SUPPORTING INFORMATION

Towards redox-switchable organocatalysts based on bidentate halogen bond donors.

E. Engelage,[‡ [a]] H. Hijazi,[‡ [b]] M. Gartmann,[[a]] L.-M. Chamoreau,[[c]] B. Schöllhorn,[[b]]* S. M. Huber,[[a]]* C. Fave [[a]]*

[a] Fakultät für Chemie und Biochemie, Ruhr-Universität Bochum, Universitätsstrasse 150, 44801 Bochum, Germany
[b] Université de Paris, Laboratoire d'Electrochimie Moléculaire, CNRS 7591, F-75006 Paris, France
[c] Institut Parisien de Chimie Moléculaire, IPCM, CNRS, Sorbonne Université, 4 place Jussieu, 75252 Paris, France

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1. General Methods

1.1 Chemicals

All reactions were performed under exclusion of air and water using oven dried flasks, dry solvents and argon gas, unless otherwise noted. Small volumes for reactions were transferred using plastic *NORMJECT* syringes and *BRAUN* Luer cannulas. Exact volumetric manipulations were carried out with the aid of Hamilton gastight syringes (RN) of the 1700 series and 800 series, for volumes between 1 µL and 10 µL. Hamilton syringes were stored under dry Argon atmosphere prior to use. Thin layer chromatography (TLC) was performed on *Merck TLC aluminium sheets* (silical gel 60, F254) and column chromatography with silica gel (grain size 0.04-0.063 cm, *Macherey-Nagel Si60*) at atmospheric pressure.

Chemicals were bought from *ABCR*, *Acros*, *Alfa Aesar*, *Baker*, *Carbolution Chemicals*, *Carl Roth*, *Chempur*, *Fluorochem* and *Honeywell*. 4-Picolin and isonicotinaldehyde were distilled, halopyridines sublimed. Octyl triflate was synthesized according to literature.[1] Methylene chloride (DCM), diethyl ether, ethyl acetate (EtOAc), tetrahydrofuran (THF) and petrol ether (PE) (60-80) were bought in technical grade quality and distilled prior to further use. Dimethyl formamide (DMF) was bought in peptide grade quality, distilled and dried twice over 3 Å molecular sieves. Diisopropylamine (*Acros*), fresh bottles were opened, molecular sieves were added, and the bottles closed with AcroSeals (black), obtained from old *n*-BuLi bottles. DCM, Ether and THF were pre-dried over molecular sieves before subjecting to a *MBRAUN* MP-SPS-800. Deuterated Solvents were obtained from *Deutero* ($CDCl_3$, DMSO-d_6) and Eurisotop (Acetonitrile-d_3, Methylenechloride-d_2) and dried over molecular sieves. The Water content of solvents was monitored by Karl Fischer titration using *a SI Analytics/Xylem* TitroLine 7500 KF trace with a *Honeywell* (former *Fluka*) Hydranal-Coulomat-AD solution and kept below 40 ppm for synthetic purpose and 25 ppm for NMR titrations and kinetic measurements. Kugelrohr distillations were performed on a customized *Heidolph* rotavapor, using a heat gun as the temperature source and two ice or dry ice cooled NS14 or NS29 Kugelrohr flasks as traps for products and byproducts. The part behind the motor was closed using a home-made glass adapter with a single valve for the attachment to a Schlenk line.

1.2 Materials and Methods

NMR spectra were recorded on the following Bruker devices: DPX-200 (200 MHz), DPX-250 (250 MHz), DRX-400 (400 MHz), AVIII-300 (300 MHz) and AVIII-400 (400 MHz). Kinetic experiments were performed at the AVIII-300, titrations in DMF-H_7 on the AVIII-400 using solvent suppression techniques. Shifts are given in parts per million (ppm). The generated data was analyzed with TopSpin and MestReNova 11.[2]

GC-MSD spectra were measured on an *Hewlett Packard* 5890 SERIES II gas chromatograph coupled to a 5970 Mass Selective Detector and an Agilent 7820A GC with 5877B MSD, both equipped with a 30 m HP5MS column using Helium as carrier gas.

IR-Spectra were recorded on a *Shimadzu IR Affinity – 1S* spectrometer with a *Specac-Quest* ATR module.

UV-Spectra were recorded on a *UV/vis Varian Cary 60 Spectrophotometer*.

Elemental analysis (C, H, N, S) was performed on a *vario Micro cube* from *Elementar Analysentechnik*.

Melting points were determined on a *Büchi* Melting point M565 device, and are reported uncorrected.

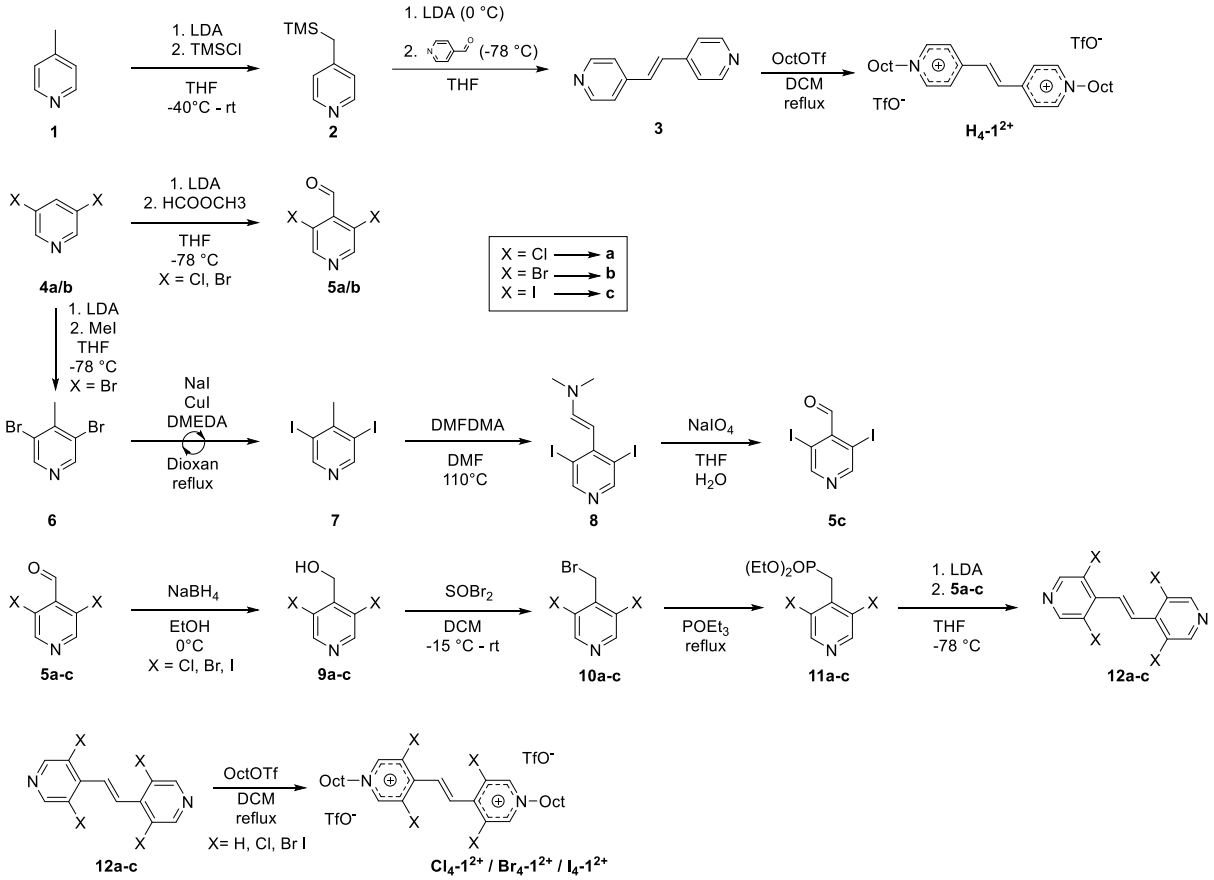
Single crystals (in Bochum, DE) were analyzed on a *Rigaku* XtaLAB mini, equipped with a 600 W Mo micro-fine focus glass sealed tube, graphite monochromator (Mo K_α) and CCD detector; a *Rigaku* Synergy dual source device, with Co and Mo micro focus sealed tubes (Cu & Mo K_α) using mirror monochromators and a HyPix-6000HE: Hybrid photon counting X-ray detector. Crystals were mounted in *Hampton* CrypLoops using Parabar/Paratone or *GE/Bayer* silicone grease. Data on both systems was recorded and reduced using the CrysalisPro[3] Software. Structures were solved using WinGX[4] in combination with ShelXT[5] and refined with shelXle[6] and ShelXL. The structure (in Paris, F) was analysed using a *Bruker* APEX-II with graphite monochromator, Cu K_α radiation from a microfocus sealed tube. The Structure was solved using the Olex2 software package in combination with ShelXL and ShelXT. Tables for the publication were generated using a modified version of Ciftab. Pictures of the structures were generated with Diamond 4.[7]

All liquids substrates were filtered over activated neutral aluminum oxide. Cyclic voltammetry experiments were performed using a Metrohm AUTOLAB instrument for classical electrochemical. The measurements were performed in a standard one-compartment three electrode cell containing 0.1 M solution of nBu_4PF_6 in anhydrous DMF thermostated at 298 K. A mechanically polished glassy carbon disk electrode (carbon rod of 3

mm diameter embedded in an insoluble polymer matrix, CHI Instruments. Inc., USA) was used as working electrode and a platinum wire as auxiliary electrode. A salt bridge containing the electrolyte was used to connect the electrochemical cell with a saturated calomel reference electrode (SCE). Electrolyte and solvent were put into the electrochemical cell equipped with the working, auxiliary and reference electrode under anhydrous argon atmosphere. The solvents were degassed for a few minutes prior to the experiment. After taking a background scan, a solution containing the XB donor was added and the cyclic voltammogram was recorded.

In the titration experiments, used to determine the corresponding affinity constants, the added solutions systematically contained the respective Lewis bases in form of commercially available nBu_4X salts, the supporting electrolyte salt as well as the electrochemical probe (**X_4-1** derivative) in order to keep the concentrations of the two latter compounds constant during all experiments. In representative CV experiments it has been verified that ohmic drop compensation was not necessary at the applied and relatively slow scan rate of 0.1 V/s. The determination of the potential shift was performed on the basis of the data from the original CV's without background subtraction.

2. Syntheses and Characterization



Scheme S1. General reaction scheme for the synthesis of **X_4-1^{2+},OTf_2** (X = H, Cl, Br, I) starting from 4-picolin or 3,5-dihalo-pyridines.

4-Picolinyl-trimethylsilane (2)[8]

An oven dried 250 mL Schlenk round bottom flask was flushed with Argon ,equipped with a rubber septum, a Teflon coated stirring bar and filled with 100 mL of THF, 15.9 mL of diisopropylamine (113 mmol, 1.1 eq) and cooled to -40°C before 45 mL of *n*-BuLi (2.5 M in hexane, 113 mmol, 1.1 eq) was added rapidly. After 5 min of stirring 10 mL of freshly distilled 4-picoline (103 mmol) were added slowly (~2 min) and the solution was stirred for 30 min before 15 mL of TMSCl (118 mmol, 1.15 eq) were added dropwise (~10 min). After stirring to room temperature, the mixture was poured onto the same volume of ice-cold water $NaHCO_3$-sol. Phases were separated and the aqueous phase extracted twice with EtOAc. The combined organic phases were washed with brine once and dried over Na_2SO_4. The solvents were removed in vacuo and the yellow-brown residue subjected to Kugelrohr distillation at 10^{-3} mbar, to obtain 11.5 g of 4-(Trimethylsilylmethyl)-pyridine a clear colourless liquid (68%), which slowly turns red and decomposes over several weeks.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.38 (d, *J* = 4.5 Hz, 2H), 6.90 (d, *J* = 6.0 Hz, 2H), 2.09 (s, 2H), 0.06 (s, 9H).

E-4,4'-diazastilbene (3)[9,10]

LDA was freshly prepared from 3.57 mL diisopropylamine (25.4 mmol, 1.05 eq) and 10.2 mL *n*-BuLi (2.5 M, 1.05 eq) at -40°C in a 50 mL Schelenktube, containing 20 mL of THF. 4 g of **2** (24.2 mmol) were added using a syringe. The solution was stirred to room temperature for ~15 min, kept there for another 20 min and cooled to -78°C before 2.5 mL freshly distilled isonicotinaldehyde (26.6 mmol, 1.1 eq) were added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for another 10 h. After quenching by pouring the solution into saturated $NaHCO_3$-sol., the phases were separated, and the aqueous phase extracted with the same amount of chloroform. The THF phase was washed with brine combined with the chloroform phase and dried over Na_2SO_4

before the solvent was removed in vacuo, leaving a reddish oil behind. The oil was diluted with 5 mL of DCM and the product precipitated using pentane, filtered off and resolubilized using DCM. This was repeated twice, yielding 2.47 g of **3** (56%) as a white powder. *Cis* product could not be observed.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.61 (dd, *J* = 4.4 Hz and 1.7 Hz, 4H), 7.39 (dd, *J* = 5.2 Hz and 1.6 Hz, 4H), 7.21 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ = 150.53, 143.53, 130.65, 121.30.
EI-MSD (m/z): M^+ = 182.2

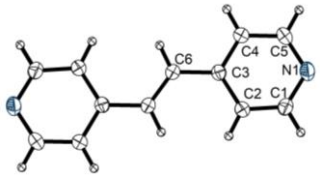


Figure S1. Crystal structure of **3**.

3,5-Dihalo-isonicotinaldehydes (Cl (5a) and Br (5b))

The compounds were prepared in a manner similar to Stewart et al.[11] 30 mL THF and 3.1 mL diisopropylamine (23 mmol, 1.1 eq) were introduced into an oven dried 250 mL round bottom Schlenk flask attached to a 50 mL dropping funnel. While cooling to -78°C, 9.2 mL *n*-BuLi (2.5 M in hexane, 23 mmol, 1.1 eq) were added. 21 mmol of the dihalopyridine (1eq, Cl = 3.11 g; Br = 4.97 g) were dissolved in 25/40 mL of THF and added over the course of about 2.5 h to the stirred LDA solution.[a] The dropping funnel was rinsed with another 10-20 mL of THF. The solution turns from bright yellow to orange (Cl) or dark red (Br) and is stirred for another 30 min, before 2.6 mL methyl formate (42 mmol, 2eq) in 30 mL THF were added over 30 min.[b] After further 1.5 h the reaction mixture was transferred onto 100 mL of an ice cold well stirred sat. Na_2CO_3 solution.
Phases were separated and the aqueous phase extracted thrice with the same amount of ethyl acetate. The organic phases were combined, washed with brine, filtered over a short pad of silica or diatomaceous earth, dried over Na_2SO_4 and the solvents were removed in vacuo, leaving a mostly brownish residue with white needles.
The products can be purified by flash column chromatography with Petrolether/EtOAc 100:6, but it was found to be more efficient to transfer the residue into a tube and separate starting material and product by sublimation through glass wool at 10^{-3} mbar. The condenser part was kept at room temperature or cooled with water. The sublimation temperatures were ~40°C for **5a** and 60-80°C for **5b**, yielding 2.8 g **5a** (73%) or 4.0 g **5b** (72%). Both products were obtained as white off crystalline powder, which turned yellow over time.

5a 3,5-Dichloroisonicotinaldehyde
^{1}H NMR (200 MHz, DMSO-d_6) δ = 10.31 (s, 1H), 8.80 (s, 2H).
^{13}C NMR (63 MHz, DMSO-d_6) δ = 188.78, 149.24, 136.36, 130.29.
EI-MSD (m/z): M^+ = 173.9, 174.9, 176.9
E_{calc}: C, 40.95%; H, 1.94%; N, 7.96%; Cl, 40.29%. **E_{obs}**: C, 40.12%; H, 1.94%; N, 7.93%.

5b 3,5-Dibromoisonicotinaldehyde
^{1}H NMR (200 MHz, DMSO-d_6) δ = 10.08 (s, 1H), 8.89 (s, 2H).
^{13}C NMR (50 MHz, DMSO-d_6) δ = 191.35, 151.86, 139.74, 119.48.
EI-MSD (m/z): M^+ = 262.8, 264.8, 266.8
E_{calc}: C, 27.20%; H, 1.14%; N, 5.29%; Br, 60.33%; O, 6.04%. **E_{obs}**: C, 27.32%; H, 1.29%; N, 5.25%.

3,5-Dibromo-4-picolin (6)

The compound is synthesized similar to the method described above (from 3,5-dibromopyridine), but instead of methyl formate 2.6 mL of methyl iodide (42 mmol, 2 eq) were used. The solution was stirred to room temperature overnight and quenched by adding 50 mL of half concentrated ammonia solution. After workup, as

FOOTNOTES
[a] When scaling up the reaction (for yields > 20 g) best results were obtained when the cooling bath was kept around -90 °C, otherwise larger amounts of dimerization were observed. For proper stirring a mechanical (KPG) stirrer was used.
[b] When dry DMF (workup with NH_4Cl) instead of methylformate was used the yields dropped to ~30%.

above, the product was purified by fractionate sublimation (80-95°C, 10^{-3} mbar), yielding 4.3 g of **6** (82%) as white off crystalline lumps.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.56 (s, 2H), 2.56 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ = 150.12, 146.46, 123.58, 22.98.
EI-MSD (m/z): M^+ = 248.9, 250.9, 252.9
E_{calc}: C, 28.72%; H, 2.01%; N, 5.58%; Br, 63.69%. **E_{obs}**: C, 40.61%; H, 2.89%; N, 7.85%.

3,5-Diiodo-4-picolin (7)

According to Lützen et al,[12] 10 g of **6** (39.9 mmol) were suspended in 500 mL of dry degassed 1,4-dioxane, containing (in order of addition) 760 mg copper(I) iodide (4 mmol, 0.1 eq), 900 µL N,N'-dimethylethylenediamine (8 mmol, 0.2 eq) and 24 g sodium iodide (160 mmol, 4 eq). The mixture was refluxed for 24 h at 110°C, cooled to room temperature, poured into 200 mL half concentrated aqueous ammonia solution and stirred for 10 min. The product is filtered off, washed with ammonia solution and ether, and is dried in vacuo, before checking the conversion, with GC-MSD or NMR, which is after the first cycle about 75% **7**, 24% of 3-bromo-5-iodopicolin and 1% of **6**. The procedure was repeated until only **7** was left, normally two times. The crude product was sublimed at 90-95°C at 10^{-3} mbar through glass wool, to remove remaining copper traces, and obtain **7** as white off needles or chunks. The yield varied between 4.1 g and 6.9 g (30% to 50%).

^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.75 (s, 2H), 2.69 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ = 156.74, 152.39, 99.76, 34.07.
EI-MSD (m/z): M^+ = 344.9.
E_{calc}: C, 20.89%; H, 1.46%; N, 4.06%; I, 73.58%. **E_{obs}**: C, 21.29%; H, 1.49%; N, 4.06%.

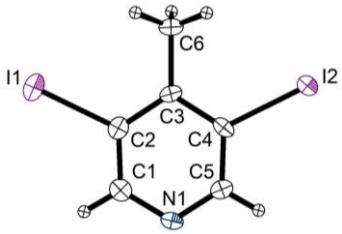


Figure S2. Crystal structure of **7.**

3,5-Diiodoisonicotinaldehyde (5c)

In a 100 mL oven-dried round bottom flask 1 g of **7** (2.9 mmol) were dissolved in 20 mL dry DMF to which 700 µL dimethylformamid dimethylacetal (5.3 mmol 1.8 eq) were added. The mixture was stirred at 90°C over 16 h before cooling to room temperature and removing the DMF in vacuo, leaving a yellow residue which consisted of 25% - 50% of **7** and 3,5-diiodo-4-(2-N,N-dimethylamino-trans-vinyl)-pyridine (**8**).[13]

^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.67 (s, 2H), 7.35 (d, *J* = 13.5 Hz, 1H), 4.97 (d, *J* = 13.5 Hz, 1H), 2.95 (s, 6H); EI-MSD (m/z): M^+ = 399.9)

The crude mixture was oxidized according to literature,[14] by dissolving it in 50 mL THF and dropwise addition of 2.3 g $NaIO_4$ in 50 mL water. The solution turns immediately yellow and white precipitate forms after 20 min. Product formation can be traced by TLC (PE/EtOAc 10:1). After 24 h the mixture is filtered and the white solid washed with DCM. The filtrate is extracted with more DCM, and the organic layer dried over Na_2SO_4. The solvent was removed and the yellow solid subjected to column chromatography PE/EtOAc/Toluene 100:10/1, yielding **5c** in 50% - 75% yield as a fine yellow powder. Single crystals were obtained by sublimation in a glass tube at 100-120 °C at 10^{-3} mbar.

^{1}H NMR (300 MHz, DMSO-d_6) δ = 11.95 (s, 1H), 11.29 (s, 2H).
^{13}C NMR (75 MHz, DMSO-d_6) δ = 196.06, 157.61, 144.28, 95.17.
EI-MSD(m/z): M^+ = 358.8
E_{calc}: C, 20.08%; H, 0.84%; I, 70.72%; N, 3.90%; O, 4.46%. **E_{obs}**: C, 20.00%; H, 0.95%; N, 3.92%.
IR [cm^{-1}]: 1705 (ν-CO)

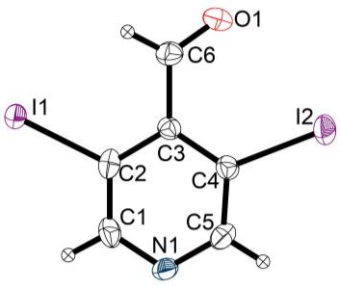


Figure S3. Crystal structure of **5c.**

3,5-dihalo-4-pyridinecarbinol (9a-c)

2.8 mmol of the corresponding isonicotinaldehydes **5a-c** (Cl = 500 mg; Br = 750 mg; I = 1 g) were dissolved in 50 mL MeOH. At 0°C 500 mg of $NaBH_4$ (13.2 mmol, 4.7 eq) were added portion wise over 30 min. The mixture was stirred to room temperature, poured into 50 mL sat. $NaHCO_3$ solution and extracted thrice with the same volume of DCM, which was then dried over $NaSO_4$ and removed in vacuo. **9a-c** were obtained in 90% - 99% yield as colorless to yellowish powders (**9a** = 498 mg; **9b** = 730 mg, **9c** = 960 mg).

9a: 3,5-dichloro-4-pyridinecarbinol
^{1}H NMR (200 MHz, CDCl3) δ = 8.51 (s, 2H), 4.94 (d, *J* = 7.0 Hz, 2H), 2.23 (t, *J* = 7.0 Hz, 1H).
^{13}C NMR (63 MHz, CDCl3) δ = 148.17, 143.32, 132.88, 59.30
EI-MSD (m/z): M^+ 176.9, 178.9.
E_{calc}: C, 40.48%; H, 2.83%; N, 7.87%; Cl, 39.83%. **E_{obs}**: C, 40.61%; H, 2.89%; N, 7.85%.

9b: 3,5-dibromo-4-pyridinecarbinol
^{1}H NMR (250 MHz, CDCl3) δ = 8.65 (s, 2H), 4.96 (s, 2H).
^{13}C NMR (63 MHz, CDCl3) δ = 151.22, 123.40, 100.14, 64.32
EI-MSD (m/z): M^+ 264.9, 266.8, 268.8.

9c: 3,5-diiodo-4-pyridinecarbinol
^{1}H NMR (300 MHz, DMSO-d_6) δ = 8.81 (s, 2H), 5.40 (t, *J* = 5.1 Hz, 1H), 4.68 (d, *J* = 5.1 Hz, 2H).
^{13}C NMR (75 MHz, DMSO-d_6) δ = 156.89, 152.18, 100.71, 71.34.
EI-MSD (m/z): M^+ 360.9
E_{calc}: C, 19.97; H, 1.40; I, 70.32; N, 3.88; O, 4.43. **E_{obs}**: C, 20.31%; H, 1.37%; N, 3.95%.

3,5-Dihalo-4-picolinyl bromide (10a-c)

Under Argon 2.5 mmol of **9a-c** (Cl = 445 mg; Br = 667 mg; I = 900 mg) and one drop of DMF were dissolved in 50 mL dry DCM, which was cooled to about -15°C. 200 µL of fresh $SOBr_2$ (2.6 mmol, 1.04 eq) were added dropwise, stirred for further 30 in at -15°C – 0°C and 1.5 h at ambient temperature. The reaction was stopped by pouring the solution into 50 mL ice cold saturated $NaHCO_3$. The phases were separated, the aqueous phase extracted twice with 25 mL Chloroform. The solvent of the combined organic phases were directly evaporated leaving reddish oils behind, which solidified on standing. (**10a** = 83%; **10b** = 87%; **10c** = 57%).

10a: 3,5-dichlor-4-(bromomethyl)-pyridine
^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.52 (s, 2H), 4.64 (s, 2H).
Mp: Decomposition T > 70°C
EI-MSD (m/z): M^+ 238.9, 240.8, 242.8.

10b: 3,5-dibromo-4-(bromomethyl)-pyridine
^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.64 (s, 2H), 4.69 (s, 2H).
Mp: Decomposition T > 70°C
EI-MSD (m/z): M^+ 326.8, 328.8, 330.8, 332.8.

10c:3,5-diiodo-4-(bromomethyl)-pyridine[c]
^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.84 (s, 2H), 4.95 (s, 2H).
Mp: Decomposition T > 70°C
EI-MSD (m/z): M^+ 422.75, 424.75.

Diethyl 3,5-dihalo-4-picolinyl phosphonate (11a-c)

The residues from the previous step were transferred into weighted 10 mL Schlenktubes, by dissolving them in DCM, which was evaporated thereafter. 1 mL of freshly distilled triethylphosphite (excess) was added, the vessels sealed with a glass stopper and heated to 110°C for 5-6 h. Bromoethane and solvent were evaporated at 10^{-3}

FOOTNOTES
[c] Analogous to the lithiation of 4-picolin it is possible to apply LDA to **6b** at temperatures between -78°C and -40°C and quench the reaction with 1,2-dibromo-tetrafluoroethane. But due to the availability and price of the bromination reagent we generally stuck to the reduction-bromination method. Brominations and silylations with elemental bromine, CBr_4, 1,2-dibromo-tetrachloroethane, or TMSCl failed.

mbar until the mass of the tubes were constant. Products were obtained as sticky brown solids, which were used in the next step without further purification (**11a**= 613 mg, **11b** = 834 mg; **11c** = 680 mg).

