

Elucidation of Charge Contribution in Iridium-Chelated Hydrogen-Bonding Systems

Barbora Balónová, Barry A. Blight*

^aDepartment of Chemistry, University of New Brunswick, Fredericton, Canada E3B 5A3

Supplementary Material

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S1: Synthetic Procedures and Characterization Data

Synthesis of complex 1H+

Iridium dimer complex $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ ^[S1] (68 mg, 6.4×10^{-5} mol) and 1-(1H benzo[d]imidazol-2-yl)-3-butylguanidine^[S2] (2.5 equiv.) were added to 15 mL of dry toluene. The reaction mixture was refluxed for 24 h under N_2 atmosphere. The reaction was cooled and a saturated solution of NH_4PF_6 in MeOH was added in excess while stirring (~2 mL). The reaction mixture was stirred overnight at room temperature and the solvent was removed under reduced pressure. The sample was dissolved in DCM and extracted with water (2 x 20 mL) to remove the excess of NH_4PF_6 . Further purification included column chromatography (silica gel, DCM: MeOH, 20:1). The title compound **1H+** was obtained as yellow powder in 59% yield.

¹H NMR (400 MHz, 298 K, CDCl_3): δ 9.38 (s, 1H), 8.61 (d, $J = 5.3$ Hz, 1H), 8.23 (s, 1H), 8.09 (d, $J = 5.7$ Hz, 1H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.84 – 7.76 (m, 2H), 7.72 (dd, $J = 7.4, 1.1$ Hz, 1H), 7.61 (t, $J = 7.4$ Hz, 2H), 7.26 (s, 1H), 7.24 (s, 1H), 7.18 – 7.13 (m, 1H), 7.08 – 7.02 (m, 2H), 6.95 (dt, $J = 10.6, 7.3$ Hz, 2H), 6.86 – 6.70 (m, 3H), 6.40 (d, $J = 7.4$ Hz, 1H), 6.19 (t, $J = 8.0$ Hz, 2H), 5.36 (t, $J = 4.9$ Hz, 1H), 4.79 (s, 1H), 3.00–2.84 (m, 2H), 1.47–1.43 (m, 2H), 1.26–1.23 (m, 2H), 0.82 (t, $J = 7.3$ Hz, 3H).

¹³C NMR (100 MHz, 298K, CDCl_3): δ 169.02, 168.06, 151.55, 149.80, 149.27, 148.57, 144.48, 144.23, 143.76, 140.19, 137.33, 132.90, 131.98, 131.05, 129.99, 124.72, 124.26, 123.46, 123.01, 122.26, 122.13, 121.65, 119.15, 117.77, 110.83, 77.16, 41.17, 30.36, 19.83, 13.72.

³¹P NMR (162 MHz, CDCl_3) δ -132.49, -134.32, -138.74, -143.16, -147.58, -152.00, -154.26.

EI-MS m/z calcd.: 732.24, **Found:** 732.2438.

Anal. calcd. for $\text{C}_{34}\text{H}_{33}\text{F}_6\text{IrN}_7\text{P}$: C, 46.57; H, 3.59; N, 11.18. **Found:** C, 46.43; H, 3.59; N, 11.31.

Synthesis of complex 2H+

Iridium dimer complex $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ ^[S1] (202 mg, 3.77×10^{-4} mol) and 1 (1Hbenzo[d]imidazol-2-yl)-3-butylthiourea^[S3] (116 mg, 0.471 mmol) were added in ~ 15 mL of dry toluene. Nitrogen was bubbled through the mixture for 15 min then the reaction was heated to reflux for 24 h and then cooled to room temperature. Solvent was removed under reduced pressure and the sample was re-dissolved in dichloromethane and saturated solution of KPF_6 (~10 equiv. in MeOH) was added dropwise while stirring. Total volume added ~ 3 mL. The solution was stirred for 21 h at room temperature and then extracted with dichloromethane and water, organic phases were combined, dried over magnesium sulfate and solvent was removed under reduced pressure. The product (yellow powder) was dried on Schlenk line under vacuum for 24 h. TLC control revealed one bright spot for product ($R_f = 0.53$, DCM: MeOH, 10:0.5). The product was further purified through precipitation from solvent mixture of dichloromethane and hexane

and dried in vacuum for 48 h. The final product **2H⁺** was obtained as a yellow powder in 47% yield.

¹H NMR (400 MHz, 298K, CDCl₃) δ (ppm): 9.50 (bs, 1H), 9.14 (d, 1H), 8.18 (d, 1H), 7.96 (d, 1H), 7.83-7.71 (m, *J* = 24.9 Hz, 3H), 7.64-7.55 (m, *J* = 29.5 Hz, 2H), 7.34 (bs, 1H), 7.16 (m, 1H), 7.07 (m, 2H), 6.97-6.91 (m, 2H), 6.86 (t, 1H), 6.81-6.74 (m, 2H), 6.53 (d, 1H), 6.36 (d, 1H), 6.21 (d, 1H), 3.49 (m, 2H), 1.59 (m, 2H), 1.32 (m, 2H), 0.90 (t, 3H).

¹³C NMR (101 MHz, 298K, CDCl₃) δ (ppm): 172.73, 168.77, 168.13, 153.65, 150.39, 150.07, 145.88, 143.81, 140.46, 137.70, 137.43, 131.89, 131.67, 130.97, 130.19, 130.15, 124.72, 124.38, 124.12, 123.33, 122.71, 122.65, 122.51, 122.21, 119.57, 119.36, 118.57, 111.08, 77.36, 45.99, 30.15, 19.92, 13.73.

³¹P NMR (121 MHz, CDCl₃) δ (ppm): -148.30, -154.62, -160.51, -166.40, -172.57.

HRMS *m/z* calcd.: 749.2033. **Found:** 749.2028 [*M*⁺].

Anal. calcd. for C₃₄H₃₂F₆IrN₆SP: C, 46.45; H, 3.55; N, 9.29. **Found:** C, 46.03; H, 3.63; N, 9.49.

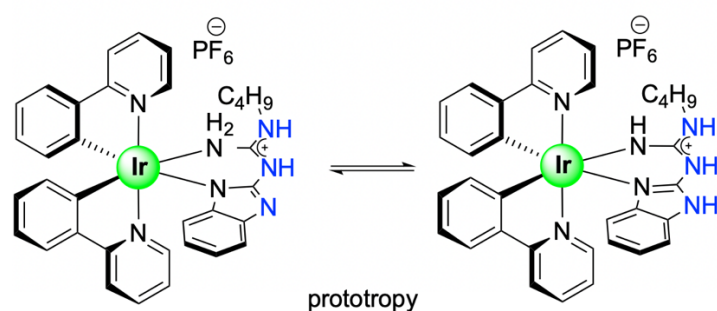


Figure S1. Illustrating prototropy of **1H⁺** where the H-bonding arrays can equilibrate between a ADD and DDD array.

S2: Copies of ^1H and ^{13}C NMR and Mass Spectra

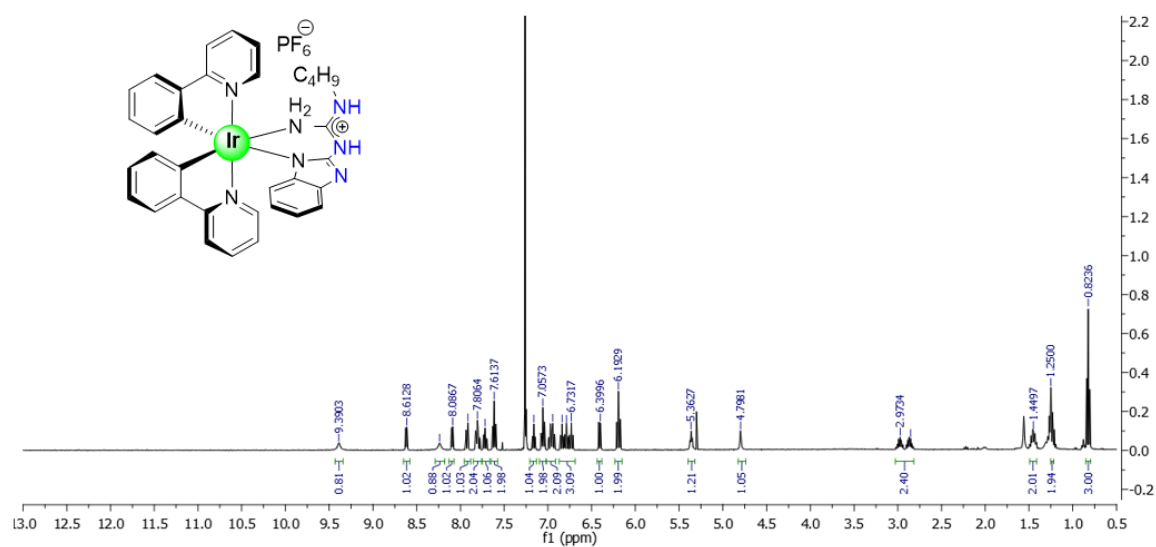


Figure S2. ^1H (400 MHz) NMR spectrum of 1H^+ in chloroform- d , 298 K.

