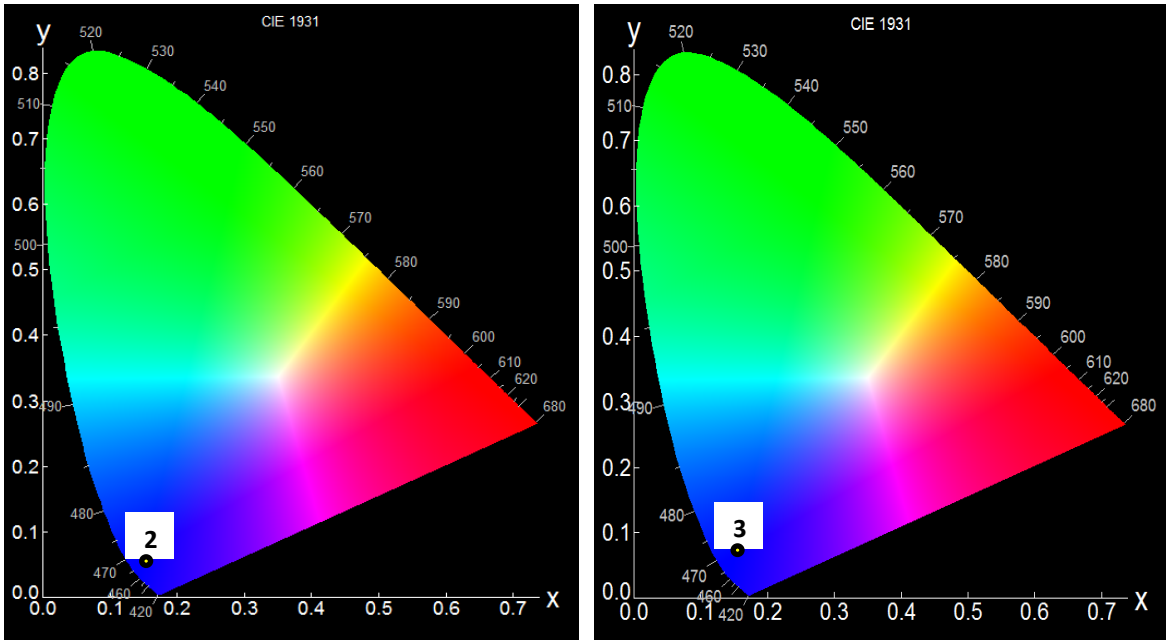
Figure S33 Results from the UV-vis titration studies for the co-system **4•3** in $CHCl_3$/ DMSO (99:1).

S5: Chromaticity Diagrams



sample	x	y
4	0.235	0.526
4•2	0.171	0.135
4•3	0.165	0.074

Figure S34. CIE 1931 Diagram from emission studies of **4, 4•2** and **4•3** in chloroform with CIEx, y coordinates assigned in the table, excited at 360 nm. Solutions of co-systems are in 1:1 ratio.



sample	x	y
2	0.154	0.052
3	0.156	0.072

Figure S35. CIE 1931 Diagrams from emission studies of **2** and **3** in chloroform with CIEx,y, coordinates assigned in the table, excited at 360 nm.

S6: Crystallographic Data

Compound 1

Table S1 Crystal data and structure refinement for Compound 1

Identification code	BBalo-135-43-blocks-final-ref
Empirical formula	$C_{12}H_{16}N_4S$
Formula weight	248.35
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	29.7869(8)
b/Å	4.44193(11)
c/Å	19.2530(5)
α/°	90
β/°	107.232(3)
γ/°	90
Volume/Å^3	2433.05(12)
Z	8
ρ_{calc}g/cm^3	1.356
μ/mm^{-1}	2.220
F(000)	1056.0
Crystal size/mm^3	0.068 × 0.047 × 0.023
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.214 to 145.746
Index ranges	-36 ≤ h ≤ 36, -5 ≤ k ≤ 5, -23 ≤ l ≤ 23
Reflections collected	16716
Independent reflections	2397 [R_{int} = 0.0394, R_{sigma} = 0.0233]
Data/restraints/parameters	2397/0/218
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0292, wR_2 = 0.0682
Final R indexes [all data]	R_1 = 0.0358, wR_2 = 0.0715
Largest diff. peak/hole / e Å^{-3}	0.27/-0.22