11a: Diethyl 3,5-dichloro-4-picolyl-phosphonate
^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.38 (s, 2H), 4.03 (p, *J* = 7.2 Hz, 4H), 3.49 (d, *J* = 23.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (63 MHz, $CDCl_3$) δ = 147.49 (d, *J* = 3.2 Hz), 138.33 (d, *J* = 10.1 Hz), 132.94 (d, *J* = 6.1 Hz), 62.49 (d, *J* = 6.8 Hz), 29.60 (d, *J* = 138.1 Hz), 16.26 (d, *J* = 6.2 Hz).
^{31}P NMR (101 MHz, $CDCl_3$) δ = 21.91-20.58 (m).
EI-MSD (m/z): M^+ 296.0, 298.1, 300.1.
E_{calc}: C, 40.29%; H, 4.73%; N, 4.70%; Cl, 23.78%; O, 16.10%; P, 10.39%. **E_{obs}**: C, 40.32%; H, 4.31%; N, 4.86%.

11b: Diethyl 3,5-dibromo-4-picolyl-phosphonate
^{1}H NMR (200 MHz, DMSO-d_6) δ = 8.73 (s, 2H), 4.03 (dt, *J* = 14.8 Hz and 7.1 Hz, 4H), 3.60 (d, *J* = 22.4 Hz, 2H), 1.21 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (63 MHz, $CDCl_3$) δ = 150.72 (d, *J* = 3.2 Hz), 141.60 (d, *J* = 10.0 Hz), 123.69 (d, *J* = 6.4 Hz), 62.58 (d, *J* = 6.7 Hz), 34.99 (d, *J* = 137.7 Hz), 16.34 (d, *J* = 6.2 Hz).
^{31}P NMR (101 MHz, $CDCl_3$) δ = 21.91-20.66 (m).
EI-MSD (m/z): M^+ 384.0, 385.9 387.9.
E_{calc}: C, 31.04%; H, 3.62%; N, 3.65%; Br, 41.29%; O, 12.40%; P, 8.00%. **E_{obs}**: C, 31.48%; H, 3.55%; N, 4.29%.

11c: Diethyl 3,5-diiodo-4-picolyl-phosphonate
^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.82 (s, 2H), 4.10 - 4.04 (m, 4H), 3.75 (d, *J* = 23.0 Hz, 1H), 1.40 - 1.27 (m, 6H).
EI-MSD (m/z): M^+ 481.0.

E-4,4'-Diaza-2,2',6,6'-tetrahalostilben (12a-c)

Calculated for 1 mmol of phosphonate **11a-c**:
Fresh LDA was prepared from 150 µL diisopropylamine (1.07 mmol, 1.07 eq) and 420 µL *n*-BuLi (2.5 M in hexanes, 1.05 mmol, 1.05 eq) in 20 mL THF at -78°C in a 50 mL Schlenk tube. The solution was stirred for 10 min at -78°C. The sticky residue from the last step was dissolved in 5-10 mL THF and added dropwise over 5 min. The reaction mixture was stirred for 30 min, before the corresponding aldehydes (1.1 mmol, 1.1 eq, **5a**: 294 mg **5b**: 291 mg **5c**: 395 mg), dissolved in 5-10 mL THF were added dropwise over 10 min. The solution was left in its cooling bath and slowly stirred to ambient temperature, while the products precipitated as white (**12a**, **12b**) or yellow (**12c**) powders. After stirring for 5 h at room temperature 10 mL sat. $NaHCO_3$ sol was added, the precipitate filtered off and washed with a 2 mL THF. For **12a** and **12b** the phases were separated, the THF washed with brine once, dried and evaporated, though only very small amounts, containing mostly aldehyde and carbninol were obtained this way. The filtered off solid was triturated with ether and pentane, as well as small amounts of ice-cold DCM, to obtain **12a-c** in pure, partially crystalline form. **12a** (51%) and **12b** (46%) form asbestos like, brittle white needles, while **12c** (31%) was always obtained as a yellow powder, which can be recrystallized from refluxing chloroform. The general solubility drops rapidly from the in the order Cl>Br>I.[15]

12a: *E*-4,4'-Diaza-2,2',6,6'-tetrachlorostilben
^{1}H-NMR (250 MHz, $CDCl_3$) δ = 8.57 (s, 4H), 7.38 (s, 2H).
^{13}C-NMR (63 MHz, $CDCl_3$) δ = 148.40, 140.31, 131.35, 131.14.
Mp: 196.5°C (decomposition at ~205°C)
EI-MSD (m/z): M+ 317.9, 320.0, 321.9
E_{calc}: C, 45.04%; H, 1.89%; N, 8.75%; Cl, 44.31%. **E_{obs}**: C, 45.94%; H, 2.22%; N, 8.52%.

12b: *E*-4,4'-Diaza-2,2',6,6'-tetrabromostilben[d]
^{1}H-NMR (200 MHz, $CDCl_3$) δ = 8.78 (s, 4H), 7.18 (s, 2H).
^{13}C-NMR (50 MHz, $CDCl_3$) δ = 151.30, 143.74, 134.54, 121.57.
Mp: 224.1°C
EI-MSD (m/z): M^+ 493.6, 495.7, 497.6, 499.8, 501.9.

FOOTNOTES
[d] Without addition of vanadium pentoxide no proper elemental analysis was obtained.

E_{calc}: C, 28.95%; H, 1.21%; N, 5.63%; Br, 64.20%. **E_{obs}:** C, 28.99%; H, 1.22%; N, 5.64 %.

12c: *E*-4,4'-Diaza-2,2',6,6'-tetraiodostilben
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.85 (s, 4H), 6.66 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.41, 149.90, 140.71, 96.83.
EI-MSD (m/z): M^+ 685.8
E_{calc}: C, 21.02%; H, 0.88%; N, 4.08%; I, 74.02%. **E_{obs}:** C, 21.22%; H, 0.91%; N, 4.10 %.

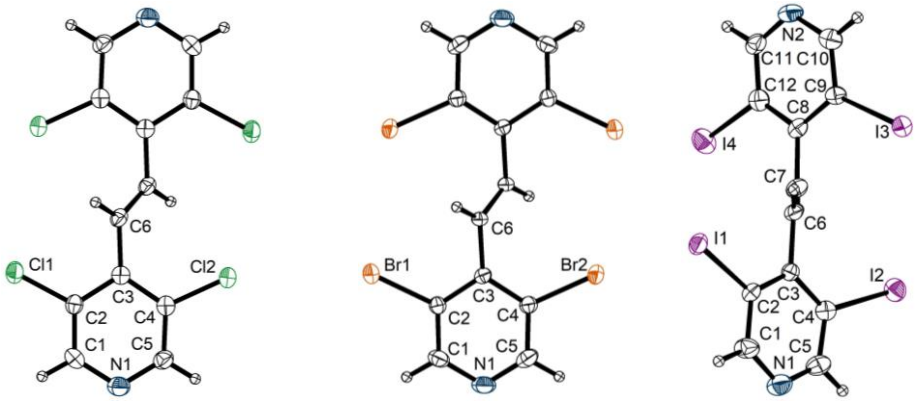


Figure S4. Juxtaposition of the crystal structures of **12a**, **12b**, and **12c**.

***E*-(2,2',6,6'-tetrahalo-)4,4'-di-octyl-4,4'-diaza-stilbenbisium bistriflate) (X_4-1)**
For the octylation according to Walter et al.[16] 1 mmol of the corresponding diazastilbene derivatives **12a-c** was suspended in 10 mL DCM, to which 2.2 mmol (2.2 eq) octyltriflate were added. The flask was closed and the contents heated to reflux for 1 h, whilst stirring. The DCM was decanted off (if necessary centrifugation) and the residual solid dissolved in MeCN. After precipitation with diethyl ether, decantation resolubilization with MeCN and a second precipitation, the filtered off solids were dried in vacuo. The yields varied between 90% and 95%.

H_4-1^{2+}: E-4,4'-di-octyl-4,4'-diaza-stilbenbisium bistriflate
^{1}H NMR (400 MHz, MeCN-d_3) δ = 8.68 (dt, *J* = 7.0 Hz and 1.7 Hz, 4H), 8.18 (dt, *J* = 7.1 Hz and 2.0 Hz, 4H), 7.85 (t, *J* = 2.1 Hz, 2H), 4.50 (t, *J* = 7.5 Hz, 4H), 1.98 (d, *J* = 7.2 Hz, 4H), 1.39 – 1.25 (m, 22H), 0.89 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (101 MHz, MeCN-d_3) δ = 151.64, 145.33, 134.43, 126.50, 62.04, 31.99, 31.40, 29.28, 29.15, 26.16, 22.89, 13.93.
^{19}F NMR (377 MHz, Acetonitrile-d_3) δ = -79.32.
EI-MS (m/z): pos: 610.69 ($-H^+$); neg: 148.89 (triflate)
E_{calc} (·$2H_2O$): C, 48.51%; H, 6.51%; F, 15.35%; N, 3.77%; O, 17.23%; S, 8.63% **E_{obs}** (·$2H_2O$): C, 48.70%; H, 6.51%; N, 3.76%.
FT-IR [cm^{-1}]: 405.05 (w), 513.07 (m), 530.42 (s), 578.64 (s), 640.37 (s), 671.23 (w), 725.23 (w), 758.02 (w), 781.17 (w), 852.54 (m), 862.18 (m), 877.61 (w), 974.05 (m), 989.48 (m), 1035.77 (s), 1149.57 (s), 1165.00 (s), 1207.44 (s), 1226.73 (s), 1240.23 (s), 1253.73 (s), 1273.02 (s), 1340.53 (w),1373.32 (w), 1467.83 (m), 1521.84 (w), 1570.06 (w), 1637.56 (m), 2856.58 (m), 2926.01 (m), 3061.03 (w), 3124.68 (w), 3387.00 (w), 3568.31 (w).

Cl_4-1^{2+} (was not analyzed further) E-2,2',6,6'-tetrachloro-4,4'-di-octyl-4,4'-diaza-stilbenbisium bistriflate
^{1}H NMR (250 MHz, MeCN-*d*3) δ = 8.95 (s, 4H), 7.50 (s, 2H), 4.73–4.44 (m, 4H), 3.43 - 3.38 (m, 4H), 1.38 - 1.30 (m, 20H), 0.94 - 0.89 (m, 6H).
E_{calc}: C, 42.66%; H, 4.77%; Cl, 16.79%; F, 13.50%; N, 3.32%; O, 11.37%; S, 7.59%. **E_{obs}**: C, 42.66%; H, 4.88%; N, 2.90%.

Br_4-1^{2+}: E-2,2',6,6'-tetrabromo-4,4'-di-octyl-4,4'-diaza-stilbenbisium bistriflate
^{1}H NMR (400 MHz, MeCN-d_3) δ = 9.06 (s, 4H), 7.29 (s, 2H), 4.52 (t, *J* = 7.7 Hz, 4H), 2.07 - 2.00 (m, 4H), 1.46 - 1.28 (m, 24H), 0.93 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (101 MHz, MeCN-d_3) δ = 153.45, 146.16, 135.99, 124.13, 62.76, 31.99, 31.21, 29.27, 29.11, 26.08, 22.91, 13.94.
EI-MS (m/z): pos: 610.69 (-1x octyl); neg: 148.68 (triflate).

E_{calc}: C, 35.24%; H, 3.94%; Br, 31.26%; F, 11.15%; N, 2.74%; O, 9.39%; S, 6.27%. **E_{obs}:** C, 35.51%; H, 3.94%; N, 2.74%.
FT-IR [cm^{-1}]: 416.62 (w), 516.92 (s), 543.93 (w), 572.86 (s), 634.58 (vs), 734.88 (m), 758.02 (m), 773.46 (m), 885.33 (m), 923.90 (m), 950.91 (s), 1026.13 (vs), 1153.43 (vs), 1188.15 (s), 1222.87 (s), 1244.09 (s), 1261.45 (s), 1379.10 (w), 1450.47 (m), 1467.83 (m), 1616.35 (m), 2856.58 (w), 2927.94 (m), 3012.81 (w), 3080.32 (w).

I_4-1^{2+}: E-2,2',6,6'-tetraiodo-4,4'-di-octyl-4,4'-diaza-stilbenbisium bistriflate
^{1}H NMR (400 MHz, MeCN-d_3) δ = 9.11 (s, 4H), 6.97 (s, 2H), 4.40 (t, *J* = 7.6 Hz, 4H), 1.99 (d, *J* = 7.0 Hz, 4H), 1.40 - 1.26 (m, 22H), 0.90 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (101 MHz, MeCN-d_3) δ = 160.01, 151.79, 142.15, 97.06, 62.24, 32.42, 31.70, 29.70, 29.52, 26.54, 23.33, 14.38.
^{19}F NMR (377 MHz, MeCN-d_3) δ = -79.30.
EI-MS (m/z): pos: 686.31 (-2x octyl); neg: 148.69 (triflate).
E_{calc}: C, 29.77%; H, 3.33%; F, 9.42%; I, 41.94%; N, 2.31%; O, 7.93%; S, 5.30%. **E_{obs}:** C, 29.94%; H, 3.35%; N, 2.25%.
FT-IR [cm^{-1}]: 514.99 (m), 572.86 (m), 634.58 (s), 738.74 (m), 883.40 (w), 910.40 (w), 927.76 (m), 952.84 (m), 1028.06 (vs), 1151.50 (vs), 1222.87 (vs), 1247.94 (vs), 1421.54 (m), 1438.90 (m), 1467.83 (m), 1512.19 (w), 1602.85 (m), 2850.79 (m), 2926.01 (m), 3018.60 (w), 3074.53 (w).

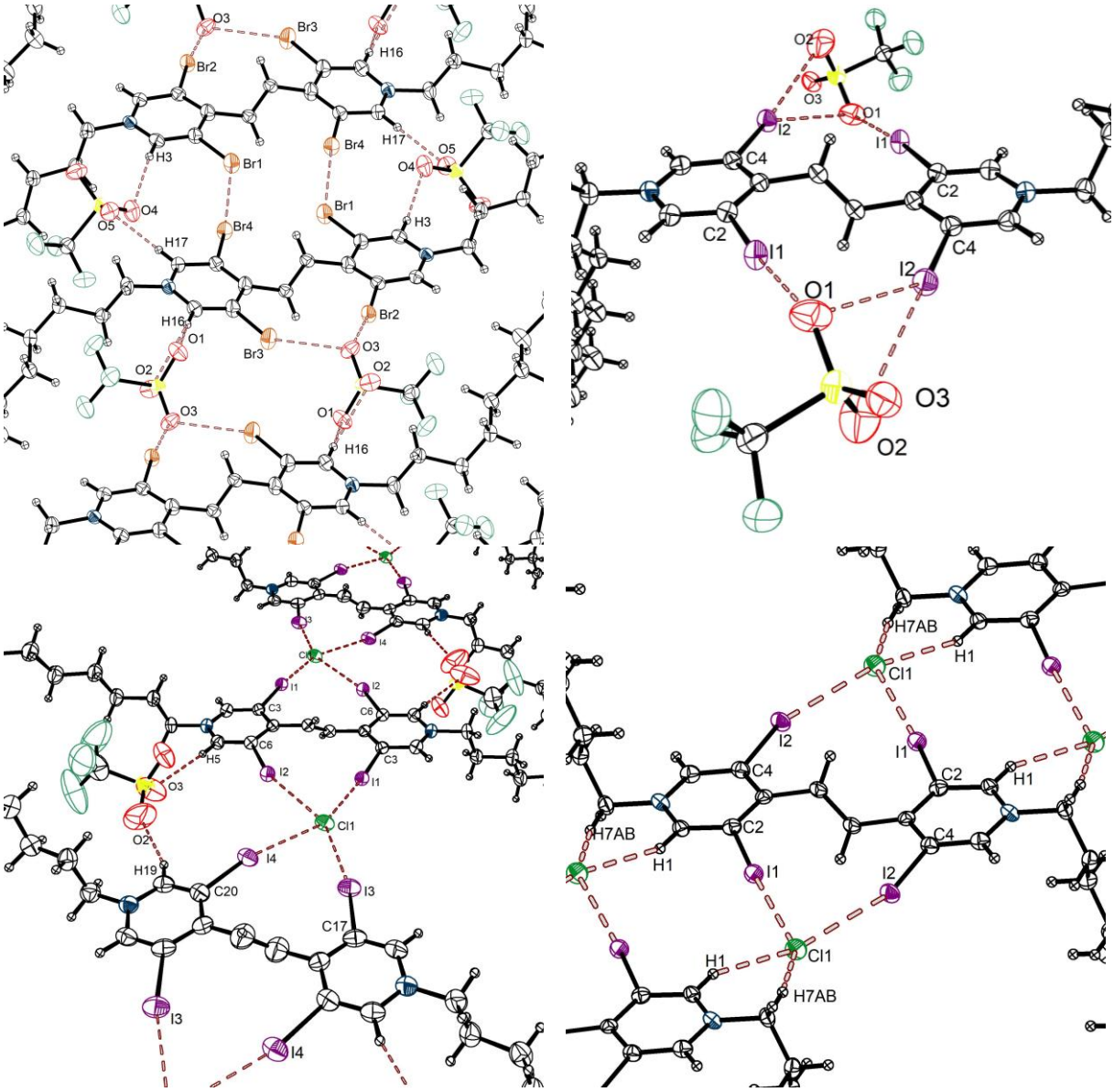


Figure S5. Crystal structures of **[Br_4-1^{2+}, $(OTf^-)_2$]** (top left), **[I_4-1^{2+}, $(OTf^-)_2$]** (top right), **[I_4-1^{2+}, (OTf^-) (Cl^-)]** (bottom left), **[I_4-1^{2+}, Cl^-_2]** (bottom right).

3. Electrochemical Characterization

Table S1. Electrochemical data

	$E^{o'}_1$ [a]	$E^{o'}_2$ [a]	D [b]
H_4-1^{2+}	-0.46	-0.66	2.17
Br_4-1^{2+}	-0.20	-	1.64
I_4-1^{2+}	-0.27	-	1.19

[a] in V; [b] in 10^{-6} mol·cm^{-2}

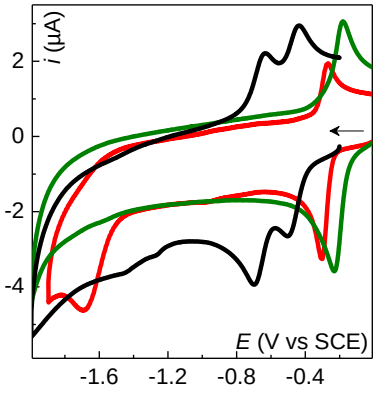


Figure S6. CVs of 0.1 mM of **I_4-1^{2+}** (red trace), **Br_4-1^{2+}** (green trace) and **H_4-1^{2+}** (black trace) in 0.1 M nBu_4PF_6/DMF on a glassy carbon electrode (3 mm-diameter) at 298 K. ν = 0.1 V.s^{-1}.

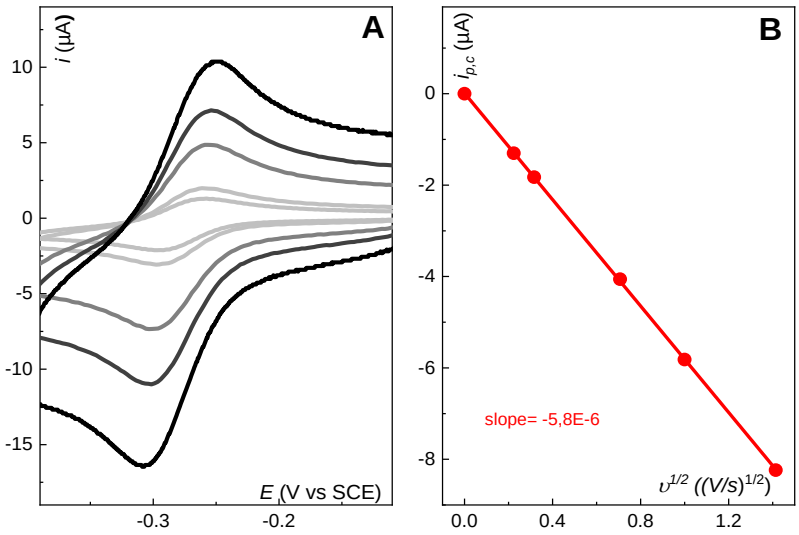


Figure S7. A) CV of **I_4-1^{2+}** recorded at different scan rate (from top to bottom 2, 1, 0.5, 0.1 and 0.05 V.s^{-1}) on GC electrode. B) Plot of the cathodic peak current ($i_{p,c}$) as a function of the square root of the scan rate.

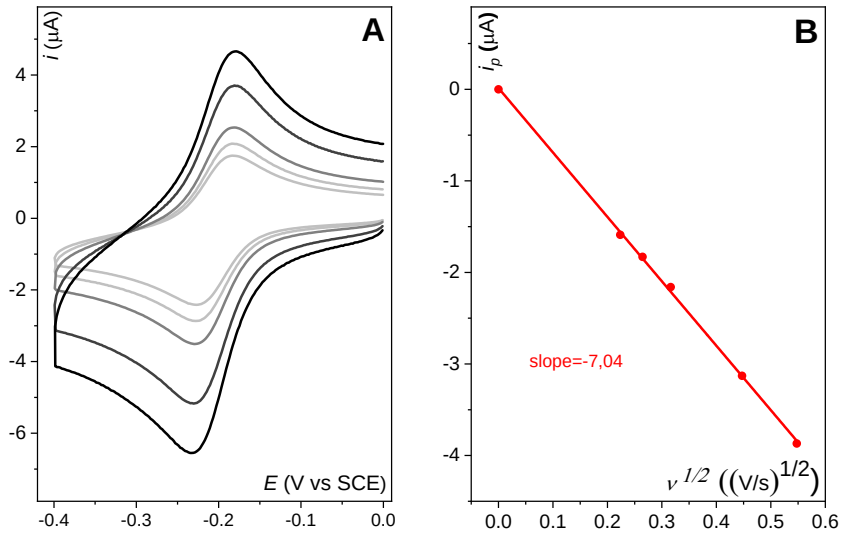


Figure S8. A) CV of **Br_4-1^{2+}**recorded at different scan rate (from top to bottom 300, 200, 100, 70 and 50 mV.s^{-1}) on GC electrode. B) Plot of the cathodic peak current ($i_{p,c}$) as a function of the square root of the scan rate.

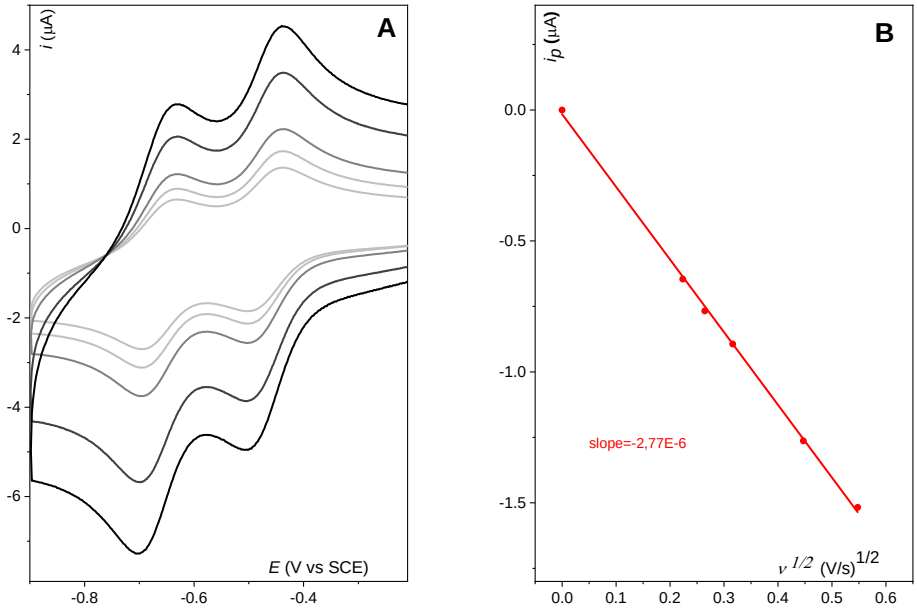


Figure S9. A) CV of **H_4-1^{2+}**recorded at different scan rate (from top to bottom 300, 200, 100, 70 and 50 mV.s^{-1}) on GC electrode. B) Plot of the cathodic peak current ($i_{p,c}$) as a function of the square root of the scan rate.