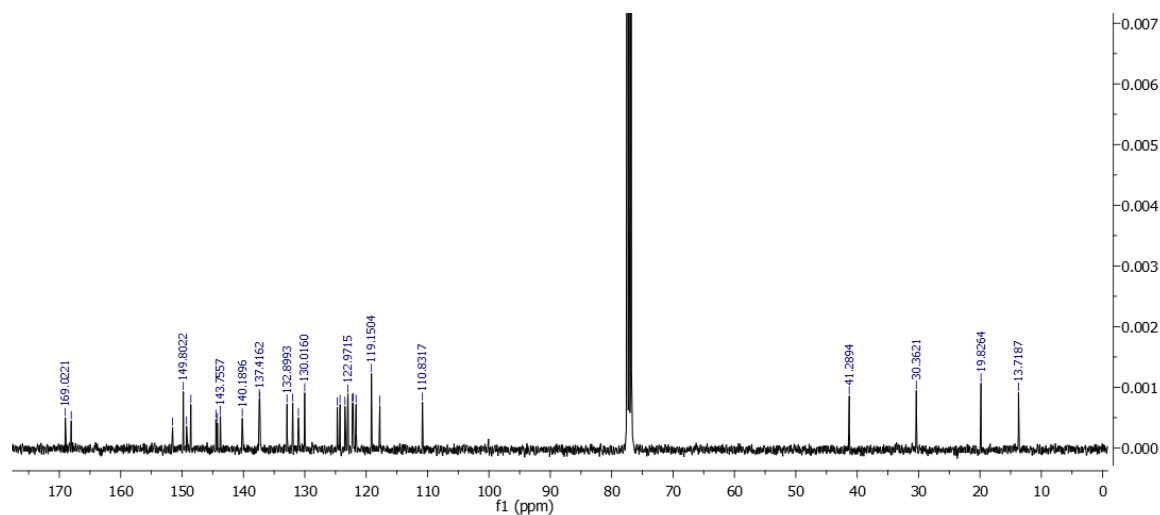


Figure S3. ^{13}C (100 MHz) NMR spectrum of 1H^+ in chloroform- d , 298 K.

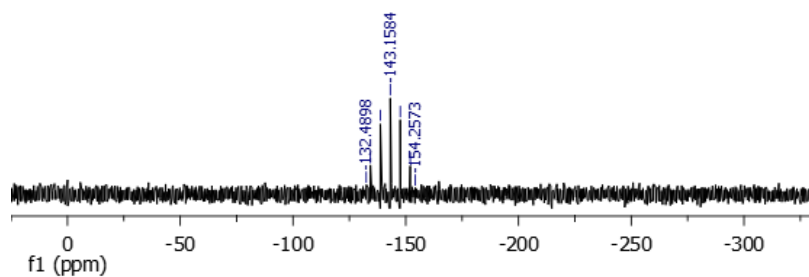


Figure S4. ^{31}P (162 MHz) NMR spectrum of 1H^+ in chloroform- d , 298 K.

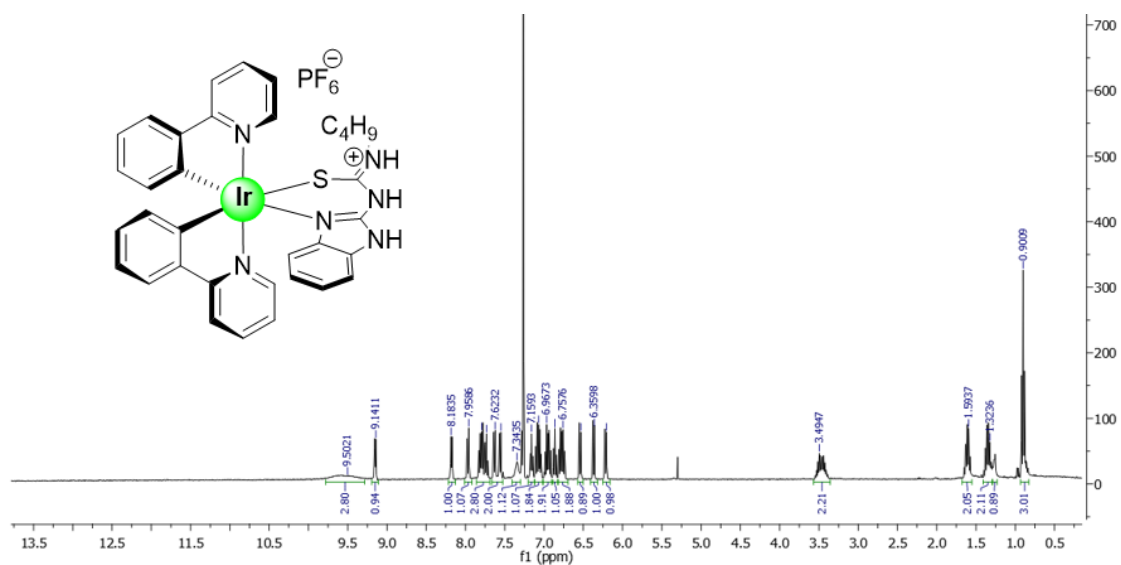


Figure S5. ^1H (400 MHz) NMR spectrum of 2H^+ in chloroform- d , 298 K.

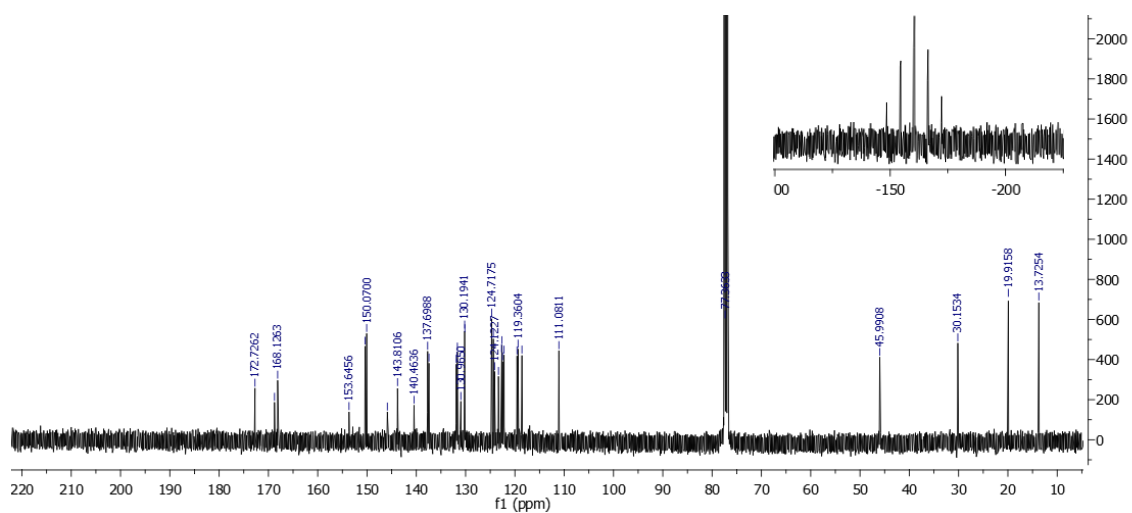


Figure S6. ^{13}C (100 MHz) NMR spectrum with inset of ^{31}P NMR spectrum (top right corner) of 2H^+ measured in chloroform- d .

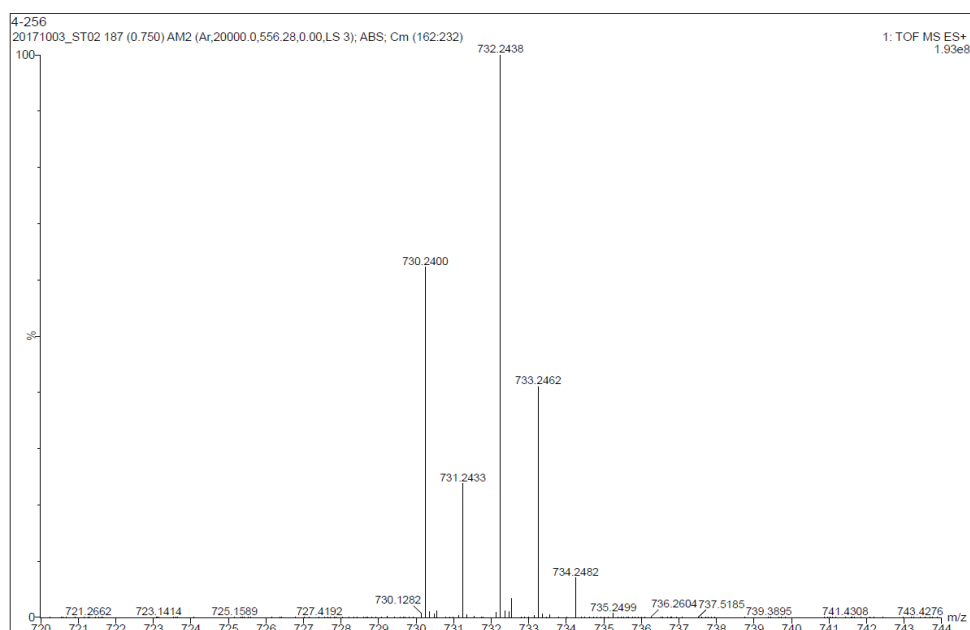


Figure S7. Mass spectrum of iridium complex $1H^+$.