Table S2 Bond Lengths for Compound 1

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C5	1.6990(14)	C7	C12	1.400(2)
N4	C6	1.3137(18)	C7	C8	1.390(2)
N4	C12	1.3983(18)	C12	C11	1.394(2)
N3	C6	1.3642(19)	C10	C11	1.385(2)

N3	C7	1.3909(18)	C10	C9	1.405(2)
N1	C5	1.3185(19)	C2	C1	1.521(2)
N1	C4	1.4652(18)	C2	C3	1.525(2)
N2	C6	1.3830(18)	C4	C3	1.523(2)
N2	C5	1.3738(19)	C8	C9	1.385(2)

Table S3 Bond Angles for Compound 1

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	N4	C12	104.05(12)	C11	C12	C7	120.17(13)
C6	N3	C7	105.77(12)	C11	C10	C9	121.50(14)
C5	N1	C4	124.05(12)	C10	C11	C12	117.72(14)
C5	N2	C6	126.36(12)	N1	C5	S1	123.72(11)
N4	C6	N3	114.56(12)	N1	C5	N2	117.41(13)
N4	C6	N2	125.95(13)	N2	C5	S1	118.87(11)
N3	C6	N2	119.49(12)	C1	C2	C3	113.14(13)
N3	C7	C12	105.58(12)	N1	C4	C3	109.64(12)
C8	C7	N3	131.90(14)	C9	C8	C7	116.79(14)
C8	C7	C12	122.51(13)	C8	C9	C10	121.29(14)
N4	C12	C7	110.03(12)	C4	C3	C2	113.95(12)
C11	C12	N4	129.79(13)				

Compound 2

Table S4 Crystal data and structure refinement for Compound 2.

Identification code	DAA X ray
Empirical formula	$C_{11}H_8N_4$
Formula weight	196.21
Temperature/K	100
Crystal system	N/A
Space group	P1
a/Å	7.2852(6)
b/Å	7.6006(6)
c/Å	9.4873(7)
α/°	74.100(6)
β/°	86.330(6)
γ/°	61.450(8)
Volume/Å^3	442.40(7)
Z	2
ρ_{calc}g/cm^3	1.473
μ/mm^{-1}	0.762

F(000)	204.0
Crystal size/mm^3	0.180 × 0.160 × 0.080
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.724 to 145.668
Index ranges	-9 ≤ h ≤ 8, -9 ≤ k ≤ 9, -11 ≤ l ≤ 11
Reflections collected	8289
Independent reflections	3094 [R_{int} = 0.025, R_{sigma} = 0.038]
Data/restraints/parameters	3094/15/288
Goodness-of-fit on F^2	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0585, wR_2 = 0.1661
Final R indexes [all data]	R_1 = 0.0617, wR_2 = 0.1693
Largest diff. peak/hole / e Å^{-3}	0.44/-0.28
Flack parameter	-0.1(2)

Table S5 Bond Lengths for Compound 2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	N2	1.357(5)	C11	C23	1.386(6)
C1	N9	1.374(5)	C11	C24	1.371(6)
C1	C13	1.402(5)	C12	C16	1.425(5)
N2	C15	1.342(4)	C12	N19	1.374(5)
C3	N9	1.316(5)	C13	C14	1.409(5)
C3	C10	1.427(6)	C15	N29	1.322(5)
N4	C12	1.342(4)	C16	C17	1.455(5)
N4	C26	1.322(5)	C16	C25	1.392(6)
C5	C10	1.398(5)	C17	C23	1.410(6)
C5	C21	1.370(6)	C17	C27	1.403(5)
N6	C14	1.324(5)	N19	C22	1.303(4)
N6	C15	1.373(5)	N20	C25	1.312(5)
C7	C10	1.413(5)	N20	C26	1.386(4)
C7	C13	1.443(5)	C22	C23	1.427(5)
C7	C18	1.385(6)	C24	C28	1.394(6)
C8	C18	1.380(5)	C26	N31	1.352(5)
C8	C21	1.399(5)	C27	C28	1.381(6)

