Folding of a Dynamic Macrocyclic System to Stabilize its Cation Radical State

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Table of contents

1. General information

NMR Spectroscopy. ^{1}H NMR spectra were recorded on a high-field spectrometer (^{1}H 600.15 MHz and 400 MHz, ^{13}C 150 MHz and 100 MHz), equipped with a broadband inverse gradient probehead. Spectra were referenced to the residual solvent signal (chloroform-d, 7.26 ppm, dichloromethane-d2 5.32 ppm). Two-dimensional NMR spectra were recorded with 2048 data points in the t2 domain and up to 1024 points in the t1 domain, with a 1s recovery delay.

Mass Spectrometry. The ESI-MS analysis was performed on Bruker qTOF (Bremen, Germany) equipped with a standard ESI source. Spectra were recorded using DCM or MeOH. The instruments parameters were as follows: positive-ion mode, calibration with the Tunemix™ mixture (Agilent Technologies, Palo Alto, CA, USA), mass accuracy was better than 5 ppm, scan range: 50 - 1600 m/z; drying gas: nitrogen; flow rate: 3.0 L/min, temperature: 200 ^{o}C; potential between the spray needle and the orifice: 4.5 kV, analyte was introduced to the ESI source by pump (New Era Pump Systems, Inc., USA) with a flow rate: 3 µL/min.

UV-Vis Spectroscopy. Electronic spectra were recorded on a Varian Carry-50 Bio spectrophotometer with a 1 cm optical path in solutions in HPLC grade CH_2Cl_2 in 298 K using standard quartz cuvettes.

Fluorescence. Steady state fluorescence spectra were recorded with a Hitachi F-7000 spectrofluorometer apparatus. Time-dependent experiments (life-time measurements) was conducted with a picosecond Horiba Jobin Yvon spectrofluorometer (UV-Vis-NIR). The fluorescence quantum yield was established using a thiomethoxy BODIPY as a reference (QY = 0.03 in DMSO).

EPR spectroscopy. EPR spectra were measured with a Bruker ELEXSYS E500 X-band spectrometer equipped with a super-high-sensitivity ER 4122 SHQE cavity operating at 9.7 GHz and 100 kHz magnetic field modulation. XEpr software was used for spectra acquisition and manipulation. An ER 4111 variable temperature unit was used for precise temperature control. In typical experiments, the spectra were acquired with the microwave power of 2 mW, the modulation amplitude of 1 G, conversion time 83.89 ms, time constant 40.96 ms, and 1 scan were applied. EPR spectra were simulated with the EasySpin software package.

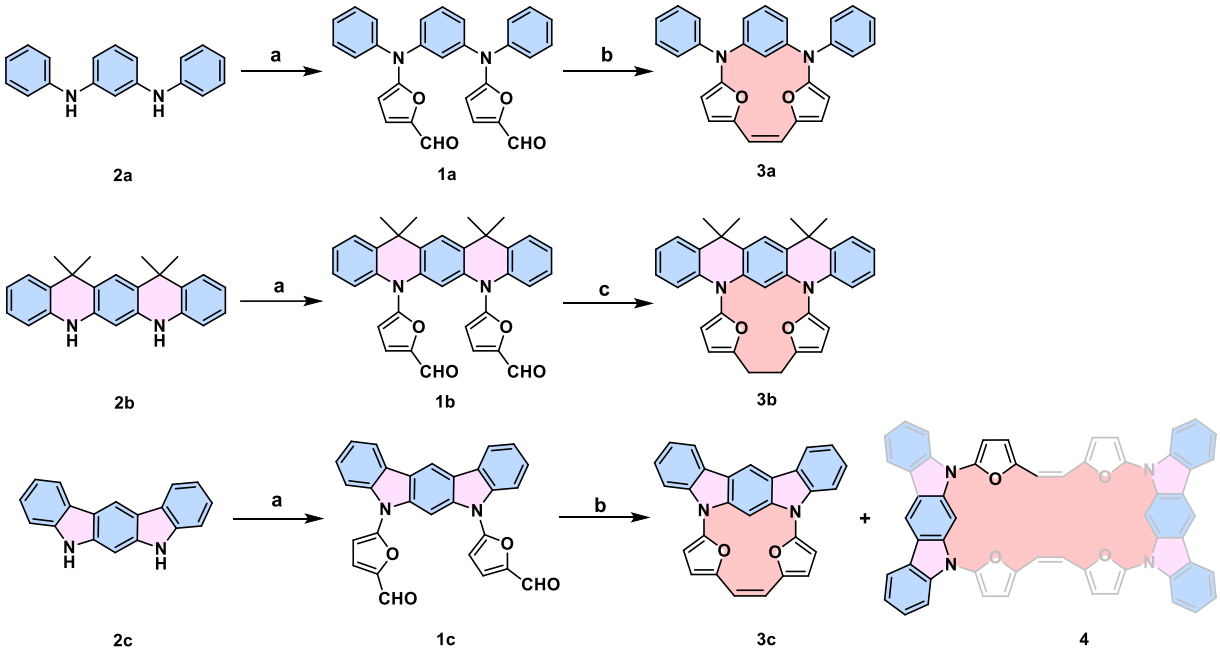
X-Ray Analysis. X-Ray quality crystals were prepared by diffusion method from HPLC grade DCM / hexane solvent combination (**1a, 3a, 1b, 3b, 3c**) and slow evaporation method with chloroform (**4**) . **1b, 3b, 3c** were performed using Bruker D8 Quest Eco diffractometer at 100K equipped with Photon II CPAD detector, MoKα (λ = 0.71073 Å) sealed tube radiation source and Triumph® optics. For structures **1a, 3a,** and **4** diffraction data were collected on a Rigaku Oxford Diffraction XtaLAB Synergy-R DW diffractometer equipped with a HyPix ARC 150° Hybrid Photon Counting (HPC) detector using CuKα (λ = 1.54184 Å) at 100 K. Data were processed using the CrystAlisPro software. The structures were solved by intrinsic phasing with SHELXT (2015 release) and refined by full-matrix least-squares methods based F2 using SHELXL. For all structures, H atoms bound to C atoms were placed in the geometrically idealized positions and treated in riding mode, with C-H = 0.95Å and Uiso(H) = 1.2Ueq(C) for C-H groups, and C-H = 0.98Å and Uiso(H) = 1.5Ueq(C) for CH_3 groups .

Theoretical calculations. Geometry optimization for all analysed structures was carried out with the Gaussian 091 software package within unconstrained C1 symmetry, with starting coordinates derived from semi-empirical calculations. Becke's three-parameter exchange functional with the gradient-corrected correlation formula of Lee, Yang and Parr (DFT-B3LYP)[2] were used with the 6- 31G(d,p) basis set. The polarizable continuum model of solvation was used (PCM, standard chloroform parametrization) for all optimizations. Harmonic vibrational frequencies were calculated using analytical second derivatives as a verification of local minimum achievement with no negative frequencies observed. GIAO predicted chemical shifts for all structures were calculated for fully optimized geometries. The analysis of diatropic currents present in analysed systems were performed via calculation of NICS value and AICD currents calculated with Gaussian 09 software and visualized with the software provided by the Authors. The charge distribution has been performed with NBO calculations and visualized with GaussView 5.0 package. The open-shell derivatives were calculated with UB3LYP-6- 31G(d,p), PCM set of funstional and database.

2. Experimental section

All solvents (MeOH, Ethyl Acetate, $CHCl_3$, n-hexane, toluene, acetone, water) if not indicated differently were used without purification. CH_2Cl_2 was distilled over CaH_2. Chloroform-*d* was prepared directly before using by passing through a basic alumina column. All reactions were performed under inert atmosphere.

2.1 Experimental procedures



Scheme S1. Conditions: a) 5-Bromo-2-furaldehyde, $Pd_2(dba)_3$, RuPhos, K_3PO_4, toluene, reflux, 24 h; b) $TiCl_4$, Zn, CuI (or, pyridine), THF (or, 1,4-dioxane), reflux; c) $TiCl_4$, Zn, CuI, 1,4-dioxane, reflux.

Compound 1a. A Schlenk tube was charged with compound **2a** (0.20 g, 0.77 mmol), 5-Bromo-2-furaldehyde (0.28 g, 1.61 mmol), $Pd_2(dba)_3$ (0.10 g, 0.12 mmol), RuPhos (0.21 g, 0.46 mmol), and K_3PO_4 (3.26 g, 15.37 mmol) and was allowed to dry under high vacuum for 3 hours. Then 40 mL of degassed toluene was added to the tube and the reaction mixture was allowed to reflux with heat-on block for 24 hours. After completion of the reaction, the crude product was allowed to cool to room temperature and passed through celite and washed with dichloromethane. The obtained solution was dried under reduced pressure and subjected to silica gel column chromatography using petroleum ether / ethyl acetate (7:3) as eluent to afford the compound as orange solid. Yield (0.27 g): 78 %; **^{1}H NMR (400 MHz, $CDCl_3$, 298 K)**, δ(ppm): 9.25 (s, 2H), 7.39-7.34 (m, 4H), 7.28-7.25 (m, 2H), 7.24-7.19 (m, 9H), 7.04 (t, ^4J = 2.2 Hz, 1H), 6.88 (dd, ^3J = 8.1, ^4J = 2.2 Hz, 2H), 5.72 (d, ^3J = 3.8 Hz, 2H).**^{13}C NMR (101 MHz, $CDCl_3$, 298 K)**, δ(ppm):159.2, 145.9, 144.6, 143.1, 130.6, 130.5, 129.9, 129.1, 126.3, 125.3, 120.5, 119.7, 111.1, 96.0. ; **HRMS (ESI)**: *m/z*: calculated for $C_{28}H_{20}N_2O_4$ $[M+Na]^+$: 471.1321; found: 471.1316.

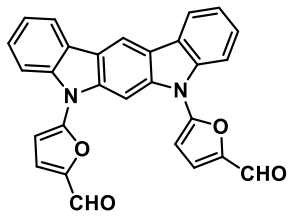
Compound 3a. To a 500 mL three necked round bottom flask containing Zn dust (2.19 g, 33.44 mmol) and CuI (0.20 g, 1.06 mmol) in 100 mL dry, degassed THF under inert gas atmosphere, $TiCl_4$ (1.85 mL, 16.94 mmol) was added. The mixture was refluxed for 2 h under argon atmosphere with heat-on block and gradual changes of colour from green to grey were observed. To this generated low valent titanium (0) species, solution of the compound **1a** (0.20 g, 0.445 mmol) in 100 mL of degassed THF was added dropwise. The mixture was refluxed for 1.5 hour with heat-on block and quenched with 10 % aq. Solution of K_2CO_3 (115 mL), extracted with ethyl acetate. The organic layer was washed with water two times, dried with Na_2SO_4, and evaporated. The crude product was subjected to silica gel column chromatography using hexane / ethyl acetate (9:1) and reduced under pressure to obtain the desired compound as red powder. Yield (0.17 g): 92 % ; **^{1}H NMR** (500 MHz, C_6D_6, 298 K), δ(ppm): 7.92 (t, ^4J = 2.21 Hz, 1H), 7.21 (d, ^3J = 8.59 Hz, 4H), 7.08 (dd, ^3J = 8.49, ^3J = 7.39 Hz, 4H), 6.93 (dd, ^3J = 7.72, ^3J = 6.95 Hz, 2H), 6.75 (t, ^3J = 8.11 Hz, 1H), 6.51 (dd, ^3J = 8.23, ^4J = 2.32 Hz, 2H), 6.06 (d, ^3J = 3.32 Hz, 2H), 5.77 (s, 2H), 6.06 (d, ^3J = 3.32 Hz, 2H); **^{13}C NMR** (126 MHz, C_6D_6, 298K), δ(ppm): 154.0, 145.6, 144.6, 143.3, 129.8, 128.5, 128.3, 127.6, 125.5, 125.2, 118.0, 117.5, 113.3, 110.5, 93.2; **HRMS (ESI):** m/z: calculated for $C_{28}H_{20}N_2O_2$ $[M]^+$: 416.1525; found: 416.1519. **UV/Vis** (CH_2Cl_2, 298K, λ(nm), log ε): 299 (4.45), 416 (3.84); **Emission** (CH_2Cl_2, 298K): 479 nm.