Analysis Info				Acquisition Date		12/3/2018 10:15:26 AM	
Analysis Name	D:\Data\Xiao\Dec 03 2018\000021.d			Operator	Administrator	57	
Method	Xiao 1.m						
Sample Name	393						
Comment							
Acquisition Parameter							
Source Type	ESI	Ion Polarity	Positive	Set Corrector Fill	45 V		
Scan Range	n/a	Capillary Exit	100.0 V	Set Pulsar Pull	400 V		
Scan Begin	50 m/z	Hexapole RF	135.0 V	Set Pulsar Push	400 V		
Scan End	1500 m/z	Skimmer 1	50.0 V	Set Reflector	1300 V		
		Hexapole 1	22.5 V	Set Flight Tube	9000 V		
				Set Detector TOF	2200 V		
Sum Formula		Sigma	m/z	Err (ppm)	Mean Err (ppm)	rdB	N Rule
C 34 H 32 Ir 1 N 6 S 1		0.13	749.2033	0.65	0.74	22.50	ok even

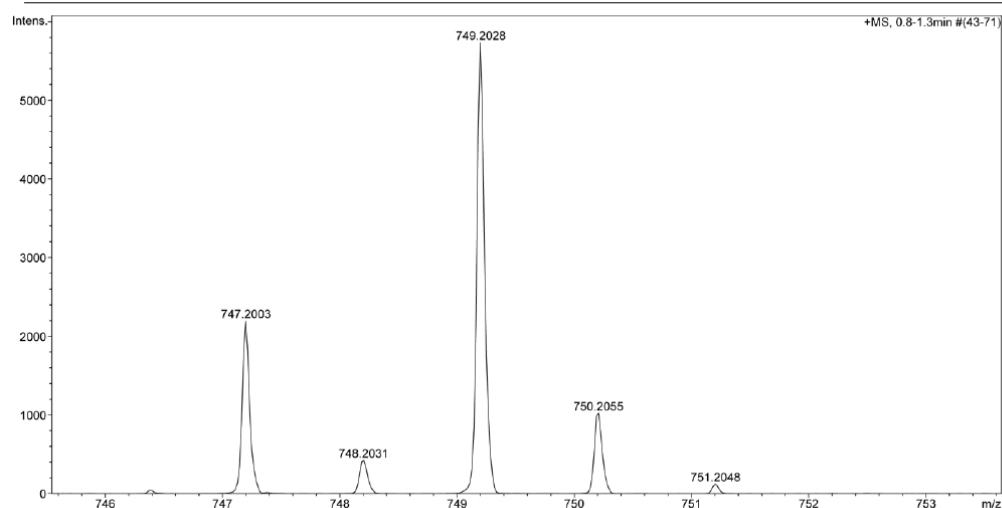


Figure S8. Mass spectrum of iridium complex $2H^+$.

S3: Elemental Analysis


 LONDON
 metropolitan
 university
Elemental Analysis Service

Please send completed form and samples to:

Stephen Boyer
 School of Human Sciences
 Science Centre
 London Metropolitan University
 29 Homsay Road
 London N7 7DD
 Telephone: 020 7133 3605
 Fax: 020 7133 2577
 Email: s.boyer@londonmet.ac.uk

Sample submitted by: <i>San Thoms</i>	
Address: <i>Ingram Building, University of Kent, Canterbury, CT2 7NH</i>	
Telephone: <i>01227 813669</i>	Email: <i>SJT51@kent.ac.uk</i>
Date Submitted: <i>15-Aug-17</i>	

Please submit ca. 5 mg of sample.

Sample Reference No.: <i>4-456</i>	
Name of Compound: <i>(pp4)2 Ir-guan⁺ PF₆⁻</i>	
Molecular Formula: <i>C₃₄H₃₃F₆IrN₇P</i>	
Stability: <i>air stable</i>	
Hazards: <i>irritant</i>	
Other Remarks:	

Element	Expected %	Found (1)	Found (2)
Carbon	<i>46.57</i>	<i>46.39</i>	<i>46.46</i>
Hydrogen	<i>3.79</i>	<i>3.54</i>	<i>3.63</i>
Nitrogen	<i>11.12</i>	<i>11.29</i>	<i>11.33</i>

Authorising Signature:

Date Completed: <i>22/07/17</i>	Signature: <i>[Signature]</i>
Comments:	

Figure S9. Copy of elemental analysis for compound **1H⁺**. Expected values highlighted in red, measured in blue.

CHN Analyzer, Perkin Elmer 2400 Series II

User's Name Barbora Balonova
 Analyzed by: Patricia Granados
 Date: 05-Dec-18
 Standard Calibration Acetanilide
 Supplier Perkin Elmer

Expected Values	Carbon %	Hydrogen %	Nitrogen %
QC:Cyclohexanone-2,4-dinitro-phenylhydrazone	51.79	5.07	20.14
BB387	78.51	4.76	5.09
BB393	46.46	3.55	9.29

Quality Control Standard Results

Sample Name	Weight mg	Carbon %	Hydrogen %	Nitrogen %
QC	3.363	52.09	5.08	20.16
	3.368	51.62	4.97	20.06

Sample Results

Sample Name	Weight mg	Carbon %	Hydrogen %	Nitrogen %
BB387	3.169	78.26	4.67	5.08
BB387b	2.700	78.29	4.58	5.08
BB393	2.787	46.16	3.66	9.49
BB393b	2.553	45.90	3.59	9.49

Figure S10. Copy of elemental analysis for compound **2H⁺**. Expected values highlighted in red, measured in blue (sample name BB393).

S4: NMR Data

^1H NMR titrations were performed in solutions of $\text{CDCl}_3/\text{DMSO-}d_6$ (99:1) with small aliquots of guest (**3** or **4**) added to host (**1**, 1H^+ , **2**, or 2H^+). Bindfit modelling was only applied to $2\text{H}^+\cdot\mathbf{4}$ because of complex precipitation as the titrations concluded. UV-Vis titrations were then performed at lower concentrations to remedy this problem.

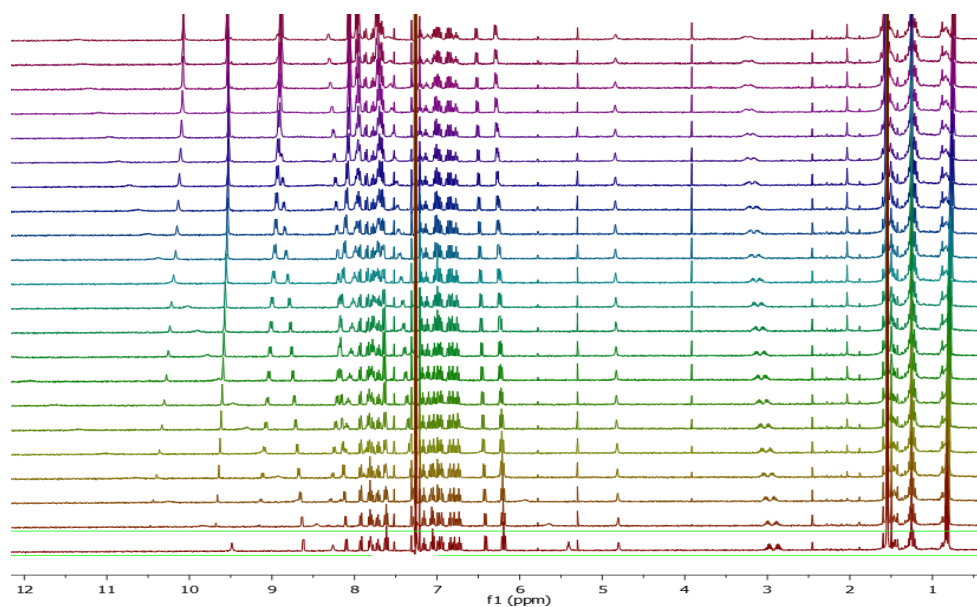


Figure S11. Stacked ^1H NMR (400 MHz, 298 K) from titration experiment for co-system $1\text{H}^+\cdot\mathbf{4}$ in $\text{CDCl}_3/\text{DMSO-}d_6$ (99:1).