4. Single Crystal XRD

Table S2. Crystal data and structure refinement for **[I_4-1^{2+}, $(OTf^-)_2$]**

CCDC-Number	1956598
Empirical formula	$C_{30}H_{40}F_6I_4N_2O_6S_2$
Formula weight [g/mol]	1210.36
Crystal system	Triclinic
Space group	P-1 (2)
Lattice parameters [Å]	
a	7.3544(2)
b	8.3505(3)
c	18.5755(6)
α	102.268(3)
β	91.823(3)
γ	112.239(3)
Density [g/cm^3]	1.963
Crystal size [mm^3]	0.058 x 0.041 x 0.038
Volume [Å^3]	1023.84(6)
Z	1
Temperature [K]	169.99(10)
Diffraction Device	XtaLAB Synergy, Dualflex, HyPix
Radiation Type	0.71073 Å (Mo K_a micro-focus sealed X-ray tube)
F(000)	580
Absorption coefficient [mm^{-1}]	3.213
Absorption correction	Gaussian
Measurement range	2.7 - 27.0
Index range	-9 < h < 9
	-10 < k < 10
	-23 < l < 23
Measured reflexes	15820
Independent	4480
Observed	3644
R(int)	0.0343
Completeness (%) / theta (°)	99.9 / 25.242
Transmission (min / max)	0.450 / 0.565
R1 (observed/all)	0.0269 / 0.0377
wR2 (observed/all)	0.0562 / 0.0589
GooF = S	1.036
Rest electron density max./min. [e-/Å^3]	-0.459 / 0.827

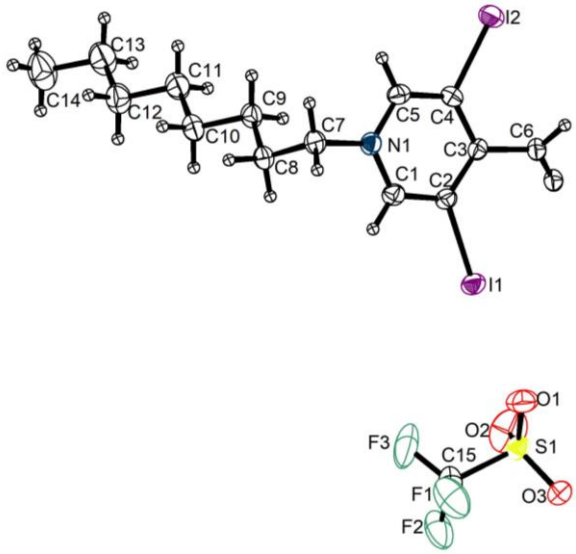


Figure S10. Crystal data for **[I_4-1^{2+}, $(OTf^-)_2$]**

Table S3. Atomic coordinates, equivalent isotropic displacement parameters [Å^2] for **[I_4-1^{2+}, (OTf^-)$_2$]**.

	x	y	z	U(eq)		x	y	z	U(eq)
I(1)	−0.76777(3)	0.51234(3)	0.14698(2)	0.03229(7)	O(3)	−1.2495(4)	0.8551(3)	0.16076(13)	0.0408(6)
I(2)	−0.21639(3)	0.19318(3)	−0.01947(2)	0.03614(7)	C(15)	−1.1024(6)	0.8259(5)	0.28173(19)	0.0435(9)
N(1)	−0.4374(4)	0.2174(3)	0.18851(14)	0.0259(5)	H(1)	−0.616596	0.328479	0.232492	0.032
C(1)	−0.5504(4)	0.3113(4)	0.19025(17)	0.0263(6)	H(5)	−0.260417	0.125388	0.129193	0.033
C(2)	−0.5729(4)	0.3835(4)	0.13215(16)	0.0245(6)	H(6)	−0.531534	0.33526	−0.045651	0.031
C(3)	−0.4789(4)	0.3581(4)	0.06850(16)	0.0235(6)	H(7A)	−0.372951	0.042394	0.236788	0.035
C(4)	−0.3629(4)	0.2576(4)	0.06961(16)	0.0252(6)	H(7AB)	−0.565395	0.071987	0.263206	0.035
C(5)	−0.3420(4)	0.1905(4)	0.12953(17)	0.0273(6)	H(8A)	−0.316025	0.209014	0.362283	0.037
C(6)	−0.5051(4)	0.4193(4)	0.00075(16)	0.0256(6)	H(8AB)	−0.360672	0.361071	0.335181	0.037
C(7)	−0.4293(5)	0.1332(4)	0.25185(16)	0.0293(7)	H(9A)	−0.072021	0.442677	0.280086	0.037
C(8)	−0.3048(5)	0.2696(4)	0.32123(17)	0.0312(7)	H(9AB)	−0.034676	0.272531	0.291779	0.037
C(9)	−0.0867(5)	0.3628(4)	0.31393(17)	0.0307(7)	H(10A)	−0.016501	0.563583	0.410522	0.045
C(10)	0.0347(5)	0.4721(5)	0.38932(18)	0.0378(8)	H(10B)	0.014797	0.39205	0.423384	0.045
C(11)	0.2547(5)	0.5640(5)	0.38608(19)	0.0398(8)	H(11A)	0.275595	0.647245	0.353402	0.048
C(12)	0.3721(5)	0.6674(5)	0.4624(2)	0.0441(9)	H(11B)	0.305943	0.473285	0.363777	0.048
C(13)	0.5906(6)	0.7649(6)	0.4604(2)	0.0534(10)	H(12A)	0.317177	0.754875	0.485291	0.053
C(14)	0.7074(6)	0.8640(7)	0.5379(2)	0.0654(12)	H(12B)	0.353962	0.583079	0.494437	0.053
S(1)	−1.07573(12)	0.83310(11)	0.18557(5)	0.03311(18)	H(13A)	0.60934	0.852088	0.429658	0.064
F(1)	−1.2613(4)	0.6871(3)	0.28712(14)	0.0728(8)	H(13B)	0.645242	0.678207	0.436297	0.064
F(2)	−1.1194(5)	0.9717(3)	0.32184(12)	0.0717(8)	H(14A)	0.8475	0.92595	0.532889	0.098
F(3)	−0.9463(5)	0.8122(3)	0.31391(14)	0.0807(9)	H(14B)	0.69401	0.777984	0.568034	0.098
O(1)	−1.0727(4)	0.6613(4)	0.15376(15)	0.0516(7)	H(14C)	0.655112	0.950953	0.561941	0.098
O(2)	−0.8958(4)	0.9802(4)	0.1887(2)	0.0756(10)					

Table S4. Anisotropic displacement parameters [Å^2] for **[I_4-1^{2+}, (OTf^-)$_2$]**.

	U11	U22	U33	U23	U13	U12
I(1)	0.02879(12)	0.04382(13)	0.03463(12)	0.01815(10)	0.01153(8)	0.02044(10)
I(2)	0.04577(14)	0.04258(14)	0.03051(12)	0.01202(9)	0.01357(9)	0.02643(11)
N(1)	0.0262(13)	0.0278(13)	0.0249(13)	0.0085(10)	0.0026(10)	0.0111(11)
C(1)	0.0212(15)	0.0279(16)	0.0293(16)	0.0087(13)	0.0050(12)	0.0079(13)
C(2)	0.0213(15)	0.0263(15)	0.0268(15)	0.0070(12)	0.0032(12)	0.0101(13)
C(3)	0.0223(14)	0.0242(15)	0.0236(15)	0.0053(12)	−0.0006(11)	0.0091(12)
C(4)	0.0263(15)	0.0264(15)	0.0231(15)	0.0057(12)	0.0070(12)	0.0105(13)
C(5)	0.0271(16)	0.0273(16)	0.0304(16)	0.0059(13)	0.0045(12)	0.0144(13)
C(6)	0.0256(15)	0.0302(15)	0.0202(15)	0.0050(12)	0.0002(12)	0.0109(13)
C(7)	0.0328(17)	0.0321(17)	0.0269(16)	0.0134(13)	0.0073(13)	0.0133(14)
C(8)	0.0376(18)	0.0401(18)	0.0234(16)	0.0129(14)	0.0072(13)	0.0206(15)
C(9)	0.0365(18)	0.0335(17)	0.0250(16)	0.0109(13)	0.0047(13)	0.0149(15)
C(10)	0.041(2)	0.049(2)	0.0249(17)	0.0090(15)	0.0034(14)	0.0189(17)
C(11)	0.040(2)	0.049(2)	0.0306(18)	0.0094(16)	0.0046(15)	0.0168(17)
C(12)	0.040(2)	0.051(2)	0.0349(19)	0.0090(16)	0.0004(16)	0.0123(18)
C(13)	0.041(2)	0.070(3)	0.039(2)	0.0114(19)	0.0047(17)	0.011(2)
C(14)	0.045(2)	0.082(3)	0.046(2)	0.010(2)	−0.0029(19)	0.003(2)
S(1)	0.0257(4)	0.0366(4)	0.0371(4)	0.0103(4)	0.0030(3)	0.0117(4)
F(1)	0.104(2)	0.0540(15)	0.0563(16)	0.0257(12)	0.0276(15)	0.0189(15)
F(2)	0.137(3)	0.0519(14)	0.0364(13)	−0.0009(10)	−0.0033(14)	0.0553(17)
F(3)	0.120(2)	0.0632(16)	0.0620(16)	0.0044(13)	−0.0409(16)	0.0500(17)
O(1)	0.0485(16)	0.0570(17)	0.0543(17)	−0.0021(13)	0.0044(13)	0.0346(14)
O(2)	0.0429(17)	0.066(2)	0.101(3)	0.0383(19)	−0.0007(17)	−0.0059(15)
O(3)	0.0421(14)	0.0518(15)	0.0359(13)	0.0060(11)	−0.0007(11)	0.0297(13)
C(15)	0.067(3)	0.0296(18)	0.0333(19)	0.0034(15)	−0.0063(17)	0.0220(19)

Table S5. Crystal data and structure refinement for **[I_4-1^{2+},(OTf^-)(Cl^-)]**

CCDC-Number	1958018
Empirical formula	$C_{29}H_{40}ClF_3I_4N_2O_3S$
Formula weight [g/mol]	1096.74
Crystal system	triclinic
Space group	P-1 (2)
Lattice parameters [Å]	
a	7.6894(4)
b	13.5299(8)
c	19.3657(11)
α	70.830(3)
β	82.860(3)
γ	79.195(3)
Density [g/cm^3]	1.953
Crystal size [mm^3]	0.15 x 0.13 x 0.07
Volume [Å^3]	1865.01(19)
Z	2
Temperature [K]	200
Diffraction Device	Bruker APEX-II CCD
Radiation Type	1.54178 Å (CuK_α microfocus)
F(000)	1048
Absorption coefficient [mm^{-1}]	27.817
Absorption correction	numerical
Measurement range	3.58 - 68.39
Index range	-8 < h < 9
	-16 < k < 16
	-23 < l < 23
Measured reflexes	37160
Independent	6845
Observed	6209
R(int)	0.0492
Completeness (%) / theta (°)	99.9 / 67.679
Transmission (min / max)	0.0408 / 0.4859
R1 (observed/all)	0.0313 / 0.0352
wR2 (observed/all)	0.0807 / 0.0840
GooF = S	1.034
Rest electron density max./min. [e-/Å^3]	-1.38 / 1.294

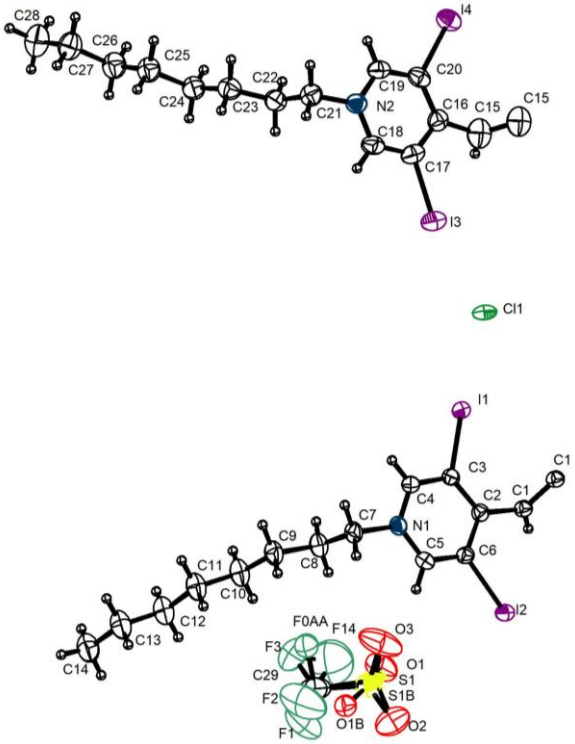


Figure S11. Asymmetric unit of **[I_4-1^{2+}, (OTf^-)(Cl^-)]**

Table S6. Atomic coordinates and equivalent isotropic displacement parameters [Å^2] for **[I_4-1^{2+},(OTf^-)(Cl^-)]**

	x	y	z	U(eq)		x	y	z	U(eq)	S.O.F.
I(1)	1.12481(3)	0.41077(2)	0.09760(2)	0.03076(8)	S(1)	1.6231(2)	0.81210(14)	0.26302(8)	0.0529(4)	0.9
I(2)	1.73254(3)	0.67032(2)	0.06902(2)	0.03313(8)	F(2)	1.4876(8)	0.9001(7)	0.3626(5)	0.156(4)	0.9
N(1)	1.2529(4)	0.6184(3)	0.20036(18)	0.0296(7)	F(3)	1.4590(14)	0.7372(9)	0.3908(4)	0.178(4)	0.9
C(1)	1.5311(5)	0.5006(3)	0.0303(2)	0.0276(8)	O(1)	1.6983(7)	0.7055(4)	0.2703(3)	0.0749(14)	0.9
C(2)	1.4272(5)	0.5421(3)	0.0878(2)	0.0275(8)	S(1B)	1.570(2)	0.8677(15)	0.2653(8)	0.055(4)	0.1
C(3)	1.2632(5)	0.5139(3)	0.1217(2)	0.0280(8)	O(1B)	1.511(5)	0.962(3)	0.2884(19)	0.043(7)	0.1
C(4)	1.1792(5)	0.5542(3)	0.1767(2)	0.0303(8)	F(0AA)	1.378(4)	0.800(3)	0.3532(19)	0.051(7)	0.1
C(5)	1.4095(6)	0.6476(3)	0.1699(2)	0.0323(9)	F(14)	1.611(14)	0.688(8)	0.347(6)	0.19(3)	0.1
C(6)	1.4965(5)	0.6115(3)	0.1148(2)	0.0279(8)	S(1B)	1.570(2)	0.8677(15)	0.2653(8)	0.055(4)	0.1
C(7)	1.1606(6)	0.6572(4)	0.2619(2)	0.0350(9)	O(1B)	1.511(5)	0.962(3)	0.2884(19)	0.043(7)	0.1
C(8)	1.2285(7)	0.5866(4)	0.3339(2)	0.0412(10)	F(0AA)	1.378(4)	0.800(3)	0.3532(19)	0.051(7)	0.1
C(9)	1.1390(7)	0.6253(4)	0.3973(3)	0.0437(11)	F(14)	1.611(14)	0.688(8)	0.347(6)	0.19(3)	0.1
C(10)	1.2237(8)	0.5659(4)	0.4690(3)	0.0492(12)	H(9A)	1.1448	0.7001	0.3853	0.052	
C(11)	1.1523(8)	0.6139(4)	0.5304(3)	0.0497(12)	H(9B)	1.0148	0.6172	0.4033	0.052	
C(12)	1.2479(8)	0.5630(5)	0.5997(3)	0.0532(13)	H(10A)	1.3509	0.5654	0.4611	0.059	
C(13)	1.1768(8)	0.6115(5)	0.6601(3)	0.0570(14)	H(10B)	1.2032	0.493	0.4844	0.059	
C(14)	1.2714(9)	0.5584(5)	0.7299(3)	0.0620(15)	H(11A)	1.1612	0.6888	0.5129	0.06	
I(3)	0.58062(4)	0.16693(2)	0.10485(2)	0.04517(9)	H(11B)	1.0276	0.6076	0.5417	0.06	
I(4)	0.12818(4)	−0.13521(2)	0.05502(2)	0.04544(10)	H(12A)	1.3727	0.5691	0.5885	0.064	
N(2)	0.0891(5)	0.0598(3)	0.1901(2)	0.0363(8)	H(12B)	1.2385	0.4882	0.6175	0.064	
C(15)	0.4974(9)	−0.0071(5)	0.0336(3)	0.0588(14)	H(13A)	1.1885	0.686	0.6427	0.068	
C(16)	0.3449(6)	0.0184(4)	0.0842(2)	0.0390(10)	H(13B)	1.0515	0.6067	0.6707	0.068	
C(17)	0.3626(6)	0.0865(4)	0.1226(3)	0.0401(10)	H(14A)	1.394	0.5673	0.7206	0.093	
C(18)	0.2359(7)	0.1062(4)	0.1742(3)	0.0404(10)	H(14B)	1.2632	0.4842	0.7467	0.093	
C(19)	0.0643(6)	−0.0054(4)	0.1548(3)	0.0384(10)	H(14C)	1.2172	0.5898	0.7667	0.093	
C(20)	0.1894(7)	−0.0276(4)	0.1027(3)	0.0388(10)	H(15)	0.6039	−0.038	0.0553	0.071	
C(21)	−0.0421(7)	0.0776(4)	0.2499(3)	0.0436(11)	H(18)	0.2509	0.1523	0.1988	0.049	
C(22)	0.0054(7)	−0.0030(4)	0.3228(3)	0.0447(11)	H(19)	−0.0384	−0.0361	0.1655	0.046	
C(23)	−0.1344(7)	0.0083(4)	0.3838(3)	0.0460(11)	H(21A)	−0.1595	0.0724	0.2394	0.052	
C(24)	−0.1030(7)	−0.0803(4)	0.4553(3)	0.0474(12)	H(21B)	−0.0446	0.1483	0.2524	0.052	
C(25)	−0.2555(7)	−0.0791(4)	0.5137(3)	0.0503(12)	H(22A)	0.119	0.0059	0.3349	0.054	
C(26)	−0.2296(8)	−0.1738(5)	0.5828(3)	0.0537(13)	H(22B)	0.0172	−0.0737	0.3189	0.054	
C(27)	−0.3810(9)	−0.1773(5)	0.6409(3)	0.0605(15)	H(23A)	−0.1349	0.0755	0.3918	0.055	
C(28)	−0.3540(10)	−0.2745(5)	0.7076(4)	0.0730(18)	H(23B)	−0.2503	0.0092	0.3686	0.055	
Cl(1)	0.92042(14)	0.27359(8)	0.04746(6)	0.0400(2)	H(24A)	0.0047	−0.0747	0.4741	0.057	
F(1)	1.7021(9)	0.7795(5)	0.3959(3)	0.1200(19)	H(24B)	−0.0848	−0.1477	0.4458	0.057	
O(2)	1.7371(12)	0.8874(7)	0.2404(4)	0.147(3)	H(25A)	−0.267	−0.0145	0.5264	0.06	
O(3)	1.4493(9)	0.8413(4)	0.2329(4)	0.104(2)	H(25B)	−0.3651	−0.0786	0.4935	0.06	
C(29)	1.5604(10)	0.8056(7)	0.3584(5)	0.080(2)	H(26A)	−0.2135	−0.2382	0.5694	0.064	
H(1)	1.6501	0.4731	0.0374	0.033	H(26B)	−0.1217	−0.1728	0.6035	0.064	
H(4)	1.0692	0.5363	0.1976	0.036	H(27A)	−0.49	−0.1759	0.6199	0.073	
H(5)	1.4591	0.6926	0.1865	0.039	H(27B)	−0.3943	−0.1145	0.656	0.073	
H(7A)	1.1807	0.729	0.2538	0.042	H(28A)	−0.3438	−0.337	0.6932	0.11	
H(7B)	1.0338	0.6583	0.2629	0.042	H(28B)	−0.4536	−0.2725	0.7426	0.11	
H(8A)	1.3557	0.5846	0.3323	0.049	H(28C)	−0.2476	−0.2758	0.7292	0.11	
H(8B)	1.2068	0.5152	0.3421	0.049						

Table S7.Anisotropic displacement parameters [Å2] for **[I_4-1^{2+},(OTf^-)(Cl^-)]**

	U11	U22	U33	U23	U13	U12
I(1)	0.02937(14)	0.03321(15)	0.03193(14)	−0.01133(10)	0.00033(10)	−0.00987(10)
I(2)	0.02917(14)	0.03841(15)	0.03605(14)	−0.01472(11)	−0.00110(10)	−0.01076(10)
N(1)	0.0281(17)	0.0353(18)	0.0267(16)	−0.0127(14)	−0.0009(13)	−0.0033(14)
C(1)	0.0242(19)	0.028(2)	0.0313(19)	−0.0104(16)	−0.0018(15)	−0.0044(15)
C(2)	0.028(2)	0.028(2)	0.0256(18)	−0.0071(16)	−0.0029(16)	−0.0039(16)
C(3)	0.031(2)	0.028(2)	0.0264(18)	−0.0080(15)	−0.0038(15)	−0.0078(16)
C(4)	0.026(2)	0.037(2)	0.0293(19)	−0.0111(17)	−0.0023(16)	−0.0075(16)
C(5)	0.034(2)	0.036(2)	0.031(2)	−0.0135(17)	−0.0057(17)	−0.0076(17)
C(6)	0.0230(19)	0.031(2)	0.0287(19)	−0.0082(16)	−0.0033(15)	−0.0039(15)
C(7)	0.033(2)	0.041(2)	0.034(2)	−0.0203(19)	0.0041(17)	−0.0009(18)
C(8)	0.048(3)	0.043(3)	0.033(2)	−0.0165(19)	0.0007(19)	−0.001(2)
C(9)	0.045(3)	0.052(3)	0.035(2)	−0.020(2)	0.002(2)	−0.001(2)
C(10)	0.058(3)	0.051(3)	0.035(2)	−0.017(2)	−0.002(2)	0.005(2)
C(11)	0.054(3)	0.055(3)	0.037(2)	−0.018(2)	−0.003(2)	0.007(2)
C(12)	0.061(3)	0.057(3)	0.038(3)	−0.017(2)	−0.004(2)	0.004(3)
C(13)	0.058(3)	0.071(4)	0.040(3)	−0.022(3)	−0.005(2)	0.005(3)
C(14)	0.062(4)	0.079(4)	0.043(3)	−0.021(3)	−0.006(3)	0.000(3)
I(3)	0.03754(17)	0.04019(17)	0.05616(19)	−0.00820(13)	−0.00870(13)	−0.01101(12)
I(4)	0.0560(2)	0.03341(16)	0.04863(18)	−0.01117(12)	−0.01564(14)	−0.00617(13)
N(2)	0.038(2)	0.0339(19)	0.0368(19)	−0.0085(15)	−0.0056(16)	−0.0086(15)
C(15)	0.063(4)	0.050(3)	0.050(3)	−0.006(2)	−0.006(3)	0.007(3)
C(16)	0.042(3)	0.035(2)	0.035(2)	−0.0030(18)	−0.0038(19)	−0.0066(19)
C(17)	0.033(2)	0.034(2)	0.047(3)	−0.0011(19)	−0.0084(19)	−0.0075(18)
C(18)	0.045(3)	0.033(2)	0.046(3)	−0.0104(19)	−0.010(2)	−0.0109(19)
C(19)	0.035(2)	0.036(2)	0.044(2)	−0.0066(19)	−0.0100(19)	−0.0098(18)
C(20)	0.046(3)	0.033(2)	0.038(2)	−0.0077(18)	−0.016(2)	−0.0037(19)
C(21)	0.042(3)	0.042(3)	0.046(3)	−0.015(2)	−0.001(2)	−0.006(2)
C(22)	0.041(3)	0.053(3)	0.045(3)	−0.021(2)	−0.003(2)	−0.008(2)
C(23)	0.043(3)	0.047(3)	0.051(3)	−0.019(2)	−0.005(2)	−0.005(2)
C(24)	0.038(3)	0.058(3)	0.046(3)	−0.018(2)	−0.004(2)	−0.002(2)
C(25)	0.046(3)	0.055(3)	0.048(3)	−0.016(2)	−0.003(2)	−0.002(2)
C(26)	0.047(3)	0.058(3)	0.053(3)	−0.019(3)	−0.001(2)	0.001(2)
C(27)	0.058(3)	0.063(4)	0.058(3)	−0.022(3)	0.007(3)	−0.005(3)
C(28)	0.084(5)	0.067(4)	0.058(4)	−0.014(3)	0.009(3)	−0.007(3)
Cl(1)	0.0341(5)	0.0375(5)	0.0547(6)	−0.0157(5)	−0.0053(4)	−0.0175(4)
S(1)	0.0656(10)	0.0431(9)	0.0530(8)	−0.0082(6)	−0.0120(7)	−0.0231(8)
F(1)	0.149(5)	0.133(4)	0.097(3)	−0.045(3)	−0.056(4)	−0.017(4)
F(2)	0.090(4)	0.203(8)	0.242(9)	−0.184(8)	−0.026(5)	0.030(4)
F(3)	0.203(9)	0.276(11)	0.089(4)	−0.046(6)	0.044(5)	−0.175(9)
O(1)	0.076(3)	0.066(3)	0.096(4)	−0.049(3)	−0.017(3)	0.008(2)
O(2)	0.191(8)	0.165(7)	0.112(5)	−0.031(5)	0.030(5)	−0.142(7)
O(3)	0.126(5)	0.065(3)	0.130(5)	−0.020(3)	−0.089(4)	−0.001(3)
C(29)	0.058(4)	0.097(5)	0.109(6)	−0.058(5)	0.006(4)	−0.031(4)

Table S8. Crystal data and structure refinement for **[I_4-1^{2+}, Cl^-_2]**

CCDC-Number	
Empirical formula	C28 H40 Cl2 I4 N2
Formula weight [g/mol]	983.12
Crystal system	Triclinic
Space group	P-1 (2)
Lattice parameters [Å]	
a	6.2514(5)
b	8.3519(7)
c	16.1830(12)
α	92.142(7)
β	90.106(7)
γ	102.190(7)
Density [g/cm^3]	1.978
Crystal size [mm^3]	0.319 x 0.259 x 0.170
Volume [Å^3]	825.26(12)
Z	1
Temperature [K]	170(2)
Diffraction Device	XtaLAB Mini (ROW)
Radiation Type	0.71073 Å (Mo K/ fine-focus sealed X-ray tube)
F(000)	468
Absorption coefficient [mm^{-1}]	3.958
Absorption correction	Analytical
Measurement range	2.5 - 26.4
Index range	-7 < h < 7
	-5 < k < 10
	-20 < l < 20
Measured reflexes	5087
Independent	3358
Observed	2775
R(int)	0.0198
Completeness (%) / theta (°)	99.4 / 25.242
Transmission (min / max)	0.456 / 0.578
R1 (observed/all)	0.0275 / 0.0371
wR2 (observed/all)	0.0609 / 0.0674
GooF = S	1.048
Rest electron density max./min. [e-/Å^3]	-0.639 / 0.84

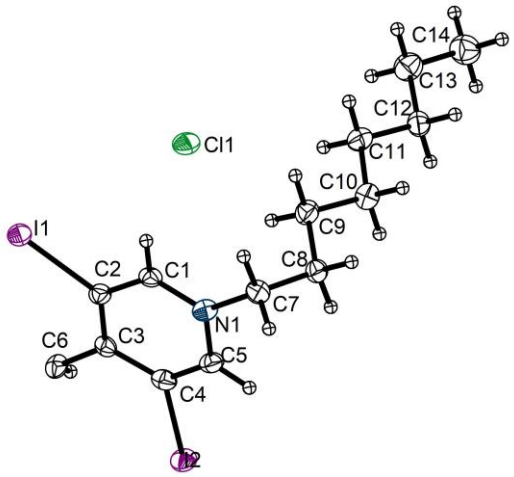


Figure S12. Crystal data for **[I_4-1^{2+}, $(Cl^-)_2$]**

Table S9. Atomic coordinates, equivalent isotropic displacement parameters [Å^2] for **[I_4-1^{2+}, Cl^-_2]**.

	x	y	z	U(eq)		x	y	z	U(eq)
I(1)	−0.76777(3)	0.51234(3)	0.14698(2)	0.03229(7)	O(3)	−1.2495(4)	0.8551(3)	0.16076(13)	0.0408(6)
I(2)	−0.21639(3)	0.19318(3)	−0.01947(2)	0.03614(7)	C(15)	−1.1024(6)	0.8259(5)	0.28173(19)	0.0435(9)
N(1)	−0.4374(4)	0.2174(3)	0.18851(14)	0.0259(5)	H(1)	−0.616596	0.328479	0.232492	0.032
C(1)	−0.5504(4)	0.3113(4)	0.19025(17)	0.0263(6)	H(5)	−0.260417	0.125388	0.129193	0.033
C(2)	−0.5729(4)	0.3835(4)	0.13215(16)	0.0245(6)	H(6)	−0.531534	0.33526	−0.045651	0.031
C(3)	−0.4789(4)	0.3581(4)	0.06850(16)	0.0235(6)	H(7A)	−0.372951	0.042394	0.236788	0.035
C(4)	−0.3629(4)	0.2576(4)	0.06961(16)	0.0252(6)	H(7AB)	−0.565395	0.071987	0.263206	0.035
C(5)	−0.3420(4)	0.1905(4)	0.12953(17)	0.0273(6)	H(8A)	−0.316025	0.209014	0.362283	0.037
C(6)	−0.5051(4)	0.4193(4)	0.00075(16)	0.0256(6)	H(8AB)	−0.360672	0.361071	0.335181	0.037
C(7)	−0.4293(5)	0.1332(4)	0.25185(16)	0.0293(7)	H(9A)	−0.072021	0.442677	0.280086	0.037
C(8)	−0.3048(5)	0.2696(4)	0.32123(17)	0.0312(7)	H(9AB)	−0.034676	0.272531	0.291779	0.037
C(9)	−0.0867(5)	0.3628(4)	0.31393(17)	0.0307(7)	H(10A)	−0.016501	0.563583	0.410522	0.045
C(10)	0.0347(5)	0.4721(5)	0.38932(18)	0.0378(8)	H(10B)	0.014797	0.39205	0.423384	0.045
C(11)	0.2547(5)	0.5640(5)	0.38608(19)	0.0398(8)	H(11A)	0.275595	0.647245	0.353402	0.048
C(12)	0.3721(5)	0.6674(5)	0.4624(2)	0.0441(9)	H(11B)	0.305943	0.473285	0.363777	0.048
C(13)	0.5906(6)	0.7649(6)	0.4604(2)	0.0534(10)	H(12A)	0.317177	0.754875	0.485291	0.053
C(14)	0.7074(6)	0.8640(7)	0.5379(2)	0.0654(12)	H(12B)	0.353962	0.583079	0.494437	0.053
S(1)	−1.07573(12)	0.83310(11)	0.18557(5)	0.03311(18)	H(13A)	0.60934	0.852088	0.429658	0.064
F(1)	−1.2613(4)	0.6871(3)	0.28712(14)	0.0728(8)	H(13B)	0.645242	0.678207	0.436297	0.064
F(2)	−1.1194(5)	0.9717(3)	0.32184(12)	0.0717(8)	H(14A)	0.8475	0.92595	0.532889	0.098
F(3)	−0.9463(5)	0.8122(3)	0.31391(14)	0.0807(9)	H(14B)	0.69401	0.777984	0.568034	0.098
O(1)	−1.0727(4)	0.6613(4)	0.15376(15)	0.0516(7)	H(14C)	0.655112	0.950953	0.561941	0.098
O(2)	−0.8958(4)	0.9802(4)	0.1887(2)	0.0756(10)					

Table S10. Anisotropic displacement parameters [Å^2] for **[I_4-1^{2+}, Cl^-_2]**.

