Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

About the relevance of anion-π interactions in water

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Contents

S1. Materials and Methods

Starting materials, if commercially available, were purchased and used as such. The solvents used were of spectroscopic or equivalent grade. When known compounds had to be prepared by literature procedures, pertinent references are given. Melting points or ranges (m.p.) given were determined on a Büchi B-545 heated stage. ^{1}H and (^{1}H decoupled) ^{13}C nuclear magnetic resonance (NMR) spectra were recorded at 300 and 75 MHz. Chemical shifts are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual deuterated methanol. Coupling constants (J) are given in Hz. Coupling patterns are abbreviated as, for example, s (singlet), d (doublet), t (triplet), q (quartet), td (triplet of doublets), m (multiplet), app. s (apparent singlet) and br. (broad). COSY and DEPT/ed-HSQC experiments were performed for all compounds. IR spectra were recorded using FT-IR ATR. HRMS were recorded using TOF electro-spray ionization (ESI-positive). UV-Visible spectra were measured on an Agilent 8453 spectrometer. The emission spectra were recorded with a PTI MO- 5020 spectrofluorimeter in the 300–700 nm range.

S2. NMR Spectra.

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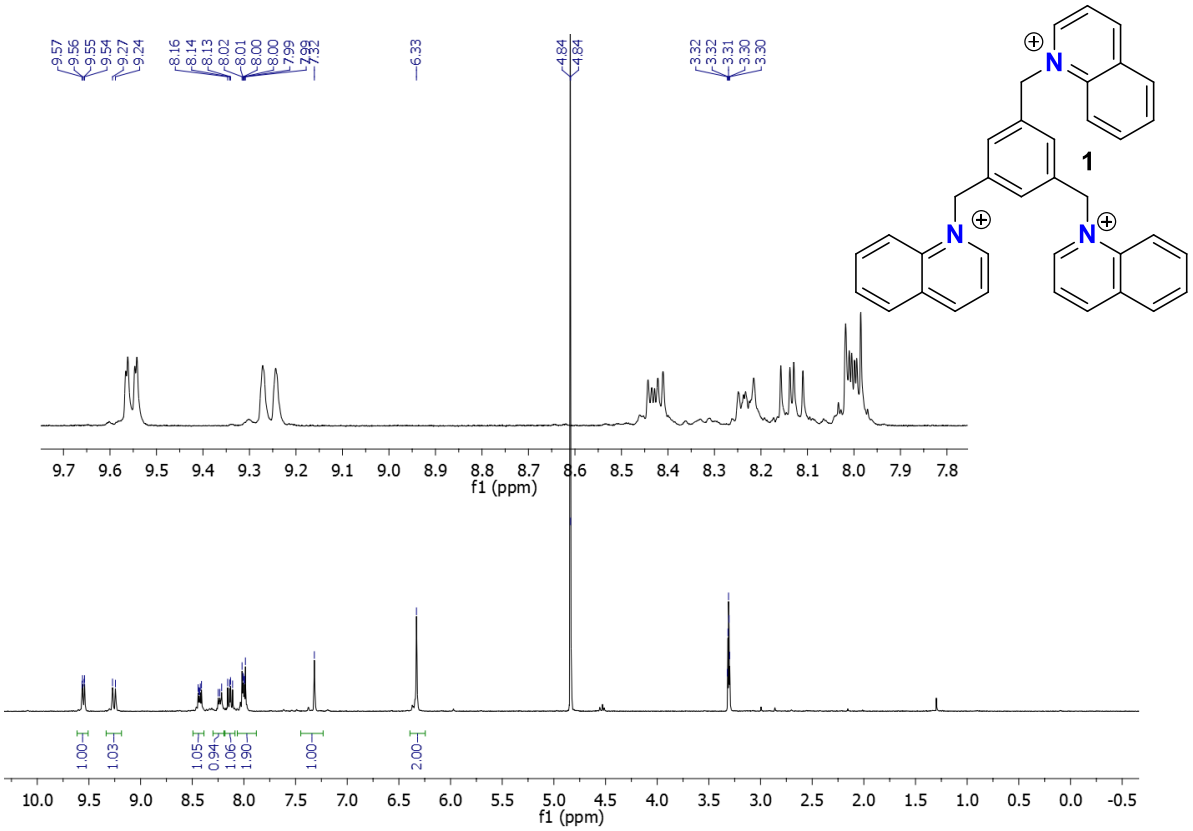
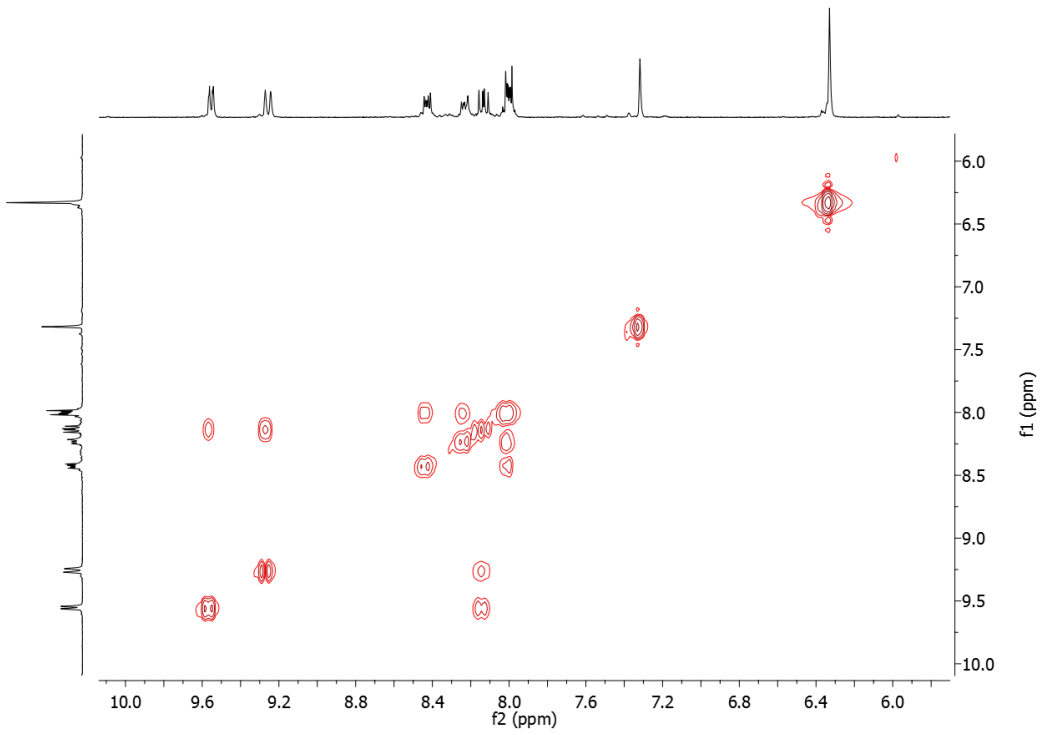


COSY of **1**



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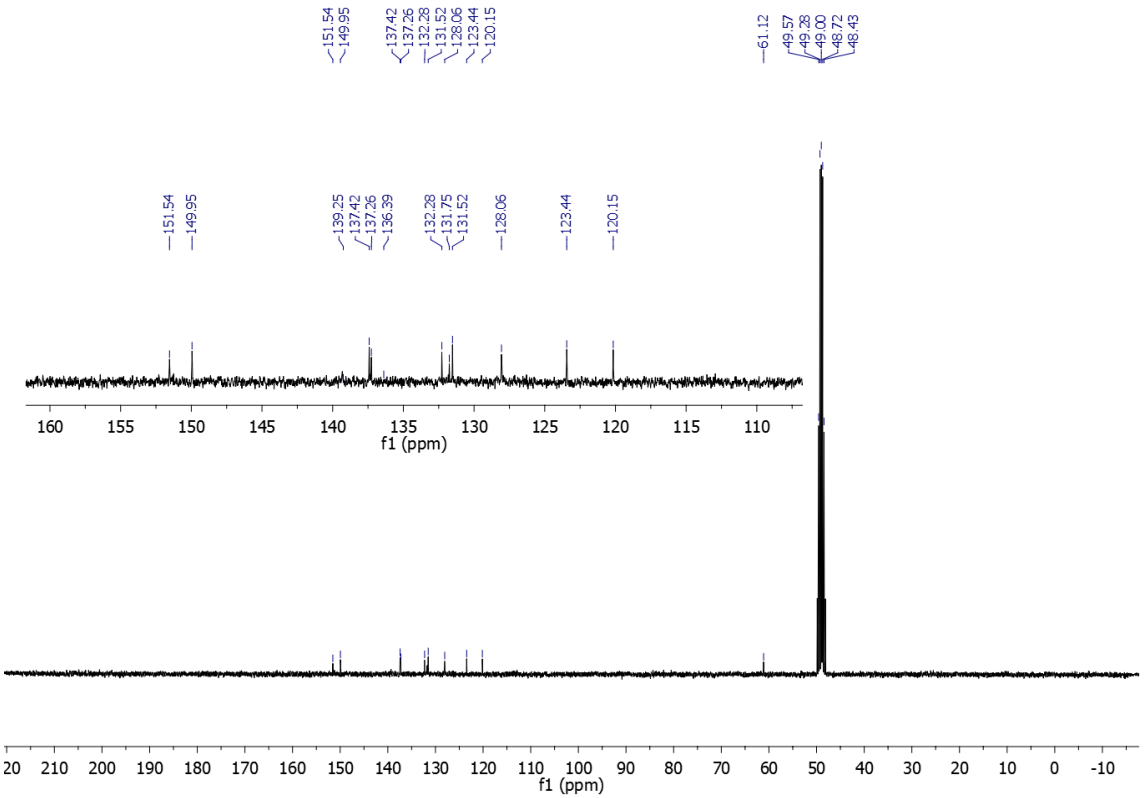
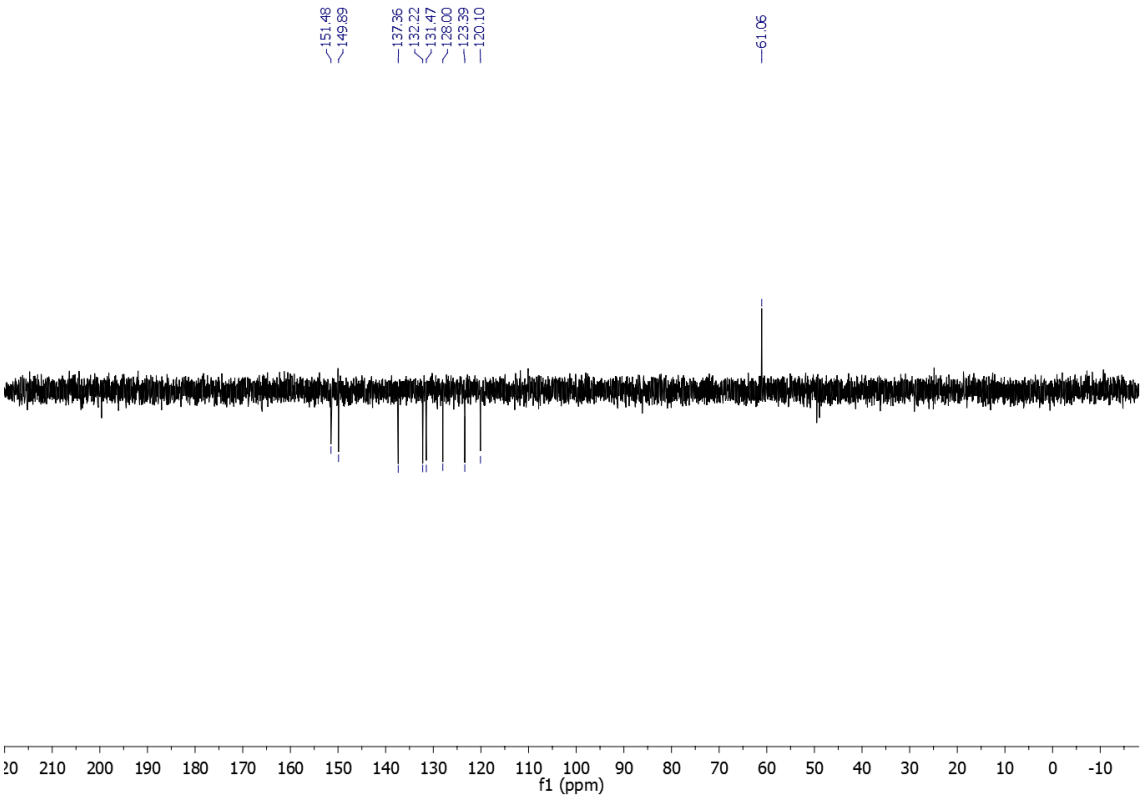