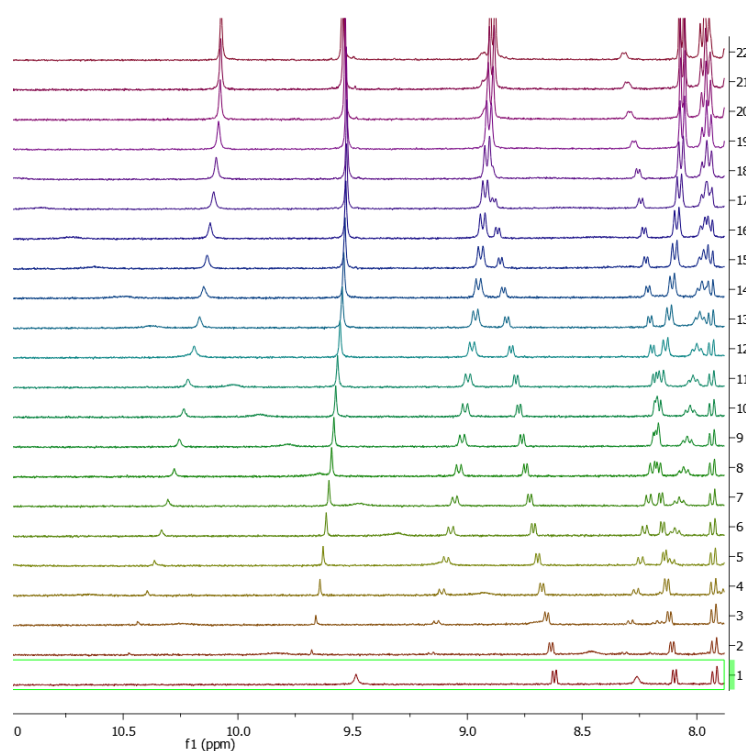


Figure S12. Stacked ^1H NMR (400 MHz, 298 K), expanded into the aromatic region from titration experiment for co-system $1\text{H}^+\bullet 4$ in $\text{CDCl}_3/\text{DMSO-}d_6$ (99:1).

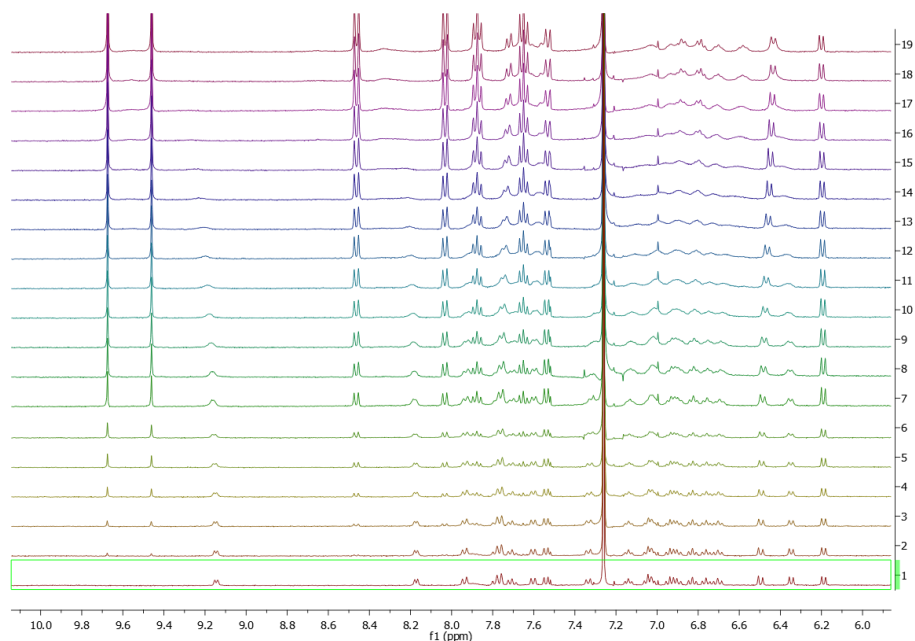


Figure S13. Stacked ^1H NMR (400 MHz, 298 K), expanded, from titration experiment for co-system $2\text{H}^+\bullet 3$ in $\text{CDCl}_3/\text{DMSO-}d_6$ (99:1).

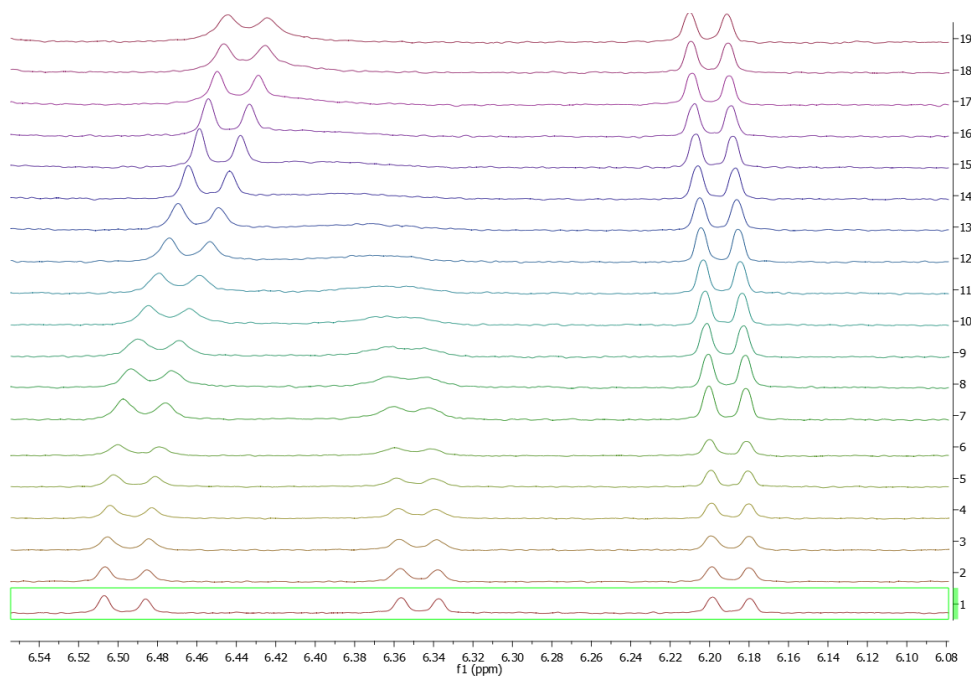


Figure S14. Stacked ^1H NMR (400 MHz, 298 K), expanded into 6.0-6.5 ppm, from titration experiment for co-system $2\text{H}^+\bullet 3$ in $\text{CDCl}_3/\text{DMSO-}d_6$ (99:1).

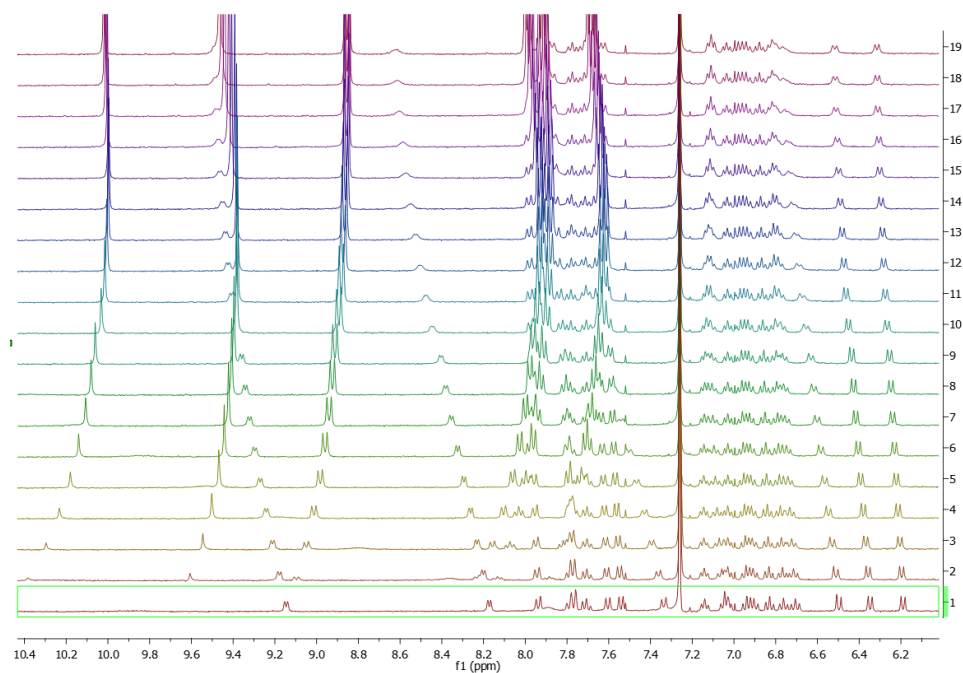


Figure S15. Stacked ^1H NMR (400 MHz, 298 K), zoomed in, from titration experiment for co-system $2\text{H}^+\bullet 4$ in $\text{CDCl}_3/\text{DMSO-}d_6$ (99:1).