	U11	U22	U33	U23	U13	U12
I(1)	0.02879(12)	0.04382(13)	0.03463(12)	0.01815(10)	0.01153(8)	0.02044(10)
I(2)	0.04577(14)	0.04258(14)	0.03051(12)	0.01202(9)	0.01357(9)	0.02643(11)
N(1)	0.0262(13)	0.0278(13)	0.0249(13)	0.0085(10)	0.0026(10)	0.0111(11)
C(1)	0.0212(15)	0.0279(16)	0.0293(16)	0.0087(13)	0.0050(12)	0.0079(13)
C(2)	0.0213(15)	0.0263(15)	0.0268(15)	0.0070(12)	0.0032(12)	0.0101(13)
C(3)	0.0223(14)	0.0242(15)	0.0236(15)	0.0053(12)	−0.0006(11)	0.0091(12)
C(4)	0.0263(15)	0.0264(15)	0.0231(15)	0.0057(12)	0.0070(12)	0.0105(13)
C(5)	0.0271(16)	0.0273(16)	0.0304(16)	0.0059(13)	0.0045(12)	0.0144(13)
C(6)	0.0256(15)	0.0302(15)	0.0202(15)	0.0050(12)	0.0002(12)	0.0109(13)
C(7)	0.0328(17)	0.0321(17)	0.0269(16)	0.0134(13)	0.0073(13)	0.0133(14)
C(8)	0.0376(18)	0.0401(18)	0.0234(16)	0.0129(14)	0.0072(13)	0.0206(15)
C(9)	0.0365(18)	0.0335(17)	0.0250(16)	0.0109(13)	0.0047(13)	0.0149(15)
C(10)	0.041(2)	0.049(2)	0.0249(17)	0.0090(15)	0.0034(14)	0.0189(17)
C(11)	0.040(2)	0.049(2)	0.0306(18)	0.0094(16)	0.0046(15)	0.0168(17)
C(12)	0.040(2)	0.051(2)	0.0349(19)	0.0090(16)	0.0004(16)	0.0123(18)
C(13)	0.041(2)	0.070(3)	0.039(2)	0.0114(19)	0.0047(17)	0.011(2)
C(14)	0.045(2)	0.082(3)	0.046(2)	0.010(2)	−0.0029(19)	0.003(2)
S(1)	0.0257(4)	0.0366(4)	0.0371(4)	0.0103(4)	0.0030(3)	0.0117(4)
F(1)	0.104(2)	0.0540(15)	0.0563(16)	0.0257(12)	0.0276(15)	0.0189(15)
F(2)	0.137(3)	0.0519(14)	0.0364(13)	−0.0009(10)	−0.0033(14)	0.0553(17)
F(3)	0.120(2)	0.0632(16)	0.0620(16)	0.0044(13)	−0.0409(16)	0.0500(17)
O(1)	0.0485(16)	0.0570(17)	0.0543(17)	−0.0021(13)	0.0044(13)	0.0346(14)
O(2)	0.0429(17)	0.066(2)	0.101(3)	0.0383(19)	−0.0007(17)	−0.0059(15)
O(3)	0.0421(14)	0.0518(15)	0.0359(13)	0.0060(11)	−0.0007(11)	0.0297(13)
C(15)	0.067(3)	0.0296(18)	0.0333(19)	0.0034(15)	−0.0063(17)	0.0220(19)

Table S11 Crystal data and structure refinement for **[Br_4-1^{2+}·(TfO^-)$_2$]**.

CCDC-Number	1956599
Empirical formula	C30 H40 Br4 F6 N2 O6 S2
Formula weight [g/mol]	1022.4
Crystal system	Triclinic
Space group	P-1 (2)
Lattice parameters [Å]	
a	7.34720(10)
b	12.7880(2)
c	21.3894(3)
α	73.6040(10)
β	82.8800(10)
γ	80.2290(10)
Density [g/cm^3]	1.793
Crystal size [mm^3]	0.365 x 0.281 x 0.077
Volume [Å^3]	1893.81(5)
Z	2
Temperature [K]	170.00(10)
Diffraction Device	XtaLAB Synergy, Dualflex, HyPix
Radiation Type	1.54184 Å (Cu K_a micro-focus sealed X-ray tube)
F(000)	1016
Absorption coefficient [mm^{-1}]	6.867
Absorption correction	Gaussian
Measurement range	3.6 - 66.5
Index range	-8 < h < 8
	-15 < k < 15
	-23 < l < 25
Measured reflexes	26386
Independent	6654
Observed	6195
R(int)	0.0399
Completeness (%) / theta (°)	99.9 / 66.500
Transmission (min / max)	0.135 / 1.000
R1 (observed/all)	0.0311 / 0.0331
wR2 (observed/all)	0.0795 / 0.0810
GooF = S	1.038
Rest electron density max./min. [e-/Å^3]	-0.742 / 0.808

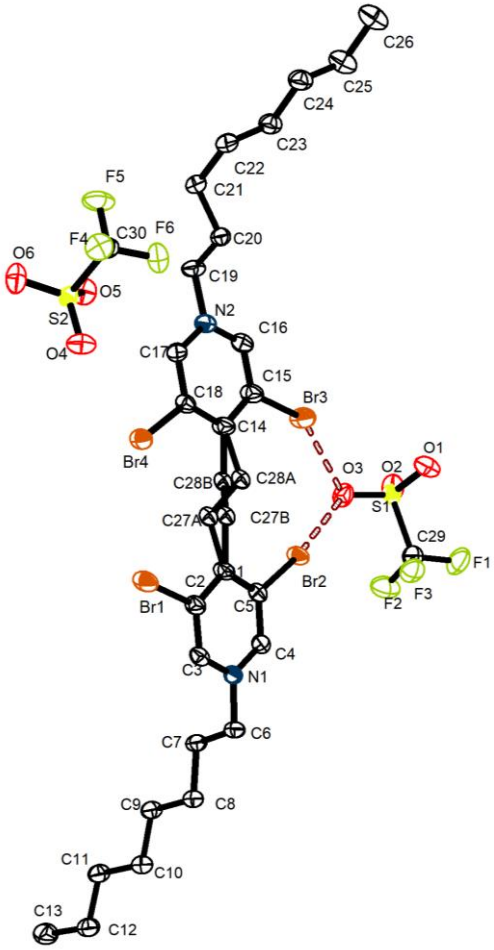


Figure S13. Asymmetric unit of **[Br_4-1^{2+}·(TfO^-)$_2$]**.

Table S12. Atomic coordinates and equivalent isotropic displacement parameters [Å^2] for **[Br_4-1^{2+}·(TfO^-)$_2$]**.

	x	y	z	U(eq)	S.O.F		x	y	z	U(eq)
Br(1)	−0.02787(4)	0.07571(3)	0.56664(2)	0.04119(9)	1	F(5)	0.7263(2)	0.10252(16)	0.13626(8)	0.0524(5)
Br(2)	0.40778(4)	0.33616(2)	0.65156(2)	0.03327(9)	1	F(6)	0.5560(2)	0.21507(13)	0.18422(8)	0.0454(4)
Br(3)	0.75137(4)	0.38167(3)	0.50587(2)	0.04449(10)	1	O(4)	0.3732(3)	0.03485(19)	0.27730(9)	0.0459(5)
Br(4)	0.34403(3)	0.09742(2)	0.42848(2)	0.03326(9)	1	O(5)	0.7076(3)	0.01671(16)	0.27986(9)	0.0384(4)
N(1)	−0.0562(3)	0.19746(15)	0.72376(9)	0.0246(4)	1	O(6)	0.5773(3)	−0.08959(16)	0.22383(10)	0.0448(5)
N(2)	0.8175(3)	0.22639(16)	0.36152(9)	0.0264(4)	1	C(30)	0.5672(3)	0.1185(2)	0.17137(11)	0.0300(5)
C(1)	0.1798(3)	0.2086(2)	0.61052(11)	0.0313(5)	1	H(3)	−0.1944	0.107784	0.687932	0.032
C(2)	0.0252(3)	0.1522(2)	0.62459(11)	0.0290(5)	1	H(4)	0.109544	0.287202	0.745043	0.031
C(3)	−0.0910(3)	0.14670(19)	0.68019(11)	0.0268(5)	1	H(6A)	−0.30299	0.17975	0.779416	0.036
C(4)	0.0879(3)	0.25251(19)	0.71334(11)	0.0262(5)	1	H(6AB)	−0.17614	0.248329	0.804023	0.036
C(5)	0.2064(3)	0.26020(19)	0.65743(11)	0.0260(5)	1	H(7A)	0.029539	0.086434	0.843914	0.035
C(6)	−0.1743(3)	0.1840(2)	0.78671(11)	0.0296(5)	1	H(7AB)	−0.08701	0.016813	0.816247	0.035
C(7)	−0.0969(3)	0.0796(2)	0.83555(11)	0.0295(5)	1	H(8A)	−0.21633	0.114149	0.922098	0.035
C(8)	−0.2153(3)	0.0550(2)	0.90051(11)	0.0290(5)	1	H(8AB)	−0.34445	0.053659	0.892247	0.035
C(9)	−0.1403(3)	−0.0556(2)	0.94563(11)	0.0292(5)	1	H(9A)	−0.12462	−0.11247	0.9214	0.035
C(10)	−0.2621(3)	−0.0928(2)	1.00841(11)	0.0313(5)	1	H(9AB)	−0.01623	−0.050631	0.957192	0.035
C(11)	−0.1874(3)	−0.2065(2)	1.04980(11)	0.0319(5)	1	H(10A)	−0.38834	−0.094007	0.997252	0.038
C(12)	−0.3043(4)	−0.2471(2)	1.11341(12)	0.0351(5)	1	H(10B)	−0.27122	−0.038797	1.034356	0.038
C(13)	−0.2256(4)	−0.3606(2)	1.15301(13)	0.0431(6)	1	H(11A)	−0.17839	−0.259957	1.023523	0.038
C(14)	0.5535(3)	0.2414(2)	0.46514(11)	0.0336(6)	1	H(11B)	−0.06061	−0.20487	1.060305	0.038
C(15)	0.7084(4)	0.2970(2)	0.45150(12)	0.0327(5)	1	H(12A)	−0.31291	−0.194278	1.140101	0.042
C(16)	0.8384(3)	0.2886(2)	0.40039(11)	0.0297(5)	1	H(12B)	−0.43131	−0.249071	1.103211	0.042
C(17)	0.6696(3)	0.17287(19)	0.37090(10)	0.0264(5)	1	H(13A)	−0.29631	−0.378748	1.19568	0.065
C(18)	0.5381(3)	0.17923(19)	0.42209(11)	0.0259(5)	1	H(13B)	−0.09552	−0.361335	1.159284	0.065
C(19)	0.9596(3)	0.2144(2)	0.30655(11)	0.0314(5)	1	H(13C)	−0.23426	−0.415188	1.129626	0.065
C(20)	0.9165(3)	0.2987(2)	0.24225(10)	0.0270(5)	1	H(16)	0.942583	0.32685	0.392671	0.036
C(21)	1.0405(4)	0.2610(2)	0.18732(11)	0.0327(5)	1	H(17)	0.655819	0.13057	0.342162	0.032
C(22)	1.0504(4)	0.3499(2)	0.12236(11)	0.0337(5)	1	H(19A)	0.967711	0.139579	0.30077	0.038
C(23)	1.1755(4)	0.4332(2)	0.12148(11)	0.0333(5)	1	H(19B)	1.081955	0.222087	0.318241	0.038
C(24)	1.1978(4)	0.5187(2)	0.05590(12)	0.0367(6)	1	H(20A)	0.94076	0.371951	0.243282	0.032
C(25)	1.3247(4)	0.5995(3)	0.05672(14)	0.0470(7)	1	H(20B)	0.78438	0.304243	0.234843	0.032
C(26)	1.3504(5)	0.6847(3)	−0.00892(15)	0.0559(8)	1	H(21A)	1.167372	0.23548	0.201652	0.039
C(27A)	0.3266(6)	0.1868(4)	0.5581(2)	0.0246(6)	0.566(4)	H(21B)	0.994021	0.197404	0.180145	0.039
C(28A)	0.4025(6)	0.2672(4)	0.5151(2)	0.0246(6)	0.566(4)	H(22A)	1.096211	0.314191	0.086814	0.04
C(27B)	0.2733(9)	0.2331(5)	0.5416(3)	0.0246(6)	0.434(4)	H(22B)	0.924067	0.388936	0.113505	0.04
C(28B)	0.4542(9)	0.2193(5)	0.5338(3)	0.0246(6)	0.434(4)	H(23A)	1.299444	0.393339	0.133401	0.04
S(1)	0.19560(7)	0.48527(5)	0.34277(3)	0.02653(13)	1	H(23B)	1.124928	0.471918	0.155311	0.04
F(1)	0.3663(3)	0.35738(15)	0.27100(9)	0.0526(4)	1	H(24A)	1.247945	0.480364	0.021831	0.044
F(2)	0.3833(3)	0.52977(17)	0.22853(8)	0.0547(4)	1	H(24B)	1.074517	0.559577	0.044058	0.044
F(3)	0.5481(2)	0.43720(14)	0.30781(8)	0.0427(4)	1	H(25A)	1.447368	0.558288	0.069232	0.056
O(1)	0.2119(3)	0.38856(17)	0.39725(9)	0.0414(4)	1	H(25B)	1.27364	0.638239	0.090487	0.056
O(2)	0.0323(2)	0.50094(15)	0.30839(9)	0.0385(4)	1	H(26A)	1.436516	0.733225	−0.00555	0.084
O(3)	0.2406(2)	0.58314(16)	0.35400(9)	0.0378(4)	1	H(26B)	1.230464	0.728566	−0.020588	0.084
H(27A)	0.365709	0.113063	0.555975	0.03	0.566(4)	H(26C)	1.400519	0.647061	−0.042706	0.084
H(28A)	0.361519	0.341514	0.5157	0.03	0.566(4)	C(29)	0.3820(4)	0.4508(2)	0.28436(12)	0.0338(5)
H(27B)	0.201559	0.257987	0.504832	0.03	0.434(4)	S(2)	0.55404(8)	0.00749(5)	0.24668(3)	0.02853(13)
H(28B)	0.524461	0.195441	0.570918	0.03	0.434(4)	F(4)	0.4307(2)	0.12533(14)	0.13462(7)	0.0425(4)

Table S13. Anisotropic displacement parameters ($Å^2$) for **[Br_4-1^{2+}·(TfO^-)$_2$]**.

	U11	U22	U33	U23	U13	U12
Br(1)	0.04466(17)	0.05401(18)	0.03589(15)	−0.01995(12)	0.00739(11)	−0.03135(13)
Br(2)	0.03521(15)	0.04110(16)	0.03039(14)	−0.01427(11)	0.00602(10)	−0.02251(11)
Br(3)	0.04185(17)	0.0616(2)	0.04527(17)	−0.03146(14)	0.01148(12)	−0.03075(14)
Br(4)	0.03061(14)	0.04226(16)	0.03413(14)	−0.01660(11)	0.00205(10)	−0.01741(11)
N(1)	0.0227(9)	0.0227(9)	0.0253(9)	−0.0031(7)	0.0012(7)	−0.0030(7)
N(2)	0.0235(9)	0.0292(10)	0.0235(9)	−0.0038(7)	0.0003(7)	−0.0029(8)
C(1)	0.0302(12)	0.0379(14)	0.0299(12)	−0.0109(10)	0.0049(10)	−0.0180(11)
C(2)	0.0297(12)	0.0327(12)	0.0282(11)	−0.0100(9)	0.0010(9)	−0.0132(10)
C(3)	0.0228(11)	0.0266(11)	0.0292(11)	−0.0029(9)	−0.0011(8)	−0.0076(9)
C(4)	0.0267(11)	0.0245(11)	0.0269(11)	−0.0054(8)	−0.0015(9)	−0.0052(9)
C(5)	0.0257(11)	0.0250(11)	0.0275(11)	−0.0049(9)	−0.0013(9)	−0.0084(9)
C(6)	0.0252(11)	0.0320(12)	0.0290(11)	−0.0073(9)	0.0071(9)	−0.0049(9)
C(7)	0.0262(11)	0.0322(13)	0.0276(11)	−0.0081(9)	0.0052(9)	−0.0025(10)
C(8)	0.0279(12)	0.0301(12)	0.0276(11)	−0.0078(9)	0.0045(9)	−0.0046(9)
C(9)	0.0269(11)	0.0330(12)	0.0267(11)	−0.0089(9)	0.0029(9)	−0.0034(10)
C(10)	0.0298(12)	0.0336(13)	0.0294(11)	−0.0089(9)	0.0034(9)	−0.0051(10)
C(11)	0.0311(12)	0.0360(13)	0.0269(11)	−0.0093(10)	0.0030(9)	−0.0029(10)
C(12)	0.0356(13)	0.0371(14)	0.0298(12)	−0.0084(10)	0.0050(10)	−0.0037(11)
C(13)	0.0506(16)	0.0426(16)	0.0301(12)	−0.0043(11)	0.0044(11)	−0.0050(13)
C(14)	0.0318(13)	0.0448(15)	0.0304(12)	−0.0157(11)	0.0063(10)	−0.0192(11)
C(15)	0.0305(12)	0.0427(14)	0.0301(12)	−0.0136(10)	0.0029(9)	−0.0170(11)
C(16)	0.0248(11)	0.0344(13)	0.0294(11)	−0.0055(9)	−0.0001(9)	−0.0092(10)
C(17)	0.0265(11)	0.0288(12)	0.0240(10)	−0.0072(9)	−0.0018(8)	−0.0038(9)
C(18)	0.0248(11)	0.0295(12)	0.0250(10)	−0.0061(9)	−0.0026(8)	−0.0101(9)
C(19)	0.0245(11)	0.0391(14)	0.0263(11)	−0.0072(10)	0.0052(9)	−0.0010(10)
C(20)	0.0256(11)	0.0293(12)	0.0254(11)	−0.0081(9)	0.0017(8)	−0.0033(9)
C(21)	0.0379(13)	0.0299(12)	0.0286(11)	−0.0099(9)	0.0070(10)	−0.0035(10)
C(22)	0.0398(14)	0.0371(13)	0.0247(11)	−0.0113(10)	0.0030(9)	−0.0055(11)
C(23)	0.0328(13)	0.0348(13)	0.0284(11)	−0.0044(10)	−0.0002(9)	−0.0026(10)
C(24)	0.0384(14)	0.0394(14)	0.0275(12)	−0.0038(10)	0.0013(10)	−0.0039(11)
C(25)	0.0489(17)	0.0498(17)	0.0365(14)	0.0009(12)	−0.0005(12)	−0.0141(14)
C(26)	0.060(2)	0.0536(19)	0.0454(16)	0.0040(14)	0.0041(14)	−0.0193(16)
C(27A)	0.0259(18)	0.0239(18)	0.0245(16)	−0.0043(14)	−0.0028(11)	−0.0078(13)
C(28A)	0.0259(18)	0.0239(18)	0.0245(16)	−0.0043(14)	−0.0028(11)	−0.0078(13)
C(27B)	0.0259(18)	0.0239(18)	0.0245(16)	−0.0043(14)	−0.0028(11)	−0.0078(13)
C(28B)	0.0259(18)	0.0239(18)	0.0245(16)	−0.0043(14)	−0.0028(11)	−0.0078(13)
S(1)	0.0235(3)	0.0266(3)	0.0307(3)	−0.0076(2)	−0.0029(2)	−0.0063(2)
F(1)	0.0569(11)	0.0505(10)	0.0622(10)	−0.0370(9)	−0.0004(8)	−0.0057(8)
F(2)	0.0599(11)	0.0625(11)	0.0338(8)	−0.0018(7)	0.0045(7)	−0.0118(9)
F(3)	0.0280(7)	0.0473(9)	0.0544(9)	−0.0192(7)	−0.0010(6)	−0.0021(6)
O(1)	0.0339(10)	0.0444(11)	0.0384(9)	0.0021(8)	0.0000(7)	−0.0095(8)
O(2)	0.0312(9)	0.0377(10)	0.0506(10)	−0.0137(8)	−0.0141(8)	−0.0047(8)
O(3)	0.0310(9)	0.0375(10)	0.0528(11)	−0.0239(8)	−0.0025(8)	−0.0072(8)
C(29)	0.0352(13)	0.0330(13)	0.0350(12)	−0.0109(10)	−0.0029(10)	−0.0062(10)
S(2)	0.0301(3)	0.0300(3)	0.0267(3)	−0.0083(2)	−0.0018(2)	−0.0066(2)
F(4)	0.0410(8)	0.0497(9)	0.0369(8)	−0.0101(7)	−0.0132(6)	−0.0020(7)
F(5)	0.0334(8)	0.0609(11)	0.0457(9)	−0.0005(8)	0.0139(7)	0.0048(8)
F(6)	0.0468(9)	0.0300(8)	0.0604(10)	−0.0103(7)	−0.0114(7)	−0.0059(7)
O(4)	0.0373(10)	0.0577(13)	0.0395(10)	−0.0114(9)	0.0099(8)	−0.0099(9)
O(5)	0.0401(10)	0.0399(10)	0.0382(9)	−0.0125(8)	−0.0138(8)	−0.0027(8)
O(6)	0.0601(13)	0.0300(10)	0.0487(11)	−0.0137(8)	−0.0166(9)	−0.0039(9)
C(30)	0.0242(11)	0.0318(13)	0.0322(12)	−0.0088(9)	0.0002(9)	−0.0007(9)

Table S14. Crystal data and structure refinement for 3,5-Diiodo-4-picolin **7**

CCDC-Number	1956597
Empirical formula	$C_6H_5I_2N$
Formula weight [g/mol]	344.91
Crystal system	Orth orhombic
Space group	Pnma (62)
Lattice parameters [Å]	
a	12.3509(8)
b	6.9326(5)
c	9.5351(5)
a	90
b	90
g	90
Density [g/cm3]	2.806
Crystal size [mm3]	0.327 x 0.117 x 0.058
Volume [Å3]	816.43(9)
Z	4
Temperature [K]	170(2)
Diffraction Device	XtaLAB Mini (ROW)
Radiation Type	0.71073 Å (Mo K/ fine-focus sealed X-ray tube)
F(000)	616
Absorption coefficient [mm-1]	7.619
Absorption correction	Gaussian
Measurement range	02.07.2027
Index range	-11 < h < 15
	-8 < k < 8
	-11 < l < 12
Measured reflexes	3449
Independent	961
Observed	872
R(int)	0.0258
Completeness (%) / theta (°)	100.0 / 25.242
Transmission (min / max)	0.306 / 0.776
R1 (observed/all)	0.0223 / 0.0259
wR2 (observed/all)	0.0539 / 0.0565
GooF = S	1.074
Rest electron density max./min. [e-/Å³]	-0.949 / 0.673

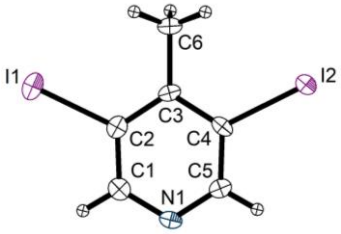


Figure S14 Asymmetric unit of 3,5-Diiodo-4-picolin (**7**).

Table S15. Atomic coordinates, equivalent isotropic displacement parameters [Å^2] and site occupancy factors (S.O.F.) for **7**.

	x	y	z	U(eq)	S.O.F.
I(1)	0.53980(3)	0.25	0.84809(3)	0.03486(14)	1
N(1)	0.3637(3)	0.25	0.4585(4)	0.0228(8)	1
I(2)	0.66031(3)	0.25	0.22406(3)	0.02478(12)	1
C(1)	0.3958(4)	0.25	0.5930(5)	0.0258(10)	1
C(2)	0.5038(5)	0.25	0.6325(5)	0.0220(10)	1
C(3)	0.5872(4)	0.25	0.5315(5)	0.0209(10)	1
C(4)	0.5501(4)	0.25	0.3922(5)	0.0207(9)	1
C(5)	0.4405(4)	0.25	0.3621(5)	0.0232(10)	1
C(6)	0.7048(4)	0.25	0.5679(5)	0.0314(12)	1
H(1)	0.342066	0.25	0.6643	0.031	1
H(5)	0.419295	0.25	0.266313	0.028	1
H(6A)	0.730313	0.116732	0.576937	0.047	0.5
H(6B)	0.715536	0.317907	0.656991	0.047	0.5
H(6C)	0.745666	0.315361	0.493765	0.047	0.5

Table S16. Anisotropic displacement parameters [Å2] for **7**.