DEPT-135 of **1**



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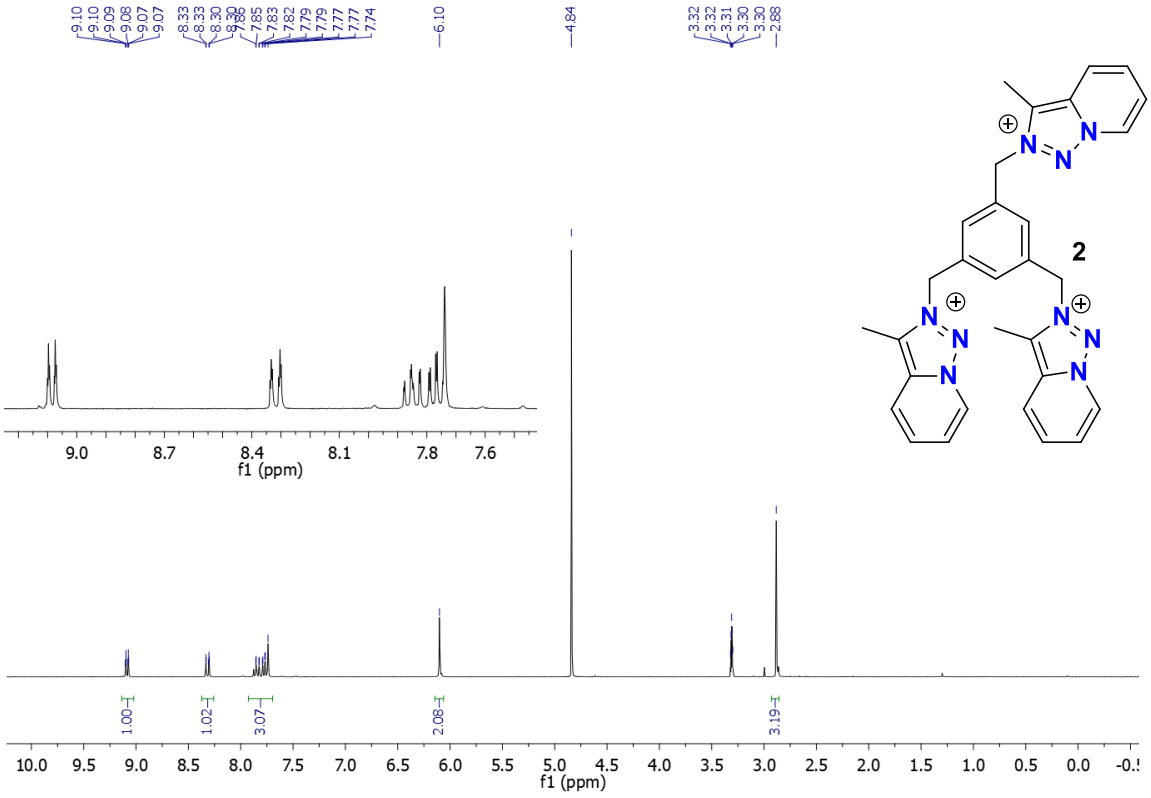
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9.10
9.09
9.08
9.07
9.07
8.33
8.33
8.30
8.30
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7.83
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7.79
7.79
7.77
7.77
7.77
7.74
6.10
4.84
3.32
3.32
3.31
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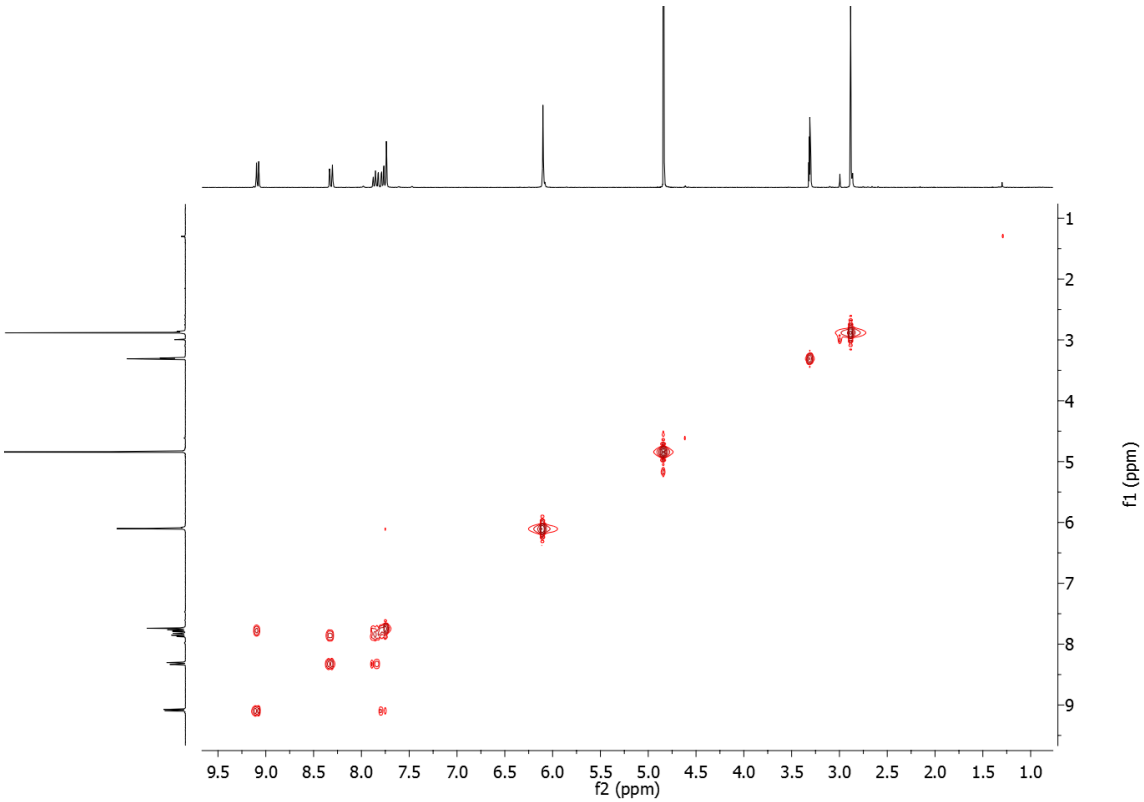
3.07
2.08
3.19
f1 (ppm)

COSY of **2**


f2 (ppm)
f1 (ppm)