Compound 1b. A Schlenk tube was charged with compound **2b** (0.10 g, 0.29 mmol), 5-Bromo-2-furaldehyde (0.11 g, 0.61 mmol), $Pd_2(dba)_3$ (0.04 g, 0.044 mmol), RuPhos (0.08 g, 0.176 mmol), and K_3PO_4 (1.24 g, 5.87 mmol) and was allowed to dry under high vacuum for 3 hours. Then 40 mL of degassed toluene was added to the tube and the reaction mixture was allowed to reflux with heat-on block for 24 hours. After completion of the reaction, the crude product was allowed to cool to room temperature and passed through celite and washed with dichloromethane. The obtained solution was dried under reduced pressure and subjected to silica gel column chromatography using petroleum ether / ethyl acetate (7:3) as eluent to afford the compound as orange solid. Yield (0.12 g): 78 %; **^{1}H NMR** (300 MHz, $CDCl_3$, 298 K) δ 9.44 (s, 2H), 7.51 (s, 1H), 7.47 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 2H), 7.38 (d, ^3J = 3.8 Hz, 2H), 7.22 – 7.17 (m, 2H), 7.17 – 7.11 (m, 4H), 7.06 (s, 1H), 6.39 (d, ^3J = 3.8 Hz, 2H), 1.64 (s, 12H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.0, 155.9, 148.4, 139.3, 137.8, 136.8, 132.8, 127.4, 126.1, 125.2, 125.1, 121.1, 119.5, 110.4, 101.2, 37.5, 29.9; **HRMS (ESI)** *m/z* calculated for $C_{34}H_{28}N_2O_4$ $[M+Na]^+$: 551.1947; found : 551.1941.

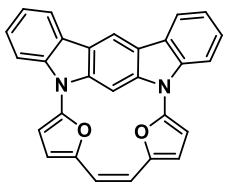
Compound 3b. To a 250 mL three necked round bottom flask containing Zn dust (0.74 g, 11.35 mmol) and CuI (0.07 g, 0.36 mmol) in 80 mL dry, degassed 1,4-dioxane under inert gas atmosphere, $TiCl_4$ (0.63 mL, 5.75mmol) was added. The mixture was refluxed with heat-on block for 2 h under argon atmosphere and gradual changes of colour from green to grey were observed. To this generated low valent titanium (0) species, solution of the compound **1b** (0.08 g, 0.15 mmol) in 40 mL of degassed 1,4-dioxane was added dropwise. The mixture was refluxed for 1.5 hour with heat-on block and after cooling down to room temperature the reaction mixture was quenched with 10 % aq. Solution of K_2CO_3 (43 mL), extracted with ethyl acetate. The organic layer was washed with water two times, dried with Na_2SO_4, and evaporated. The crude product was subjected to silica gel

column chromatography using hexane / ethyl acetate (9:1) and reduced under pressure to obtain the desired compound as yellow solid. Yield (0.05 g): 68 % ; **^{1}H NMR** (400 MHz, $CDCl_3$, 293 K), δ (ppm): 7.42 (d, ^{3}J = 7.8, 2H), 7.37 (s, 1H), 7.06 (t, ^{3}J = 8.4, 2H), 6.95 (t, ^{3}J = 7.9, 2H), 6.84 (d, ^{3}J = 7.9, 2H), 6.21 (d, ^{3}J = 3.1 Hz, 2H), 6.15 (d, ^{3}J = 3.1 Hz, 2H), 4.41 (s, 1H), 3.07 (s, 4H), 1.64 (s, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$, 298 K), δ(ppm): 151.8, 145.8, 139., 139.5, 130.6, 126.6, 125.6, 124.2, 121.5, 121.0, 114.0, 109.0, 108.7, 103.0, 77.4, 77.1, 76.8, 35.7, 31.4, 27.1; **HRMS (ESI):** m/z: calculated for $C_{34}H_{30}N_2O_2$ $[M+Na]^+$: 521.2205; found: 521.2199. **UV/Vis** (CH_2Cl_2, 298K, λ(nm), log ε): 271 (4.62); **Emission** (CH_2Cl_2, 298K): 363 nm.

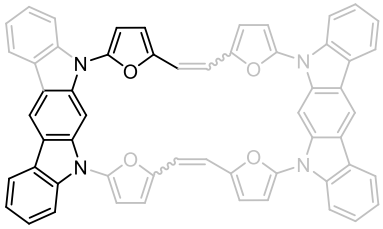
Compound 1c. A Schlenk tube was charged with compound **2c** (0.40 g, 1.56 mmol), 5-Bromo-2-furaldehyde (0.57 g, 3.28 mmol), $Pd_2(dba)_3$ (0.26 g, 0.234 mmol), RuPhos (0.50 g, 0.936 mmol), and K_3PO_4 (6.50 g, 31.21 mmol) and was allowed to dry under high vacuum for 3 hours. Then 80 mL of degassed toluene was added to the tube and the reaction mixture was allowed to reflux with heat-on block for 24 hours. After completion of the reaction, the crude product was allowed to cool to room temperature and passed through celite and washed with dichloromethane. The obtained solution was dried under reduced pressure and subjected to silica gel column chromatography using petroleum ether / ethyl acetate (7:3) as eluent to afford the compound as orange solid. Yield (0.5 g): 72 %; **^{1}H NMR** (600 MHz, $CDCl_3$, 298K), δ(ppm): 9.68 (s, 2H), 8.66 (s, 1H), 8.44 (s, 1H), 8.18 (d, ^{3}J = 7.6 Hz, 2H), 7.87 (d, ^{3}J = 8.2 Hz, 2H), 7.54 (d, ^{3}J = 3.8 Hz, 2H), 7.54 – 7.50 (d, ^{3}J = 7.8 Hz, 2H), 7.43 (t, ^{3}J = 7.4 Hz, 2H), 6.73 (d, ^{3}J = 3.7 Hz, 2H).; **^{13}C NMR** (151 MHz, $CDCl_3$, 298K), δ(ppm): 176.1, 151.3, 147.8, 139.1, 138.5, 126.7, 125.0, 122.7, 121.1, 120.1, 111.8, 111.5, 99.7, 95.4; **HRMS (ESI):** m/z: calculated for $C_{28}H_{16}N_2O_4$ $[M+Na]^+$: 467.1008; found: 467.1004.



Compound 3c & 4. To a 250 mL double necked round bottom flask containing Zn dust (0.66 g, 10.12 mmol) and CuI (0.06 g, 0.32 mmol) in 80 mL dry, degassed THF under inert gas atmosphere, $TiCl_4$ (0.56 mL, 5.13 mmol) was added. The mixture was refluxed with heat-on block for 2 h under nitrogen atmosphere and gradual changes of colour from green to grey were observed. To this generated low valent titanium (0) species, solution of the compound **1c** (0.06 g, 0.134 mmol) in 30 mL of degassed THF was added dropwise. The mixture was refluxed for 1.5 hours with heat-on block and quenched with 10 % aq. Solution of K_2CO_3 (35 mL), extracted with ethyl acetate. The organic layer was washed with water two times, dried with Na_2SO_4 and evaporated. The mixture was subjected to the SEC column to separate the dimer from the monomer by using THF as an eluent. The first fraction was consisting of dimer (**4**) which was further purified by precipitation using DCM and hexane to obtain the dimer as orange solid. Yield of compound **4** (0.025 g): 45%. The last fraction was consisting of the monomer (**3c**) which was further purified by precipitation method from dichloromethane/hexane solvents to give yellow solid. Yield of compound **3c** (0.022 g): 40 %.

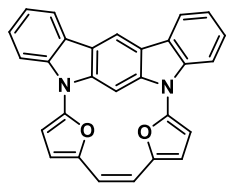


3c

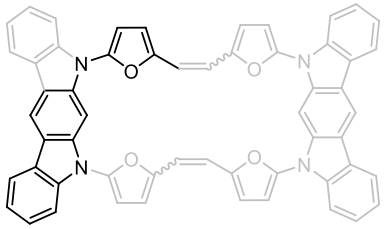


4

Compound 3c & 4 (Alternative procedure). In the three-neck round bottom flask zinc dust (0.15 g, 2.25 mmol) was dried under vacuum for 1 h. Then 30 mL of dry, degassed 1,4-dioxane was added via syringe under the argon atmosphere, following by the addition of pyridine (0.001 mL, 0.011 mmol) and titanium tetrachloride (0.12 mL, 1.12 mmol). The mixture was refluxed with heat-on block for 2 h and the solution of the dialdehyde **1c** (0.1 g, 0.225 mmol) in 20 mL dry, degassed 1,4-dioxane was added dropwise. The resulting solution was refluxed with heat-on block for additional 2 h. Then the heating bath was removed, 20 mL of saturated aqueous solution of NH_4Cl was added and the suspension was stirred for 20 min and extracted with ethyl acetate and dried over Na_2SO_4. The mixture was subjected to the SEC column to separate the dimer from the monomer by using THF as an eluent. The first fraction was consisting of dimer (**4**) which was further purified by precipitation using DCM and hexane to obtain as orange solid. Yield of compound **4** (0.022 g): 24 %. The last fraction was consisting of the monomer (**3c**) which was further purified by precipitation from dichloromethane/hexane solvents to give yellow solid. Yield of compound **3c** (0.036 g): 39 %.



3c

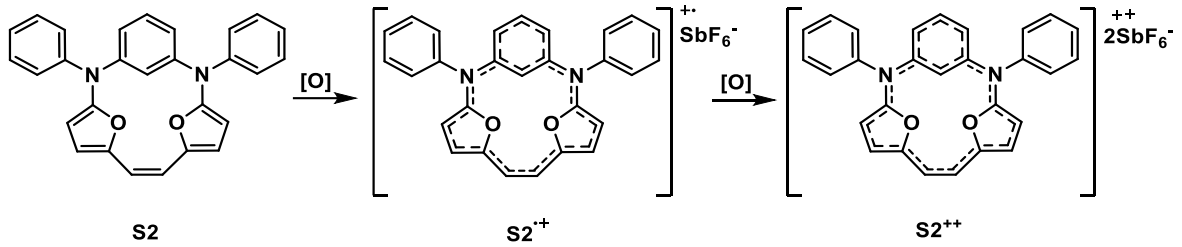


4

Compound 3c: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ(ppm): 9.41 (s, 1H), 8.35 (s, 1H), 8.04 (d, ^3J = 7.6 Hz, 2H), 7.49 (d, ^3J = 8.43 Hz, 2H), 7.40 (t, ^3J = 8.1 Hz, 2H), 7.30 (td, ^{3}J = 7.5, ^{4}J = 1.1 Hz, 2H), 6.36 (d, ^3J = 3.3 Hz, 2H), 6.28 (d, ^3J = 3.3 Hz, 2H), 5.75 (s, 2H).; **^{13}C NMR** couldn't be collected due to poor solubility; **HRMS (ESI)**: *m/z*: calculated for $C_{28}H_{16}N_2O_2$ $[M]^+$: 412.1212; found: 412.1211. **UV/Vis** (CH_2Cl_2, 298K, λ(nm), log ε): 276 (4.24), 311 (4.18); **Emission** (CH_2Cl_2, 298K): 498 nm.

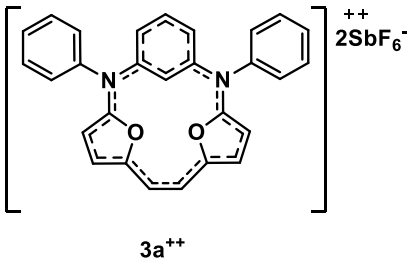
Compound 4: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ(ppm): 8.73 (s, 1H), 8.35 (s, 1H), 8.22 (d, ^3J = 8.4 Hz, 2H), 7.65 (d, ^3J = 8.1 Hz, 2H), 7.48 (t, ^3J = 8.2 Hz, 2H), 7.37 (t, ^3J=8.1 Hz, 2H), 6.71 (s, 2H), 6.44 (d, ^3J = 3.4 Hz, 2H), 6.42 (d, ^3J = 3.35 Hz, 2H).; **^{13}C NMR** (101 MHz, $CDCl_3$, 298K), δ(ppm): 149.0, 145.1, 140.5, 139.8, 125.9, 124.8, 121.3, 120.2, 119.7, 113.7, 110.9, 110.5, 101.3, 77.4, 77.1, 76.8.; **HRMS (ESI)**: *m/z*: calculated for $C_{56}H_{32}N_4O_4$ $[M]^+$: 824.2424; found: 824.2573. **UV/Vis** (CH_2Cl_2, 298K, λ(nm), log ε): 302 (4.96), 357(4.56); **Emission** (CH_2Cl_2, 298K): 459 nm.

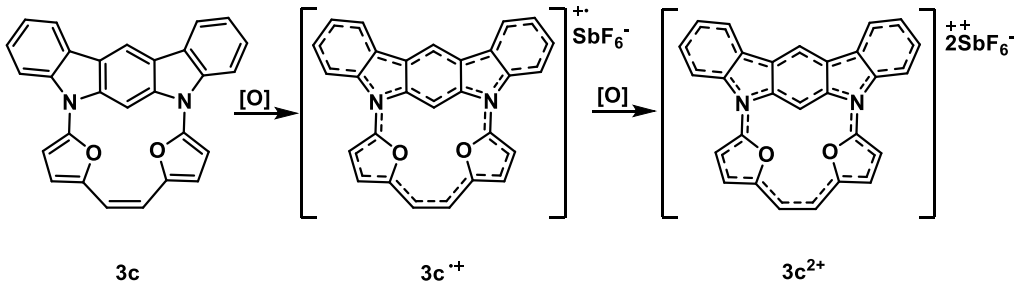
General procedure of oxidation: 1 mg of compound (**3a** or **3c or 4**) was dissolved in 500 µL of CD_3CN / CD_2Cl_2 in a glove-box conditions. To this solution $NOSbF_6$ (10 mg in 200 µl of CD_3CN prepared in glove-box conditions) was added gradually every half equivalent and the reaction was controlled by NMR spectroscopy.