	U11	U22	U33	U23	U13	U12
I(1)	0.0408(3)	0.0435(2)	0.02027(19)	0	-0.00362(13)	0
N(1)	0.0144(19)	0.026(2)	0.028(2)	0	0.0001(16)	0
I(2)	0.01902(19)	0.0314(2)	0.02389(19)	0	0.00310(11)	0
C(1)	0.025(3)	0.025(2)	0.027(2)	0	0.002(2)	0
C(2)	0.027(3)	0.018(2)	0.021(2)	0	-0.0017(19)	0
C(3)	0.017(2)	0.022(2)	0.024(2)	0	-0.0061(18)	0
C(4)	0.016(2)	0.020(2)	0.026(2)	0	0.0060(19)	0
C(5)	0.021(2)	0.026(2)	0.024(2)	0	-0.0044(19)	0
C(6)	0.016(3)	0.047(3)	0.031(3)	0	-0.005(2)	0

Table S17. Crystal data and structure refinement for 3,5-diiodoisonicotinaldehyde **5c**

CCDC-Number	1956593
Empirical formula	$C_6H_3I_2NO$
Formula weight [g/mol]	358.89
Crystal system	Monoclinic
Space group	P21/c (14)
Lattice parameters [Å]	
a	8.0122(10)
b	14.3857(10)
c	7.6116(9)
α	90
β	116.531(15)
γ	90
Density [g/cm³]	3.037
Crystal size [mm³]	0.337 x 0.084 x 0.084
Volume [Å³]	784.94(17)
Z	4
Temperature [K]	170(2)
Diffraction Device	XtaLAB Mini (ROW)
Radiation Type	0.71073 Å (Mo K/ fine-focus sealed X-ray tube)
F(000)	640
Absorption coefficient [mm^{-1}]	7.941
Absorption correction	Gaussian
Measurement range	2.8 - 27.0
Index range	-10 < h < 5
	-17 < k < 18
	-9 < l < 9
Measured reflexes	2930
Independent	1709
Observed	1347
R(int)	0.0237
Completeness (%) / theta (°)	100.0 / 25.242
Transmission (min / max)	0.364 / 0.615
R1 (observed/all)	0.0337 / 0.0503
wR2 (observed/all)	0.0696 / 0.0786
GooF = S	1.066
Rest electron density max./min. [e-/Å³]	-0.951 / 1.483

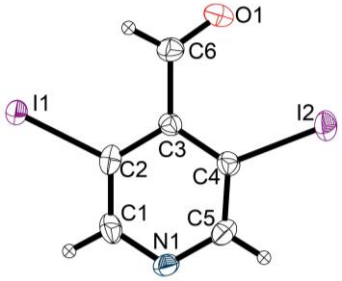


Figure S15. Asymmetric unit of 3,5-diiodoisonicotinaldehyde (**5c**)

Table S18. Atomic coordinates, equivalent isotropic displacement parameters [Å^2] for **5c**.

	x	y	z	U(eq)
I(1)	0.11624(6)	0.45792(3)	0.31324(7)	0.02956(15)
I(2)	0.62656(6)	0.12440(3)	0.36295(7)	0.03393(16)
O(1)	0.6458(7)	0.3378(4)	0.3425(9)	0.0450(14)
N(1)	0.0811(7)	0.1612(4)	0.3155(9)	0.0302(14)
C(1)	0.0555(9)	0.2523(5)	0.3116(10)	0.0305(16)
C(2)	0.1880(9)	0.3164(4)	0.3235(9)	0.0244(14)
C(3)	0.3603(8)	0.2872(4)	0.3386(9)	0.0222(13)
C(4)	0.3857(8)	0.1902(4)	0.3434(9)	0.0238(14)
C(5)	0.2444(9)	0.1314(5)	0.3304(10)	0.0293(15)
C(6)	0.5044(9)	0.3561(5)	0.3488(10)	0.0292(15)
H(1)	−0.060572	0.274701	0.299942	0.037
H(5)	0.264748	0.066285	0.332236	0.035
H(6)	0.480414	0.419815	0.361399	0.035

Table S19. Anisotropic displacement parameters (Å^2) for **5c**.

	U11	U22	U33	U23	U13	U12
I(1)	0.0237(2)	0.0210(2)	0.0435(3)	−0.0015(2)	0.0146(2)	0.00179(17)
I(2)	0.0266(2)	0.0294(3)	0.0429(3)	0.0009(2)	0.0130(2)	0.00837(19)
O(1)	0.037(3)	0.035(3)	0.077(4)	−0.006(3)	0.038(3)	−0.009(2)
N(1)	0.022(3)	0.021(3)	0.043(4)	0.003(3)	0.010(3)	−0.003(2)
C(1)	0.021(3)	0.034(4)	0.032(4)	0.000(3)	0.008(3)	0.008(3)
C(2)	0.027(3)	0.024(3)	0.016(3)	−0.003(3)	0.004(3)	0.006(3)
C(3)	0.019(3)	0.024(3)	0.022(3)	−0.003(3)	0.008(3)	−0.002(3)
C(4)	0.021(3)	0.025(3)	0.026(3)	0.004(3)	0.010(3)	0.003(3)
C(5)	0.033(4)	0.020(3)	0.032(4)	−0.001(3)	0.012(3)	−0.001(3)
C(6)	0.025(3)	0.027(4)	0.032(4)	−0.003(3)	0.010(3)	−0.005(3)

Table S20. Crystal data and structure refinement for 4,4'-diazastilben. **3**

CCDC-Number	1956596
Empirical formula	$C_{12}H_{10}N_2$
Formula weight [g/mol]	182.22
Crystal system	Monoclinic
Space group	P21/c (14)
Lattice parameters [Å]	
a	5.74648(16)
b	10.5539(3)
c	7.6448(2)
a	90
b	92.025(2)
g	90
Density [g/cm3]	1.306
Crystal size [mm3]	0.590 x 0.270 x 0.106
Volume [Å3]	463.35(2)
Z	2
Temperature [K]	169.96(10)
Diffraction Device	XtaLAB Synergy, Dualflex, HyPix
Radiation Type	1.54184 Å (Cu K/ micro-focus sealed X-ray tube)
F(000)	192
Absorption coefficient [mm-1]	0.618
Absorption correction	Gaussian
Measurement range	7.2 - 66.5
Index range	-6 < h < 6
	-12 < k < 10
	-8 < l < 9
Measured reflexes	2215
Independent	810
Observed	752
R(int)	0.0261
Completeness (%) / theta (°)	99.3 / 66.485
Transmission (min / max)	0.261 / 1.000
R1 (observed/all)	0.0362 / 0.0384
wR2 (observed/all)	0.1025 / 0.1056
GooF = S	1.085
Rest electron density max./min. [e-/Å³]	-0.127 / 0.223

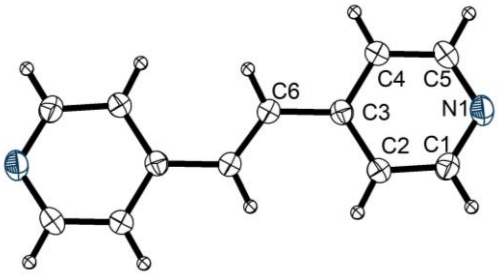


Figure S16. Asymmetric unit of 4,4'-diazastilben **3**.

Table S21 Atomic coordinates, equivalent isotropic displacement parameters [Å^2] for **3**.

	x	y	z	U(eq)
N(1)	0.50412(17)	0.15817(9)	0.34454(13)	0.0330(3)
C(1)	0.46732(19)	0.28177(10)	0.31961(15)	0.0307(4)
C(2)	0.62057(18)	0.37654(11)	0.37011(14)	0.0278(3)
C(3)	0.83173(18)	0.34394(10)	0.45437(13)	0.0238(3)
C(4)	0.87304(19)	0.21533(10)	0.47859(15)	0.0293(4)
C(5)	0.7076(2)	0.12753(11)	0.42283(15)	0.0337(4)
C(6)	1.00398(17)	0.43796(10)	0.51701(13)	0.0254(3)
H(1)	0.324725	0.306345	0.262754	0.037
H(2)	0.583029	0.462852	0.347889	0.033
H(4)	1.014956	0.187617	0.533481	0.035
H(5)	0.740865	0.040293	0.441396	0.04
H(6)	1.131706	0.407952	0.587638	0.031

Table S22. Anisotropic displacement parameters (Å^2) for **3**.

	U11	U22	U33	U23	U13	U12
N(1)	0.0328(6)	0.0290(6)	0.0368(6)	−0.0044(4)	−0.0014(4)	−0.0069(4)
C(1)	0.0277(6)	0.0308(7)	0.0330(6)	−0.0035(5)	−0.0051(5)	−0.0016(5)
C(2)	0.0286(6)	0.0230(6)	0.0314(6)	−0.0011(4)	−0.0030(5)	−0.0002(4)
C(3)	0.0253(6)	0.0233(7)	0.0228(6)	−0.0007(4)	0.0017(4)	−0.0014(4)
C(4)	0.0288(6)	0.0240(7)	0.0348(7)	0.0022(4)	−0.0044(5)	−0.0006(4)
C(5)	0.0377(7)	0.0211(6)	0.0421(7)	0.0000(5)	−0.0020(5)	−0.0035(5)
C(6)	0.0238(6)	0.0247(6)	0.0274(6)	−0.0001(4)	−0.0028(4)	−0.0011(4)

Table S23. Crystal data and structure refinement for ee-Cl_4-Diazastilben **12a**.

CCDC-Number	1956595
Empirical formula	C12H6Cl4N2
Formula weight [g/mol]	319.99
Crystal system	Monoclinic
Space group	P21/n (14)
Lattice parameters [Å]	
a	3.83015(11)
b	7.3483(2)
c	21.5681(6)
α	90
β	94.518(3)
γ	90
Density [g/cm^3]	1.756
Crystal size [mm^3]	0.121 x 0.089 x 0.025
Volume [Å^3]	605.15(3)
Z	2
Temperature [K]	170.00(10)
Diffraction Device	XtaLAB Synergy, Dualflex, HyPix
Radiation Type	1.54184 Å (Cu K/ micro-focus sealed X-ray tube)
F(000)	320
Absorption coefficient [mm^{-1}]	8.721
Absorption correction	Gaussian
Measurement range	4.1 - 66.5
Index range	-4 < h < 4
	-8 < k < 8
	-25 < l < 25
Measured reflexes	3275
Independent	1068
Observed	993
R(int)	0.0392
Completeness (%) / theta (°)	99.8 / 66.470
Transmission (min / max)	0.503 / 1.000
R1 (observed/all)	0.0380 / 0.0398
wR2 (observed/all)	0.1051 / 0.1074
GooF = S	1.079
Rest electron density max./min. [e-/Å^3]	-0.276 / 0.395

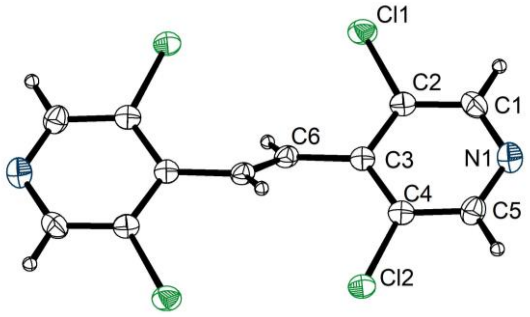


Figure S17. Asymmetric unit of ee-Cl_4-Diazastilben **12a**.

Table S24. Atomic coordinates, equivalent isotropic displacement parameters [Å^2] for ee-Cl_4-Diazastilben **12a**.

	x	y	z	U(eq)
Cl(1)	0.73831(14)	0.77631(8)	0.37510(3)	0.0295(3)
Cl(2)	0.17744(14)	0.13564(7)	0.44823(2)	0.0273(2)
N(1)	0.4759(5)	0.3168(3)	0.28855(10)	0.0305(5)
C(1)	0.5870(6)	0.4849(4)	0.30286(11)	0.0278(5)
C(2)	0.5801(6)	0.5576(3)	0.36182(11)	0.0226(5)
C(3)	0.4581(5)	0.4573(3)	0.41128(10)	0.0206(5)
C(4)	0.3450(6)	0.2816(3)	0.39466(11)	0.0228(5)
C(5)	0.3557(6)	0.2181(3)	0.33435(11)	0.0271(6)
C(6)	0.4488(6)	0.5401(3)	0.47331(10)	0.0215(5)
H(1)	0.674566	0.557621	0.271137	0.033
H(5)	0.273501	0.098377	0.325109	0.033
H(6)	0.362428	0.661012	0.475207	0.026

Table S25. Anisotropic displacement parameters (Å^2) for ee-Cl_4-Diazastilben **12a**.

	U11	U22	U33	U23	U13	U12
Cl(1)	0.0334(4)	0.0221(4)	0.0334(4)	0.0025(2)	0.0052(3)	-0.0039(2)
Cl(2)	0.0317(4)	0.0215(4)	0.0290(4)	0.0013(2)	0.0041(2)	-0.0052(2)
N(1)	0.0349(12)	0.0313(12)	0.0255(11)	-0.0022(9)	0.0034(8)	0.0028(9)
C(1)	0.0284(12)	0.0320(14)	0.0234(11)	0.0051(10)	0.0051(9)	-0.0001(10)
C(2)	0.0220(11)	0.0195(12)	0.0264(11)	0.0016(9)	0.0015(8)	0.0014(9)
C(3)	0.0170(10)	0.0214(12)	0.0230(11)	0.0013(9)	-0.0002(8)	0.0033(8)
C(4)	0.0198(11)	0.0224(12)	0.0261(12)	0.0020(9)	0.0010(9)	0.0018(9)
C(5)	0.0321(12)	0.0220(13)	0.0269(13)	-0.0025(9)	-0.0001(10)	0.0016(9)
C(6)	0.0208(11)	0.0177(11)	0.0262(11)	-0.0030(9)	0.0037(8)	-0.0005(8)

Table S27. Crystal data and structure refinement for ee-Br_4-diazastilben **12b**.

Compound	ee-br4-diazastilben
CCDC-Number	1956592
Empirical formula	$C_{12}H_6Br_4N_2$
Formula weight [g/mol]	497.83
Crystal system	Monoclinic
Space group	P21/c (14)
Lattice parameters [Å]	
a	10.635(2)
b	3.9131(5)
c	16.157(3)
α	90
β	104.01(2)
γ	90
Density [g/cm^3]	2.534
Crystal size [mm^3]	0.890 x 0.069 x 0.037
Volume [Å^3]	652.4(2)
Z	2
Temperature [K]	170(2)
Diffraction Device	XtaLAB Mini (ROW)
Radiation Type	0.71073 Å (Mo K/ fine-focus sealed X-ray tube)
F(000)	464
Absorption coefficient [mm^{-1}]	12.318
Absorption correction	Gaussian
Measurement range	2.6 - 28.3
Index range	-14 < h < 4
	-4 < k < 5
	-21 < l < 21
Measured reflexes	3090
Independent	1610
Observed	1144
R(int)	0.0328
Completeness (%) / theta (°)	99.9 / 25.242
Transmission (min / max)	0.421 / 0.688
R1 (observed/all)	0.0373 / 0.0643
wR2 (observed/all)	0.0814 / 0.0953
GooF = S	1.031
Rest electron density max./min. [e-/Å^3]	-0.772 / 0.834

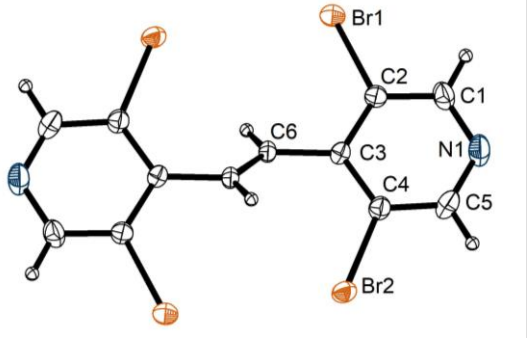


Figure S18. Asymmetric unit of ee-Br_4-diazastilben **12b**.

Table S28. Atomic coordinates, equivalent isotropic displacement parameters [Å^2] for ee-Br$_4$-diazastilben **12b**.

	x	y	z	U(eq)
Br(1)	0.23911(5)	0.78609(14)	0.59400(3)	0.02840(17)
Br(2)	0.39854(5)	0.21427(13)	0.30619(3)	0.02558(17)
N(1)	0.0593(4)	0.5777(13)	0.3452(3)	0.0335(11)
C(1)	0.0887(5)	0.6759(13)	0.4273(4)	0.0278(12)
C(2)	0.2125(5)	0.6368(12)	0.4795(3)	0.0213(10)
C(3)	0.3146(5)	0.5017(11)	0.4496(3)	0.0174(10)
C(4)	0.2793(5)	0.4092(13)	0.3632(3)	0.0225(11)
C(5)	0.1529(5)	0.4509(14)	0.3144(3)	0.0298(12)
C(6)	0.4444(4)	0.4555(13)	0.5086(3)	0.0206(10)
H(1)	0.022992	0.774792	0.450325	0.033
H(5)	0.133575	0.384565	0.256119	0.036
H(6)	0.447922	0.354832	0.562649	0.025

Table S29.Anisotropic displacement parameters (Å^2) for ee-Br$_4$-diazastilben **12b**.

	U11	U22	U33	U23	U13	U12
Br(1)	0.0262(3)	0.0380(3)	0.0228(3)	−0.0038(2)	0.0095(2)	0.0036(2)
Br(2)	0.0260(3)	0.0327(3)	0.0192(3)	−0.0044(2)	0.0077(2)	−0.0013(2)
N(1)	0.020(2)	0.049(3)	0.029(3)	0.007(2)	0.001(2)	0.000(2)
C(1)	0.018(3)	0.037(3)	0.029(3)	0.005(2)	0.006(2)	0.002(2)
C(2)	0.020(3)	0.026(3)	0.019(2)	0.001(2)	0.007(2)	−0.001(2)
C(3)	0.018(2)	0.019(2)	0.015(2)	0.0028(18)	0.0038(18)	−0.0034(19)
C(4)	0.020(3)	0.029(3)	0.019(2)	0.001(2)	0.005(2)	−0.002(2)
C(5)	0.029(3)	0.037(3)	0.020(3)	0.000(2)	0.000(2)	−0.007(2)
C(6)	0.014(2)	0.030(3)	0.016(2)	−0.001(2)	0.0016(19)	0.002(2)

Table S30. Crystal data and structure refinement for ee-I_4-diazastilben **12c**.

CCDC-Number	1956599
Empirical formula	C12 H6 I4 N2
Formula weight [g/mol]	685.79
Crystal system	Monoclinic
Space group	P21/c (14)
Lattice parameters [Å]	
a	14.4001(8)
b	12.4931(7)
c	8.8901(5)
α	90
β	104.251(6)
γ	90
Density [g/cm^3]	2.939
Crystal size [mm^3]	0.164 x 0.125 x 0.092
Volume [Å^3]	1550.13(16)
Z	4
Temperature [K]	170(2)
Diffraction Device	XtaLAB Mini (ROW)
Radiation Type	0.71073 Å (Mo K/ fine-focus sealed X-ray tube)
F(000)	1216
Absorption coefficient [mm^{-1}]	8.025
Absorption correction	Gaussian
Measurement range	2.2 - 26.5
Index range	-18 < h < 17
	-15 < k < 14
	-11 < l < 10
Measured reflexes	6796
Independent	3213
Observed	2689
R(int)	0.0252
Completeness (%) / theta (°)	99.9 / 25.242
Transmission (min / max)	0.423 / 0.575
R1 (observed/all)	0.0271 / 0.0368
wR2 (observed/all)	0.0588 / 0.0625
GooF = S	1.036
Rest electron density max./min. [e-/Å^3]	-0.552 / 0.899

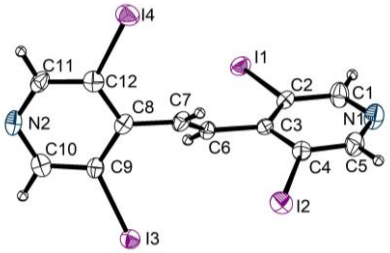


Figure S19. Asymmetric unit of ee-I_4-diazastilben **12c**.

Table S31. Atomic coordinates, equivalent isotropic displacement parameters [Å^2] for ee-I_4-diazastilben **12c**.

	X	y	z	U(eq)
I(1)	0.44244(2)	0.53860(3)	0.25568(4)	0.02708(10)
C(1)	0.4841(4)	0.3124(4)	0.3553(7)	0.0318(13)
I(2)	0.20204(2)	0.20436(3)	0.50924(4)	0.03092(10)
C(2)	0.4160(3)	0.3917(4)	0.3520(6)	0.0228(11)
N(2)	0.0445(3)	0.7583(3)	0.4826(5)	0.0301(10)
I(3)	0.02505(2)	0.46352(3)	0.22860(4)	0.02524(10)
C(3)	0.3354(3)	0.3701(4)	0.4077(5)	0.0196(10)
I(4)	0.29127(3)	0.64992(3)	0.82387(4)	0.03725(11)
C(4)	0.3257(4)	0.2636(4)	0.4529(6)	0.0244(11)
N(1)	0.4761(3)	0.2125(3)	0.4032(6)	0.0343(11)
C(9)	0.0757(3)	0.5824(4)	0.3959(5)	0.0216(10)
C(8)	0.1599(4)	0.5723(4)	0.5146(5)	0.0211(10)
C(10)	0.0212(4)	0.6751(4)	0.3867(6)	0.0299(12)
C(11)	0.1218(4)	0.7473(4)	0.6000(6)	0.0275(12)
C(12)	0.1783(4)	0.6567(4)	0.6224(6)	0.0255(11)
C(7)	0.2272(4)	0.4818(4)	0.5249(6)	0.0246(11)
C(6)	0.2643(3)	0.4566(4)	0.4074(6)	0.0218(10)
C(5)	0.3969(4)	0.1901(4)	0.4501(6)	0.0304(12)
H(1)	0.539707	0.33046	0.321433	0.038
H(10)	−0.036293	0.679455	0.306918	0.036
H(11)	0.138843	0.804665	0.671664	0.033
H(7)	0.244147	0.440804	0.617672	0.029
H(6)	0.243829	0.497321	0.314902	0.026
H(5)	0.389057	0.11915	0.483507	0.037

Table S32. Anisotropic displacement parameters (Å^2) for ee-I_4-diazastilben **12c**.

	U11	U22	U33	U23	U13	U12
I(1)	0.02902(19)	0.02089(18)	0.0314(2)	−0.00152(14)	0.00761(15)	−0.00453(13)
C(1)	0.032(3)	0.031(3)	0.038(3)	0.003(2)	0.019(3)	0.006(2)
I(2)	0.02903(19)	0.0320(2)	0.0328(2)	0.00679(15)	0.00975(15)	−0.00300(15)
C(2)	0.026(3)	0.017(2)	0.026(3)	−0.003(2)	0.006(2)	−0.001(2)
N(2)	0.035(3)	0.024(2)	0.035(3)	0.001(2)	0.015(2)	0.009(2)
I(3)	0.02494(18)	0.02715(19)	0.02383(18)	−0.00103(14)	0.00637(14)	−0.00072(13)
C(3)	0.021(2)	0.020(3)	0.018(2)	−0.0044(19)	0.003(2)	0.0006(19)
I(4)	0.0292(2)	0.0483(2)	0.0331(2)	−0.01246(17)	0.00545(16)	0.00089(17)
C(4)	0.026(3)	0.025(3)	0.022(3)	0.000(2)	0.006(2)	0.001(2)
N(1)	0.038(3)	0.027(3)	0.043(3)	0.002(2)	0.019(2)	0.004(2)
C(9)	0.025(3)	0.023(3)	0.020(3)	0.000(2)	0.010(2)	0.003(2)
C(8)	0.028(3)	0.019(2)	0.020(3)	0.002(2)	0.014(2)	−0.002(2)
C(10)	0.029(3)	0.032(3)	0.030(3)	0.004(2)	0.009(2)	0.004(2)
C(11)	0.030(3)	0.022(3)	0.035(3)	−0.007(2)	0.018(2)	−0.002(2)
C(12)	0.026(3)	0.029(3)	0.025(3)	0.003(2)	0.013(2)	−0.002(2)
C(7)	0.032(3)	0.021(3)	0.022(3)	−0.003(2)	0.008(2)	0.002(2)
C(6)	0.024(3)	0.016(2)	0.024(3)	0.001(2)	0.004(2)	0.002(2)
C(5)	0.039(3)	0.024(3)	0.028(3)	0.008(2)	0.007(2)	0.005(2)

5. DFT Calculations

5.1 Method

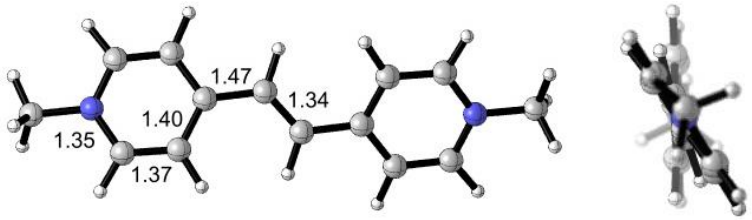
Density Functional Theory (DFT) calculations were performed with the Gaussian 09 suite of programs, Revision E.01.[17] To this end, the M062X[18] functional with D3 dispersion corrections[19] and the def2-TZVP[20] basis set was used in combination with an ultrafine grid. Dicationic and neutral compounds were modeled with closed-shell wavefunctions, while monocationic species (radicals) were treated with open-shell ones. All geometries were optimized without restraints and the nature of the obtained structures as minima was confirmed by frequency calculations and the absence of imaginary frequencies (unless noted otherwise below). All calculations were performed in the gas phase and counterions were omitted (except for halogen bond accepting anions). To reduce computational costs, all octyl groups were replaced by methyl.

5.2 Geometries

In the following, the geometries of all three oxidations states (dicationic, monocationic and neutral) will be given for **H_4-1'** and **I_4-1'** (where the prime symbol indicates replacement of octyls with methyl groups). A "front" (left) and "side" (right) view will be presented to allow a quick assessment of the structure. In addition, for the radical (monocationic species), the spin density plots (isosurface = 0.001) will be shown and for **I_4-1' $^{2+}$**, the structures of three halide (with chloride, bromide, iodide) adducts will be given. Coordinates and distances are in Å.

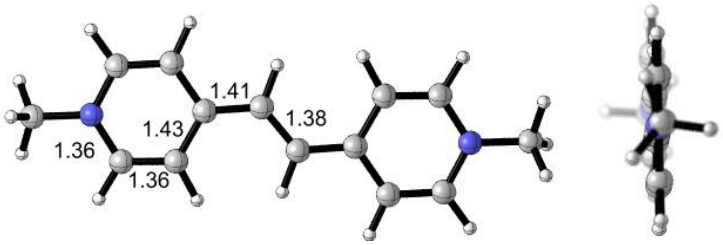
Coordinates of H_4-1' $^{2+}$:

This structure still features one imaginary frequency connected with a methyl rotation, which could not be eliminated and which was finally ignored. We do not expect this rotation to significantly influence the core structure of the molecule.