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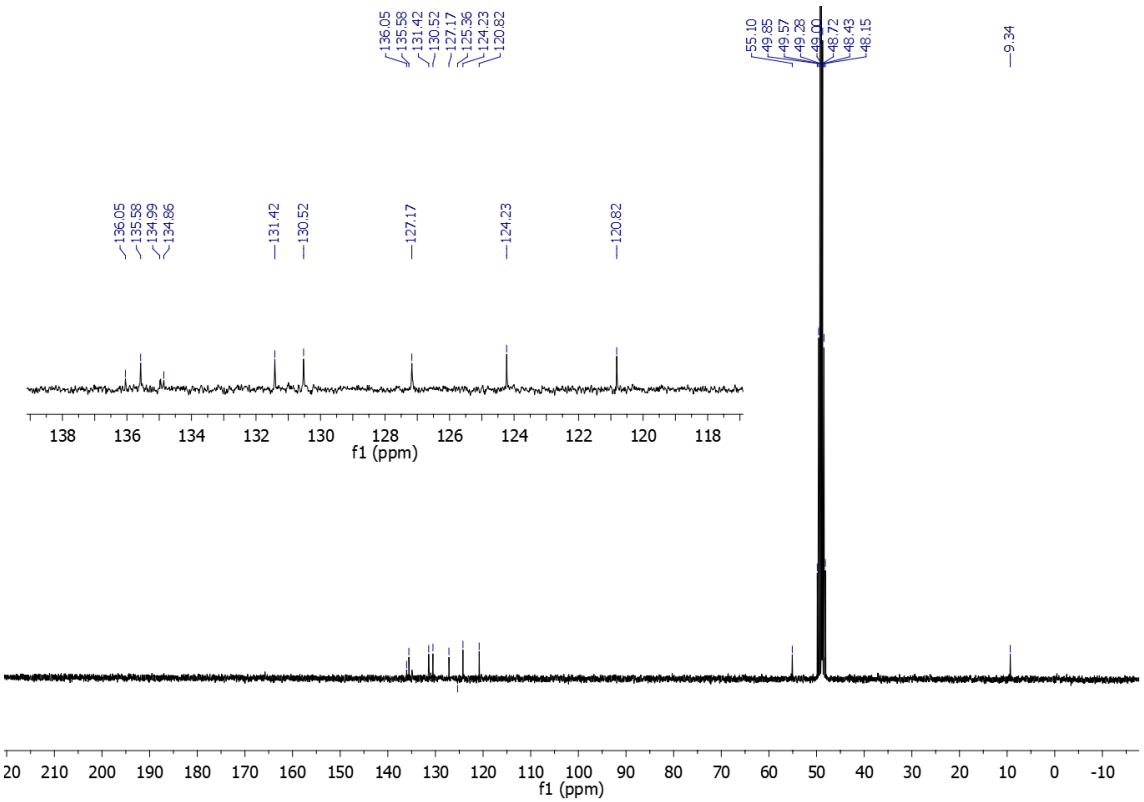
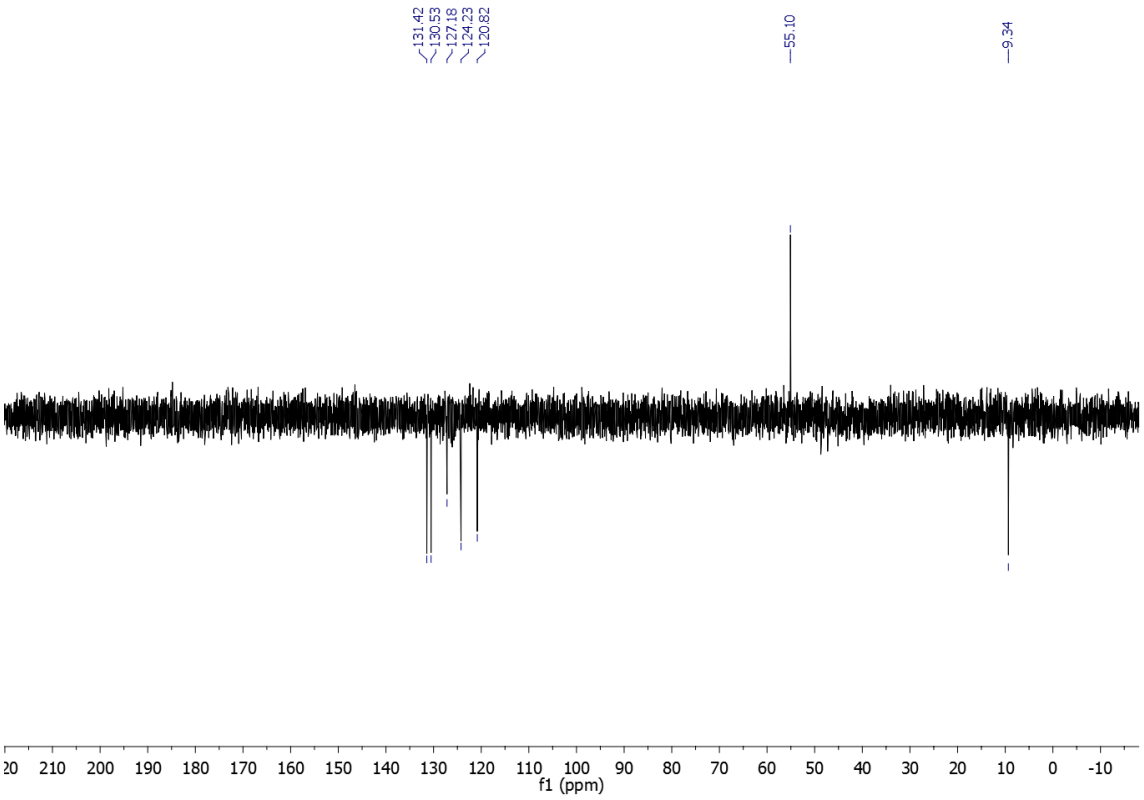
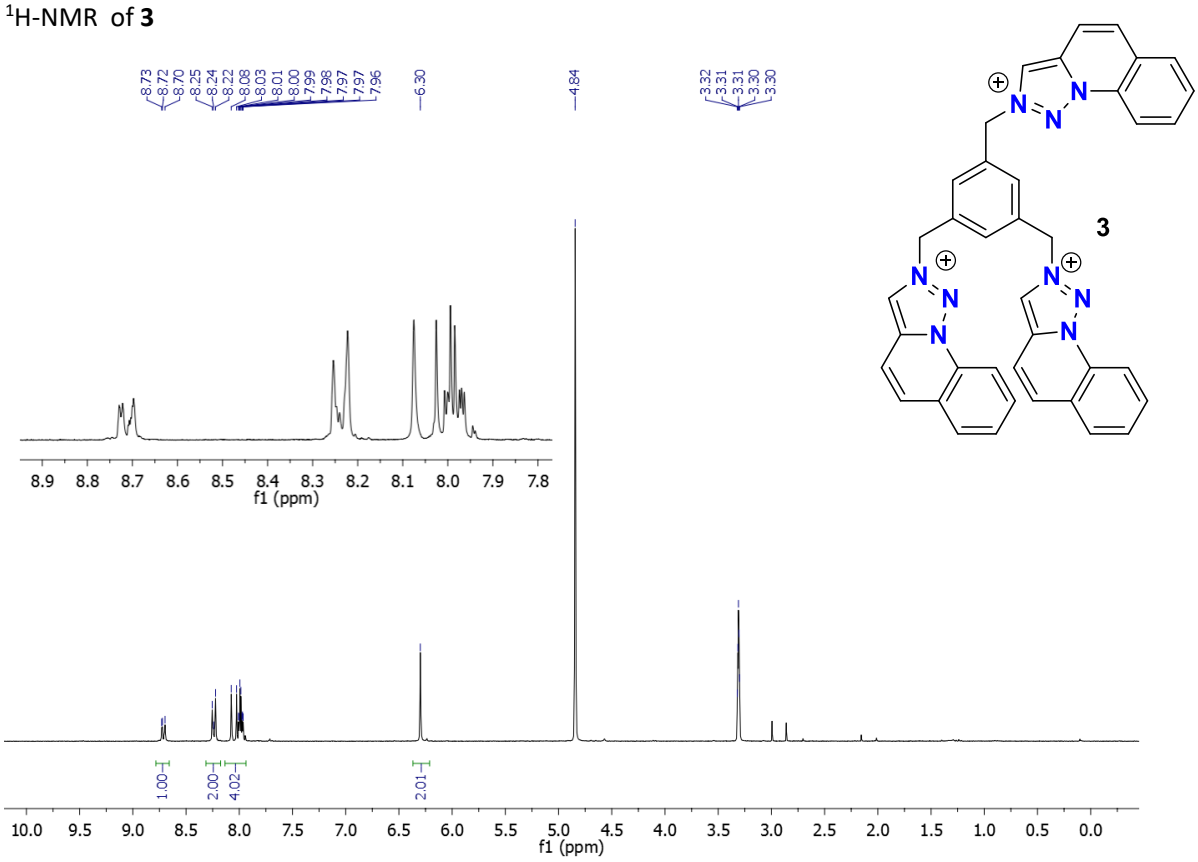


DEPT-135 of **2**



^{1}H-NMR of **3**



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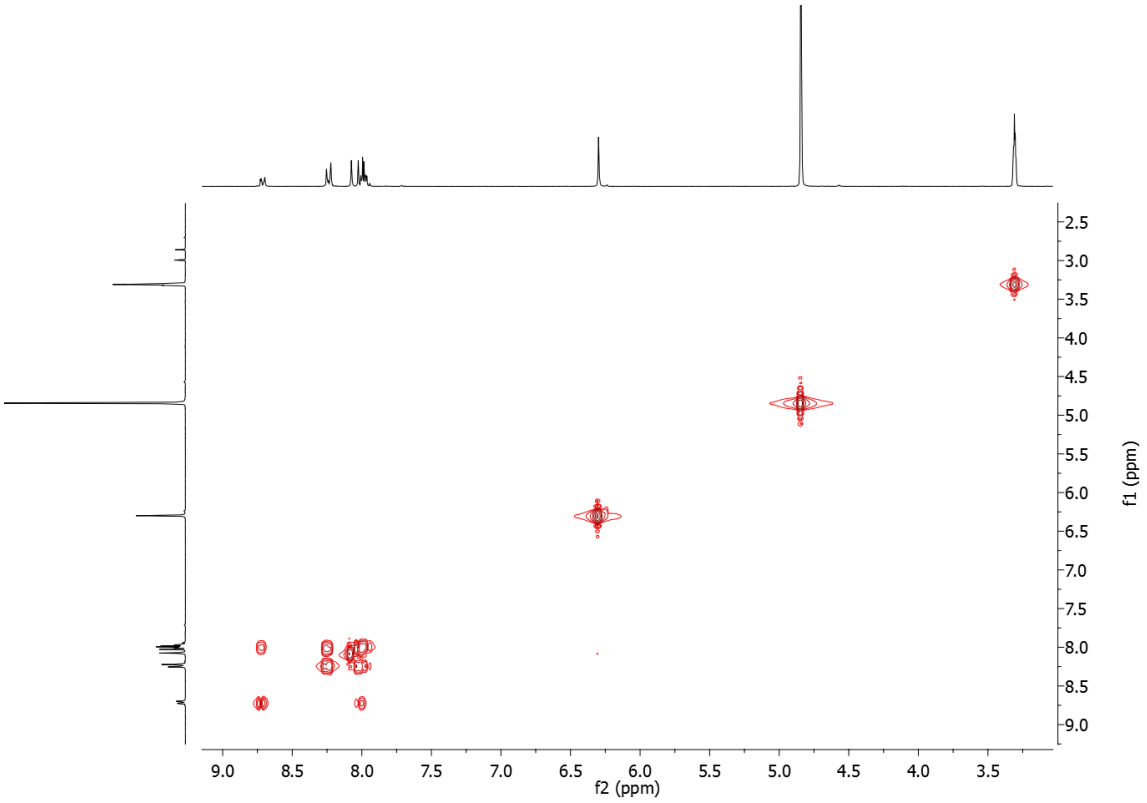
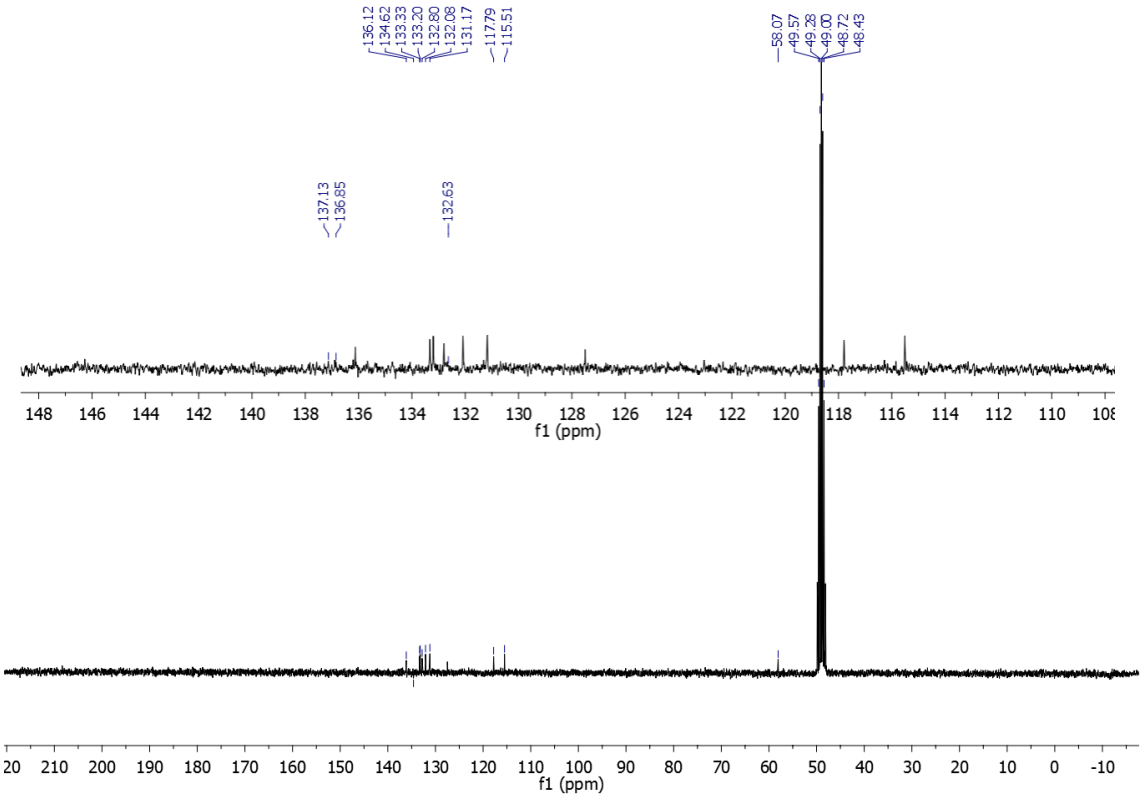