Scheme S2. Oxidation experiments for **3a**.

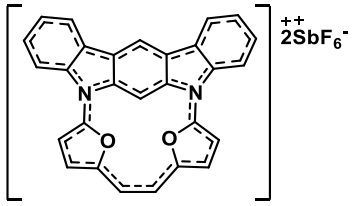
Compound $3a^{2+}$. ^{1}H NMR (600 MHz, CD_3CN, 233K) δ(ppm): 10.86 (t, ^4J = 2.22 Hz, 1H), 7.75 (d, ^3J = 5.65 Hz, 2H), 7.65 (5H), 7.57 (4H), 7.32 (t, ^3J = 8.36 Hz, 2H), 7.09 (dd, ^3J = 8.27 Hz, 2H), 6.64 (d, ^3J = 5.57, 2H), 6.25 (s, 2H).

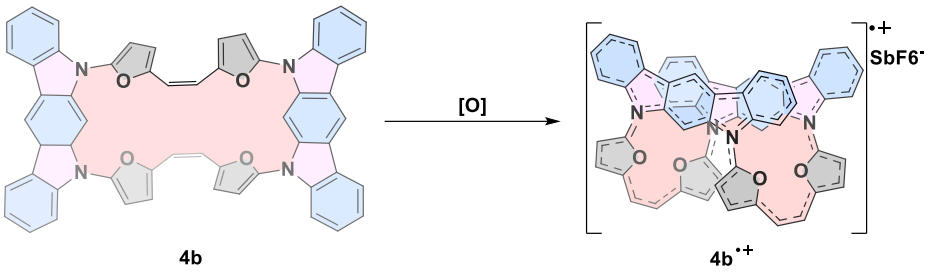




Scheme S3. Oxidation experiments for **3c**.

Compound $3c^{2+}$. **^{1}H NMR** (600 MHz, CD_3CN, 233 K) δ(ppm): 9.36 (s, 1H), 9.18 (d, ^3J = 5.3 Hz, 2H), 8.83 (d, ^3J = 5.4 Hz, 2H), 8.77 – 8.75 (m, 2H), 8.70 – 8.68 (m, 2H), 8.08 – 8.06 (m, 4H), 8.02 (s, 2H), 6.70 (s, 1H).





Scheme S4. Oxidation experiments for **4**.

3. NMR spectra

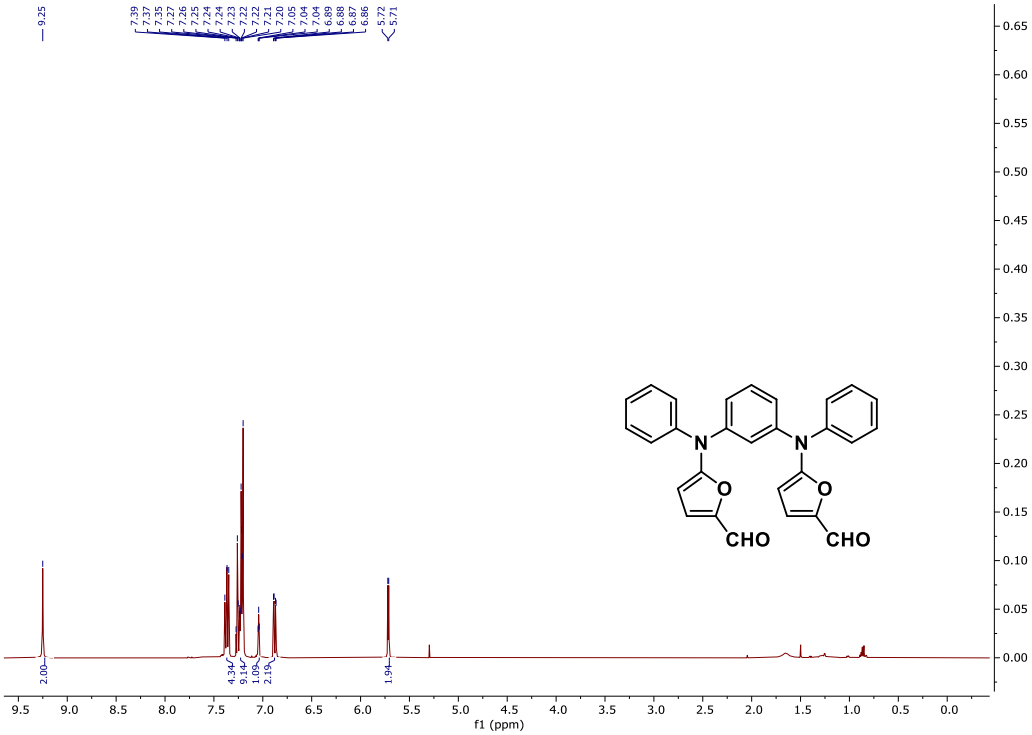


Fig. S1 ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of **1a**.

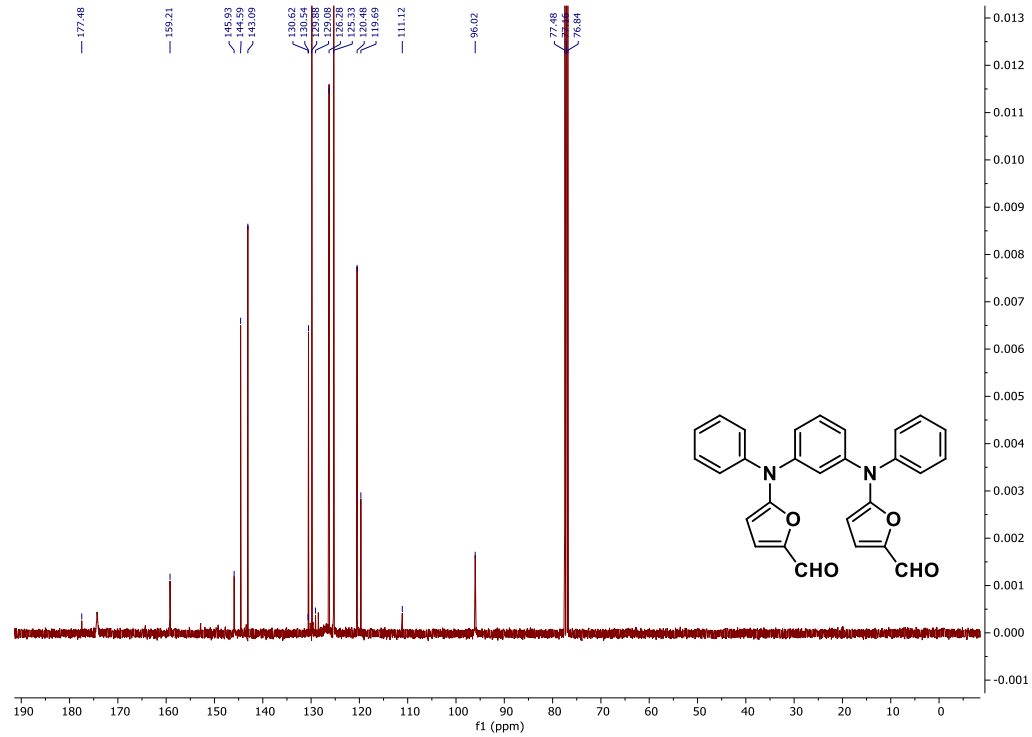


Fig. S2 ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) spectrum of **1a**.

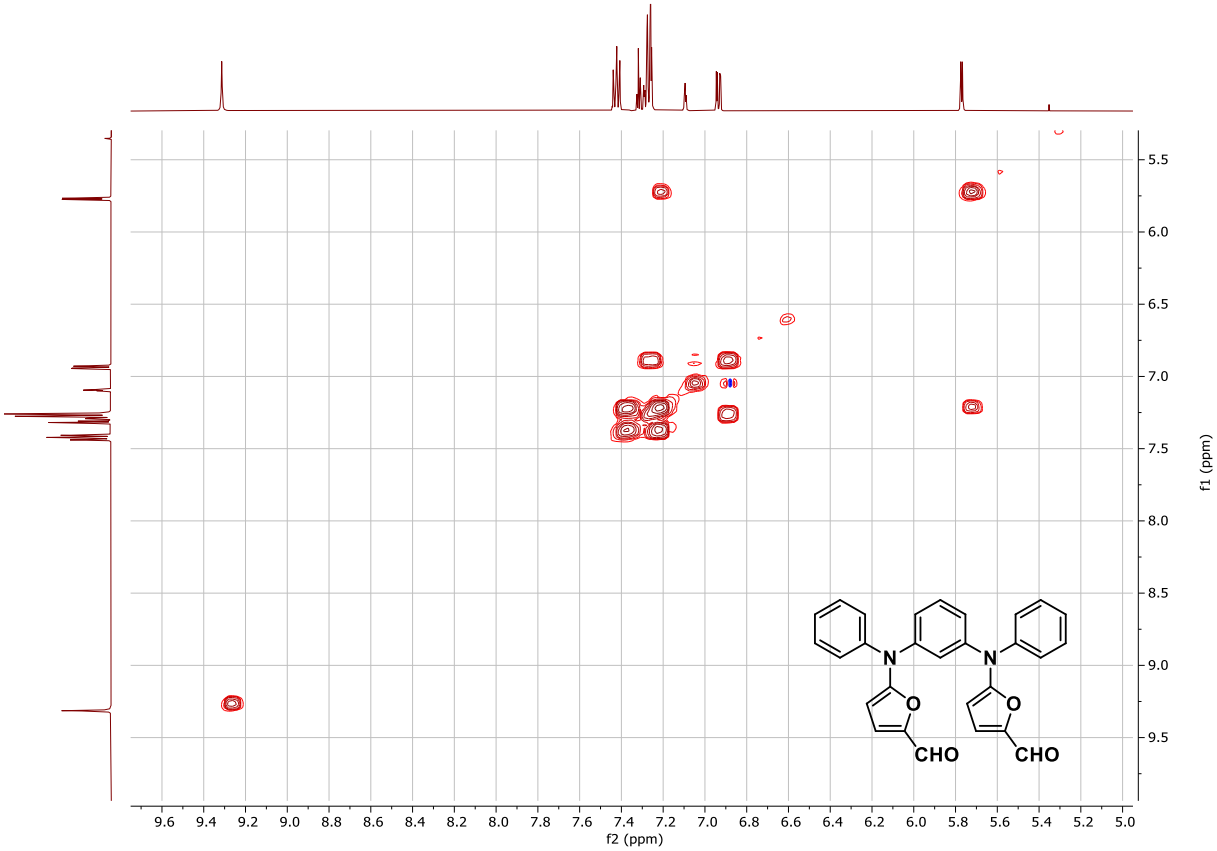


Fig. S3 ^{1}H-^{1}H COSY ($CDCl_3$, 500 MHz, 298 K) spectrum of **1a**.