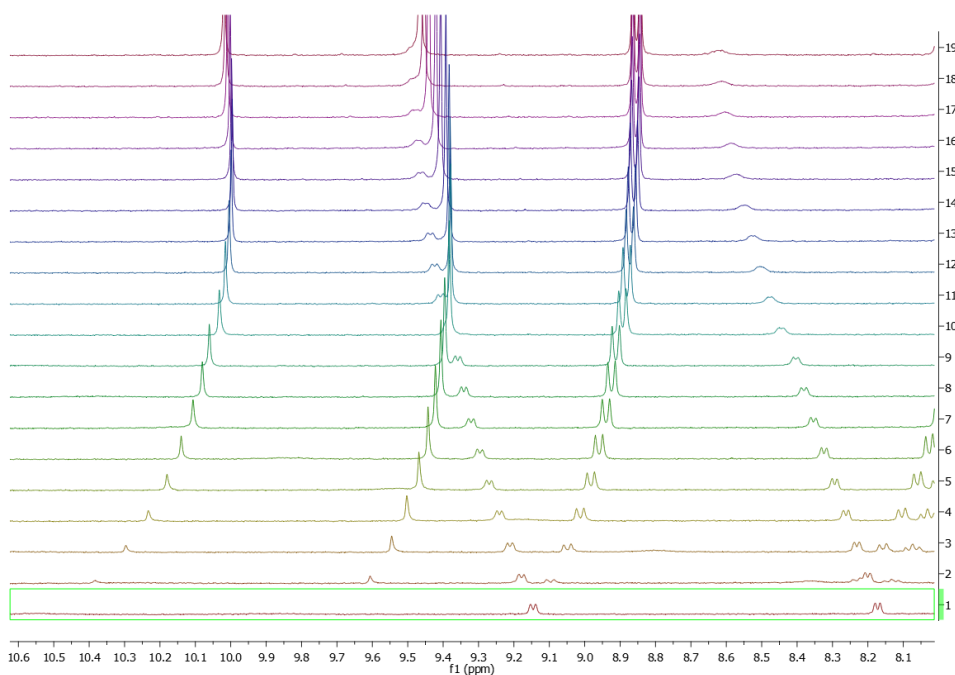


Figure S16. Stacked ^1H NMR (400 MHz, 298 K), expanded from 8.0-10.5 ppm, from titration experiment for co-system $2\text{H}^+\bullet 4$ in $\text{CDCl}_3/\text{DMSO-}d_6$ (99:1).

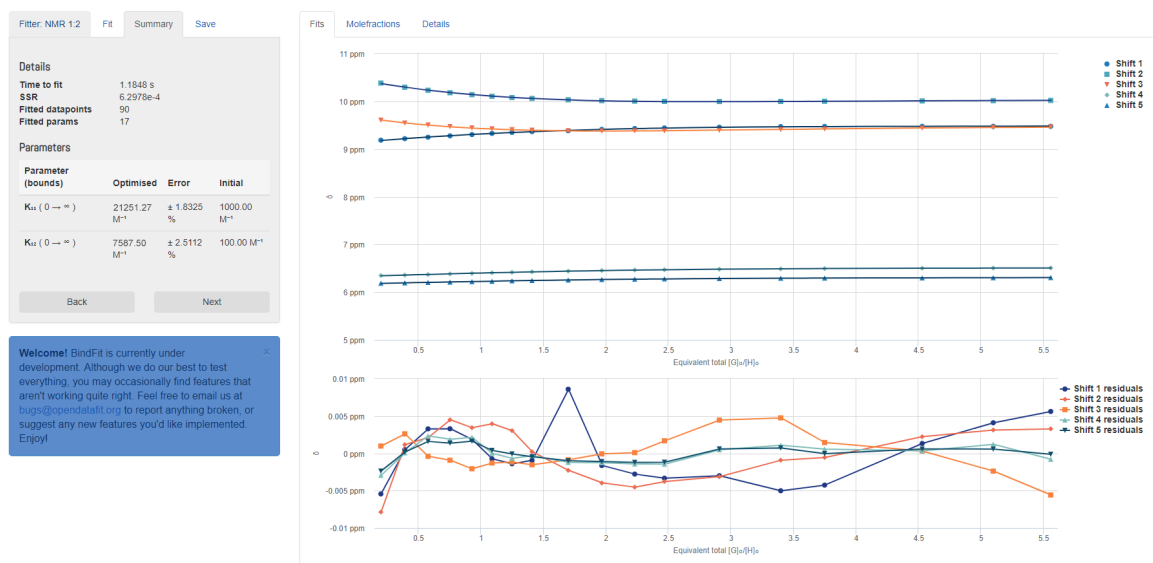


Figure S17. Results from the ^1H NMR titration studies of co-system $2\text{H}^+\cdot\mathbf{4}$ in $\text{CDCl}_3/\text{DMSO-}d_6$ (99:1).

$$K_{11}=2.1 \times 10^4 \text{ M}^{-1} \pm 1.8\% \quad K_{12}=7.6 \times 10^3 \text{ M}^{-1} \pm 2.5\%$$

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

S4: UV-vis Absorption Data

UV-Vis absorption spectroscopy titrations were performed in solutions of $\text{CHCl}_3/\text{DMSO}$ (99:1) with small aliquots of guest (**3** or **4**) added to host (**1**, **1H⁺**, **2**, or **2H⁺**). Bindfit modelling was performed on all systems. Each system was evaluated for the best 1:1 and 1:1/1:2 binding models based on percent error, the quality of the fitted data, and the randomness of the residual data (versus systematic error). Complexes **1•3** and **1H⁺•3** illustrated higher error than acceptable and as such this data was alternatively treated SIVVU modelling which gave a better fit. The output were comparable to the Bindfit results but R^2 was much more accurate. We furthermore included 1:2 binding models because these types of systems have been reported in the past.^[S4] We have also included an example of a potential 1:2 binding geometry (Below, fig S18).

Binding models were refined using <http://app.supramolecular.org/bindfit/> and <http://sivvu.org>

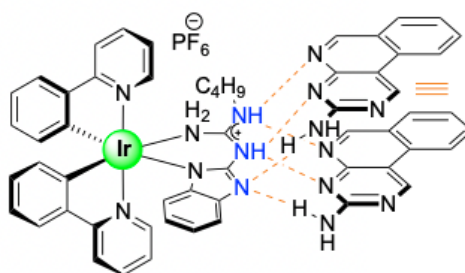


Figure S18. Proposed 1:2 intermolecular association geometry, in which **1H⁺** vertically bifurcates 2 molecules of **3** which are pi-stacking.

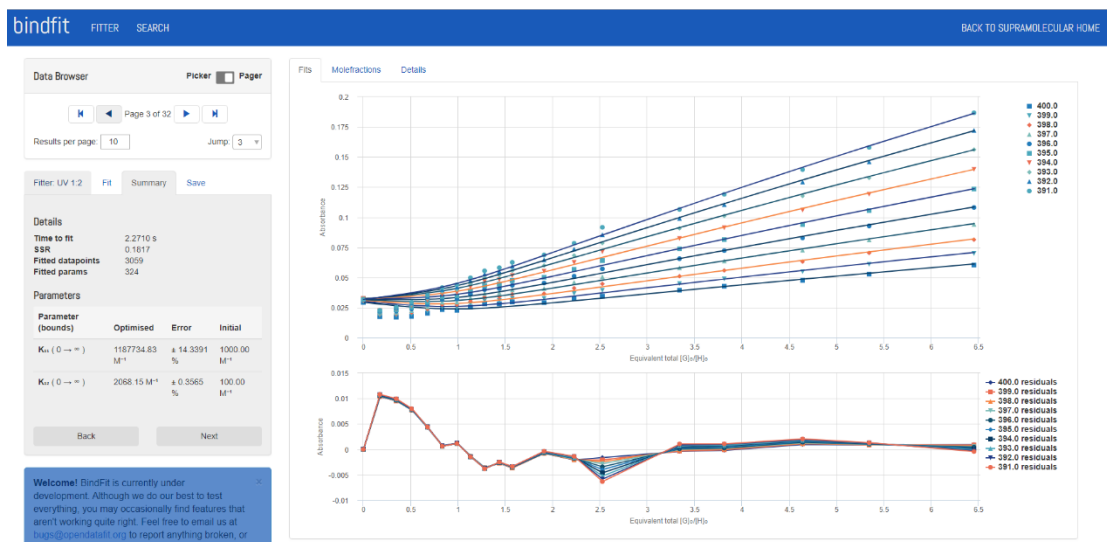


Figure S19. Results from the UV-vis absorption titration studies of co-system $1H^+ \bullet 3$ in $CHCl_3/DMSO$ (99:1).

$$K_{11} = 1.1 \times 10^6 M^{-1} \pm 14\% \quad K_{12} = 2.1 \times 10^3 M^{-1} \pm 0.4\%$$

Link to BindFit: <http://app.supramolecular.org/bindfit/view/7b10c11e-0d5f-4a6a-ba21-ffd1ca095ae9>