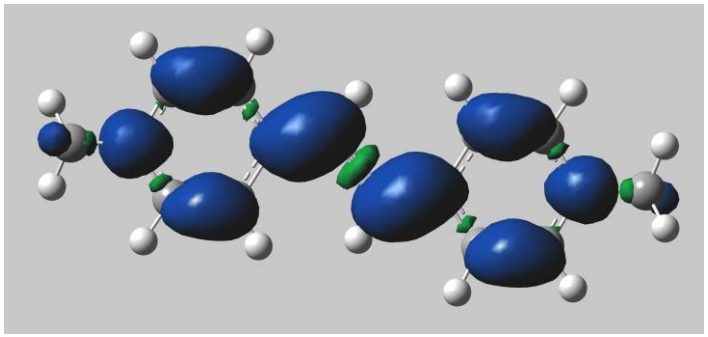


C	1.91014500	0.25757700	-0.03610900	C	-6.12444300	0.25591700	0.04937600
C	2.50168100	-0.96287600	-0.37182000	H	-6.46737900	0.41831700	-0.97037200
C	2.76029200	1.31116500	0.31247700	H	-6.59372800	-0.63100200	0.46220100
C	3.86907200	-1.09672500	-0.33509700	H	-6.35741100	1.11904500	0.66823300
C	4.12122600	1.12289800	0.33505400	C	6.12616100	-0.23628100	0.07877700
H	4.36830300	-2.02085900	-0.59020700	H	6.59865200	0.62620700	-0.38370600
H	4.81579400	1.90718500	0.60408800	H	6.42648400	-0.31732000	1.12177300
C	-1.91073200	-0.26288200	-0.02998400	H	6.40040100	-1.13773300	-0.45964300
C	-2.50401300	0.96092000	-0.36104200	H	-1.91937700	1.81395300	-0.67360700
C	-2.75860400	-1.31540600	0.31741200	H	-2.36530100	-2.28922600	0.57523000
C	-3.86859100	1.09380500	-0.31816600	H	2.36712800	2.28455600	0.57221400
C	-4.12220100	-1.12732400	0.34665000	H	1.91675500	-1.81448200	-0.68772200
H	-4.37373900	2.01694900	-0.56844400	C	-0.46044200	-0.48597900	-0.04380200
H	-4.81172200	-1.91496600	0.61604700	C	0.45986900	0.48191300	-0.04774400
N	-4.65809200	0.06161100	0.03511900	H	-0.15742800	-1.52664400	-0.00591300
N	4.65787300	-0.06693200	0.01617700	H	0.15757900	1.52292800	-0.01513900

Coordinates of H_4-1' $^{1+}$:

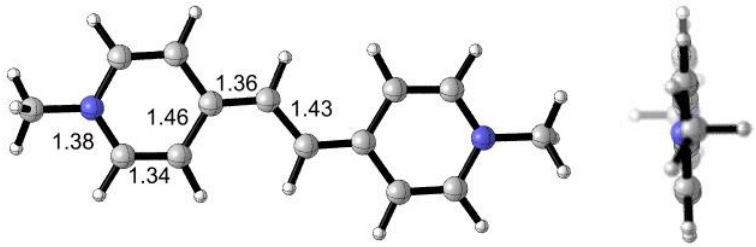


Spin Density:



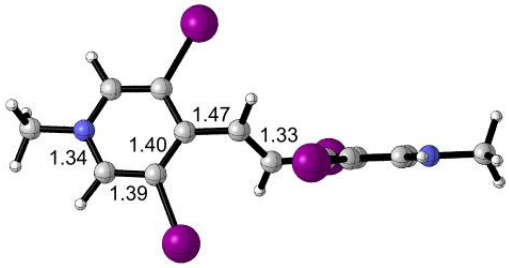
C	1.87685700	-0.26381200	0.00419600	C	-6.11681500	-0.24936400	0.03680800
C	2.48744900	1.02431800	0.00933200	H	-6.46210600	-0.19279700	1.06905600
C	2.78250000	-1.36239900	0.00670500	H	-6.59591000	0.53022300	-0.55046200
C	3.83849300	1.15550000	0.01581800	H	-6.37935600	-1.21739400	-0.38097500
C	4.12550100	-1.17072000	0.01384900	C	6.11762400	0.24424600	-0.03030100
H	4.32327600	2.12138100	0.01841300	H	6.58812900	-0.48373800	0.62667100
H	4.83073600	-1.98981300	0.01479800	H	6.47727200	0.10275600	-1.04932500
C	-1.87702100	0.26502400	-0.00554900	H	6.37471600	1.24375900	0.30861800
C	-2.48749500	-1.02334800	-0.01267000	H	-1.89460600	-1.92521100	-0.01656500
C	-2.78276600	1.36331300	-0.00619800	H	-2.40447500	2.37620800	-0.00424700
C	-3.83830600	-1.15459400	-0.01894400	H	2.40396900	-2.37521600	0.00577500
C	-4.12595900	1.17153600	-0.01289800	H	1.89477400	1.92631500	0.01088200
H	-4.32345500	-2.12037400	-0.02298500	C	-0.48708400	0.48926800	-0.00109600
H	-4.83076300	1.99088200	-0.01210700	C	0.48692400	-0.48819100	-0.00033300
N	-4.66670100	-0.07730400	-0.02373200	H	-0.18607900	1.53031700	0.00199300
N	4.66648400	0.07834600	0.02244800	H	0.18599800	-1.52926100	-0.00286900

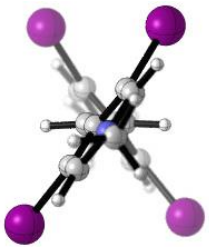
Coordinates of H_4-1' ^{0}:



C	1.85340000	-0.28585200	0.01483000	C	-6.10590500	-0.26662500	0.11160500
C	2.49079400	1.02399800	0.03092400	H	-6.37259500	-0.27248700	1.17348100
C	2.80642200	-1.38356200	0.01507800	H	-6.65230000	0.53707400	-0.38083300
C	3.82701800	1.15849700	0.05798000	H	-6.41742000	-1.21137300	-0.33166700
C	4.13282700	-1.18163400	0.04308600	C	6.10592300	0.26653400	-0.11094800
H	4.30552200	2.12897100	0.06703700	H	6.65236000	-0.53642000	0.38268800
H	4.84347300	-1.99712500	0.04188900	H	6.37288800	0.27106800	-1.17276200
C	-1.85339100	0.28587100	-0.01533400	H	6.41713600	1.21191500	0.33115900
C	-2.49079400	-1.02397800	-0.03046900	H	-1.89354000	-1.92337500	-0.02800600
C	-2.80642600	1.38358200	-0.01591700	H	-2.43742200	2.40066100	-0.00091100
C	-3.82702600	-1.15848500	-0.05710500	H	2.43742000	-2.40063400	-0.00058400
C	-4.13284100	1.18164200	-0.04344100	H	1.89351600	1.92337900	0.02894900
H	-4.30553700	-2.12896400	-0.06543800	C	-0.51044100	0.50285600	-0.00190500
H	-4.84347100	1.99714500	-0.04246800	C	0.51045400	-0.50281400	0.00087300
N	-4.68752500	-0.08312000	-0.09294900	H	-0.19569300	1.54077300	0.00675300
N	4.68751000	0.08311100	0.09345500	H	0.19568600	-1.54072100	-0.00836500

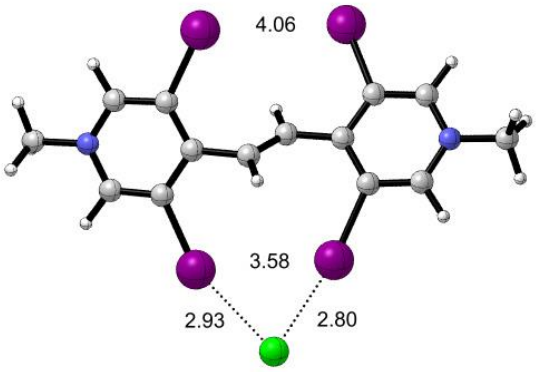
Coordinates of I_4-1' $^{2+}$:

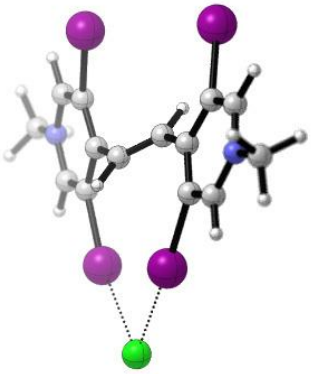




C	1.92291400	0.00417300	0.10409900	I	-1.99454200	-2.46901600	-1.92536100
C	2.53901600	0.93906600	-0.74258300	I	-1.56917800	2.53404200	1.65868800
C	2.74458200	-0.98340400	0.67902700	I	1.99769300	-2.46549300	1.92725000
C	3.90128300	0.85596900	-0.97821500	I	1.56651500	2.53593300	-1.65854800
C	4.09506500	-1.01073700	0.40429700	C	-6.10401300	-0.16832800	0.66670000
H	4.41881600	1.55754900	-1.61641400	H	-6.35381300	0.52611500	1.46201600
H	4.76239200	-1.75229000	0.82141700	H	-6.62515700	0.10649400	-0.24794000
C	-1.92308400	0.00210500	-0.10407800	H	-6.36690800	-1.18057000	0.96302500
C	-2.74335900	-0.98751200	-0.67757400	C	6.09888600	-0.17943100	-0.69087000
C	-2.53993800	0.93574900	0.74331400	H	6.63133500	-0.26443600	0.25291800
C	-4.09285100	-1.01939500	-0.39871400	H	6.28760200	-1.05197600	-1.31277100
C	-3.90143500	0.84869600	0.98228500	H	6.40753500	0.72252400	-1.20903000
H	-4.75920200	-1.76263500	-0.81442900	C	-0.48988700	0.03587400	-0.44904100
H	-4.41959800	1.54946300	1.62086200	C	0.48958600	0.03605200	0.44862400
N	-4.64536500	-0.10979400	0.41849900	H	-0.26745800	-0.00882300	-1.51056600
N	4.64694700	-0.09947100	-0.41140800	H	0.26694100	-0.00951400	1.51006800

Coordinates of chloride complex of I_4-1' $^{2+}$:

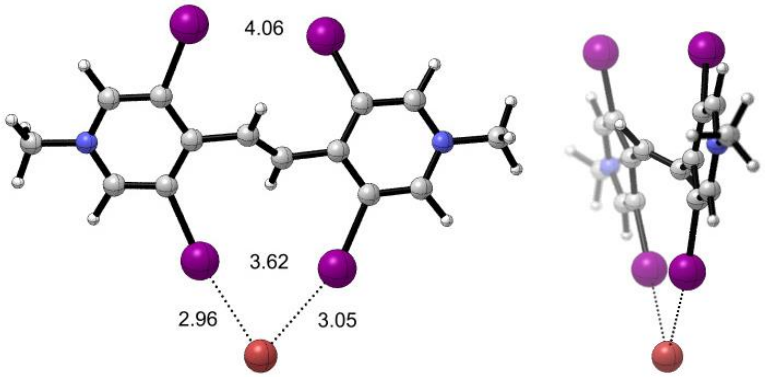




halogen bonding data:
first bond: d(I-Cl) = 2.93 Å (79 % of sum of van-der-Waals radii), Angle C-I-Cl = 160°
second bond: d(I-Cl) = 2.80 Å (75 % of sum of van-der-Waals radii), Angle C-I-Cl = 170°

C	1.35748900	-1.39459900	-0.08502300	I	-3.49367300	0.10556300	-0.19756600
C	0.65384500	-2.58342900	0.20900200	I	4.00706100	0.08334700	-0.75294700
C	2.75888100	-1.49912700	-0.21265900	I	-1.47891000	-2.83507900	0.16881800
C	1.37539300	-3.74433300	0.42977500	C	-2.78207700	5.48876600	-0.66095700
C	3.40622100	-2.69161500	0.01558900	H	-2.93163400	5.56055200	-1.73626200
H	0.88259400	-4.67716000	0.66730700	H	-3.73853700	5.53081700	-0.14712600
H	4.47835200	-2.80072000	-0.05631400	H	-2.14543200	6.29816900	-0.31846300
C	-0.91268000	1.75358000	0.12413100	C	3.43921000	-5.04087000	0.62307600
C	-0.19641300	2.95662200	0.19935000	H	4.15554800	-5.21666200	-0.17527300
C	-2.29688700	1.84047000	-0.14949500	H	3.95488000	-4.94940200	1.57673900
C	-0.82814300	4.16019200	-0.05537500	H	2.72753900	-5.85894500	0.66401200
C	-2.86270900	3.07528100	-0.38686400	C	-0.31112400	0.41959200	0.37499800
H	-0.30931100	5.10598000	-0.01535000	C	0.71838500	-0.07885100	-0.31016500
H	-3.91385900	3.19343400	-0.61256900	H	-0.80104200	-0.16633600	1.14579300
N	-2.13251400	4.20175400	-0.35219900	H	1.17737400	0.52435600	-1.08708100
N	2.71107100	-3.79011300	0.34749200	Cl	-4.27068500	-2.71326300	-0.06621100
I	1.79380300	3.11277000	0.79227700				

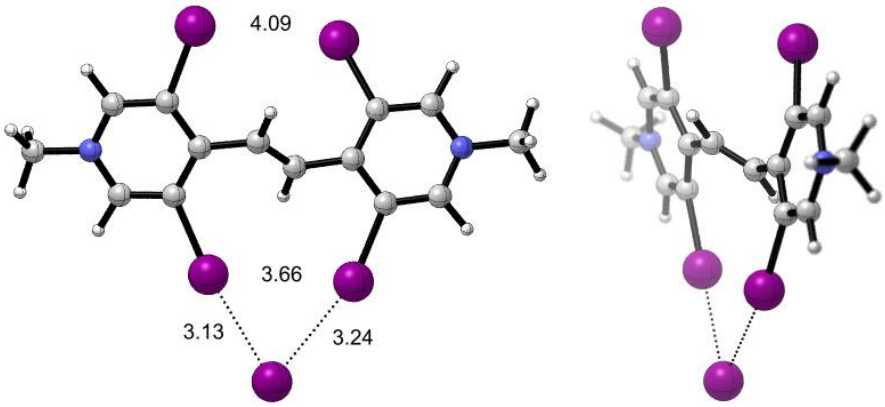
Coordinates of bromide complex of I_4-1' $^{2+}$:



halogen bonding data:
first bond: d(I-Br) = 2.96 Å (77 % of sum of van-der-Waals radii), Angle C-I-Br = 171°
second bond: d(I-Br) = 3.05 Å (80 % of sum of van-der-Waals radii), Angle C-I-Br= 162°

C	-1.06422700	-1.71416200	0.08241200
C	-0.00147100	-2.58939100	-0.23127000
C	-2.34392100	-2.29181300	0.22190700
C	-0.28581900	-3.92371500	-0.46253000
C	-2.54922800	-3.63110400	-0.01961200
H	0.49253300	-4.63119800	-0.71445700
H	-3.51945900	-4.09908700	0.05856200
C	-0.01245400	2.01813300	-0.13058500
C	-1.10189100	2.89754500	-0.21546500
C	1.25276800	2.57973500	0.14841700
C	-0.92828100	4.24592900	0.03561900
C	1.35423800	3.93486100	0.38273000
H	-1.74202700	4.95381800	-0.01198000
H	2.29822800	4.41015300	0.61259400
N	0.27932300	4.73823000	0.33911300
N	-1.52572200	-4.42279600	-0.37335200
I	-3.01906100	2.34816900	-0.81706500
I	2.98790400	1.36991700	0.20428000
I	-4.04783900	-1.23495200	0.80158000
I	2.09792100	-2.11433700	-0.19485000
C	0.43349800	6.17066800	0.65212200
H	0.43958800	6.29852600	1.73273400
H	1.37016600	6.52266300	0.22944900
H	-0.39495400	6.71975700	0.21583400
C	-1.78323200	-5.84095600	-0.67842700
H	-2.49738900	-6.23350700	0.04012500
H	-2.18323200	-5.92110000	-1.68725400
H	-0.84997200	-6.39010000	-0.60461100
C	-0.11453700	0.55804200	-0.37751000
C	-0.90963400	-0.26116700	0.31097500
H	0.54355800	0.17533600	-1.15076200
H	-1.54442400	0.14983400	1.08951300
Br	4.84669400	-1.04642900	0.06966000

Coordinates of iodide complex of I_4-1' $^{2+}$:

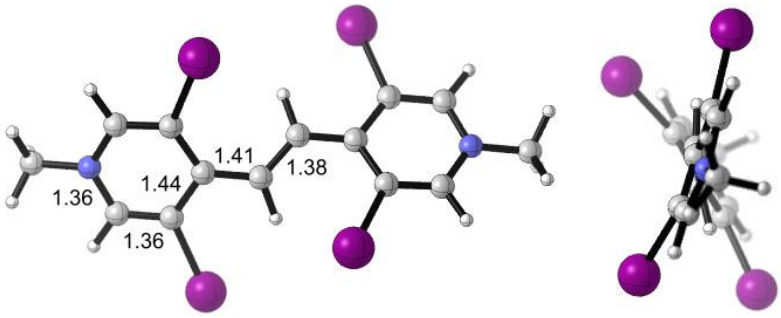


halogen bonding data:
first bond: d(I-I) = 3.13 Å (79 % of sum of van-der-Waals radii), Angle C-I-I = 171°
second bond: d(I-I) = 3.24 Å (82 % of sum of van-der-Waals radii), Angle C-I-I= 163°

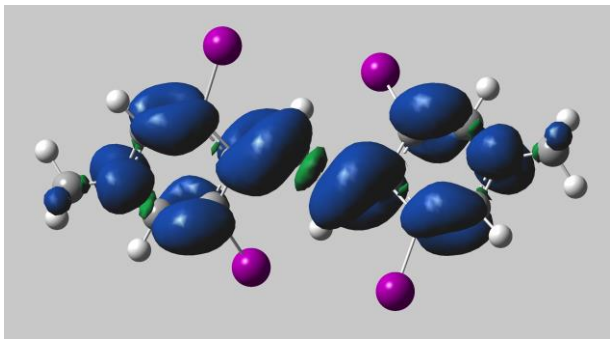
C	-1.17833200	-1.76030800	0.07141300
C	-0.04908700	-2.53308400	-0.27166200
C	-2.39820300	-2.45180200	0.23457100
C	-0.21734200	-3.88443000	-0.51499900
C	-2.48775700	-3.80048400	-0.02194600
H	0.61604700	-4.51670500	-0.79004200
H	-3.41003100	-4.35499000	0.07000900
C	-0.45980500	2.04312900	-0.14423500
C	-1.62937000	2.81218300	-0.23801400
C	0.74116400	2.72450600	0.14634200
C	-1.59012300	4.17055700	0.01676600
C	0.70901600	4.08221400	0.38203100

H	-2.46892300	4.79570700	-0.03499400
H	1.60038900	4.64689700	0.62002500
N	-0.43872700	4.77751000	0.33089500
N	-1.40604600	-4.49311300	-0.41045200
I	-3.47981500	2.07837400	-0.85341100
I	2.59713000	1.69620100	0.21916700
I	-4.17768000	-1.56181800	0.86888300
I	2.02472900	-1.89501800	-0.23571400
C	-0.42434400	6.21775100	0.64593600
H	-0.39732500	6.34368000	1.72641100
H	0.45697600	6.66592600	0.19575000
H	-1.31874000	6.67850200	0.23880200
C	-1.54754200	-5.92535700	-0.72499100
H	-2.12521200	-6.40511700	0.06069900
H	-2.05496200	-6.03113300	-1.68169200
H	-0.55983400	-6.37159400	-0.77837700
I	4.86088700	-0.61217600	0.07799700
C	-0.42098600	0.58057900	-0.38785700
C	-1.14972100	-0.30104100	0.29691300
H	0.27624500	0.25622600	-1.15350000
H	-1.82493200	0.06048500	1.06532400

Coordinates of I_4-1' $^{1+}$:

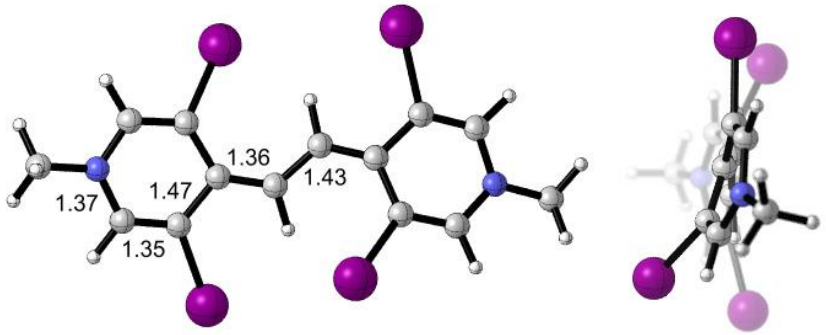


Spin Density:



C	-1.88013300	0.31936600	-0.11676800
C	-2.18152900	1.63737300	0.37356600
C	-3.03534800	-0.38096000	-0.61186200
C	-3.42574200	2.17987000	0.23473500
C	-4.25153000	0.21694700	-0.72581500
H	-3.66188400	3.17032600	0.59527000
H	-5.11256600	-0.29130600	-1.13400200
C	1.88008600	-0.31942000	-0.11687300
C	2.18161700	-1.63738400	0.37345100
C	3.03522200	0.38101700	-0.61200600
C	3.42586800	-2.17978500	0.23454700
C	4.25144500	-0.21679100	-0.72604000
H	3.66212300	-3.17021400	0.59508200
H	5.11240900	0.29153000	-1.13428800
N	4.44774500	-1.50080200	-0.33463400
N	-4.44771600	1.50096100	-0.33436800
I	0.88457300	-2.81297800	1.52157400
I	2.95410000	2.36511200	-1.25496100
I	-2.95436800	-2.36501500	-1.25495100
I	-0.88431000	2.81279900	1.52167600
C	5.74328600	-2.14452100	-0.55720200
H	5.80331300	-2.52049200	-1.57800100
H	6.53644200	-1.42110400	-0.38530300
H	5.85490100	-2.96843000	0.14201800
C	-5.74317500	2.14480800	-0.55703700
H	-5.80284100	2.52135700	-1.57764400
H	-6.53639000	1.42129200	-0.38585200
H	-5.85504800	2.96831900	0.14260400
C	0.61758100	0.30792100	-0.12502600
C	-0.61768400	-0.30808200	-0.12494200
H	0.64716200	1.37651200	-0.26018600
H	-0.64733500	-1.37668600	-0.25995900

Coordinates of I_4-1' ^{0}:

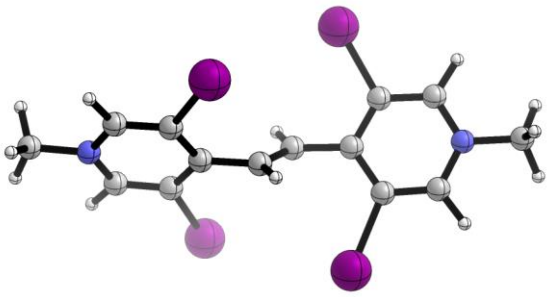


C	-1.79670400	0.52140900	-0.06760300	I	0.44801800	-3.13062400	1.12977400
C	-1.98781500	1.95395300	0.20467300	I	3.56466500	2.01523900	0.21868000
C	-3.10382600	-0.14821600	-0.13887600	I	-3.31115300	-2.03659200	-1.01663100
C	-3.13817600	2.43812300	0.71240600	I	-0.62414200	3.44615500	-0.36415200
C	-4.22424700	0.38401300	0.37764600	C	5.13891300	-2.85305600	-1.44039400
H	-3.26666700	3.48567300	0.94736300	H	5.00277700	-2.84613200	-2.52430400
H	-5.16859900	-0.14079300	0.38691500	H	6.10914500	-2.41831400	-1.20377900
C	1.81827100	-0.54702500	-0.05089800	H	5.12676300	-3.88438600	-1.09087400
C	1.87153700	-2.01292900	0.05994900	C	-5.36970200	2.11888000	1.68574000
C	3.17548900	-0.00434700	-0.16320400	H	-6.28664800	1.67918000	1.29576900
C	2.94899100	-2.71709800	-0.33681000	H	-5.26929300	1.85174200	2.74026000
C	4.21889600	-0.75109800	-0.56204100	H	-5.44214300	3.20211200	1.60197600
H	2.98838600	-3.79647200	-0.27933900	C	0.71781900	0.25018000	-0.06898200
H	5.20438200	-0.33868300	-0.72451100	C	-0.64076100	-0.18194400	-0.20382400
N	4.09803900	-2.10656300	-0.76514200	H	0.91229500	1.30742800	-0.00234700
N	-4.24209000	1.65252800	0.90591800	H	-0.77571700	-1.21963300	-0.46579900

5.3 Estimation of K_{Ox} and K_{Red}

In order to computationally estimate K_{Ox} and K_{Red}, the association of **I_4-1' $^{2+}$** and **I_4-1' ^{0}** to chloride was investigated by M06-2X-D3 def2-TZVP (see above) with the SMD18 intrinsic solvation model using parameters for DMF. Coordinates and energies will be provided below.