^{13}C-NMR of **3**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132.80
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58.07
49.57
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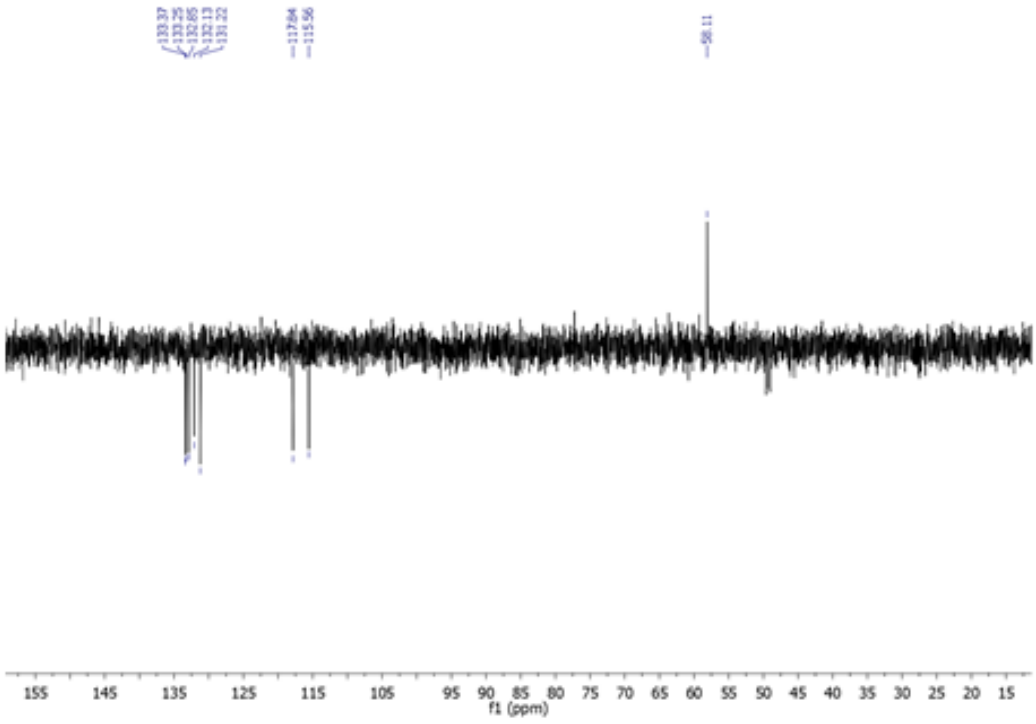
49.00
48.72
48.43
137.13
136.85
132.63
f1 (ppm)
f1 (ppm)

DEPT-135 of **3**


f1 (ppm)

S3. Single Crystal X-ray Diffraction Analyses

Single-crystal X-ray diffraction (SXRD) data for **1, 2** and **3** were collected on a Xcalibur diffractometer (Agilent Technologies, Sapphire 3 CCD detector) using a single wavelength X-ray source with MoKα radiation, λ = 0.71073 Å. The selected single crystals were mounted using Paratone-N hydrocarbon oil[1] on the top of a loop fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, analytical absorption correction, and data reduction were performed with the Oxford program suite CrysAlisPro.[2] Empirical absorption correction was applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

The data collection was performed at 120(1) K in all cases.

The crystal structures were solved with SHELXT[3], using direct methods and were refined by full-matrix least-squares methods on F^2 with SHELXL2014. All programs used during the crystal structure determination process are included in the OLEX2 software.[4]

The crystallographic details of both the crystal structures are summarized in Table S1. CCDC 1939483, 1939484 and 1939485 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement for **1, 2** and **3.**

	1	**2**	**3**
Empirical formula	$C_{36}H_{34}Br_3N_3O_2$	$C_{90}H_{98}Br_9N_{27}O_4$	$C_{78}H_{66}Br_6N_{18}O_3$
Formula weight	780.39	2341.14	1782.94
Temperature / K	120.0(1)	120.0(1)	120.0(1)
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	P21/n	Pca21	P21/c
a/Å	9.4720(4)	20.7951(4)	12.3635(9)
b/Å	29.1025(13)	30.5457(6)	23.3233(15)
c/Å	11.8612(7)	14.9217(3)	13.8839(12)
α/°	90	90	90
β/°	99.230(5)	90	113.410(10)
γ/°	90	90	90
Volume / Å^3	3227.3(3)	9478.3(3)	3674.0(5)
Z	4	4	2
ρ_{calc}g/cm^3	1.606	1.641	1.612
μ/mm^{-1}	3.788	3.872	3.342
F(000)	1568	4696	1788
2Θ range	6.618 to 51.996	6.618 to 52	6.63 to 49.998
Radiation	0.71073	0.71073	0.71073
Reflections collected	14239	43674	17947
Independent reflections	6331	14073	6452
R_{int}	0.0355	0.0502	0.0569
Data/restraints/parameters	6331/6/403	14073/135/1208	6452/10/496
GOF	1.048	0.975	1.105
R_1, wR_2[I>=2σ (I)]	0.0462, 0.0984	0.0450, 0.1010	0.0588, 0.1135
R_1, wR_2[all data]	0.0682, 0.1081	0.0661, 0.1128	0.0924, 0.1261

Structure 1

A colourless, block crystal (0.16 x 0.15 x 0.044 mm) of [($C_{36}H_{30}N_3$) $Br_3 \cdot 2H_2O$], was measured at 120(1) K using MoKα radiation, λ = 0.71073 Å.

The structure was solved by direct methods with SHELXT and was refined with SHELXL in the monoclinic space group *P*21/*n* with *Z* = 4.

ISOR SHELXL restraint had to be used to correct the thermal parameters of the atom C4. Hydrogen positions were calculated after each cycle of refinement using a riding model, with C-H = 0.97 Å and Uiso(H) = 1.2Ueq(C).

The final refinement was conducted with the reflection data within a 0.80 Å resolution limit, a total of 14239 reflections of which 6331 were independent and 4887 were greater than 2σ(*I*). Final full matrix least-squares refinement on *F*2 converged to *R*1 = 0.0462 and *wR*2 = 0.1081 (*I*>2σ(*I*)) with GOF = 1.048. Crystallographic data and additional details of data collection and refinement are summarized in Table S1. Drawings with atomic labels are represented in Figure S1.

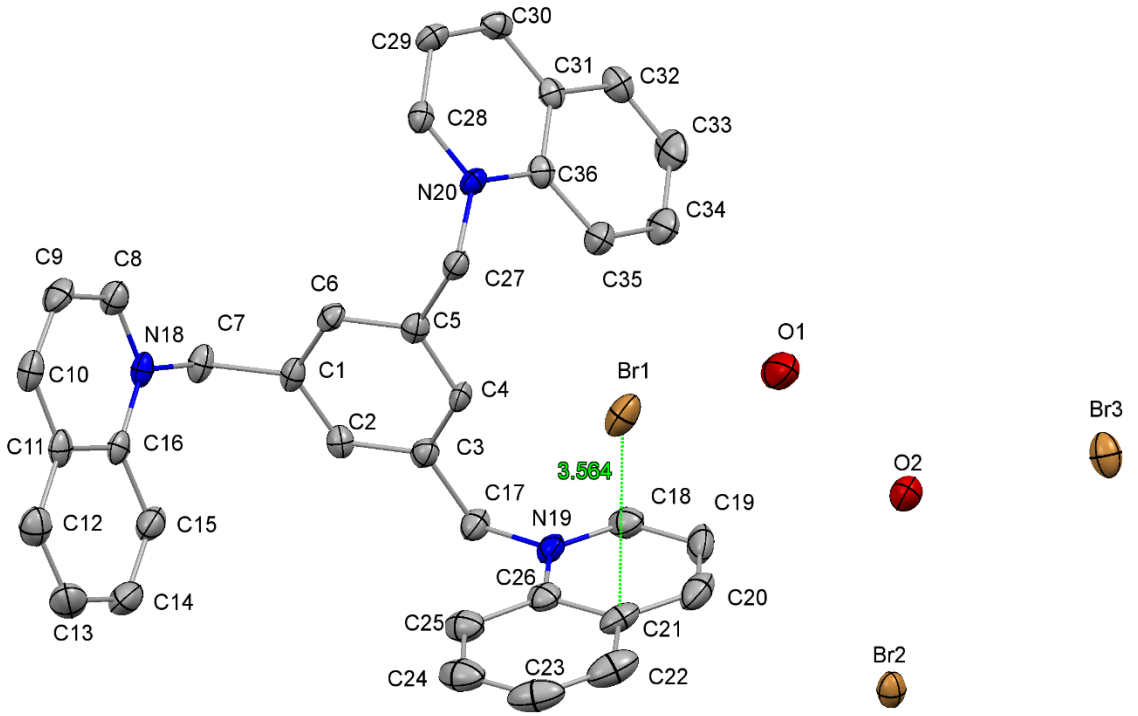


Figure S1. The asymmetric unit present in **1** with all non–hydrogen atoms represented by thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms were omitted for clarity.