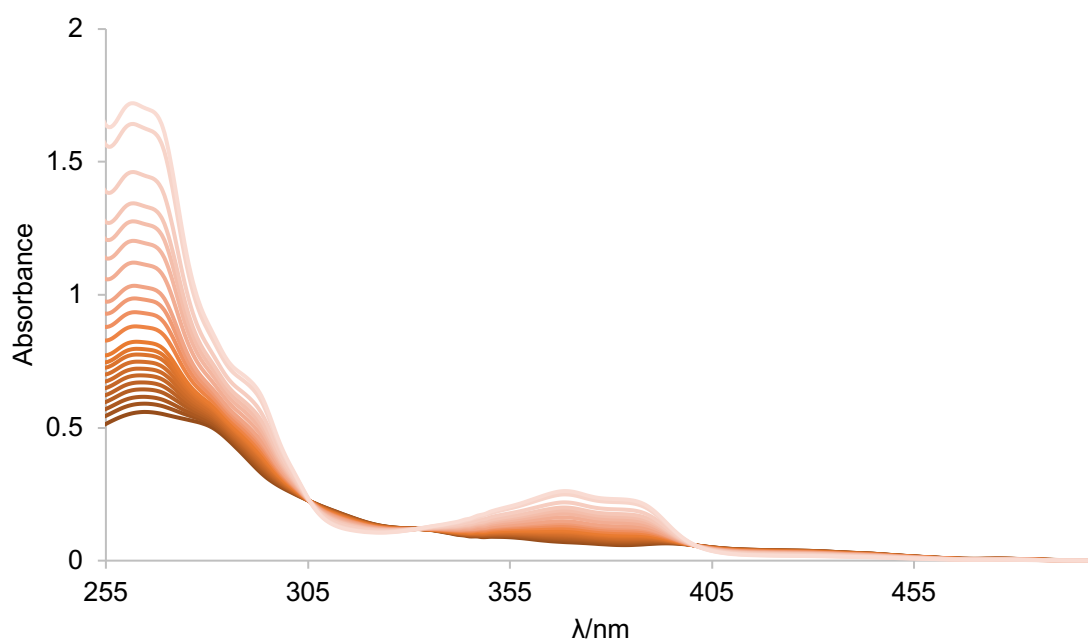


Figure S20. Results from the UV-vis absorption titration studies of co-system $1H^+ \bullet 3$ in $CHCl_3/DMSO$ (99:1).



Figure S21. Results from the UV-vis absorption titration studies of co-system $1H^+ \cdot 3$ in $CHCl_3/DMSO$ (99:1) modelled using SIVVU.org with better fit.

Calculated constants from modelled energies:

$$K_{I1} = 1.9 \times 10^6 \text{ M}^{-1} \quad K_{I2} = 3.4 \times 10^4 \text{ M}$$

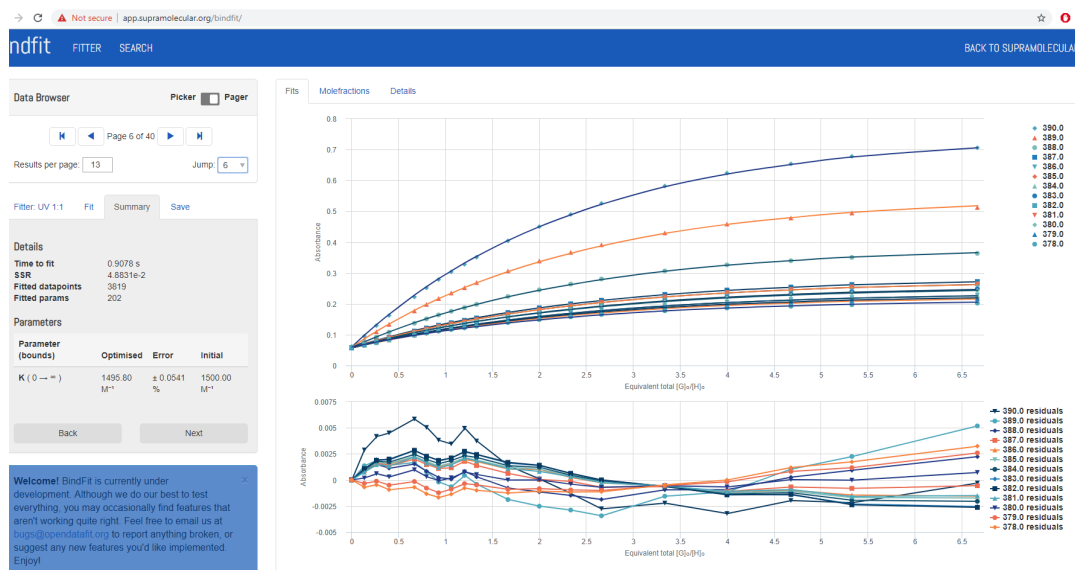


Figure S22. Results from the UV-vis absorption titration studies of co-system **1H⁺•4** in CHCl₃/DMSO (99:1).

$$K_a = 1.5 \times 10^3 \text{ M}^{-1} \pm 0.05\%$$

Link to BindFit: <http://app.supramolecular.org/bindfit/view/94dd3175-1285-4c8b-8599-a14ee7114fb2>

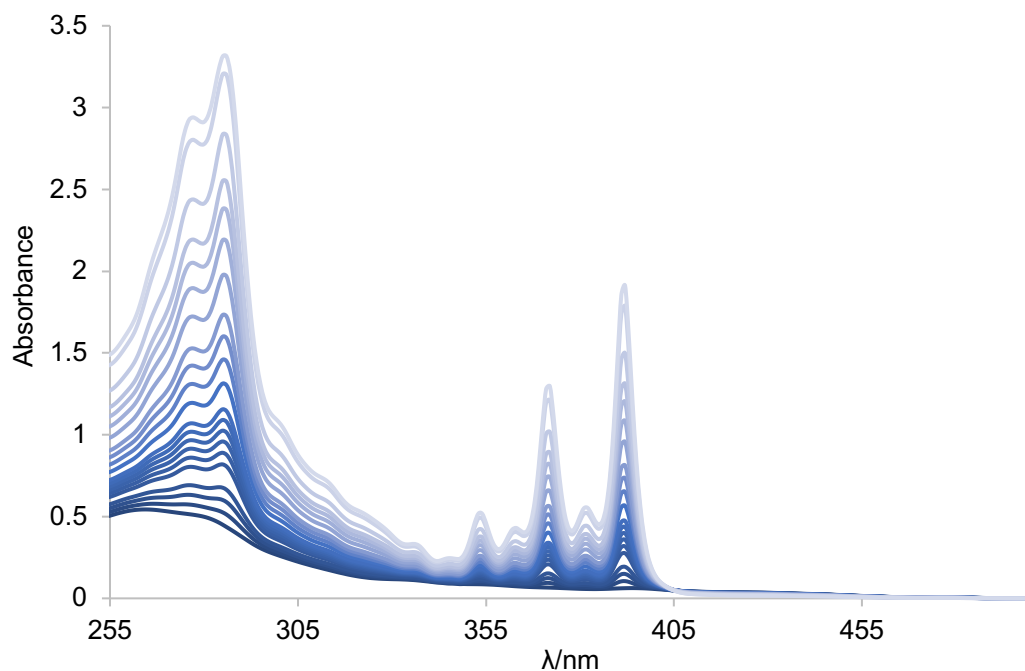


Figure S23. Results from the UV-vis absorption titration studies of co-system **1H⁺•4** in CHCl₃/DMSO (99:1).

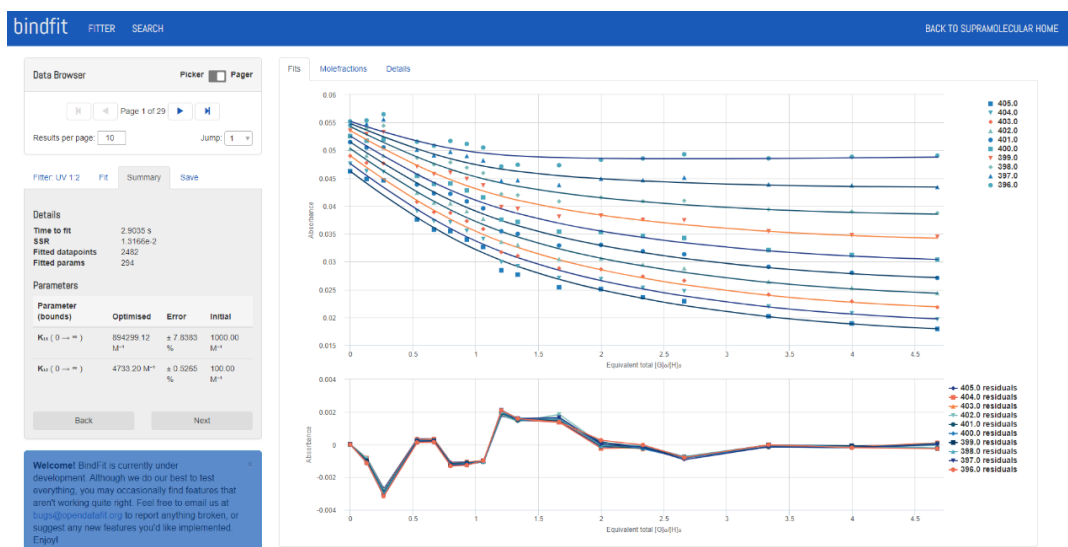


Figure S24. Results from the UV-vis absorption titration studies of co-system **1•3** in $CHCl_3/DMSO$ (99:1).