I_4-1' $^{2+}$ (DMF):



Energy (ht): -1840.353757

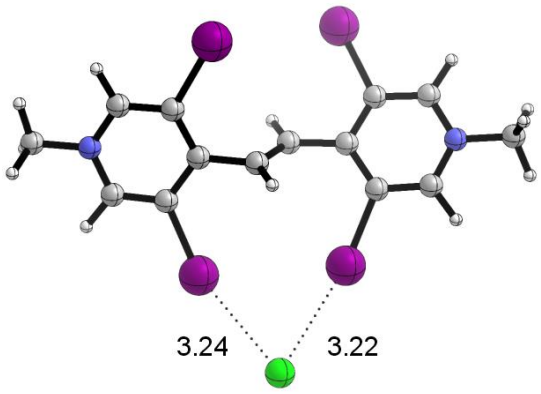
Enthalpy (ht): -1840.098711

Free enthalpy (ht): -1840.177375

C	-1.90713000	0.02742700	-0.18382500	C	4.01884900	-1.13259300	0.41651600
C	-2.59258500	1.01357600	0.53184000	C	3.95522800	0.89169100	-0.73757500
C	-2.66750800	-1.05431900	-0.65020200	H	4.64033900	-1.94997600	0.75465100
C	-3.95258300	0.89914000	0.74619100	H	4.53440500	1.63024600	-1.27335900
C	-4.01993200	-1.12438000	-0.40928600	N	4.63358200	-0.15816500	-0.26386100
H	-4.52761400	1.63833900	1.28503500	N	-4.63141800	-0.15050600	0.27731800
H	-4.64545300	-1.94039100	-0.74413700	I	1.78183500	-2.64242300	1.67703300
C	1.90633500	0.01945800	0.18326900	I	1.69677800	2.72700100	-1.28586100
C	2.66369500	-1.06226700	0.65055100	I	-1.78919000	-2.63397700	-1.68039100
C	2.59569700	1.00609900	-0.53061700	I	-1.68985100	2.73329900	1.28522900

C	6.08127500	-0.26177700	-0.53149400
H	6.21703700	-0.79741500	-1.46878500
H	6.48903200	0.74175200	-0.60285700
H	6.54367900	-0.80315300	0.28757800
C	-6.07977600	-0.26585300	0.53413000
H	-6.57313900	-0.51386200	-0.40157100
H	-6.23317700	-1.05593700	1.26571400
H	-6.43940200	0.68350100	0.91560800
C	0.46196400	0.07716600	0.47381700
C	-0.46290300	0.08171600	-0.47627100
H	0.18662000	0.04058600	1.52459900
H	-0.18852600	0.04980600	-1.52745000

Chloride complex of I_4-1' $^{2+}$ (DMF):



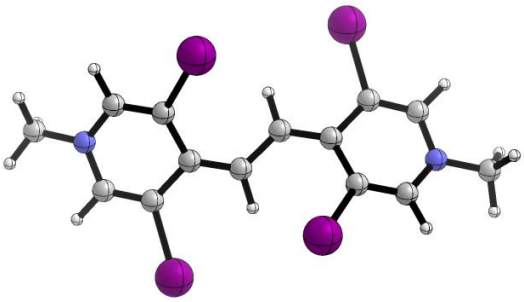
Energy (ht): -2300.741407

Enthalpy (ht): -2300.483484

Free enthalpy (ht): -2300.567858

C	1.24047400	-1.48170400	-0.14519600
C	0.54363500	-2.64119200	0.23350800
C	2.63187600	-1.61593300	-0.29042100
C	1.23818700	-3.79895500	0.52852400
C	3.27112900	-2.79489700	0.01694600
H	0.74528000	-4.70966800	0.83644300
H	4.34094900	-2.92822900	-0.05459600
C	-0.77112100	1.79987800	0.15406100
C	0.01496500	2.94686000	0.28946300
C	-2.11690000	1.99400800	-0.19411600
C	-0.50804900	4.19533300	0.00962900
C	-2.58933500	3.25955000	-0.45965700
H	0.06809400	5.10589400	0.08524100
H	-3.61230000	3.45992700	-0.74711800
N	-1.78093100	4.32459800	-0.37057100
N	2.56945300	-3.85342100	0.43680500
I	1.97112800	2.90538900	0.99974400
I	-3.44275800	0.38239100	-0.27589700
I	3.85880600	-0.08009100	-0.98593100
I	-1.54843600	-2.80535500	0.23844700
C	-2.32849600	5.65445000	-0.69803000
H	-2.56478900	5.67291800	-1.75939200
H	-3.22802300	5.80755200	-0.10771200
H	-1.58436000	6.40619500	-0.46016100
C	3.29042900	-5.08200400	0.81438300
H	4.09338900	-5.24175100	0.10099100
H	3.69382300	-4.94597400	1.81571800
H	2.59372300	-5.91381700	0.79586700
C	-0.23721600	0.43719000	0.41323000
C	0.60625900	-0.17241100	-0.41395300
H	-0.56428100	-0.03070900	1.33871200
H	0.92491500	0.33052000	-1.32256400
Cl	-4.74083900	-2.57857600	-0.07544000

I_4-1' ^{0} (DMF):



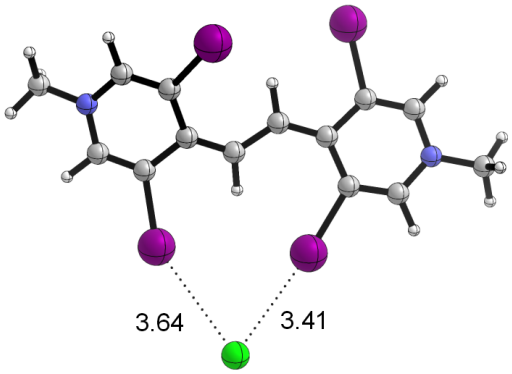
Energy (ht): -1840.645868

Enthalpy (ht): -1840.39299

Free enthalpy (ht): -1840.475121

C	-1.81970700	0.46158200	-0.31708900	I	0.57991100	-2.77097100	1.43257800
C	-1.95016500	1.85769200	0.11266400	I	3.41031000	2.14789900	-0.84487300
C	-3.13684100	-0.08184100	-0.65188000	I	-3.41648400	-2.14780000	-0.85215200
C	-3.05489000	2.59169000	-0.14449500	I	-0.57120800	2.77532000	1.41038700
C	-4.20823800	0.69677900	-0.89692000	C	5.28405000	-2.88612200	-1.13182900
H	-3.14826400	3.62738000	0.15176300	H	5.18092600	-3.15458600	-2.18425700
H	-5.16530600	0.30287800	-1.20912500	H	6.21704200	-2.34437500	-0.98764500
C	1.82128400	-0.46781700	-0.31323700	H	5.29962000	-3.79191000	-0.52970600
C	1.95743400	-1.86034400	0.12700300	C	-5.33648200	2.86604900	-1.00357500
C	3.13716400	0.08010400	-0.64466100	H	-5.82600500	2.51580900	-1.90992000
C	3.06879500	-2.59024200	-0.11398800	H	-6.03227100	2.79797800	-0.16538000
C	4.21678700	-0.69260200	-0.87233300	H	-5.03552200	3.90149300	-1.14181000
H	3.16341900	-3.62536100	0.18501800	C	0.67162300	0.25126500	-0.42895200
H	5.17185500	-0.29464000	-1.18535500	C	-0.67203700	-0.26201900	-0.42684600
N	4.17329600	-2.04951900	-0.70056400	H	0.78777500	1.30003900	-0.66223700
N	-4.14902000	2.05758500	-0.75735400	H	-0.78993000	-1.31200700	-0.65389800

Chloride complex of I_4-1' ^{0} (DMF):



Energy (ht): -2301.019959

Enthalpy (ht): -2300.764186

Free enthalpy (ht): -2300.851281

C	1.67335900	-1.03512100	-0.20693100	I	-3.75826900	-0.25494600	-0.25375400
C	1.24036600	-2.41935400	0.04062600	I	4.12617900	0.82116800	-0.75665500
C	3.13565700	-0.98356100	-0.34431800	I	-0.76903800	-3.04233100	0.26160200
C	2.11600500	-3.44620500	0.14344200	C	-3.28386200	5.03087800	-1.35717900
C	3.95049800	-2.05277500	-0.23515800	H	-3.11658500	5.08410600	-2.43444500
H	1.78921800	-4.45799200	0.33870800	H	-4.35390800	4.98008700	-1.16343400
H	5.02407700	-1.98477000	-0.33815000	H	-2.87851800	5.92546900	-0.88799000
C	-1.18955400	1.46986100	-0.21159200	C	4.36277100	-4.42146600	0.24192900
C	-0.68653900	2.81889900	0.07157600	H	5.26751000	-4.27990600	-0.34553100
C	-2.64316100	1.51537200	-0.42738000	H	4.62467300	-4.49239300	1.29901400
C	-1.38112300	3.92796500	-0.26398100	H	3.87441400	-5.34153000	-0.07176200
C	-3.28941700	2.64928900	-0.75249200	C	-0.49553000	0.30141800	-0.29595000
H	-1.00413700	4.92790500	-0.09471400	C	0.92845200	0.11119100	-0.30114400
H	-4.34570200	2.68434000	-0.98015900	H	-1.11072900	-0.56634500	-0.44624600
N	-2.63869100	3.85910700	-0.78712000	H	1.50712300	1.00807900	-0.45416500
N	3.46307400	-3.30098200	0.00588000	Cl	-4.08175900	-3.82472200	0.35511300
I	0.99951100	3.17097700	1.28469300				

Chloride (DMF):

Energy (ht): -460.371567

Enthalpy (ht): -460.369206

Free enthalpy (ht): -460.386589

6. Binding Constants

6.1 Cyclic Voltammetry

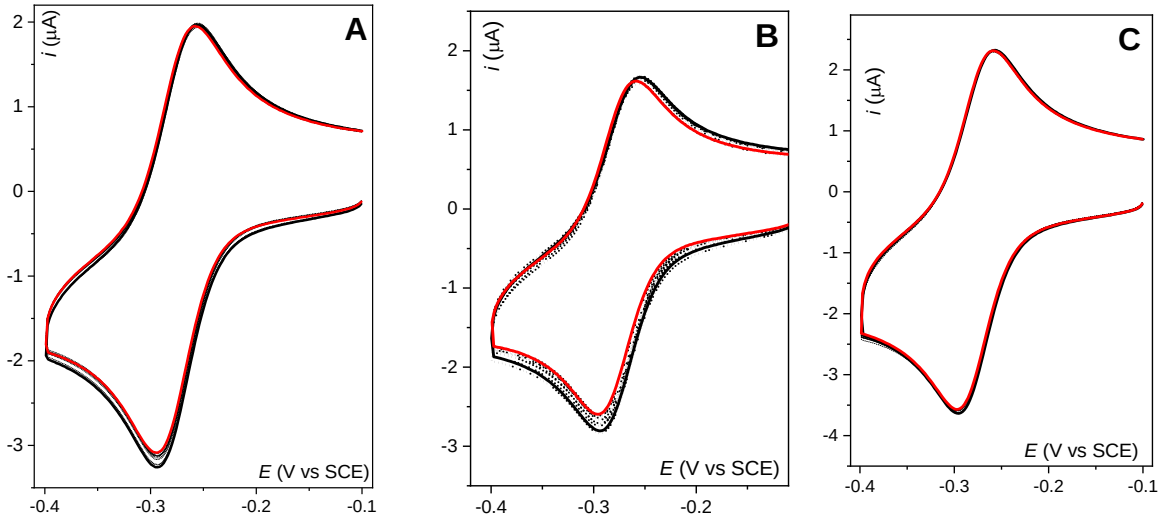


Figure S20. CVs of 0.1 mM $\mathbf{I_4\text{-}1^{2+}}$ in 0.1 M nBu_4PF_6/DMF in the absence and in the presence of increasing concentrations (from 0 to 30 mM) of nBu_4X: A) X = NO_3^-, B) X = HSO_4^- and C) X = OTf^-. T = 298K, ν = 0.1 $V.s^{-1}$.

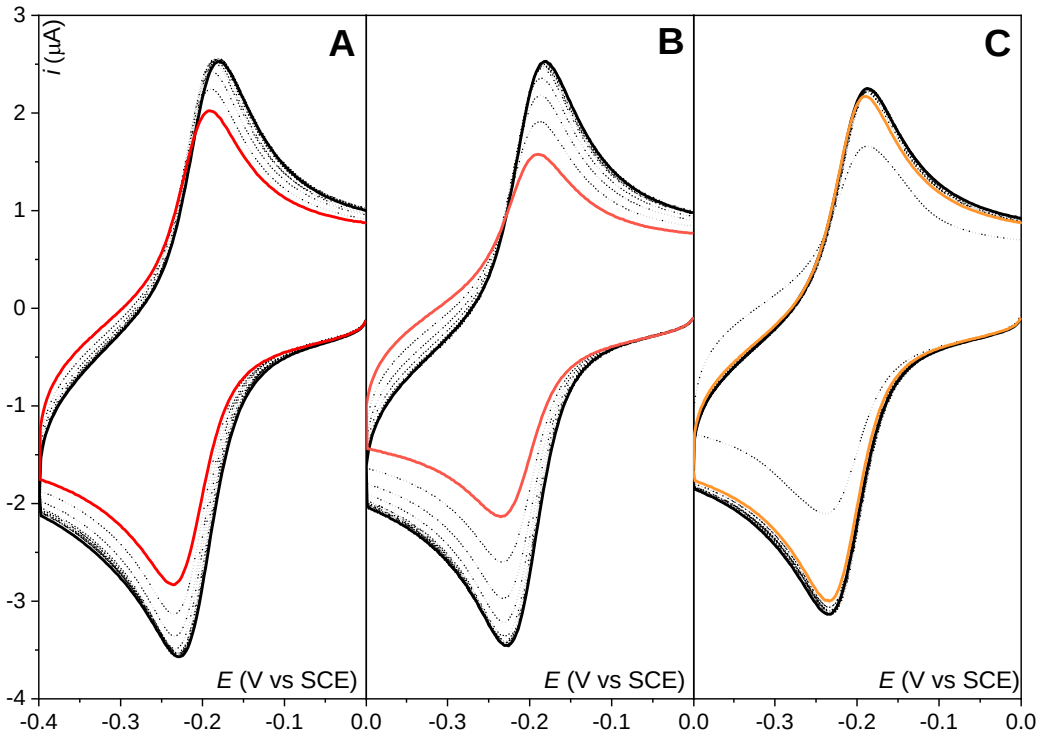


Figure S21. CVs of 0.1 mM $\mathbf{Br_4\text{-}1^{2+}}$ in 0.1 M nBu_4PF_6/DMF in the absence and in the presence of increasing concentrations (from 0 to 30 mM) of nBu_4X: A) X = Cl-, B) X = Br- and C) X = I-. T = 298K, ν = 0.1 $V.s^{-1}$.

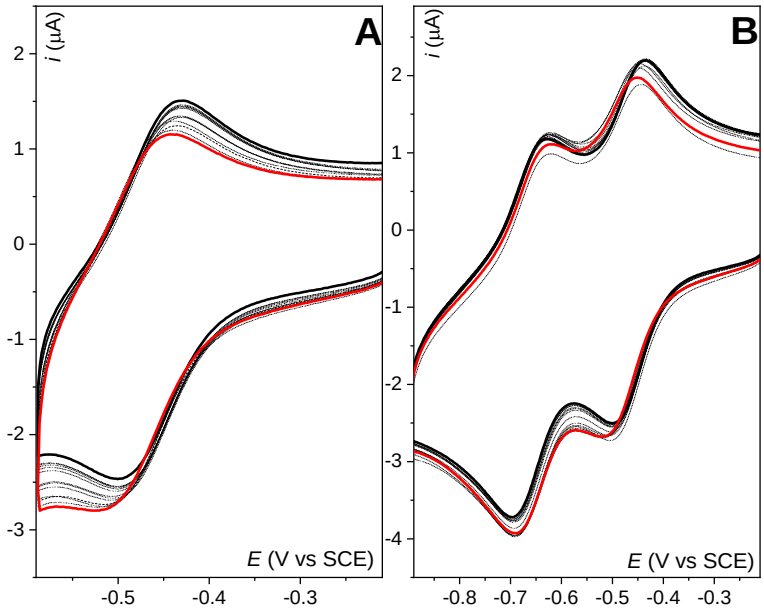


Figure S22. CVs of 0.1 mM $\mathbf{H_4\text{-}1^{2+}}$ in 0.1 M nBu_4PF_6/DMF in the absence and in the presence of increasing concentrations (from 0 to 30 mM) of nBu_4Cl: A) 1st wave, B) Both waves. T = 298K, ν = 0.1 $V.s^{-1}$.

6.2. UV-Vis

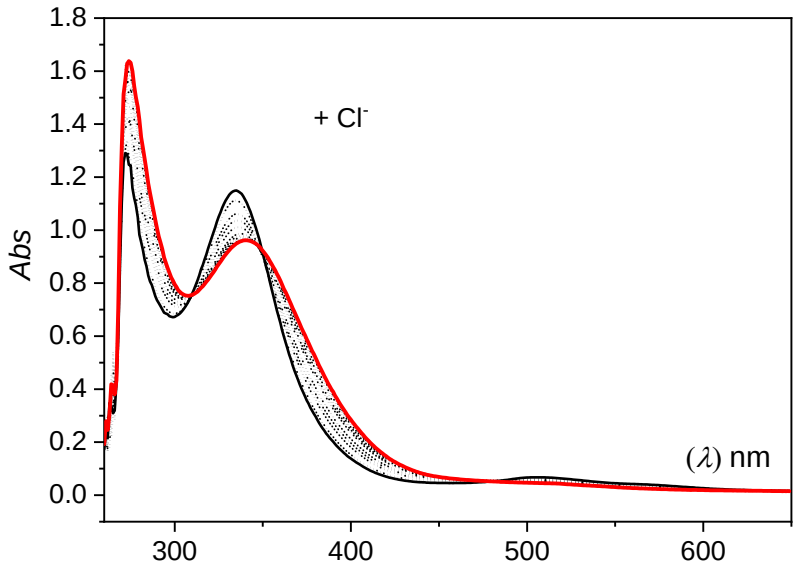


Figure S23. UV-vis spectra of 0.1 mM $\mathbf{I_4\text{-}1^{2+}}$ in pure DMF in the presence and absence of increasing equivalents of nBu_4Cl.

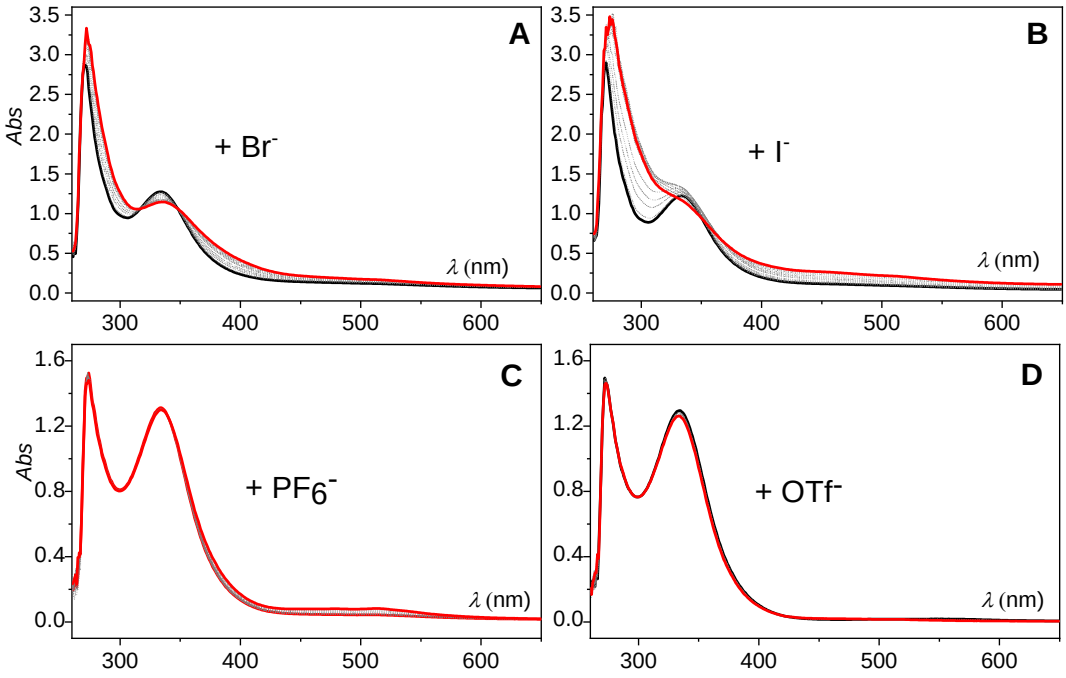


Figure S24. UV-vis spectra of 0.1 mM $\mathbf{I_4\text{-}1^{2+}}$ in pure DMF in the presence and absence of increasing equivalents of nBu_4X: A) X = Br^-, B) X = I^-, C) X = PF_6^- and D) X = OTf^-.

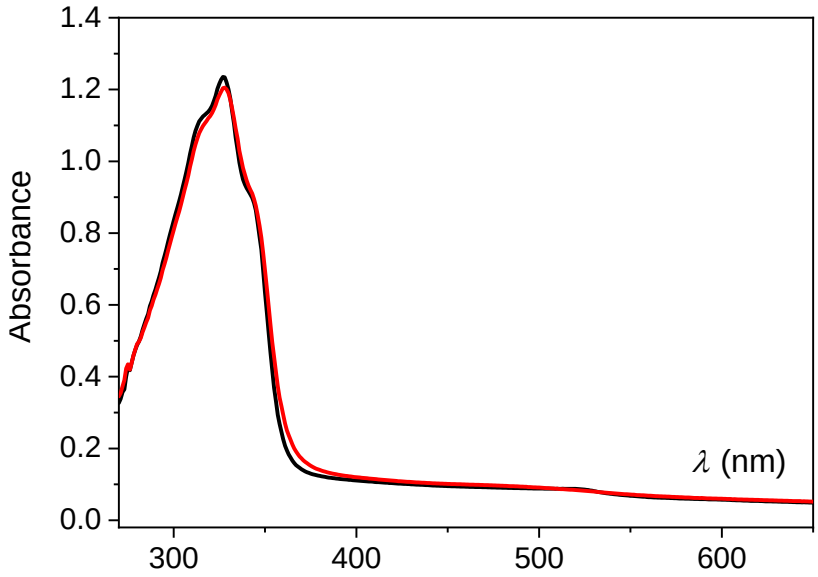


Figure S25. UV-vis spectra of 0.025 mM $\mathbf{H_4\text{-}1^{2+}}$ in pure DMF in the absence (black trace) and in the presence of 300 equivalents of nBu_4Cl.

6.3. NMR

For the NMR titrations 6 mM stock solutions of the hosts **X_4-1**, **13,** and **14,** as well as 10 mM and 100 mM guest (tetrabutylammonium chloride, bromide and iodide) solutions were prepared in dry DMF-h7. For each measurement, a single NMR tube was prepared by adding first the host, then the guest to the tube and, filling to an overall of 600 µL (see Tables S33 and S34. The tubes solutions were mixed appropriately before measurement. For the titration in 0.1 M nBu_4PF_6 separate stock solutions were prepared. Results are given in Table S35, and Figure S28. A titration of **14** was not possible since the proton signals shifted into the DMF peaks.

Table S33. **I_4-1^{2+}** with chloride in DMF

Tube Nr.	V [µL]	G/H	V_{Host} [µL]	V_{Guest} [µL]	V_{Fill} [µL]	n_{Guest} [µmol]	n_{Host} [µmol]	c_{Host} [M]	c_{Guest} [M]	H1/H5 [ppm]
1	600	0.00	50.0	0.0	550.0	0.00	0.59	0.00099142	0.00000000	9.731
2	600	0.17	50.0	10.0	540.0	0.10	0.59	0.00099142	0.00016552	9.702
3	600	0.83	50.0	50.0	500.0	0.50	0.59	0.00099142	0.00082758	9.692
4	600	1.50	50.0	90.0	460.0	0.89	0.59	0.00099142	0.00148964	9.691
5	600	2.50	50.0	150.0	400.0	1.49	0.59	0.00099142	0.00248273	9.679
6	600	5.01	50.0	300.0	250.0	2.98	0.59	0.00099142	0.00496546	9.659
7	600	20.60	50.0	120.0	430.0	12.25	0.59	0.00099142	0.02042314	9.623
8	600	61.80	50.0	360.0	190.0	36.76	0.59	0.00099142	0.06126943	9.597
9	600	85.83	50.0	500.0	50.0	51.06	0.59	0.00099142	0.08509643	9.593

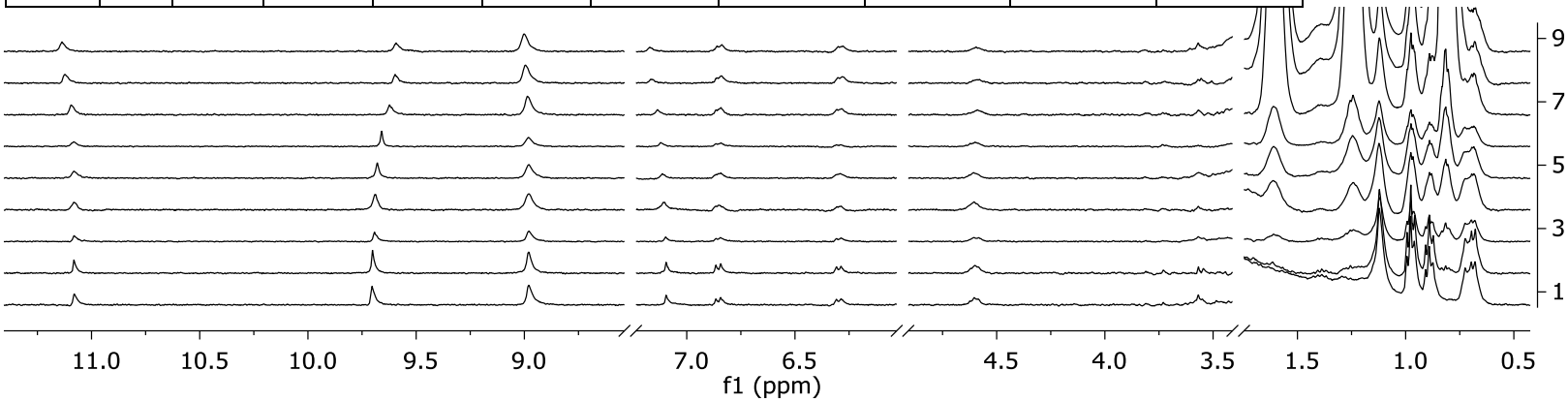


Figure S26. NMR spectra of titration of **I_4-1^{2+}** with Cl^- in DMF under standard solvent suppression conditions.

Table S34. NMR-titration table for **X_4-1^{2+}** and **13** with **Cl^-**, and **X_4-1** with Br^-, I^- and Cl^- in 0.1 M nBu_4PF_6 /DMF solution.