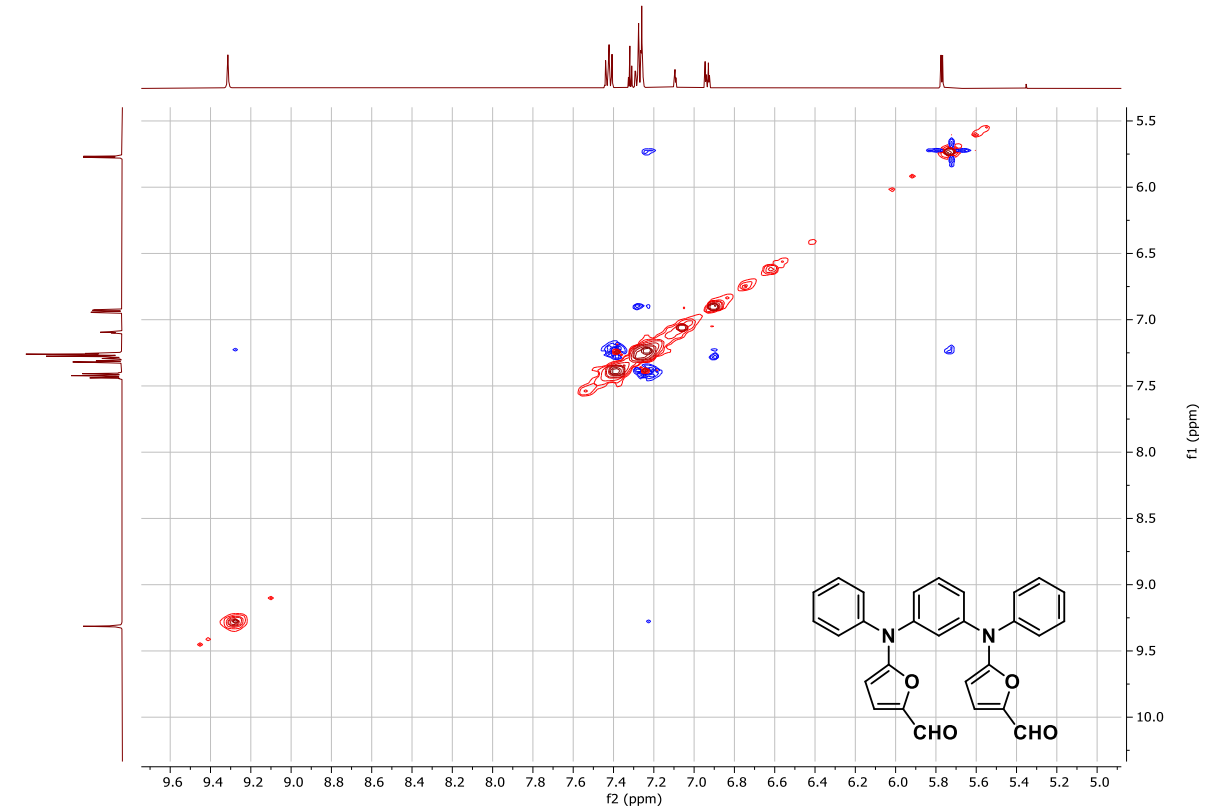


Fig. S4 ^{1}H-^{1}H NOESY NMR ($CDCl_3$, 126 MHz, 298 K) spectrum of **1a**.

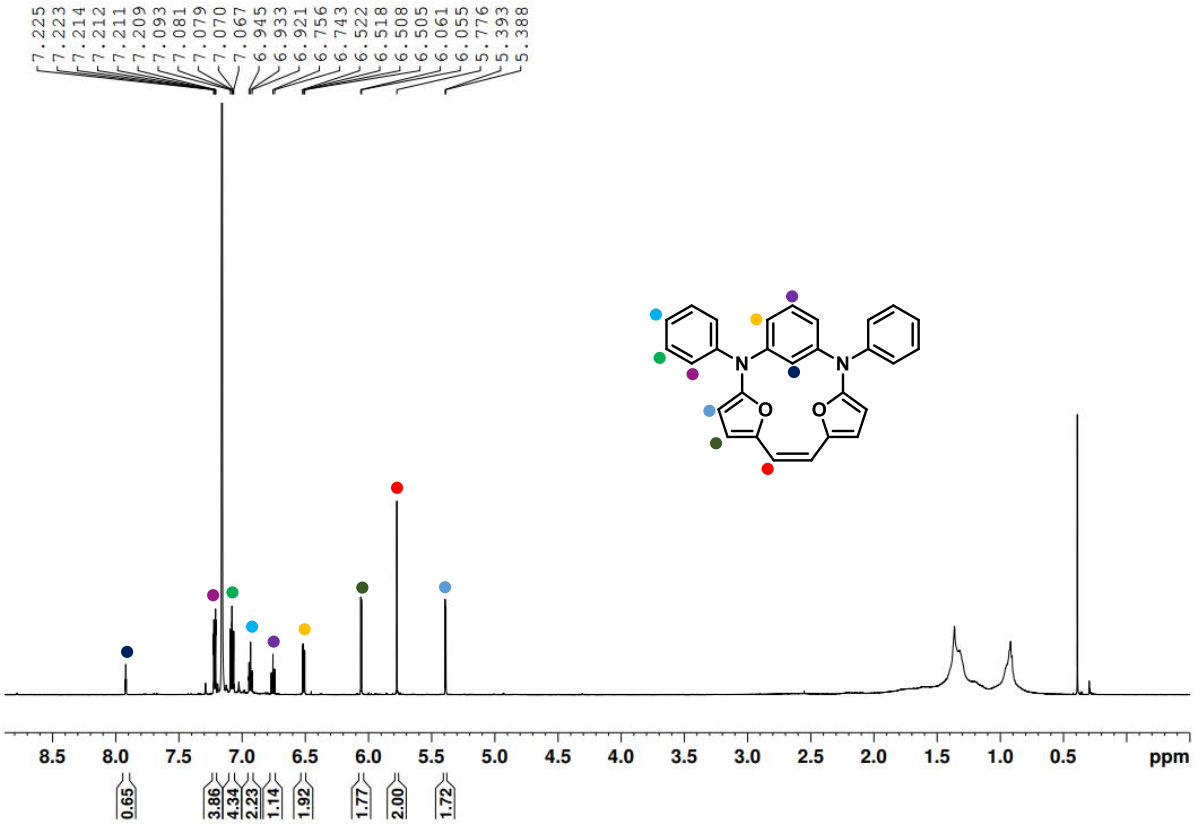


Fig. S5 ^{1}H NMR (C_6D_6, 500 MHz, 298 K) spectrum of **3a**.

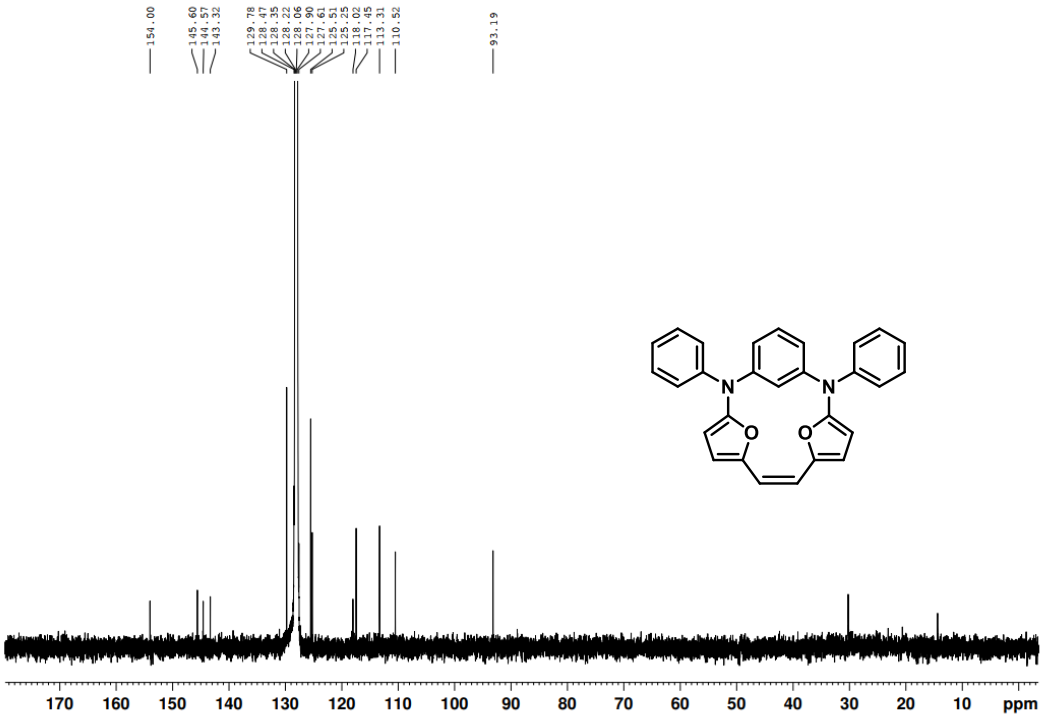


Fig. S6 ^{13}C NMR (C_6D_6, 126 MHz, 298 K) spectrum of **3a**.

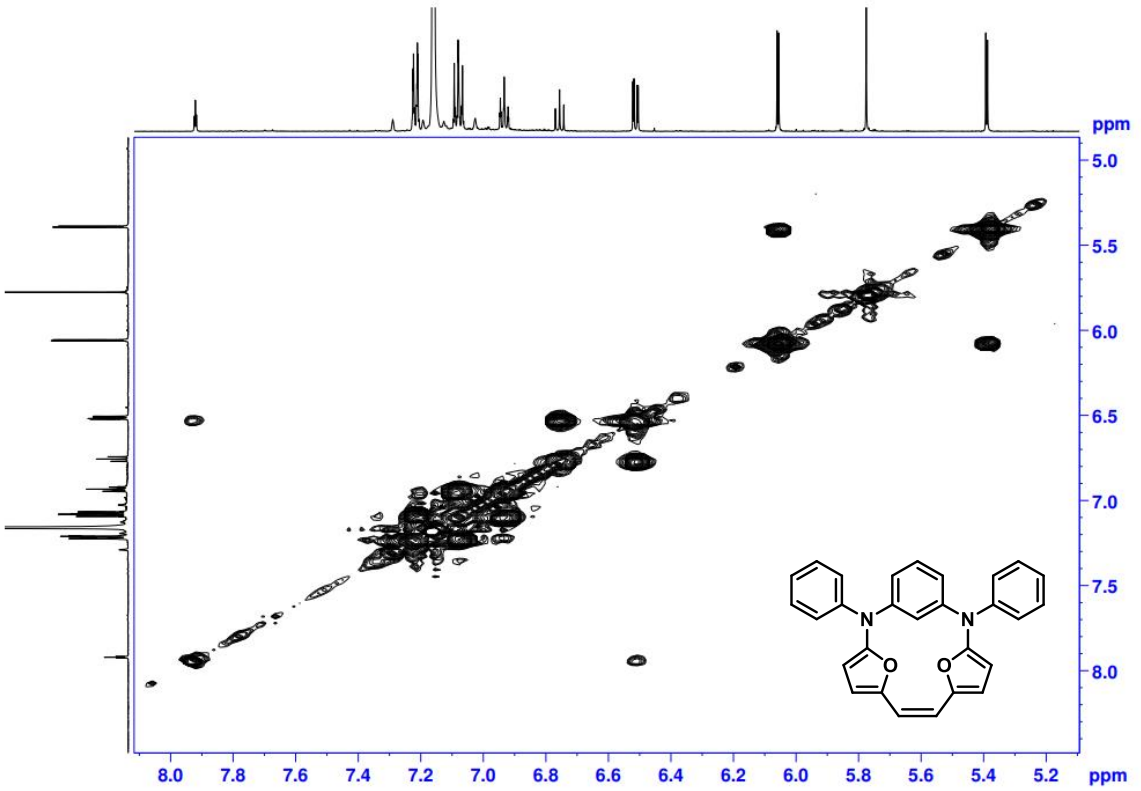


Fig. S7 ^{1}H-^{1}H COSY (C_6D_6, 500 MHz, 298 K) spectrum of **3a**.

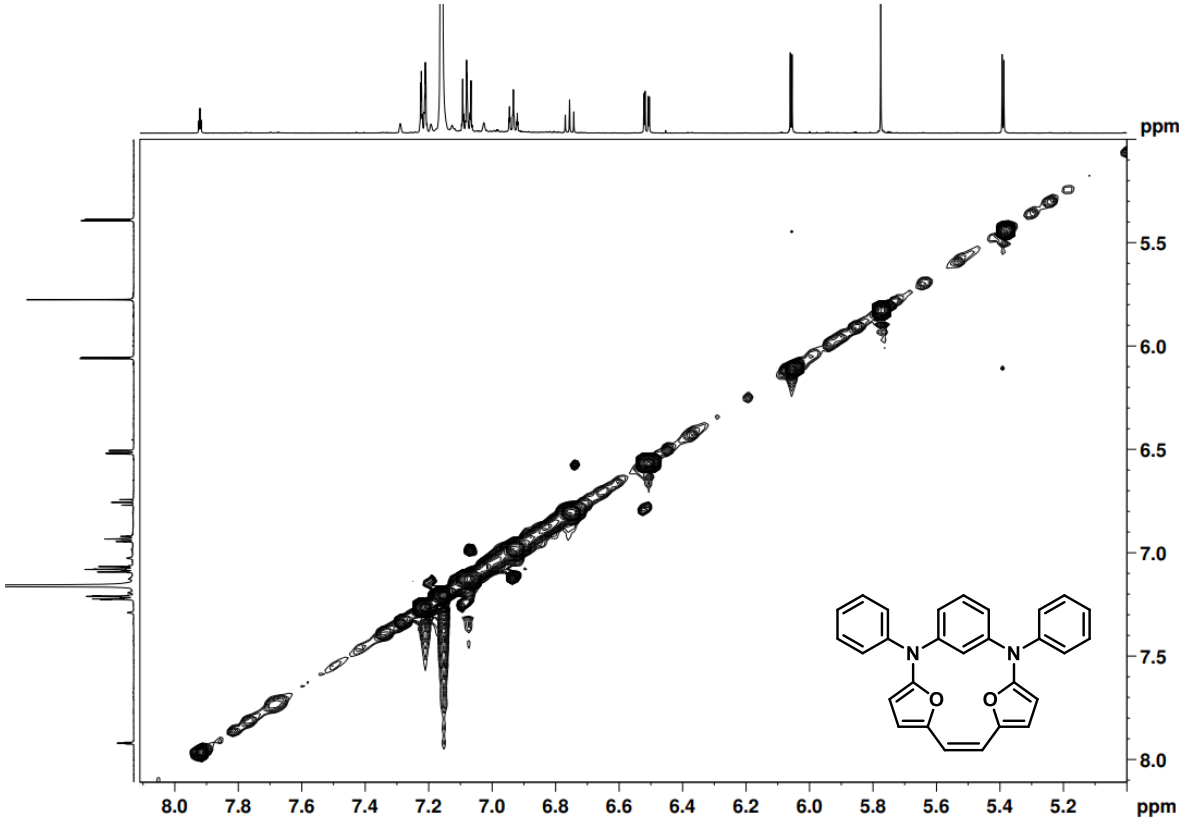


Fig. S8 ^{1}H-^{1}H NOESY (C_6D_6, 500 MHz, 298 K) spectrum of **3a**.