$$K_{11} = 8.9 \times 10^5 M^{-1} \pm 7.8\% \quad K_{12} = 4.7 \times 10^3 M^{-1} \pm 0.8\%$$

Link to BindFit: <http://app.supramolecular.org/bindfit/view/d25c5763-b8c6-444f-bcf2-cfb13b67b230>

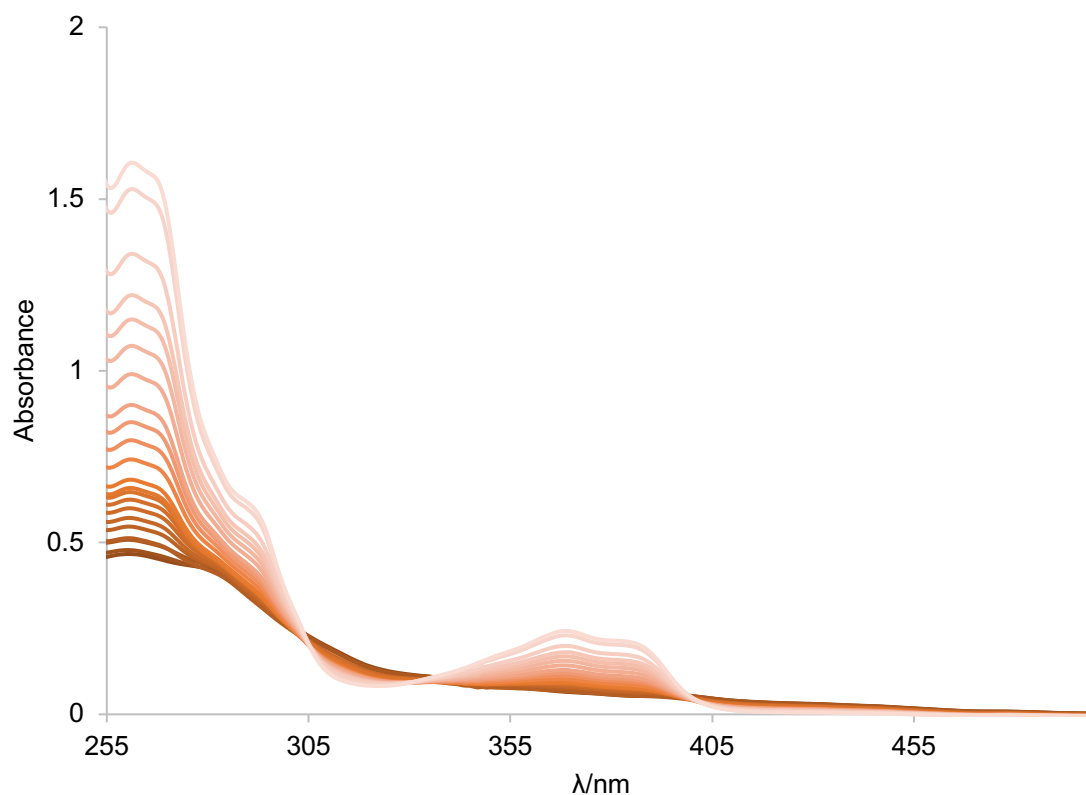


Figure S25. Results from the UV-vis absorption titration studies of co-system **1•3** in $CHCl_3/DMSO$ (99:1).



Figure S26. Results from the UV-vis absorption titration studies of co-system **1•3** in $\text{CHCl}_3/\text{DMSO}$ (99:1) modelled using SIVVU.org with better fit.

Calculated constants from modelled energies:

$$K_{I1} = 9.1 \times 10^5 \text{ M}^{-1} \quad K_{I2} = 3.2 \times 10^4 \text{ M}^{-1}$$

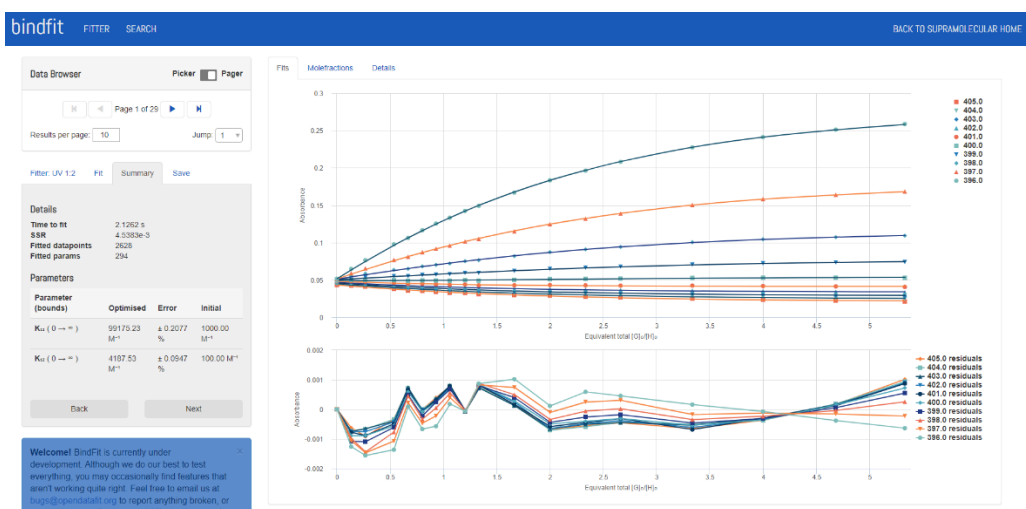


Figure S27. Results from the UV-vis absorption titration studies of co-system **1•4** in $CHCl_3/DMSO$ (99:1).

$$K_{11} = 9.9 \times 10^4 M^{-1} \pm 0.2\% \quad K_{12} = 4.2 \times 10^3 M^{-1} \pm 0.1\%$$

Link to BindFit: <http://app.supramolecular.org/bindfit/view/64e93147-18ce-4cc3-8dfc-45fb7a766f52>

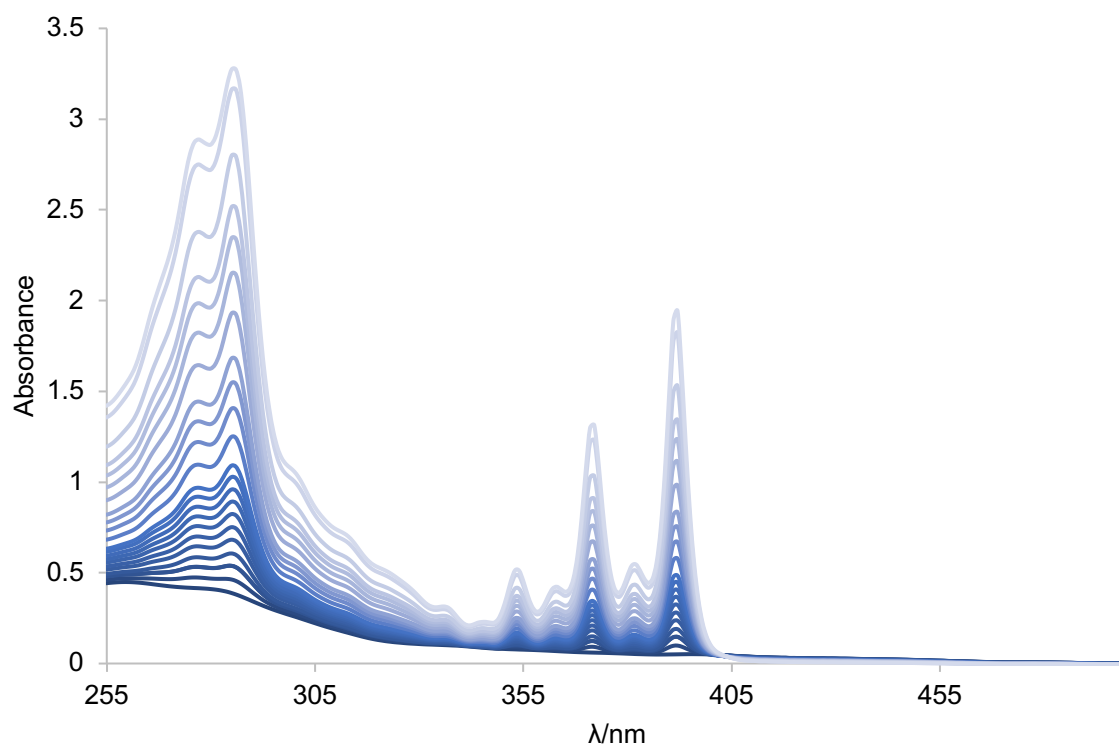


Figure S28. Results from the UV-vis absorption titration studies of co-system **1•4** in $CHCl_3/DMSO$ (99:1).