										Br_4-1^{2+}/Cl	**H_4-1^{2+}/Cl**	**13**/Cl	**$I4$-1^{2+}/Br^-**	**I_4-1^{2+}/I^-**	**I_4-1^{2+}/Cl^-PF_6**
Tube Nr.	**V [µL]**	**G/H**	**V_{Host} [µL]**	**V_{Guest} [µL]**	**V_{Fill} [µL]**	**n_{Guest} [µmol]**	**n_{Host} [µmol]**	**c_{Host} [M]**	**c_{Guest} [M]**	**H1/H5 [ppm]**	**H1/H5 [ppm]**	**[ppm]**	**H1/H5 [ppm]**	**H1/H5 [ppm]**	**H1/H5 [ppm]**
10	600	0.00	50	0	550	0.0	0.6	0.001	0.000000	9.729	8.980	8.451	9.685	10.408	10.361
20	600	0.17	50	10	540	0.1	0.6	0.001	0.000167	9.730	8.982	8.439	9.685	10.407	10.362
30	600	0.83	50	50	500	0.5	0.6	0.001	0.000834	9.737	8.982	8.538	9.685	10.402	10.360
40	600	1.50	50	90	460	0.9	0.6	0.001	0.001500	9.744	8.983	8.598	9.685	10.395	10.358
50	600	2.50	50	150	400	1.5	0.6	0.001	0.002501	9.753	8.984	8.631	9.685	10.397	10.357
60	600	5.00	50	300	250	3.0	0.6	0.001	0.005001	9.773	8.983	8.675	9.686	10.388	10.351
70	600	20.00	50	120	430	12.0	0.6	0.001	0.019999	9.843	8.988	8.843	9.685	10.360	10.325
80	600	60.00	50	360	190	36.0	0.6	0.001	0.059996	9.958	9.004	9.055	9.692	10.333	10.302
90	600	83.33	50	500	50	50.0	0.6	0.001	0.083327	9.958	9.005	9.076	9.721	10.325	10.300

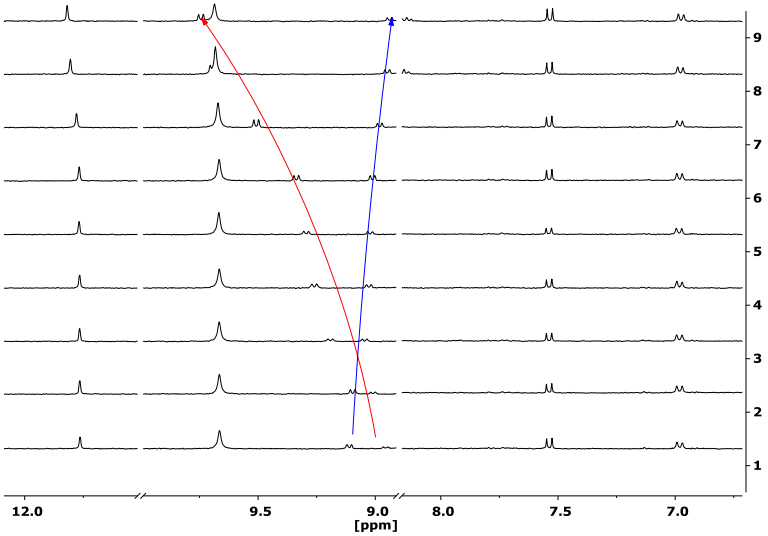


Figure S27. NMR spectra of titration of **13** with Cl^- in DMF under optimized solvent suppression conditions.

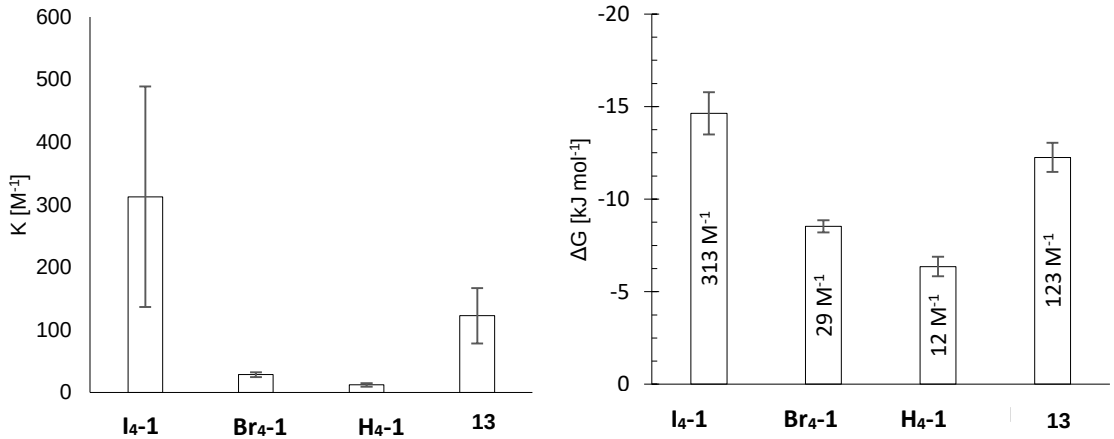


Figure S28. Graphical representation of the results of the NMR-titrations of **X_4-1** and **13** with Cl^- in K [M^{-1}] (left) and ΔG [kJ·mol^{-1}] (right).

Table S35. Determined binding constands/free energies of **X_4-1** and **13** with Cl^-, and **X_4-1** with Br^-, I^- and Cl^- in 0.1 M nBu_4PF_6/DMF solution.

Host	Guest	K [M^{-1}]	ΔG [kJ·mol^{-1}]	Error [kJ·mol^{-1}]
I_4-1^{2+}	Cl^-	312.7	-14.64	1.14
Br_4-1^{2+}		28.5	-8.53	0.33
H_4-1^{2+}		12.1	-6.36	0.53
13		122.7	-12.25	0.78
I_4-1^{2+}	Br^-	58.6	-10.37	0.36
I_4-1^{2+}	I^-	66.2	-10.68	0.50
I_4-1^{2+}	Cl^-/PF_6	33.5	-8.95	0.33

7. Benzhydryl bromide solvolysis (BHB)

For the solvolysis reaction[21] 12.36 mg (50 µmol) were dissolved in 2.0 mL dry MeCN-*d3* and 1.8 µL (100 µmol) of H_2O were added. The Halogen bond donors were prepared as 12.5 mM solutions using 6.25 µmol donor and 500 µL MeCN-*d3.* 400 µL of the donor solutions pipetted into NMR tubes. Directly before the measurements 200 µL of BHB/water solution was added (5 µmol), the tubes closed and inverted, to ensure homogeneous mixtures.

The raw integrals of the BHB and amide protons are given in the tables below. To estimate the conversion, the integral of BHB was set to one and correlated to the amide integral.

Table S36 BHB Background reaction.

#	t[s]	Integral (BHB)	% BHB	Integral (Amide)	time [h]	time [d]	BHB	Amide	% Conversion
1	0	9265.27	100.00	5.343	0.0	0.0	1	0.00	0.1
2	14668	9145.35	98.71	56.104	4.1	0.2	1	0.01	0.6
3	28738	9228.26	99.60	65.634	8.0	0.3	1	0.01	0.7
4	43067	9020.63	97.36	75.321	12.0	0.5	1	0.01	0.8
5	57083	8846.70	95.48	84.307	15.9	0.7	1	0.01	0.9
6	71943	8672.35	93.60	91.393	20.0	0.8	1	0.01	1.0
7	86210	8635.67	93.20	154.451	23.9	1.0	1	0.02	1.8
8	100290	8612.72	92.96	223.254	27.9	1.2	1	0.03	2.5
9	114475	8784.84	94.81	284.199	31.8	1.3	1	0.03	3.1
10	128876	8662.87	93.50	268.353	35.8	1.5	1	0.03	3.0
11	143281	8486.06	91.59	260.379	39.8	1.7	1	0.03	3.0
12	158404	8316.82	89.76	340.322	44.0	1.8	1	0.04	3.9
13	172927	8332.79	89.94	362.17	48.0	2.0	1	0.04	4.2
14	187205	8442.93	91.12	548.221	52.0	2.2	1	0.06	6.1
15	201676	8446.35	91.16	536.227	56.0	2.3	1	0.06	6.0
16	215964	8339.20	90.00	574.762	60.0	2.5	1	0.07	6.4
17	230302	8270.25	89.26	605.245	64.0	2.7	1	0.07	6.8
18	244767	8172.17	88.20	597.622	68.0	2.8	1	0.07	6.8
19	259168	8176.43	88.25	619.445	72.0	3.0	1	0.08	7.0
20	273504	8115.83	87.59	655.608	76.0	3.2	1	0.08	7.5
21	287912	8195.04	88.45	621.285	80.0	3.3	1	0.08	7.0
22	302346	8155.29	88.02	606.94	84.0	3.5	1	0.07	6.9
23	316833	8138.80	87.84	682.788	88.0	3.7	1	0.08	7.7
24	330512	8113.42	87.57	739.713	91.8	3.8	1	0.09	8.4
25	344989	8214.89	88.66	835.921	95.8	4.0	1	0.10	9.2
26	359268	8115.91	87.59	762.067	99.8	4.2	1	0.09	8.6
27	373736	8092.27	87.34	836.284	103.8	4.3	1	0.10	9.4
28	388059	8129.44	87.74	911.058	107.8	4.5	1	0.11	10.1
29	403638	7974.90	86.07	877.503	112.1	4.7	1	0.11	9.9
30	417086	7980.67	86.14	916.735	115.9	4.8	1	0.11	10.3
31	431354	8047.97	86.86	910.955	119.8	5.0	1	0.11	10.2
32	445755	7990.66	86.24	963.779	123.8	5.2	1	0.12	10.8
33	460037	8021.14	86.57	925.487	127.8	5.3	1	0.12	10.3

Table S37. BHB- I_4-1^{2+}

#	t[s]	Integral BHB (6.464,6.425)		Integral Amide (6.291,6.196)	time [h]	time [d]	BHB	Amide	% Conversion
1	0	8392.334	100.00	4.191	0.0	0.0	1	0.00	0.0
2	14695	7328.889	87.33	513.597	4.1	0.2	1	0.07	6.5
3	28719	6650.584	79.25	1232.72	8.0	0.3	1	0.19	15.6
4	43094	6055.102	72.15	1942.387	12.0	0.5	1	0.32	24.3
5	56820	5371.014	64.00	2578.342	15.8	0.7	1	0.48	32.4
6	71503	4778.862	56.94	3286.231	19.9	0.8	1	0.69	40.7
7	86249	4272.68	50.91	3877.699	24.0	1.0	1	0.91	47.6
8	100267	3777.547	45.01	4324.402	27.9	1.2	1	1.14	53.4
9	114632	3422.983	40.79	4935.016	31.8	1.3	1	1.44	59.0
10	129059	2946.174	35.11	5331.39	35.8	1.5	1	1.81	64.4
11	143301	2477.293	29.52	5555.718	39.8	1.7	1	2.24	69.2
12	158647	2296.718	27.37	6045.597	44.1	1.8	1	2.63	72.5
13	172983	1967.363	23.44	6416.921	48.1	2.0	1	3.26	76.5
14	187386	1646.845	19.62	6657.745	52.1	2.2	1	4.04	80.2
15	201915	1439.185	17.15	6848.677	56.1	2.3	1	4.76	82.6
16	216216	1373.427	16.37	7208.981	60.1	2.5	1	5.25	84.0
17	230583	1189.672	14.18	7432.636	64.1	2.7	1	6.25	86.2
18	244996	934.528	11.14	7498.203	68.1	2.8	1	8.02	88.9
19	259450	875.048	10.43	7731.447	72.1	3.0	1	8.84	89.8
20	273788	763.882	9.10	7880.872	76.1	3.2	1	10.32	91.2
21	288165	637.769	7.60	7983.427	80.0	3.3	1	12.52	92.6
22	302563	541.395	6.45	7938.913	84.0	3.5	1	14.66	93.6
23	317070	462.27	5.51	8169.952	88.1	3.7	1	17.67	94.6
24	330493	404.079	4.81	8244.915	91.8	3.8	1	20.40	95.3
25	344853	344.374	4.10	8367.248	95.8	4.0	1	24.30	96.0
26	359259	296.922	3.54	8414.792	99.8	4.2	1	28.34	96.6
27	373636	269.295	3.21	8493.434	103.8	4.3	1	31.54	96.9
28	388081	249.165	2.97	8547.153	107.8	4.5	1	34.30	97.2
29	403915	196.876	2.35	8700.942	112.2	4.7	1	44.20	97.8
30	416834	157.322	1.87	8513.886	115.8	4.8	1	54.12	98.2
31	431317	134.838	1.61	8785.359	119.8	5.0	1	65.15	98.5
32	445647	156.313	1.86	8985.748	123.8	5.2	1	57.49	98.3
33	459988	97.218	1.16	8807.485	127.8	5.3	1	90.60	98.9
34	475150	50.3	0.60	8723.987	132.0	5.5	1	173.44	99.4

Table S38. BHB - 2.5 µmol $\mathbf{I_4\text{-}1^{2+}}$/ 5 µmol BHB

	t[s])	Integral BHB (6.461,6.426)		Integral Amide (6.289,6.220)	time [h]	time [d}	BHB	Amide	% Conversion
1	0	7955.309	100.00	22.884	0.0	0.0	1	0.00	0.3
2	14232	7241.7	91.03	429.556	4.0	0.2	1	0.06	5.6
3	28189	6797.99	85.45	851.873	7.8	0.3	1	0.13	11.1
4	42619	6341.402	79.71	1493.433	11.8	0.5	1	0.24	19.1
5	56852	5893.667	74.08	1971.679	15.8	0.7	1	0.33	25.1
6	71538	5430.776	68.27	2438.505	19.9	0.8	1	0.45	31.0
7	86247	5053.248	63.52	2874.209	24.0	1.0	1	0.57	36.3
8	100285	4694.063	59.01	3420.913	27.9	1.2	1	0.73	42.2
9	114646	4264.321	53.60	3879.234	31.8	1.3	1	0.91	47.6
10	129084	3945.664	49.60	4206.181	35.9	1.5	1	1.07	51.6
11	143247	3706.427	46.59	4539.317	39.8	1.7	1	1.22	55.1
12	157699	3387.38	42.58	4868.595	43.8	1.8	1	1.44	59.0
13	172060	3185.951	40.05	5178.306	47.8	2.0	1	1.63	61.9
14	186455	2844.758	35.76	5389.533	51.8	2.2	1	1.89	65.5
15	200931	2675.109	33.63	5690.066	55.8	2.3	1	2.13	68.0
16	215262	2469.04	31.04	5945.277	59.8	2.5	1	2.41	70.7
17	229638	2364.005	29.72	6332.443	63.8	2.7	1	2.68	72.8
18	244103	2140.321	26.90	6333.961	67.8	2.8	1	2.96	74.7
19	258501	2020.045	25.39	6561.578	71.8	3.0	1	3.25	76.5
20	272858	1880.644	23.64	6727.34	75.8	3.2	1	3.58	78.2
21	287244	1683.03	21.16	6934.375	79.8	3.3	1	4.12	80.5
22	301653	1598.479	20.09	6913.974	83.8	3.5	1	4.33	81.2
23	316069	1580.418	19.87	7149.796	87.8	3.7	1	4.52	81.9
24	330484	1461.849	18.38	7289.229	91.8	3.8	1	4.99	83.3
25	344873	1343.756	16.89	7333.992	95.8	4.0	1	5.46	84.5
26	359253	1292.843	16.25	7441.798	99.8	4.2	1	5.76	85.2
27	373655	1203.999	15.13	7636.58	103.8	4.3	1	6.34	86.4
28	388093	1210.59	15.22	7663.968	107.8	4.5	1	6.33	86.4
29	403916	1062.51	13.36	7814.984	112.2	4.7	1	7.36	88.0
30	416846	1028.004	12.92	7946.954	115.8	4.8	1	7.73	88.5
31	431946	952.593	11.97	7849	120.0	5.0	1	8.24	89.2
32	446319	824.717	10.37	7929.892	124.0	5.2	1	9.62	90.6
33	460639	811.46	10.20	8003.961	128.0	5.3	1	9.86	90.8
34	475772	774.978	9.74	8049.824	132.2	5.5	1	10.39	91.2

Table S39. BHB - **Br_4-1^{2+}**

#	t[s]	Integral BHB (6.461,6.429)		Integral Amide (6.275,6.218)	time [h]	time [d}	BHB	Amide	% Conversion
1	0	8094.889	100.00	59.846	0.0	0.0	1	0.01	0.7
2	14702	7481.581	92.42	157.98	4.1	0.2	1	0.02	2.1
3	28762	7149.491	88.32	374.515	8.0	0.3	1	0.05	5.0
4	43086	6904.612	85.30	569.397	12.0	0.5	1	0.08	7.6
5	57055	6763.894	83.56	838.028	15.8	0.7	1	0.12	11.0
6	71928	6540.84	80.80	1031.442	20.0	0.8	1	0.16	13.6
7	86228	6411.269	79.20	1268.035	24.0	1.0	1	0.20	16.5
8	100274	6214.355	76.77	1532.364	27.9	1.2	1	0.25	19.8
9	114500	5979.317	73.87	1766.944	31.8	1.3	1	0.30	22.8
10	128887	5761.404	71.17	1985.418	35.8	1.5	1	0.34	25.6
11	143277	5577.477	68.90	2256.077	39.8	1.7	1	0.40	28.8
12	158389	5336.628	65.93	2373.6	44.0	1.8	1	0.44	30.8
13	172785	5148.038	63.60	2621.412	48.0	2.0	1	0.51	33.7
14	187156	4969.094	61.39	2889.844	52.0	2.2	1	0.58	36.8
15	201668	4857.091	60.00	3100.91	56.0	2.3	1	0.64	39.0
16	215949	4668.707	57.67	3341.564	60.0	2.5	1	0.72	41.7
17	230331	4486.385	55.42	3561.356	64.0	2.7	1	0.79	44.3
18	244748	4327.843	53.46	3667.945	68.0	2.8	1	0.85	45.9
19	259194	4209.85	52.01	3923.143	72.0	3.0	1	0.93	48.2
20	273521	4041.638	49.93	4093.323	76.0	3.2	1	1.01	50.3
21	287914	3886.607	48.01	4222.664	80.0	3.3	1	1.09	52.1
22	302296	3682.277	45.49	4429.5	84.0	3.5	1	1.20	54.6
23	316803	3576.553	44.18	4636.329	88.0	3.7	1	1.30	56.5
24	330467	3506.41	43.32	4797.172	91.8	3.8	1	1.37	57.8
25	344950	3301.44	40.78	4948.713	95.8	4.0	1	1.50	60.0
26	359294	3237.936	40.00	5061.241	99.8	4.2	1	1.56	61.0
27	373736	3019.468	37.30	5092.946	103.8	4.3	1	1.69	62.8
28	388086	2914.706	36.01	5268.529	107.8	4.5	1	1.81	64.4
29	403671	2858.992	35.32	5503.962	112.1	4.7	1	1.93	65.8
30	417046	2732.996	33.76	5553.139	115.8	4.8	1	2.03	67.0
31	431359	2712.631	33.51	5727.32	119.8	5.0	1	2.11	67.9
32	445743	2499.771	30.88	5777.135	123.8	5.2	1	2.31	69.8
33	460067	2526.994	31.22	5980.916	127.8	5.3	1	2.37	70.3
34	475186	2352.898	29.07	6009.13	132.0	5.5	1	2.55	71.9

Table S40. BHB - H_4-1^{2+}

#	t[s]	Integral BHB (6.465,6.423)		Integral Amide (6.256,6.197)	time [h]	time [d}	BHB	Amide	% Conversion
1	0	8625.614	100.00	47.247	0.0	0.0	1	0.01	0.5
2	14697	8445.237	97.91	90.687	4.1	0.2	1	0.01	1.1
3	28761	8433.581	97.77	134.76	8.0	0.3	1	0.02	1.6
4	43090	8389.836	97.27	226.479	12.0	0.5	1	0.03	2.6
5	57045	8243.212	95.57	291.372	15.8	0.7	1	0.04	3.4
6	71940	8136.028	94.32	376.265	20.0	0.8	1	0.05	4.4
7	86231	8151.032	94.50	405.252	24.0	1.0	1	0.05	4.7
8	100305	8143.773	94.41	437.401	27.9	1.2	1	0.05	5.1
9	114497	8074.509	93.61	518.768	31.8	1.3	1	0.06	6.0
10	128921	7996.052	92.70	516.904	35.8	1.5	1	0.06	6.1
11	143301	7895.546	91.54	576.34	39.8	1.7	1	0.07	6.8
12	158386	7866.119	91.19	615.069	44.0	1.8	1	0.08	7.3
13	172876	7675.839	88.99	718.531	48.0	2.0	1	0.09	8.6
14	187198	7697.723	89.24	707.847	52.0	2.2	1	0.09	8.4
15	201667	7749.364	89.84	765.245	56.0	2.3	1	0.10	9.0
16	215962	7713.334	89.42	855.638	60.0	2.5	1	0.11	10.0
17	230336	7676.624	89.00	975.287	64.0	2.7	1	0.13	11.3
18	244786	7494.172	86.88	930.445	68.0	2.8	1	0.12	11.0
19	259210	7641.514	88.59	1021.055	72.0	3.0	1	0.13	11.8
20	273510	7453.406	86.41	1016.467	76.0	3.2	1	0.14	12.0
21	287913	7547.185	87.50	1100.551	80.0	3.3	1	0.15	12.7
22	302359	7431.842	86.16	1167.682	84.0	3.5	1	0.16	13.6
23	316824	7258.544	84.15	1092.931	88.0	3.7	1	0.15	13.1
24	330537	7436.902	86.22	1141.6	91.8	3.8	1	0.15	13.3
25	344963	7288.952	84.50	1238.416	95.8	4.0	1	0.17	14.5
26	359293	7469.78	86.60	1341.304	99.8	4.2	1	0.18	15.2
27	373755	7318.259	84.84	1306.782	103.8	4.3	1	0.18	15.2
28	388083	7274.153	84.33	1435.552	107.8	4.5	1	0.20	16.5
29	403670	7297.688	84.60	1419.585	112.1	4.7	1	0.19	16.3
30	417045	7203.417	83.51	1485.327	115.8	4.8	1	0.21	17.1
31	431369	7264.607	84.22	1507.425	119.8	5.0	1	0.21	17.2
32	445756	7174.969	83.18	1527.379	123.8	5.2	1	0.21	17.6
33	460068	7170.035	83.12	1563.657	127.8	5.3	1	0.22	17.9
34	475173	7199.709	83.47	1626.084	132.0	5.5	1	0.23	18.4

Table S41. BHB – **13** [22,23]

#	X(I)	Y(X)	Y1(X)	time [h]	Time [d]	BHB	Amide	% conversion
Model	ARR_DATA(I)	Integral BHB (6.496,6.453)	Integral Amide (6.328,6.204)					
1	0	5491.451	36.171	0.0	0.0	1	0.01	0.7
2	14013	1376.261	4618.962	3.9	0.2	1	3.36	77.0
3	28380	871.606	5955.159	7.9	0.3	1	6.83	87.2
4	42773	602.67	6646.745	11.9	0.5	1	11.03	91.7
5	57184	485.518	7220.376	15.9	0.7	1	14.87	93.7
6	71581	373.93	7377.351	19.9	0.8	1	19.73	95.2
7	86852	344.261	7745.759	24.1	1.0	1	22.50	95.7
8	100379	267.485	7841.272	27.9	1.2	1	29.31	96.7
9	114777	221.884	8037.261	31.9	1.3	1	36.22	97.3
10	129263	204.869	8075.486	35.9	1.5	1	39.42	97.5
11	143577	139.667	8232.52	39.9	1.7	1	58.94	98.3
12	158418	98.013	8330.861	44.0	1.8	1	85.00	98.8
13	172856	88.949	8311.029	48.0	2.0	1	93.44	98.9
14	187252	57.044	8264.879	52.0	2.2	1	144.89	99.3
15	201165	73.701	8310.557	55.9	2.3	1	112.76	99.1
16	215586	71.875	8292.253	59.9	2.5	1	115.37	99.1
17	230165	83.087	8454.89	63.9	2.7	1	101.76	99.0
18	244588	13.258	8469.486	68.0	2.8	1	638.82	99.8
19	258831	13.98	8438.266	72.0	3.0	1	603.60	99.8
20	273173	15.017	8450.181	76.0	3.2	1	562.71	99.8
21	287564	14.233	8485.981	80.0	3.3	1	596.22	99.8
22	301959	12.865	8369.674	84.0	3.5	1	650.58	99.8
23	317066	28.468	8543.319	88.0	3.7	1	300.10	99.7
24	330930	6.345	8585.244	91.8	3.8	1	1353.07	99.9
25	345163	15.572	8447.669	95.8	4.0	1	542.49	99.8
26	359597	3.84	8528.527	99.8	4.2	1	2220.97	100.0
27	373983	13.201	8438.458	103.8	4.3	1	639.23	99.8
28	388372	5.417	8392.648	107.8	4.5	1	1549.32	99.9
29	402767	19.938	8503.949	112.1	4.7	1	426.52	99.8
30	417222	2.28	8512.883	115.8	4.8	1	3733.72	100.0
31	431567	1.32	8494.453	119.8	5.0	1	6435.19	100.0
32	445961	23.824	8505.981	123.8	5.2	1	357.03	99.7
33	460364	0.27	8439.762	127.8	5.3	1	31258.38	100.0
34	474755	17.332	8481.875	132.0	5.5	1	489.38	99.8

Table S42. BHB - **14** [24]

#	X(I)	Y(X)	Y1(X)	time [h]	time [d]	BHB	Amide	% Conversion
Model	ARR_DATA (I)	Integral BHB (6.488,6.458)	Integral Amide (6.229,6.149)					
1	0	6145.578	12.822	0.0	0.0	1	0.00	0.0
2	14016	3428.711	479.812	3.9	0.2	1	0.14	12.3
3	28375	3248.145	822.457	7.9	0.3	1	0.25	20.2
4	42758	3074.056	960.92	11.9	0.5	1	0.31	23.8
5	57174	2903.902	1389.617	15.9	0.7	1	0.48	32.4
6	71603	2866.637	1584.661	19.9	0.8	1	0.55	35.6
7	86847	2722.544	1819.915	24.1	1.0	1	0.67	40.1
8	100372	2672.616	1990.86	27.9	1.2	1	0.74	42.7
9	114763	2604.013	2103.371	31.9	1.3	1	0.81	44.7
10	129271	2548.89	2339.935	35.9	1.5	1	0.92	47.9
11	143575	2505.522	2476.121	39.9	1.7	1	0.99	49.7
12	158403	2456.736	2644.497	44.0	1.8	1	1.08	51.8
13	172842	2443.377	2852.004	48.0	2.0	1	1.17	53.9
14	187263	2291.488	3001.929	52.0	2.2	1	1.31	56.7
15	201170	2335.002	3079.85	55.9	2.3	1	1.32	56.9
16	215581	2230.468	3292.801	59.9	2.5	1	1.48	59.6
17	230246	2200.145	3386.952	64.0	2.7	1	1.54	60.6
18	244595	2162.183	3583.396	67.9	2.8	1	1.66	62.4
19	258822	2128.357	3708.145	71.9	3.0	1	1.74	63.5
20	273154	2055.89	3864.473	75.9	3.2	1	1.88	65.3
21	287623	2015.459	3905.693	79.9	3.3	1	1.94	66.0
22	301958	1950.981	4046.998	83.9	3.5	1	2.07	67.5
23	317065	1928.074	4179.916	88.1	3.7	1	2.17	68.4
24	330930	1960.662	4253.674	91.9	3.8	1	2.17	68.4
25	345184	1888.348	4358.081	95.9	4.0	1	2.31	69.8
26	359597	1866.021	4432.328	99.9	4.2	1	2.38	70.4
27	373984	1827.862	4577.979	103.9	4.3	1	2.50	71.5
28	388380	1792.289	4581.118	107.9	4.5	1	2.56	71.9
29	402747	1747.226	4736.521	111.9	4.7	1	2.71	73.1
30	417203	1773.234	4838.029	115.9	4.8	1	2.73	73.2
31	431564	1696.665	4950.862	119.9	5.0	1	2.92	74.5
32	445947	1688.69	4954.222	123.9	5.2	1	2.93	74.6
33	460347	1644.245	5139.424	127.9	5.3	1	3.13	75.8
34	474739	1644.782	5082.166	131.9	5.5	1	3.09	75.5

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