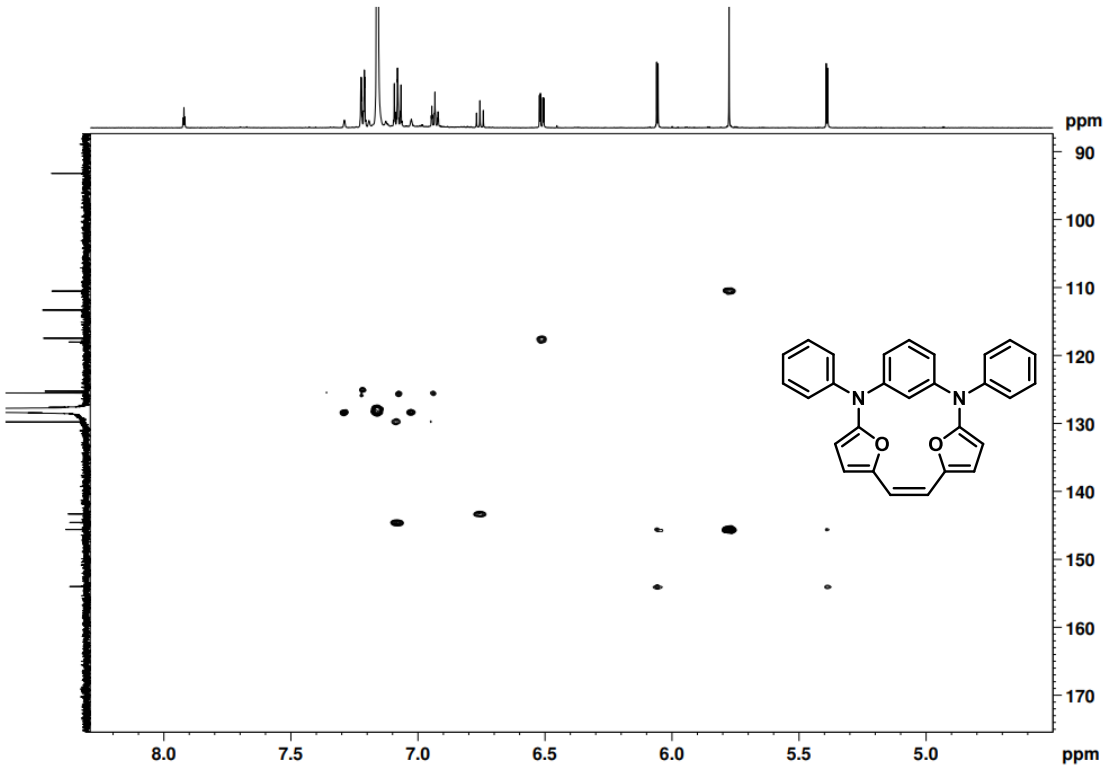


Fig. S9 ^{1}H-^{13}C HMBC (C_6D_6, 500 MHz, 298 K) spectrum of **3a**.

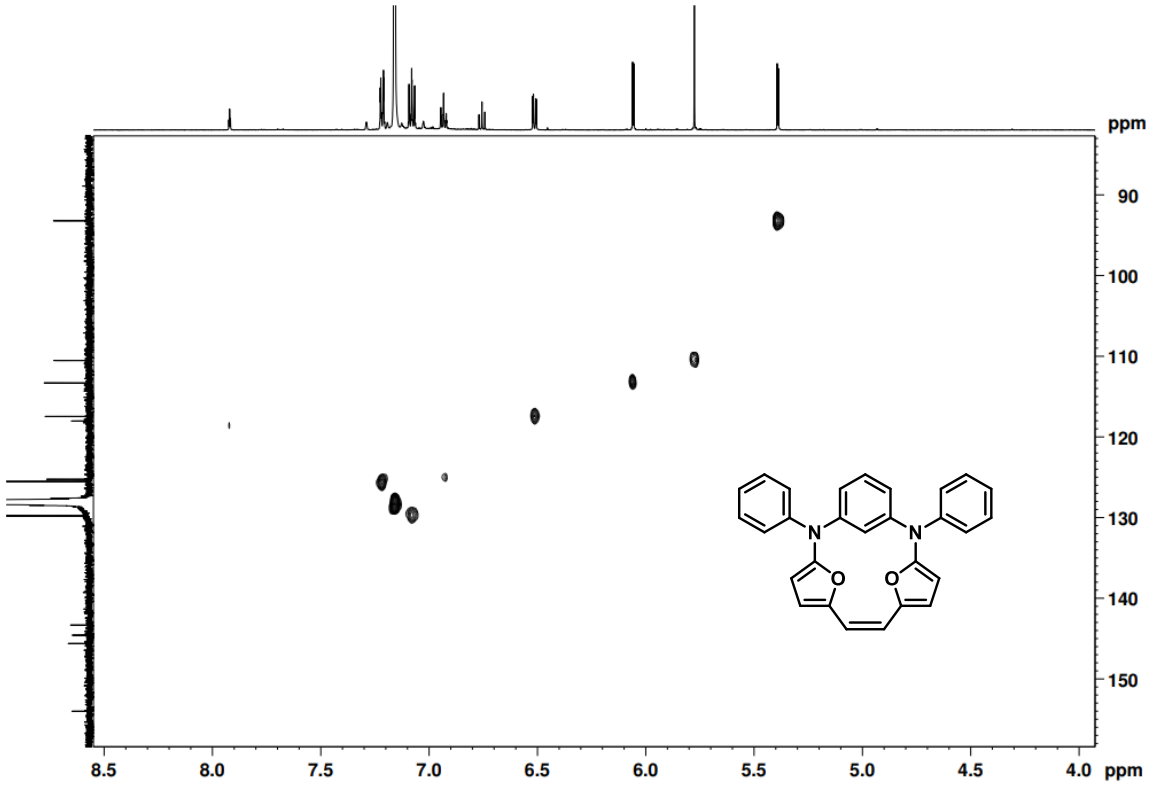


Fig. S10 ^{1}H-^{13}C HSQC (C_6D_6, 500 MHz, 298 K) spectrum of **3a**.

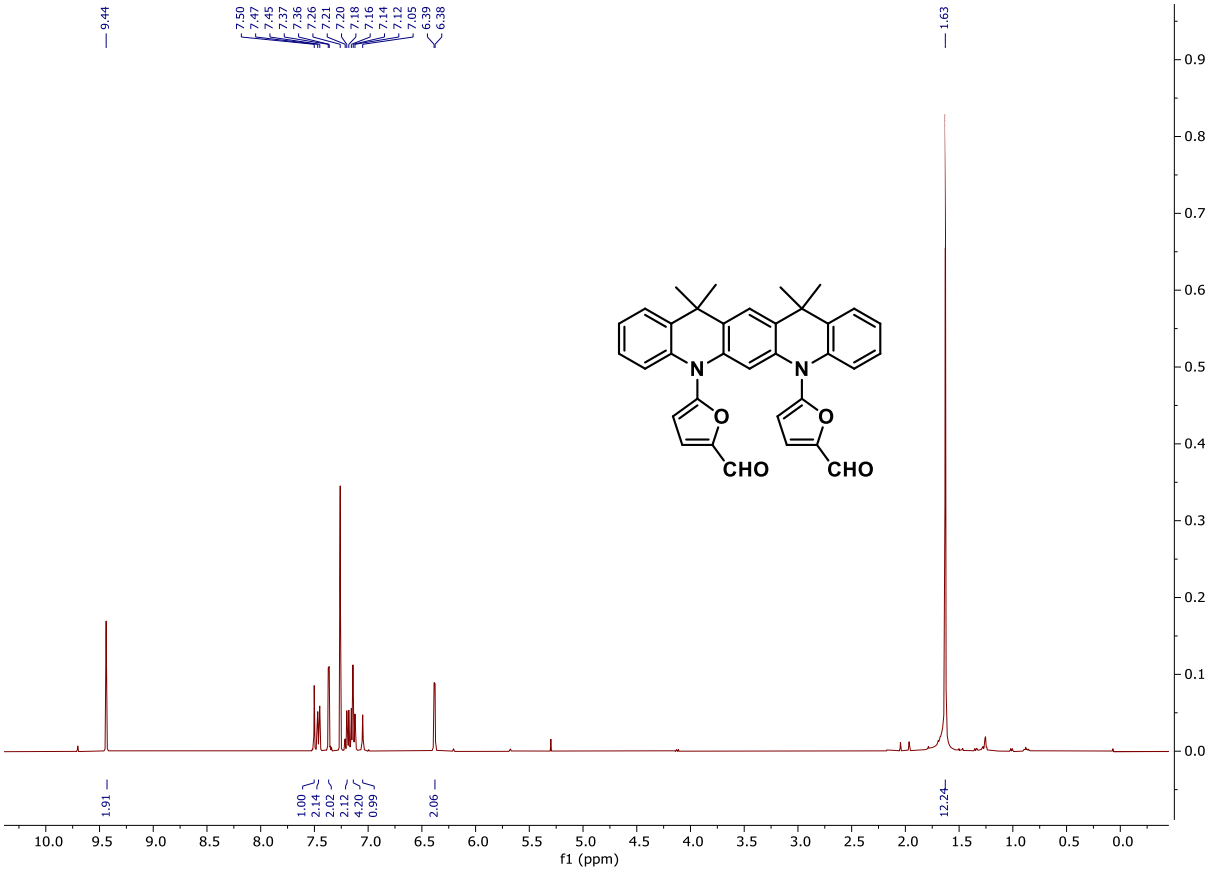


Fig. S11 ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of **1b**.

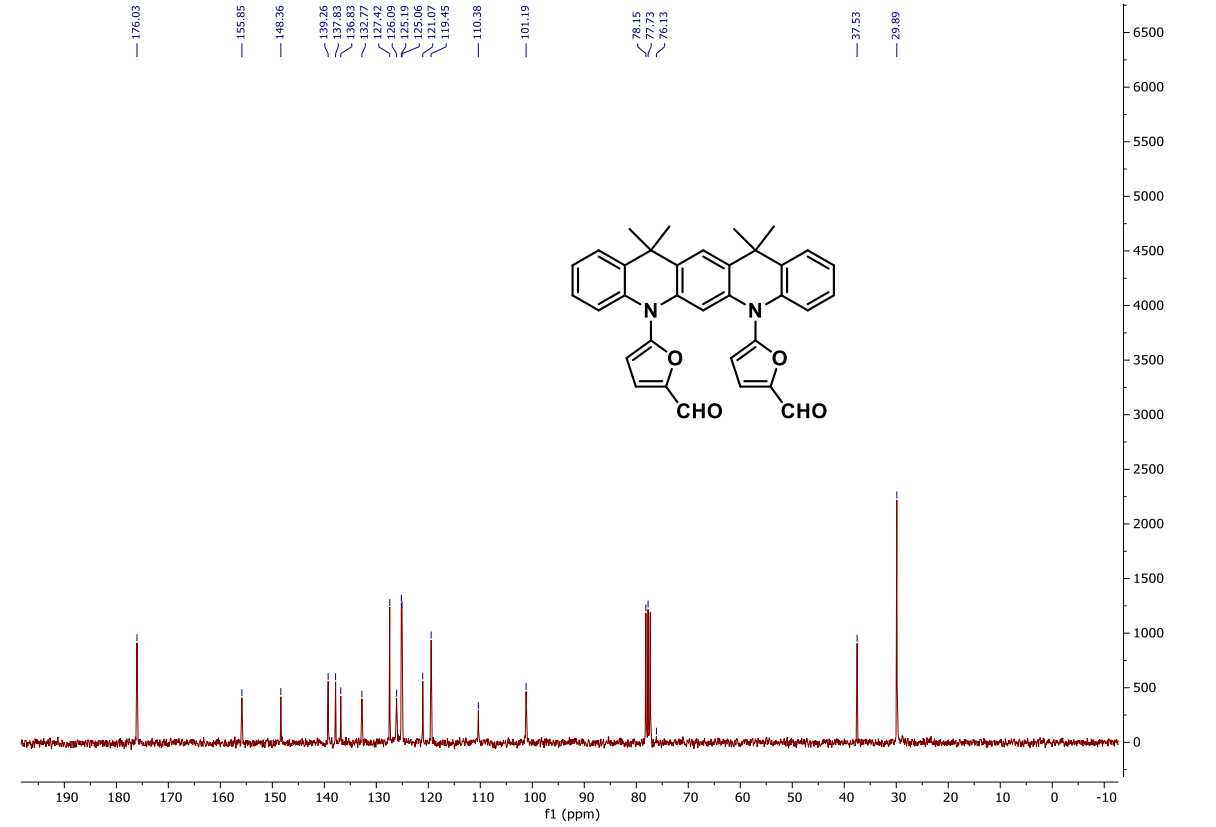


Fig. S12 ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) spectrum of **1b**.