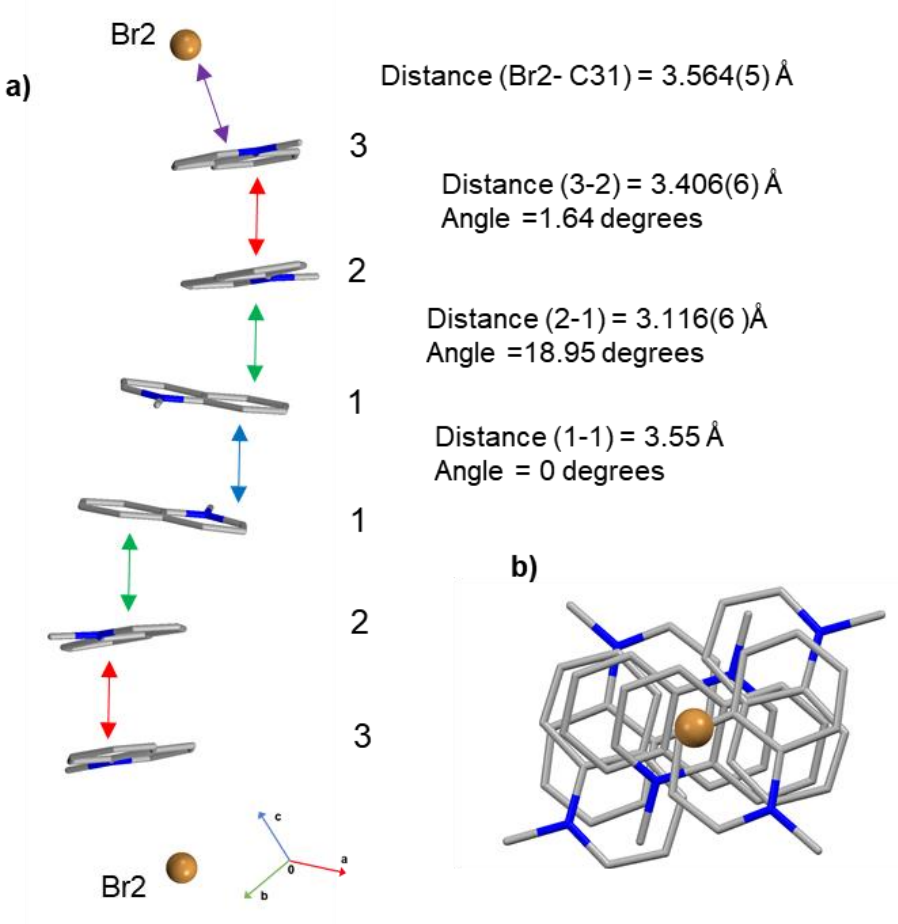


Figure S2. a) Lateral view of the π stack in compound **1** and the distances and angles between the aromatic unit. b) Upper view of the π stack. All hydrogen atoms were omitted for clarity.

Structure 2

A yellow crystal (0.35 x 0.23 x 0.156 mm) of [($C_{30}H_{30}N_3$) $3Br_9$ ·$4H_2O$] was measured at 120(1) K using MoKα radiation, λ = 0.71073 Å. The structure was solved by direct methods with SHELXT and was refined with the SHELXL software package (S3), crystallized in the orthorhombic Pca21 space group with Z =4.

Some soft SHELXL restraints (DELU, ISOR, SIMU, EADP) had to be used to correct the geometry of the disordered parts and the thermal parameters of the corresponding atoms.

Hydrogen positions were calculated after each cycle of refinement using a riding model, with C-H = 0.93 Å and Uiso(H) = 1.2Ueq(C) for aromatic H atoms, and with C-H = 0.97 Å and Uiso(H) = 1.2Ueq(C) for methyl H atoms.

The bromide Br8 and Br9 have been modelled in two different positions with an occupancies of 0.4 and 0.6 for Br 8 and 0.3 and 0.7 for Br9.

The final refinement was conducted with the reflection data within a θmax = 26.0° resolution limit, a total of 43674 reflections of which 14073 were independent and 11106 were greater than 2σ(I). Final full matrix least-squares refinement on F^2 converged to R1 = 0.0450 and wR2 = 0.1128 with GOF = 0.975. Crystallographic data and additional details of data collection and refinement are summarized in Table S2. Drawings with atomic labels are represented in Figure S3 and S4.

Crystallographic data and additional details of data collection and refinement are summarized in Table S1. Drawings with atomic labels are represented in Figure S3.

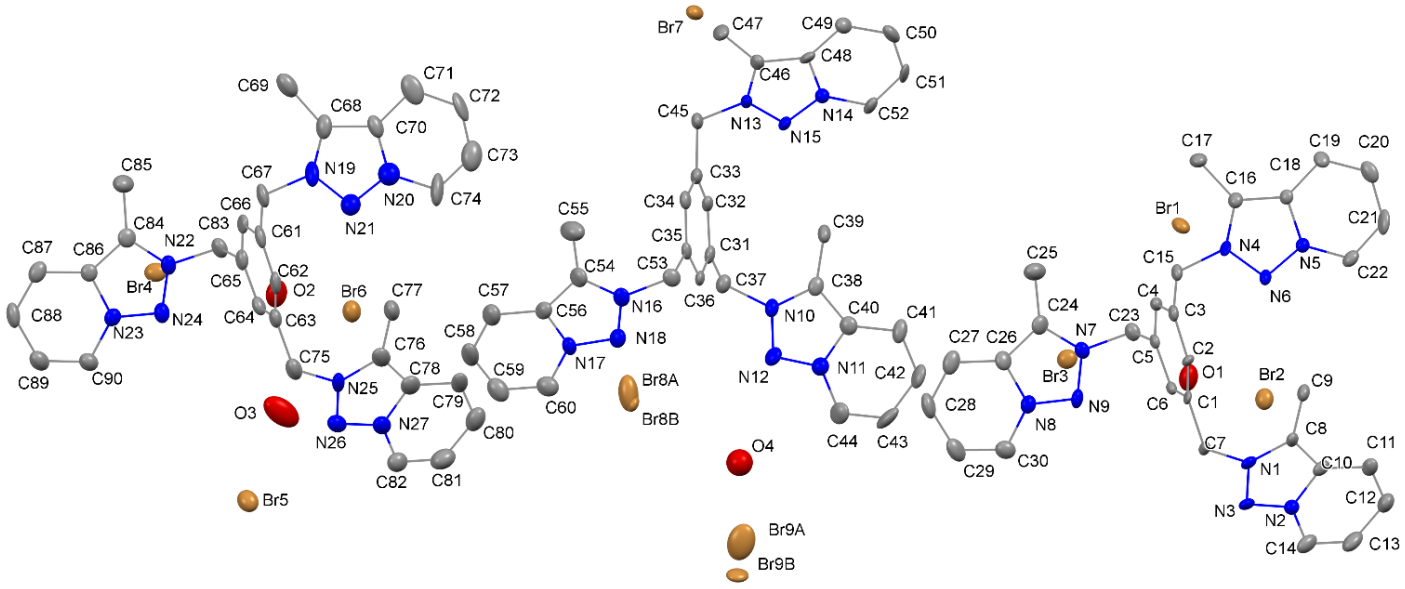


Figure S3. The asymmetric unit present in **2** with all non–hydrogen atoms represented by thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms were omitted for clarity.