Table S6 Bond Angles for Compound 2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	C1	N9	116.3(4)	N6	C15	N2	125.0(3)
N2	C1	C13	122.3(3)	N6	C15	N29	115.8(3)
N9	C1	C13	121.4(3)	N2	C15	N29	119.2(4)
C1	N2	C15	116.9(3)	C12	C16	C17	119.2(4)
N9	C3	C10	127.5(3)	C12	C16	C25	115.1(3)
C12	N4	C26	116.9(3)	C17	C16	C25	125.7(3)
C10	C5	C21	119.4(3)	C16	C17	C23	117.7(3)
C14	N6	C15	117.1(3)	C16	C17	C27	123.5(4)

C10	C7	C13	117.1(4)	C23	C17	C27	118.7(4)
C10	C7	C18	118.3(3)	C7	C18	C8	120.8(4)
C13	C7	C18	124.5(4)	C12	N19	C22	117.1(3)
C18	C8	C21	120.2(4)	C25	N20	C26	115.5(3)
C1	N9	C3	116.9(4)	C8	C21	C5	120.4(3)
C3	C10	C7	116.2(4)	N19	C22	C23	127.9(4)
C3	C10	C5	123.0(3)	C22	C23	C17	116.3(4)
C7	C10	C5	120.8(4)	C22	C23	C11	123.6(4)
C23	C11	C24	120.9(4)	C17	C23	C11	120.1(4)
N4	C12	C16	122.0(3)	C11	C24	C28	119.3(4)
N4	C12	N19	116.1(3)	C16	C25	N20	124.4(3)
C16	C12	N19	121.9(3)	N20	C26	N4	126.0(3)
C7	C13	C1	120.9(3)	N20	C26	N31	114.6(3)
C7	C13	C14	123.2(4)	N4	C26	N31	119.4(3)
C1	C13	C14	116.0(3)	C17	C27	C28	119.7(4)
C13	C14	N6	122.8(4)	C24	C28	C27	121.2(4)

Co-system 1•2

Table S7 Crystal data and structure refinement for **Co-system 1•2**

Identification code	BB-C-1b
Empirical formula	$C_{23}H_{24}N_8S$
Formula weight	444.56
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.2112(6)
b/Å	4.9417(2)
c/Å	32.3534(12)
α/°	90
β/°	90.456(4)
γ/°	90
Volume/Å^3	2112.13(15)
Z	4
ρ_{calc}g/cm^3	1.398
μ/mm^{-1}	1.598
F(000)	936.0
Crystal size/mm^3	0.271 × 0.061 × 0.058
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.464 to 133.194
Index ranges	$-15 \leq h \leq 15$, $-5 \leq k \leq 5$, $-38 \leq l \leq 26$
Reflections collected	7285

Independent reflections	3528 [R_{int} = 0.0409, R_{sigma} = 0.0520]
Data/restraints/parameters	3528/0/309
Goodness-of-fit on F^2	1.010
Final R indexes [I>=2σ (I)]	R_1 = 0.0393, wR_2 = 0.0855
Final R indexes [all data]	R_1 = 0.0587, wR_2 = 0.0945
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.22