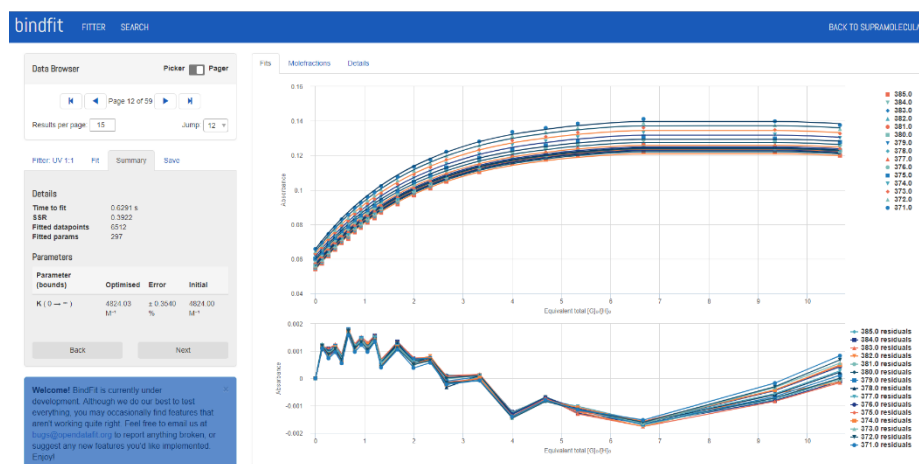


Figure S29. Results from the UV-vis absorption titration studies of co-system $2\text{H}^+\cdot\mathbf{3}$ in $\text{CHCl}_3/\text{DMSO}$ (99:1).

$$K_a = 4.8 \times 10^3 \text{ M}^{-1} \pm 0.4\%$$

Link to BindFit: <http://app.supramolecular.org/bindfit/view/e9e364b6-2db8-4e15-b74e-b48d636b60e0>

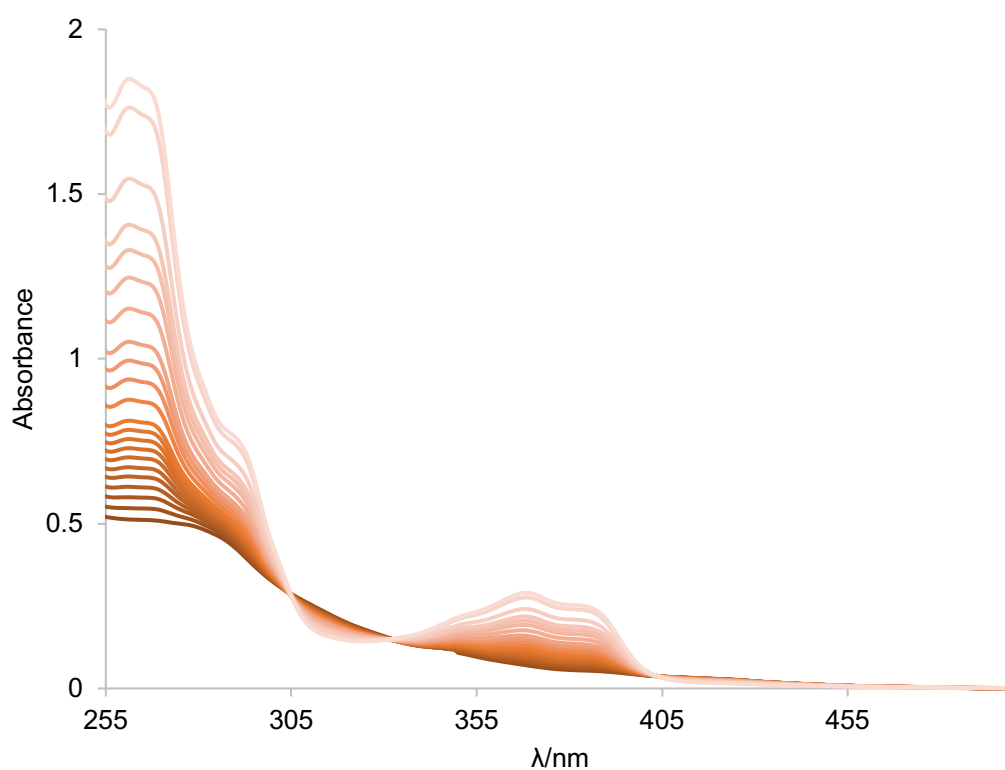


Figure S30. Results from the UV-vis absorption titration studies of co-system $2\text{H}^+\cdot\mathbf{3}$ in $\text{CHCl}_3/\text{DMSO}$ (99:1).

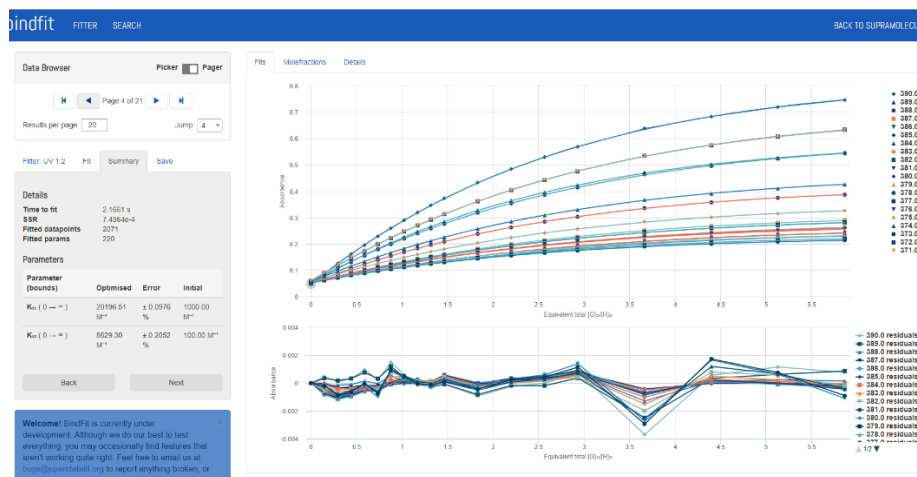


Figure S31. Results from the UV-vis absorption titration studies of co-system $2H^+ \bullet 4$ in $CHCl_3/DMSO$ (99:1).

$$K_{11} = 2.0 \times 10^4 M^{-1} \pm 0.1\% \quad K_{12} = 8.6 \times 10^3 M^{-1} \pm 0.2\%$$

Link to BindFit: <http://app.supramolecular.org/bindfit/view/0ac4a9ac-4af6-4ee3-9e34-70499995765d>

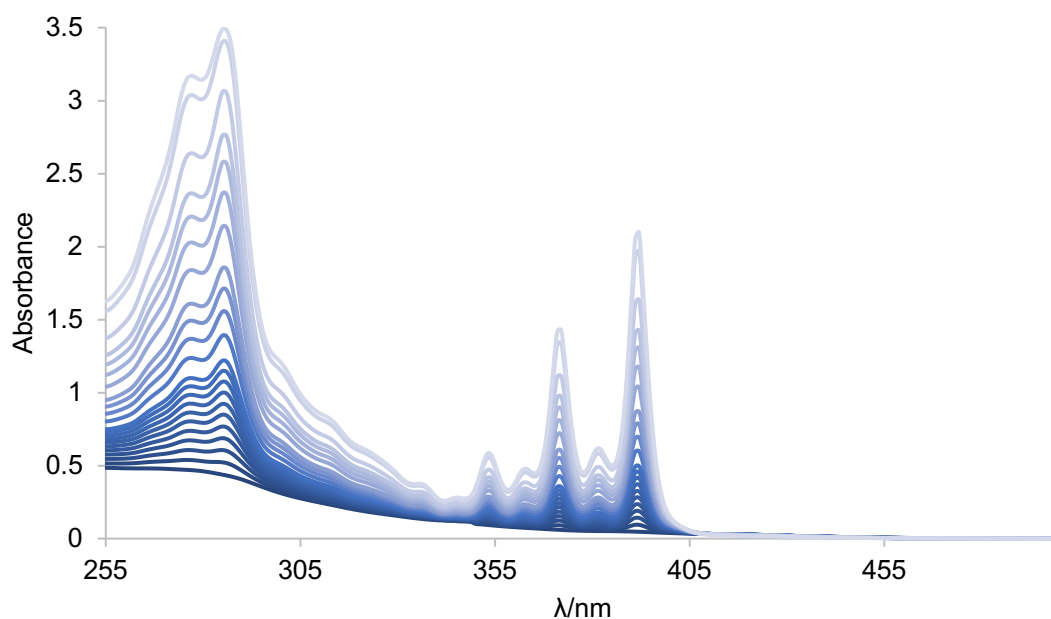


Figure S32. Results from the UV-vis absorption titration studies of co-system $2H^+ \bullet 4$ in $CHCl_3/DMSO$ (99:1).

References

- [S1] Nonoyama, M. (1974) Benzo[h]Quinolin-10-Yl-N Iridium (III) Complexes. *Bull. Chem. Soc. Jpn.* 47, 767–768.
doi: 10.1246/bcsj.47.767
- [S2] Balónová, B.; Martir, D. R.; Clark, E. R.; Shepherd, H. J.; Zysman-Colman, E.; Blight, B. A. (2018) Influencing the Optoelectronic Properties of a Heteroleptic Iridium Complex by Second-Sphere H-Bonding Interactions. *Inorg. Chem.* 57, 8581–8587.
doi: 10.1021/acs.inorgchem.8b01326
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