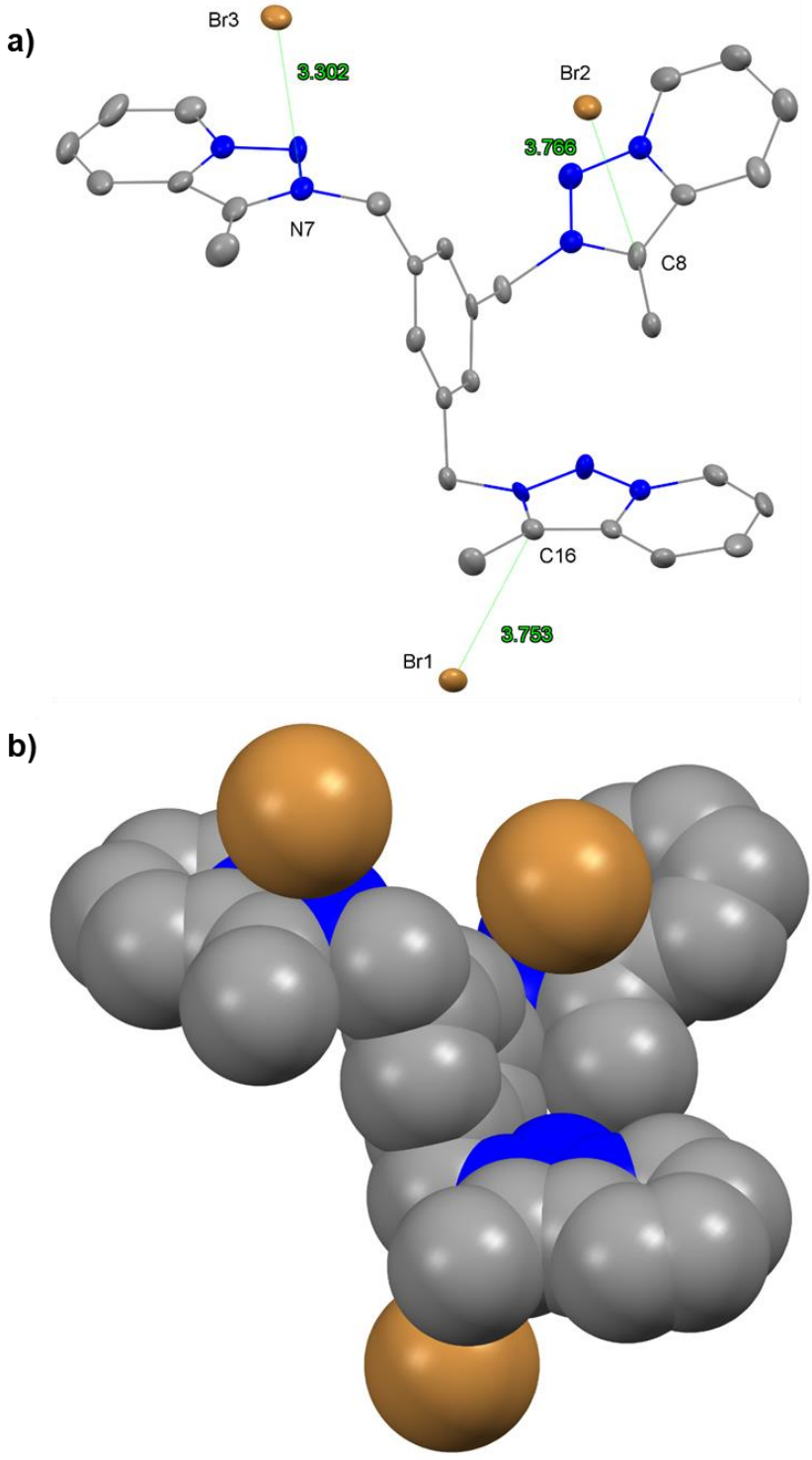


Figure S4. a) Detail the interaction and distances between one molecule of **2** and the bromide anions with all non–hydrogen atoms represented by thermal ellipsoids drawn at the 50% probability level. b) Spacefill drawing. All hydrogen atoms were omitted for clarity

Structure 3

A colourless crystal (0.17 × 0.16 × 0.07 mm) of $[(C_{39}H_{30}N_9)_2\ Br_6{\cdot}3H_2O]$, was measured at 120(1) K using MoKα radiation, λ = 0.71073 Å.

The structure was solved by direct methods with SHELXT and was refined with SHELXL in the monoclinic space group *P*21/c with *Z* = 2.

Some soft *SHELXL* restraints (*DFIX*, *ISOR*) had to be used to correct the geometry of the disordered parts and the thermal parameters of the water molecules. All hydrogen positions were calculated after each cycle of refinement using a riding model, with C-H = 0.97 Å and Uiso(H) = 1.2Ueq(C). The presence of solvent molecules could easily be seen by the residual peaks located in the open channels. The three water are modelled in different PARTs and their occupancies are 0.5 for O1, 0.75 for O2 and 0.25 for O3.

The final refinement was conducted with the reflection data within a θ_{max} = 25.0° resolution limit, a total of 17497 reflections of which 6452 were independent and 4654 were greater than 2σ(*I*). Final full matrix least-squares refinement on F^2 converged to *R*1 = 0.0588 and *wR*2 = 0.1261 with GOF = 1.105. Crystallographic data and additional details of data collection and refinement are summarized in Table S2. Drawings with atomic labels are represented in Figure S5.

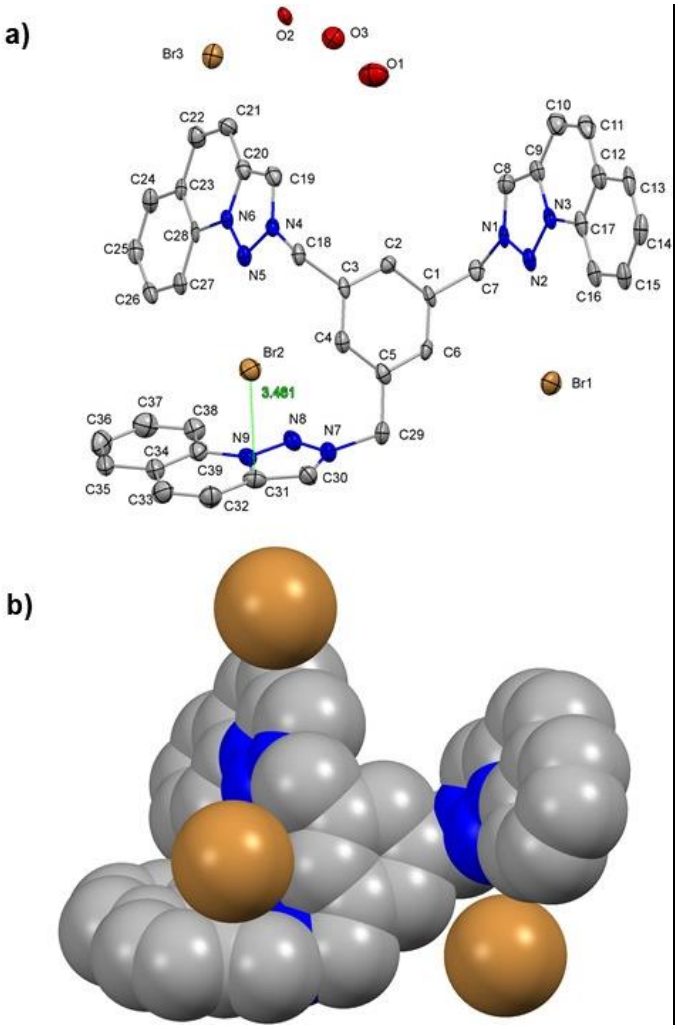


Figure S5. a) The asymmetric unit present in **3** with all non–hydrogen atoms represented by thermal ellipsoids drawn at the 50% probability level. b) Spacefill drawing. All hydrogen atoms were omitted for clarity

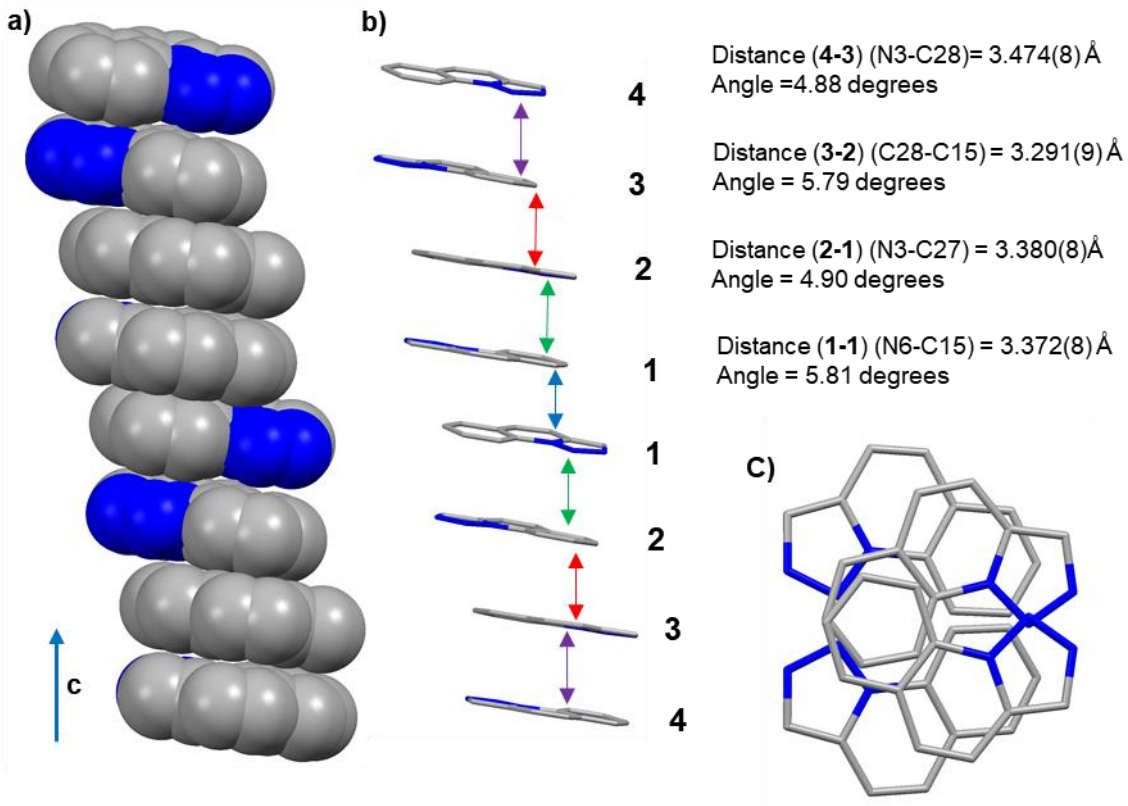
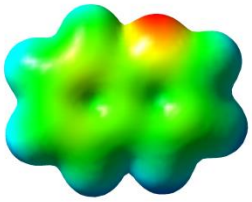
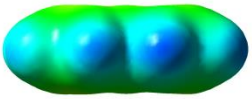
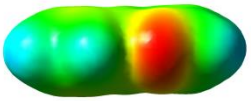
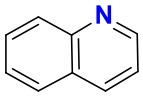


Figure S6. a) Spacefill view along the *c* axis of the π stack in compound **3.** b)Stick representation, distances and angles between the aromatic unit in compound **3**. c) Upper view of the π stack. All hydrogen atoms were omitted for clarity.