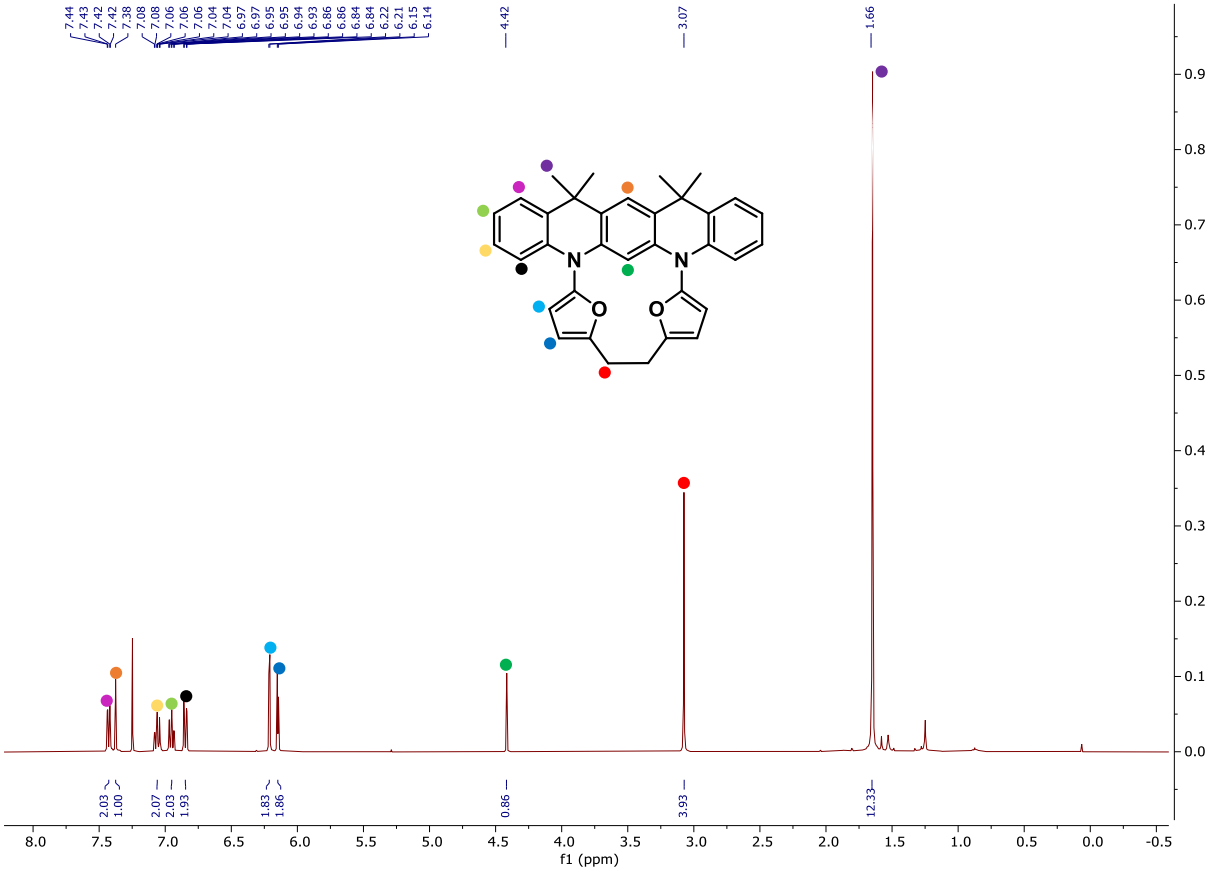


Fig. S11 ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of **3b**.

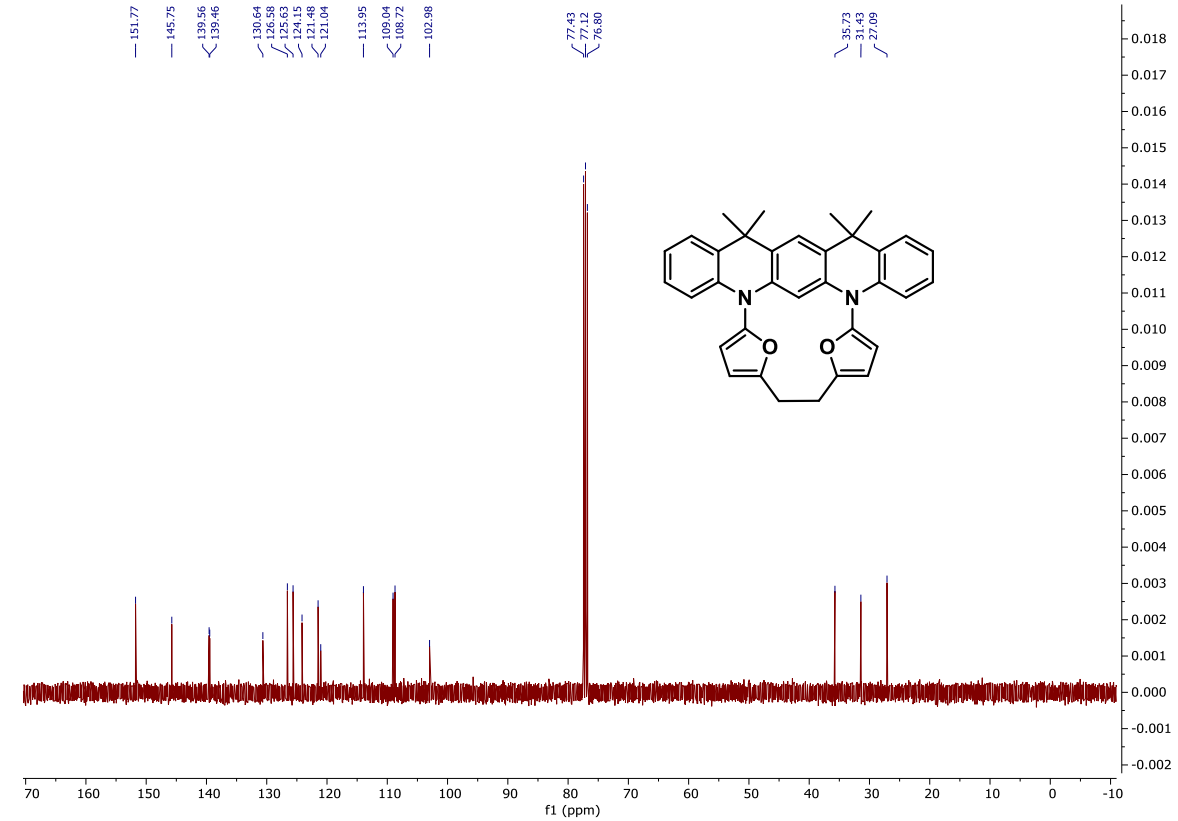


Fig. S14 ^{13}C NMR ($CDCl_3$, 101 MHz, 298 K) spectrum of **3b**.

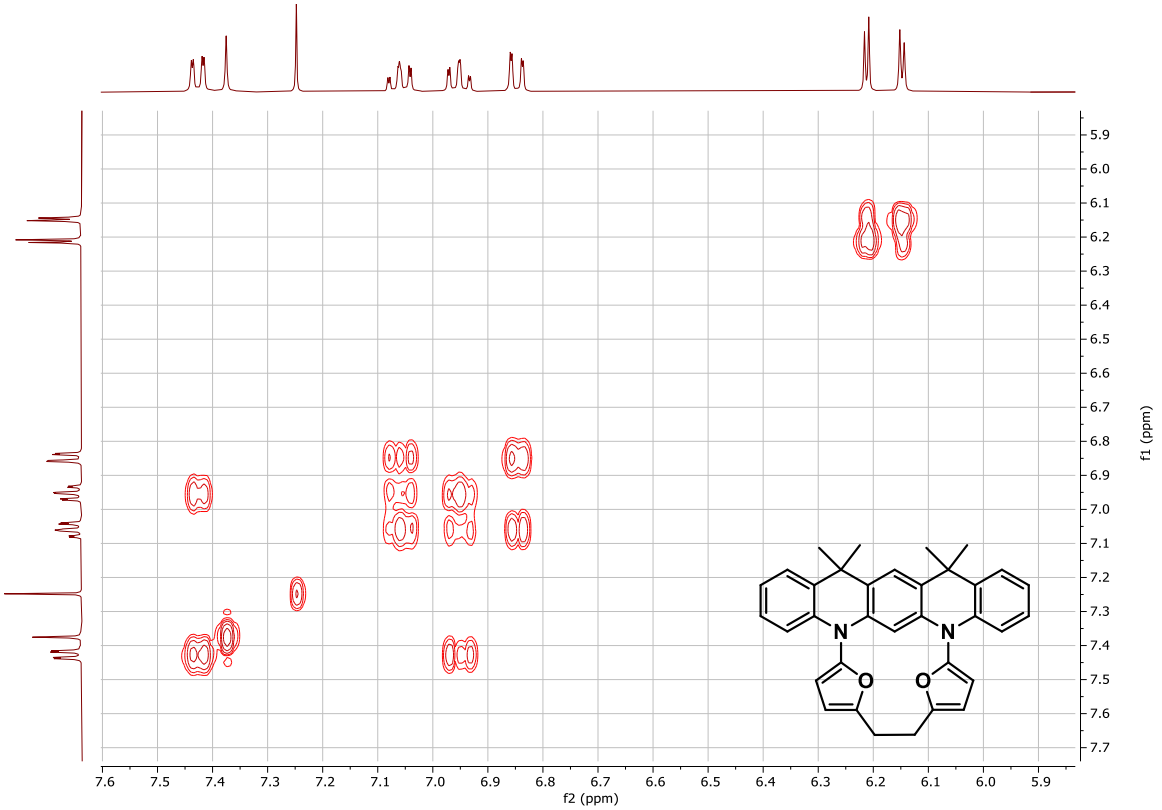


Fig. S12 ^{1}H-^{1}H COSY ($CDCl_3$, 400 MHz, 298 K) spectrum of **3b**.