Table S8 Bond Lengths for **Co-system 1•2**

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
S1	C5	1.692(2)	C18	C19	1.411(3)
N4	C6	1.356(3)	C18	C23	1.411(3)
N4	C7	1.380(3)	C18	C17	1.425(3)
N5	C16	1.383(3)	C7	C8	1.411(3)
N5	C17	1.308(3)	C7	C12	1.391(3)
N3	C6	1.325(3)	C15	C19	1.435(3)
N3	C8	1.398(3)	C9	C8	1.388(3)
N6	C13	1.342(3)	C9	C10	1.388(3)
N6	C16	1.346(3)	C22	C23	1.372(3)
N2	C6	1.378(3)	C22	C21	1.410(3)
N2	C5	1.371(3)	C11	C10	1.401(3)
N7	C13	1.337(3)	C11	C12	1.389(3)
N8	C13	1.378(3)	C19	C20	1.413(3)
N8	C14	1.315(3)	C20	C21	1.376(3)
N1	C5	1.327(3)	C4	C3	1.521(3)
N1	C4	1.461(3)	C3	C2	1.523(3)
C14	C15	1.404(3)	C2	C1	1.526(3)
C16	C15	1.412(3)			

Table S9 Bond Angles for **Co-system 1•2**

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C6	N4	C7	106.44(17)	C14	C15	C19	124.98(19)
C17	N5	C16	117.94(18)	C16	C15	C19	119.82(19)
C6	N3	C8	103.72(17)	C10	C9	C8	118.05(19)
C13	N6	C16	116.14(18)	C23	C22	C21	118.9(2)
C5	N2	C6	127.20(19)	N3	C8	C7	109.79(17)
C14	N8	C13	116.37(18)	C9	C8	N3	130.36(19)
C5	N1	C4	122.72(18)	C9	C8	C7	119.85(19)
N6	C13	N8	125.65(19)	N2	C5	S1	119.27(16)
N7	C13	N6	119.27(19)	N1	C5	S1	123.51(16)

N7	C13	N8	115.08(19)	N1	C5	N2	117.21(19)
N8	C14	C15	123.63(19)	C12	C11	C10	121.3(2)
N5	C16	C15	121.59(19)	C18	C19	C15	117.22(19)
N6	C16	N5	115.43(18)	C18	C19	C20	118.28(19)
N6	C16	C15	122.98(19)	C20	C19	C15	124.49(19)
N4	C6	N2	119.10(18)	C21	C20	C19	120.1(2)
N3	C6	N4	114.49(18)	C22	C23	C18	120.6(2)
N3	C6	N2	126.39(19)	N5	C17	C18	125.40(19)
C19	C18	C17	117.98(19)	N1	C4	C3	110.72(17)
C23	C18	C19	120.41(19)	C9	C10	C11	121.57(19)
C23	C18	C17	121.60(19)	C11	C12	C7	116.8(2)
N4	C7	C8	105.56(18)	C4	C3	C2	111.93(17)
N4	C7	C12	132.0(2)	C20	C21	C22	121.7(2)
C12	C7	C8	122.45(19)	C3	C2	C1	113.01(18)
C14	C15	C16	115.19(19)				

Co-system 1•3

Table S10 Crystal data and structure refinement for **Co-system 1•3**

Identification code	BBalo_43-135_NV-ref
Empirical formula	$C_{31}H_{27}N_7S$
Formula weight	529.65
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.23003(11)
b/Å	26.3191(4)
c/Å	13.59163(19)
α/°	90
β/°	91.7138(14)
γ/°	90
Volume/Å^3	2585.17(6)
Z	4
ρ_{calc}g/cm^3	1.361
μ/mm^{-1}	1.390
F(000)	1112.0
Crystal size/mm^3	0.211 × 0.074 × 0.072
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.716 to 146.052
Index ranges	$-8 \leq h \leq 8$, $-32 \leq k \leq 32$, $-16 \leq l \leq 12$

Reflections collected	18595
Independent reflections	5083 [R_{int} = 0.0495, R_{sigma} = 0.0362]
Data/restraints/parameters	5083/0/460
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0476, wR_2 = 0.1276
Final R indexes [all data]	R_1 = 0.0510, wR_2 = 0.1321
Largest diff. peak/hole / e $Å^{-3}$	0.54/-0.28