S4. DFT Calculations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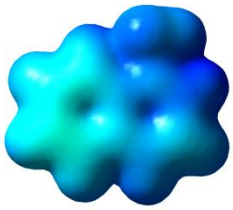	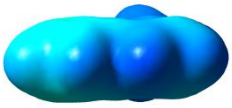	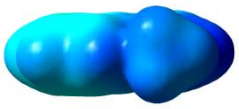	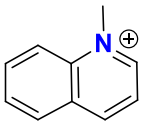
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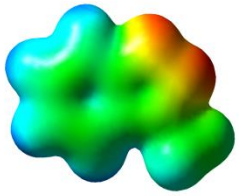	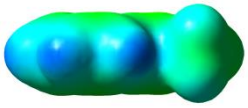	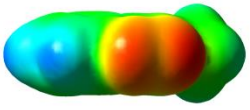	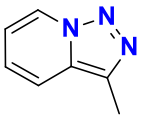
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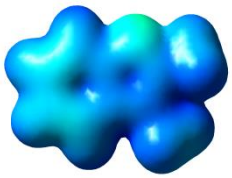
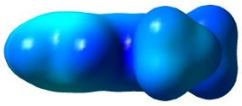
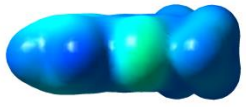
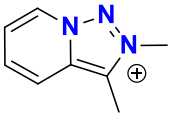
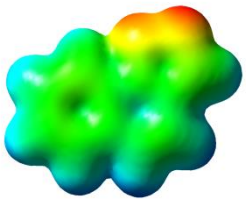
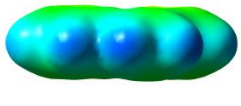
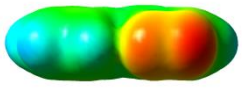
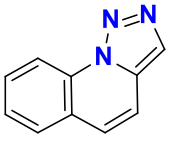
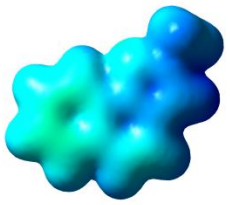
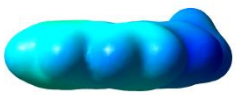
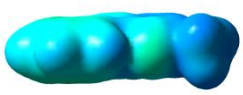
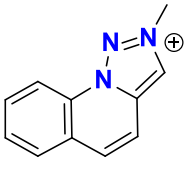
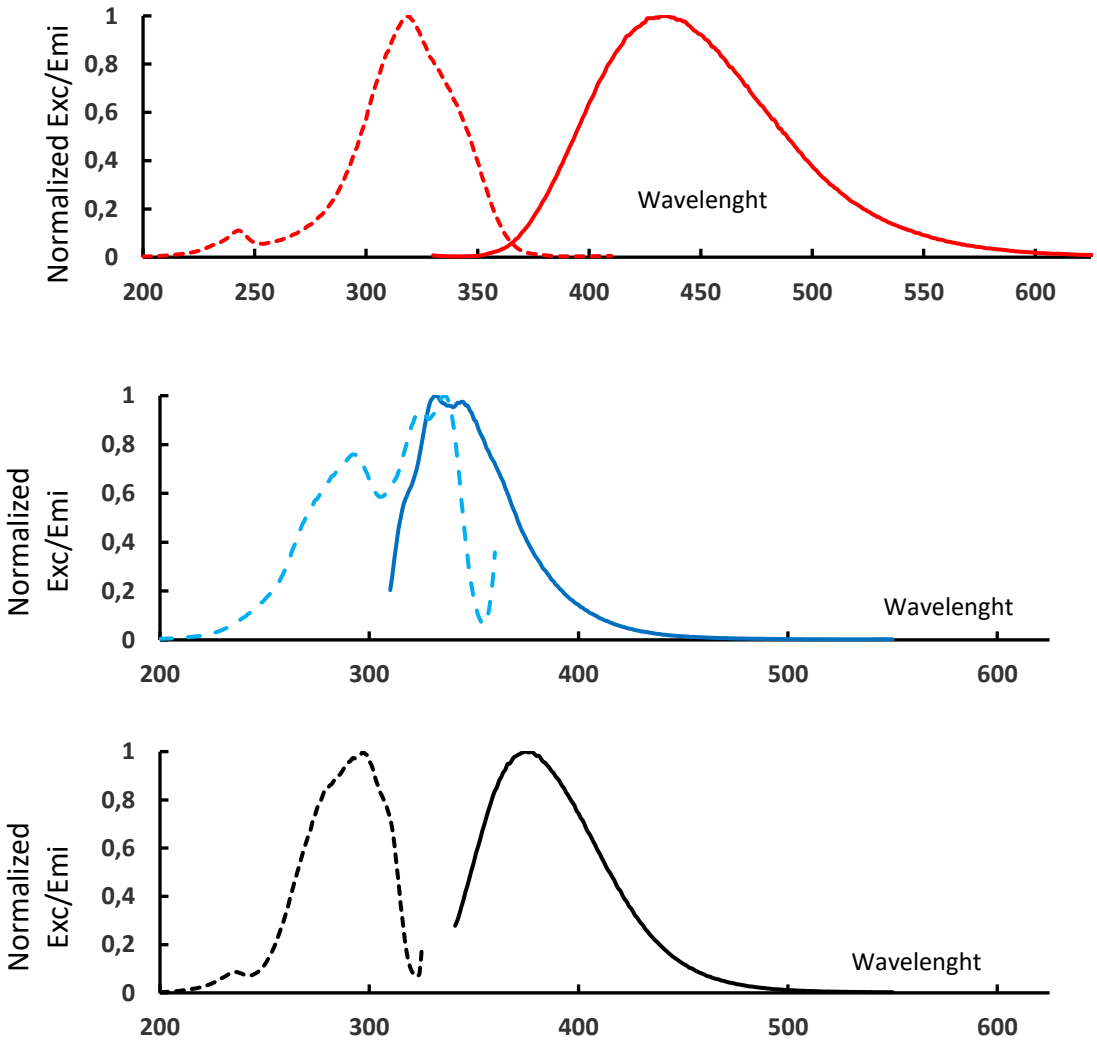
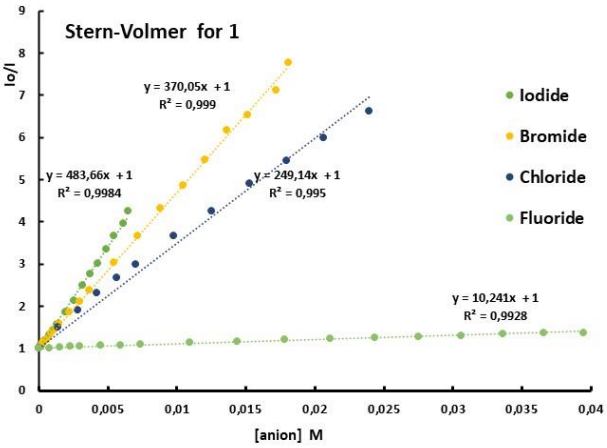
			
2a	Side view	Side view	
			
5c Q_{zz} -7.3 B	Side view	Side view	
			
3a	Side view	Side view	

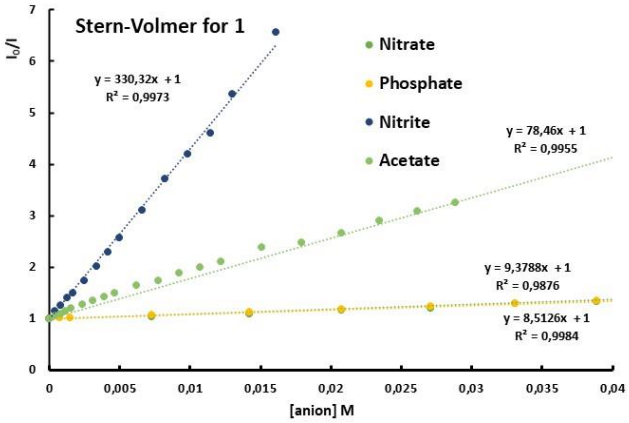
S5. Fluorescence Excitation and Emission Spectra

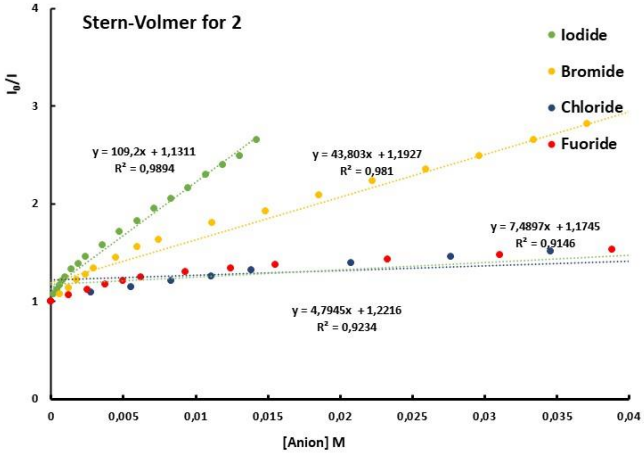
Compound	λ Excitation	λ Emission	Stokes shift
1	**319 nm**	**436 nm**	117 nm
2	**297 nm**	**340 nm**	43 nm
3	**297 nm**	**376 nm**	78 nm

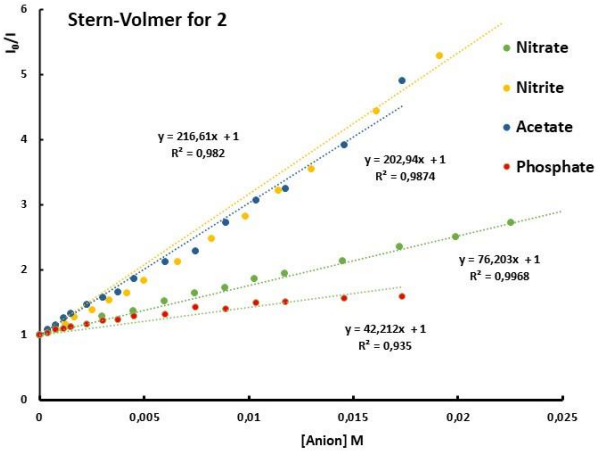


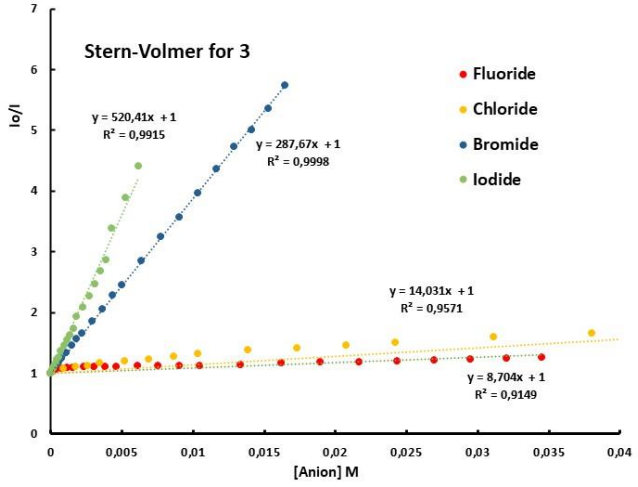
S6. Stern-Volmer plots and titration conditions

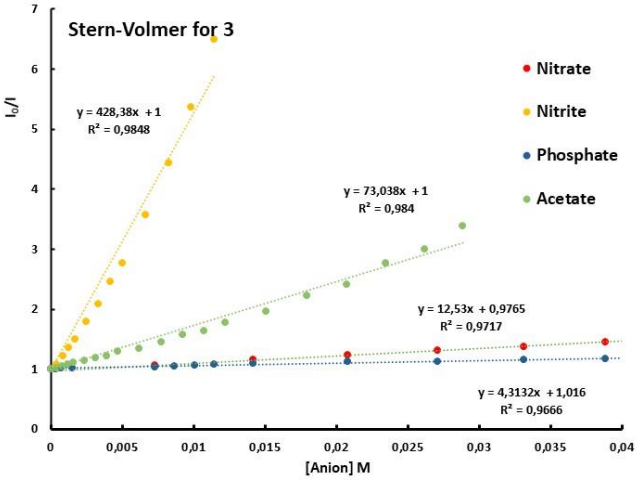












Anion titrations were done by consecutive additions of concentrated anion solutions to 0.00002 M solutions of ligands **1**, **2** or **3**. The ligand initial solution was prepared combining 0.1 mL of stock ligand solution in 1.9 mL of water. Titrations were stopped upon the addition of one millilitre of concentrated anion solution.