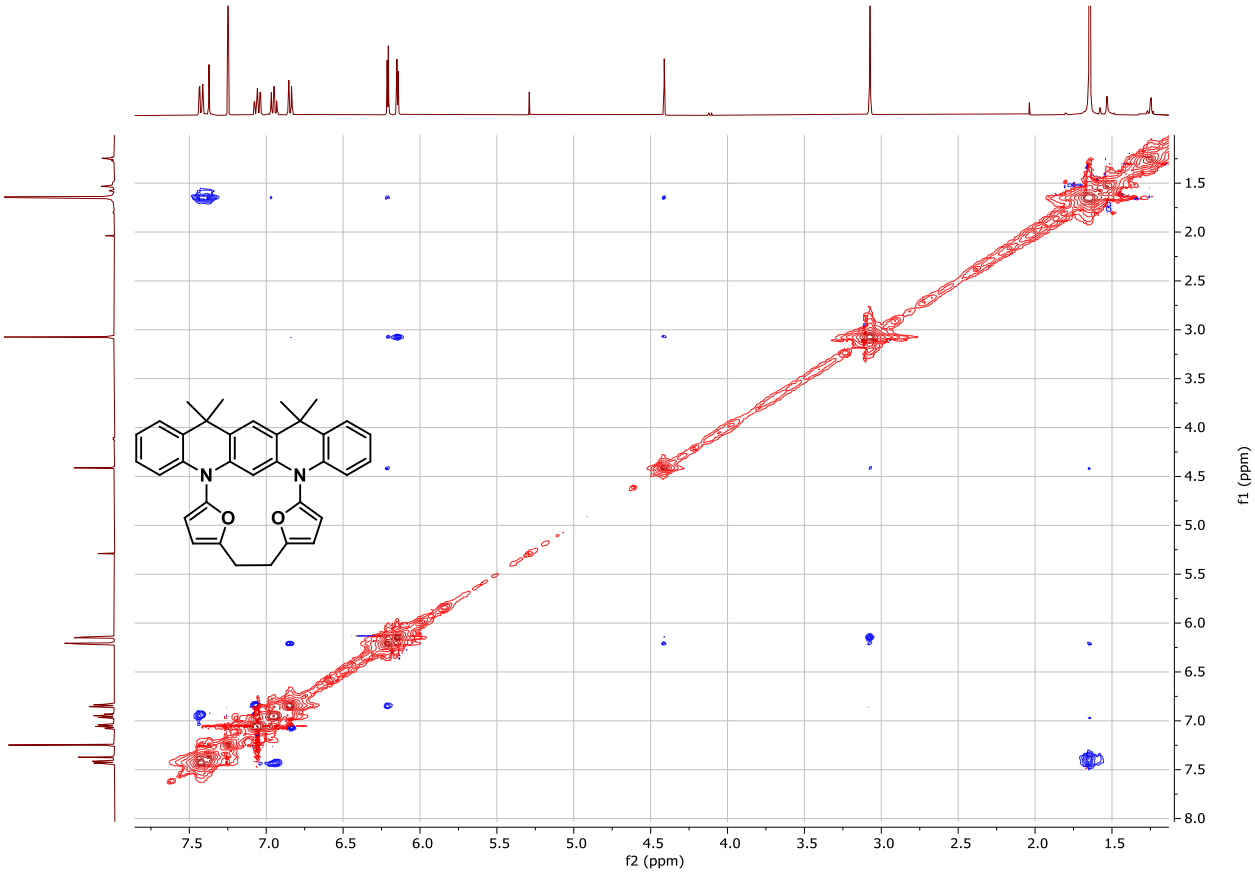


Fig. S16 ^{1}H-^{1}H NOESY ($CDCl_3$, 400 MHz, 298 K) spectrum of **3b**.

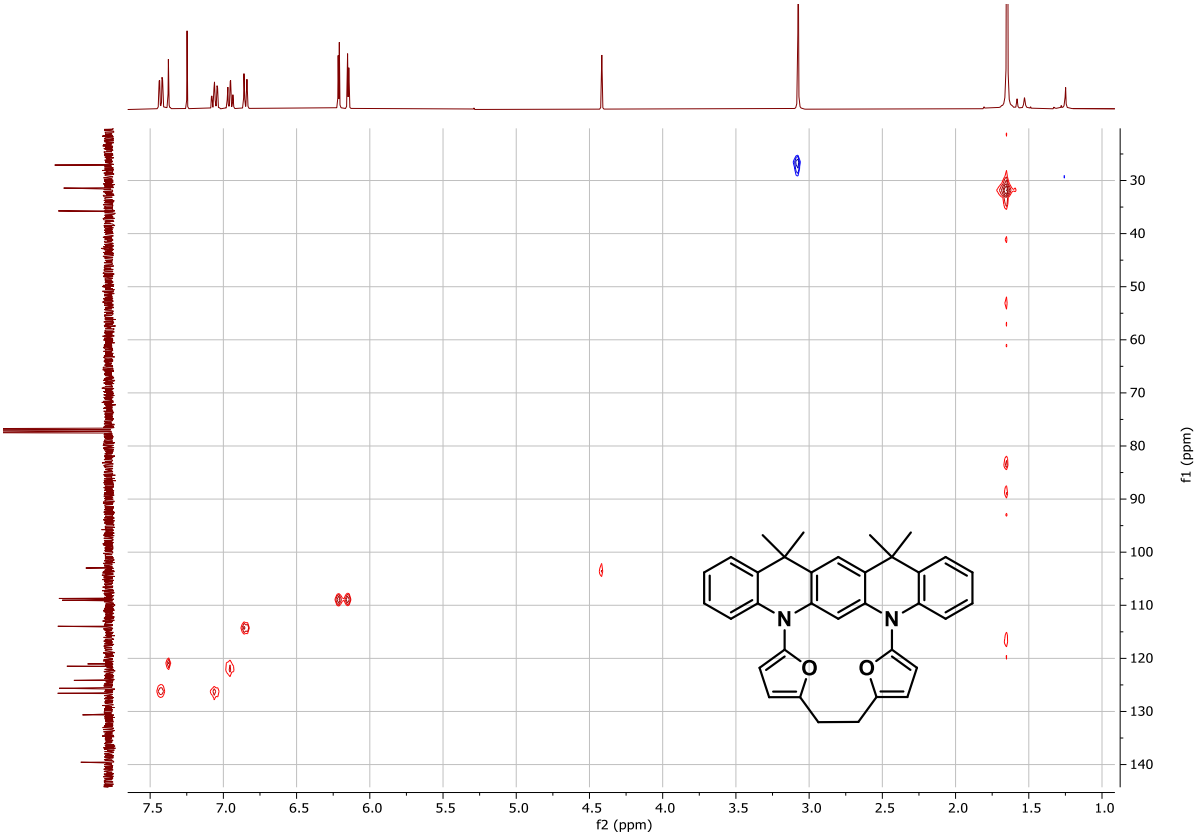


Fig. S17 ^{1}H-^{13}C HSQC ($CDCl_3$, 400 MHz, 298 K) spectrum of **3b**.

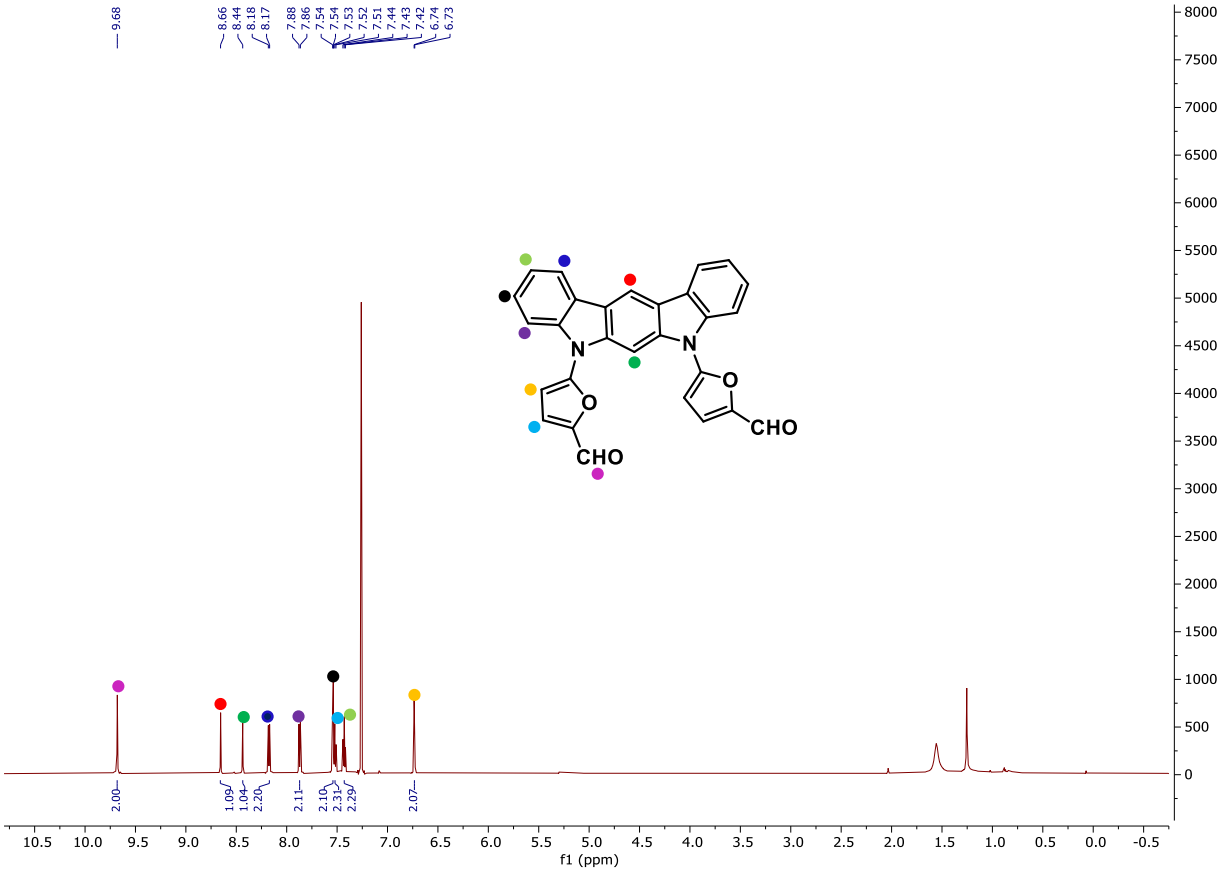


Fig. S18 ^{1}H-NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of **1c**.

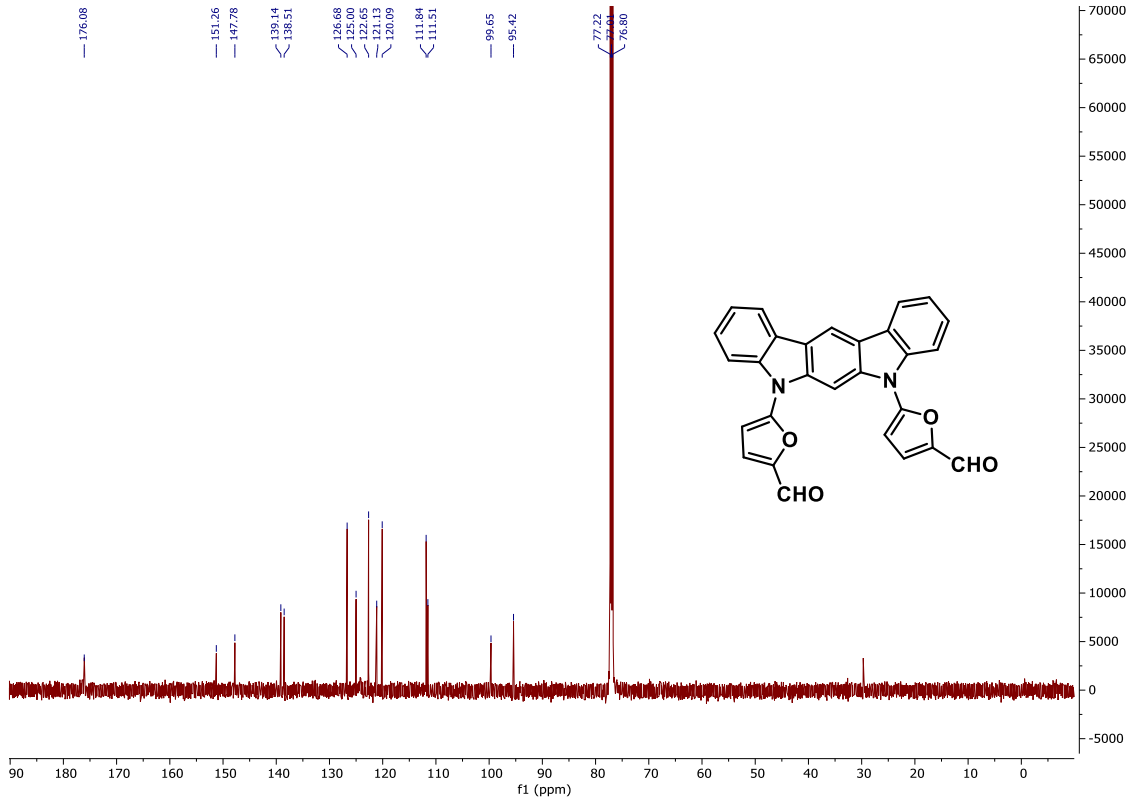


Fig. S19 ^{13}C-NMR ($CDCl_3$, 101 MHz, 298 K) spectrum of **1c**.