Table S11 Bond Lengths for **Co-system 1•3**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C24	1.6919(16)	C18	C17	1.407(2)
N2	C12	1.339(2)	C18	C19	1.440(2)
N2	C9	1.334(2)	C7	C2	1.411(2)
N6	C25	1.322(2)	C7	C6	1.405(2)
N6	C26	1.395(2)	N1	C9	1.388(2)
N4	C24	1.326(2)	N1	C1	1.292(2)
N4	C23	1.454(2)	C21	C22	1.527(2)
N5	C25	1.380(2)	C21	C20	1.526(2)
N5	C24	1.377(2)	C17	C16	1.378(3)
N3	C12	1.382(2)	C2	C3	1.401(2)
N3	C19	1.301(2)	C2	C1	1.440(2)
N7	C25	1.360(2)	C11	C10	1.391(2)
N7	C27	1.389(2)	C16	C15	1.397(3)
C12	C11	1.428(2)	C29	C30	1.403(2)
C8	C7	1.450(2)	C6	C5	1.378(2)
C8	C10	1.394(2)	C30	C31	1.387(2)
C8	C9	1.424(2)	C3	C4	1.374(3)
C13	C18	1.409(2)	C26	C31	1.396(2)
C13	C11	1.454(2)	C26	C27	1.404(2)
C13	C14	1.405(2)	C5	C4	1.407(3)
C28	C29	1.386(2)	C14	C15	1.383(2)
C28	C27	1.391(2)	C23	C22	1.519(2)

Table S12 Bond Angles for **Co-system 1•3**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	N2	C12	119.50(13)	C7	C2	C1	118.24(14)
C25	N6	C26	103.83(12)	C3	C2	C7	120.45(15)
C24	N4	C23	124.08(14)	C3	C2	C1	121.28(15)

C24	N5	C25	126.91(14)	C12	C11	C13	118.16(14)
C19	N3	C12	117.62(14)	C10	C11	C12	117.13(14)
C25	N7	C27	106.15(13)	C10	C11	C13	124.71(14)
N2	C12	N3	114.41(13)	C17	C16	C15	120.23(15)
N2	C12	C11	122.40(14)	C11	C10	C8	121.16(14)
N3	C12	C11	123.18(14)	N3	C19	C18	125.05(15)
N6	C25	N5	126.08(14)	C28	C29	C30	121.69(15)
N6	C25	N7	114.40(13)	C5	C6	C7	120.33(16)
N7	C25	N5	119.51(14)	C31	C30	C29	121.11(15)
C10	C8	C7	124.60(14)	C4	C3	C2	120.15(16)
C10	C8	C9	116.97(14)	N2	C9	C8	122.84(14)
C9	C8	C7	118.40(14)	N2	C9	N1	114.07(13)
C18	C13	C11	117.03(14)	N1	C9	C8	123.09(14)
C14	C13	C18	118.89(14)	N6	C26	C31	129.90(14)
C14	C13	C11	124.08(14)	N6	C26	C27	110.26(13)
N4	C24	S1	124.15(12)	C31	C26	C27	119.85(14)
N4	C24	N5	117.51(14)	C6	C5	C4	120.71(16)
N5	C24	S1	118.34(12)	C15	C14	C13	119.98(15)
C29	C28	C27	116.69(14)	C30	C31	C26	118.11(14)
C13	C18	C19	118.95(14)	N1	C1	C2	125.95(14)
C17	C18	C13	120.44(15)	N4	C23	C22	111.32(13)
C17	C18	C19	120.60(15)	C23	C22	C21	110.87(13)
C2	C7	C8	117.14(14)	C14	C15	C16	120.84(16)
C6	C7	C8	124.31(14)	C3	C4	C5	119.75(16)
C6	C7	C2	118.53(15)	N7	C27	C28	132.09(14)
C1	N1	C9	117.13(13)	N7	C27	C26	105.35(13)
C20	C21	C22	112.74(13)	C28	C27	C26	122.55(14)
C16	C17	C18	119.61(15)				

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