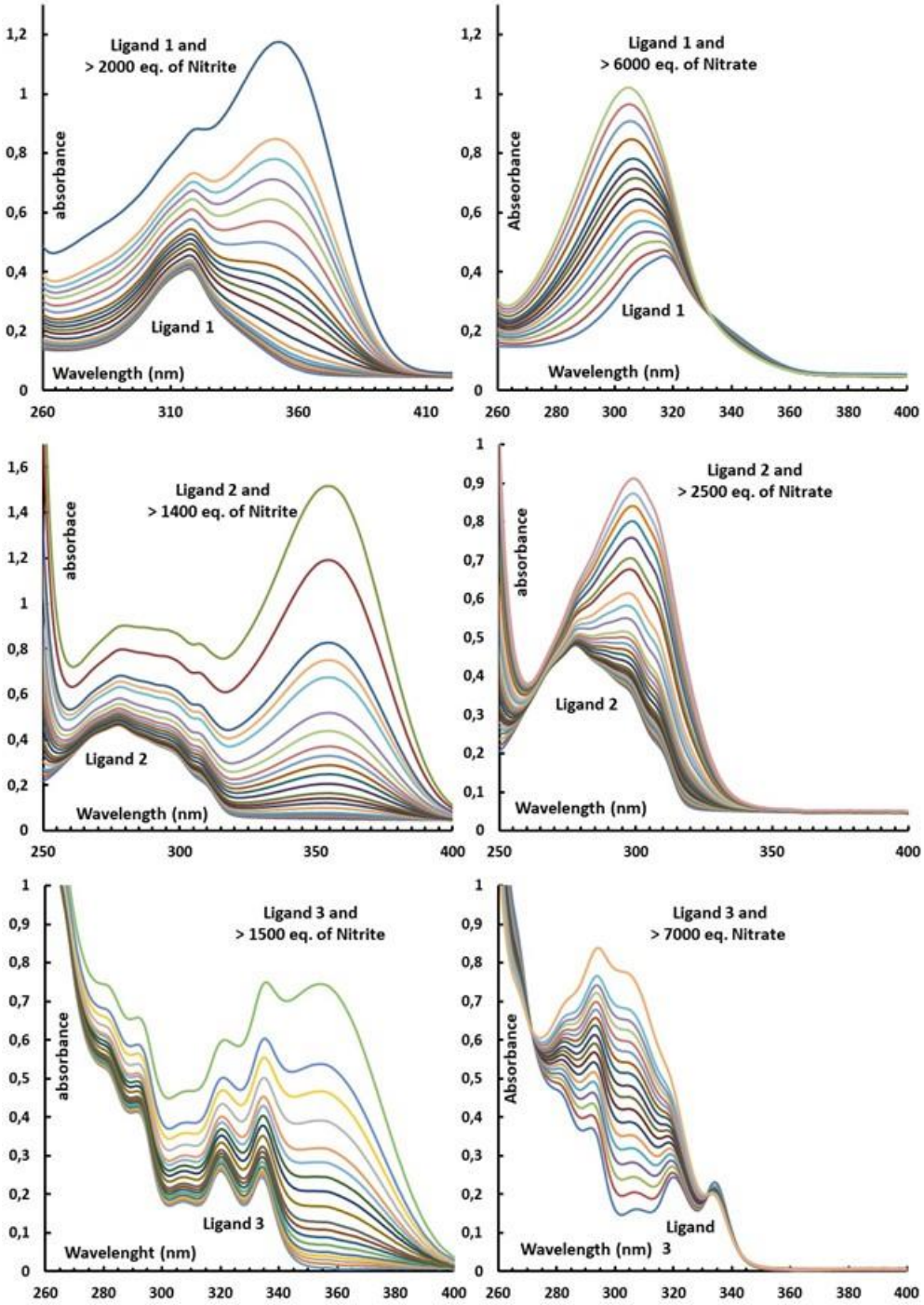
Table S2: Employed concentrations for the titration and measured initial and final pH upon the addition of 1 mL of anion solution.

[ligand 1] M	vol (mL)	v total (mL)	Anion (as tetrabutyl ammonium salt)	[anion] M	pH
0,00040419	0,1	2	*None*	-	5,38
0,00040419	0,1	2	Iodide	0,053	7,52
0,00040419	0,1	2	Bromide	0,15	4,87
0,00040419	0,1	2	Chloride	0,708	4,85
0,00040419	0,1	2	Fluoride	0,302	6,22
0,00040419	0,1	2	Nitrate	0,298	4,15
0,00040419	0,1	2	Nitrite	0,338	7,56
0,00040419	0,1	2	Phosphate	0,298	3,85
0,00040419	0,1	2	Acetate	0,317	5,6

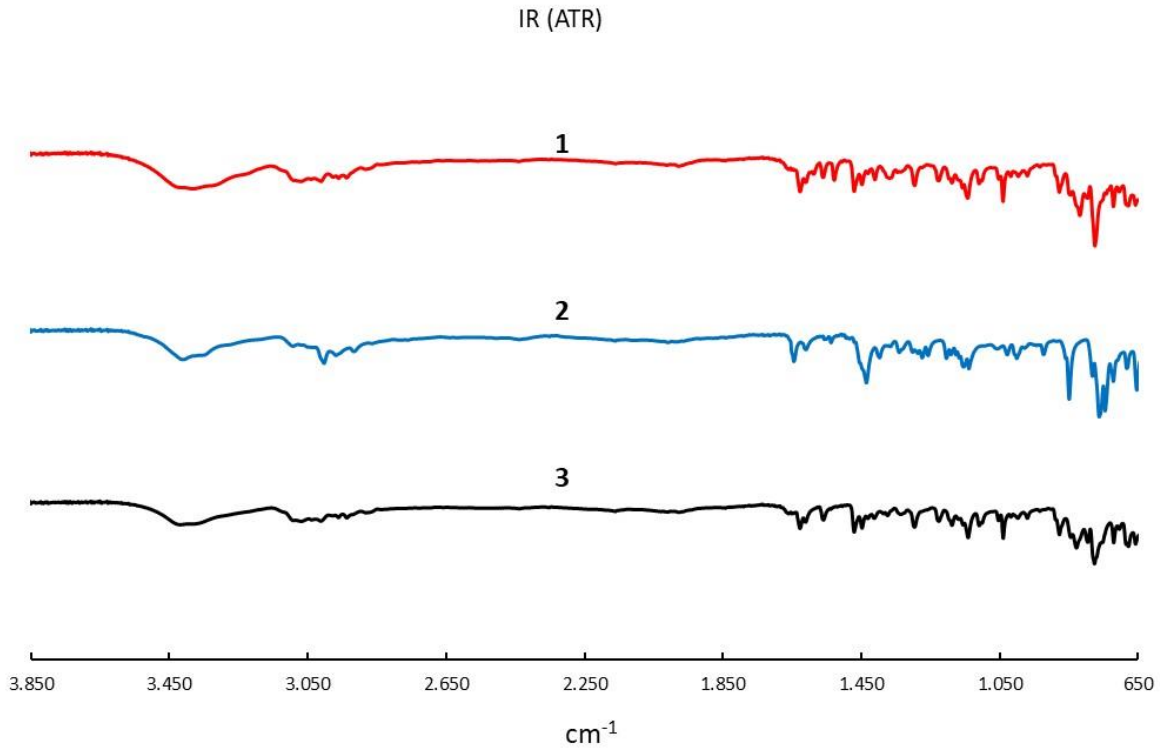
[ligand 2] M	vol (mL)	v total (mL)	Anion (as tetrabutyl ammonium salt)	[anion] M	pH
0,00039761	0,1	2	*None*	-	5,42
0,00039761	0,1	2	Iodide	0,047	7,03
0,00039761	0,1	2	Bromide	0,148	5,04
0,00039761	0,1	2	Chloride	0,691	4,92
0,00039761	0,1	2	Fluoride	0,31	6,28
0,00039761	0,1	2	Nitrate	0,304	4,09
0,00039761	0,1	2	Nitrite	0,338	7,36
0,00039761	0,1	2	Phosphate	0,306	3,92
0,00039761	0,1	2	Acetate	0,306	5,54

[ligand 3] M	vol (mL)	v total (mL)	Anion (as tetrabutyl ammonium salt)	[anion] M	pH
0,00039829	0,1	2	*None*	-	5,38
0,00039829	0,1	2	Iodide	0,047	6,52
0,00039829	0,1	2	Bromide	0,148	5,15
0,00039829	0,1	2	Chloride	0,691	4,91
0,00039829	0,1	2	Fluoride	0,31	6,28
0,00039829	0,1	2	Nitrate	0,298	4,13
0,00039829	0,1	2	Nitrite	0,338	7,32
0,00039829	0,1	2	Phosphate	0,298	3,88
0,00039829	0,1	2	Acetate	0,317	5,59

S7. UV/Vis spectra with excess of nitrite and nitrate.



S8. IR Spectra



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[2]Agilent (2014). *CrysAlis PRO*. Agilent Technologies Ltd, Yarnton, Oxfordshire, England.

[3] Sheldrick, G. M. (2015). Acta Cryst. A71, 3-8.

[4]O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann,*J. Appl. Cryst. (2009). 42, 339-341*.