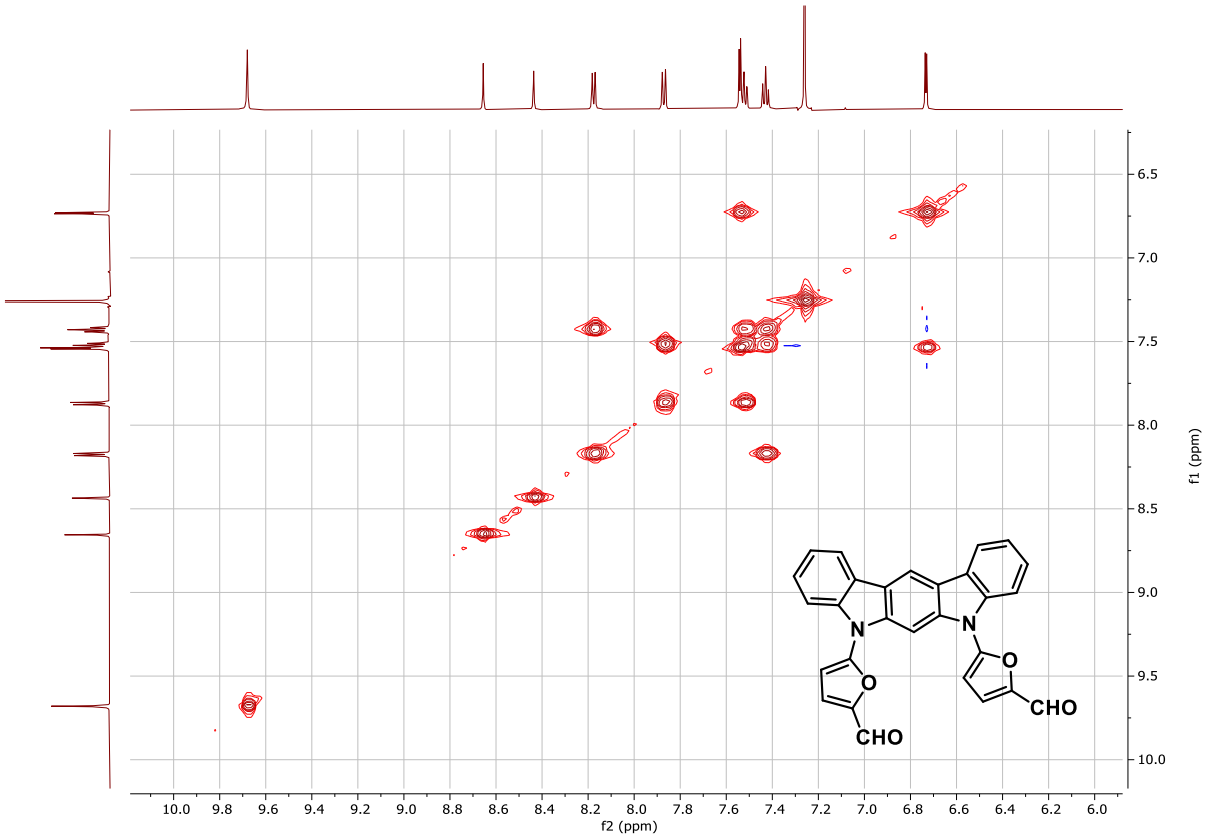


Fig. S20 ^{1}H-^{1}H COSY ($CDCl_3$, 400 MHz, 298 K) spectrum of **1c**.

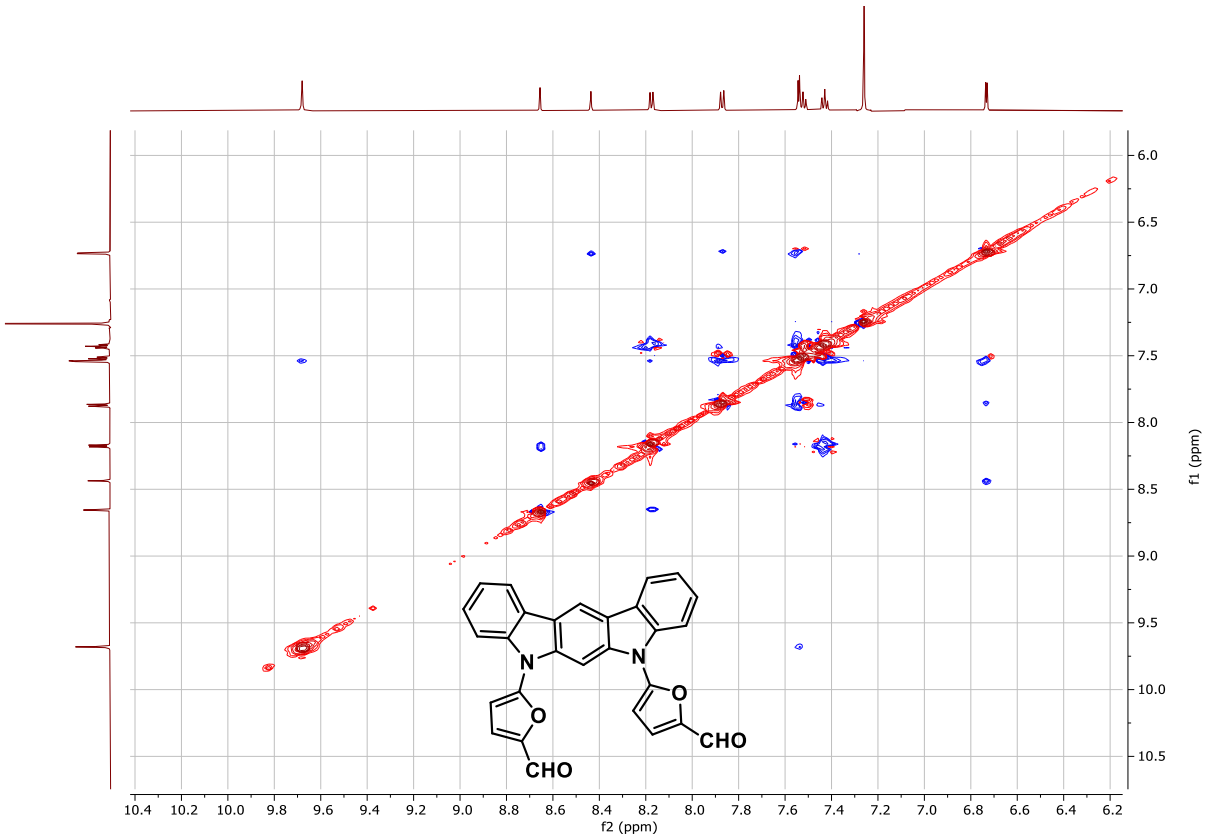


Fig. S21 ^{1}H-^{1}H NOESY ($CDCl_3$, 400 MHz, 298 K) spectrum of **1c**.

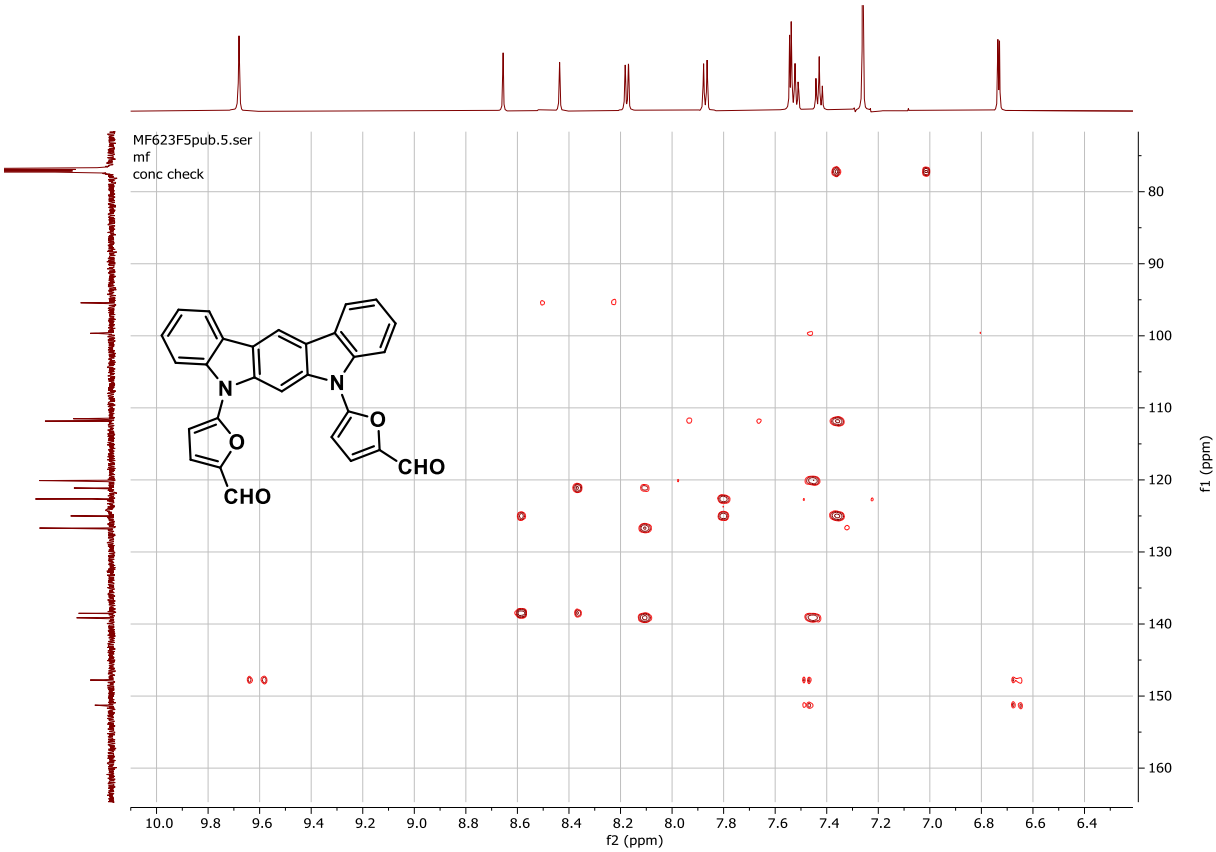


Fig. S22 ^{1}H-^{13}C HMBC ($CDCl_3$, 400 MHz, 298 K) spectrum of **1c**

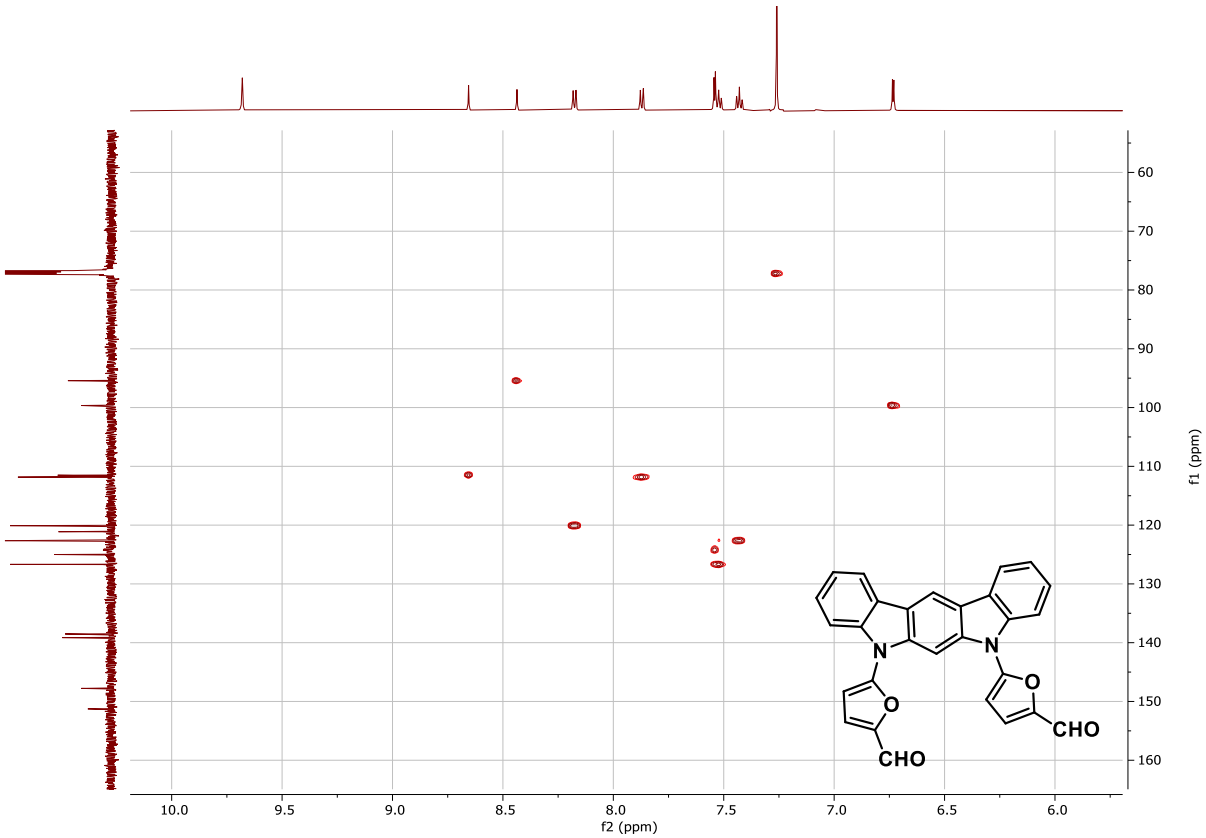


Fig. S23 ^{1}H-^{13}C HSQC ($CDCl_3$, 400 MHz, 298 K) spectrum of **1c**.

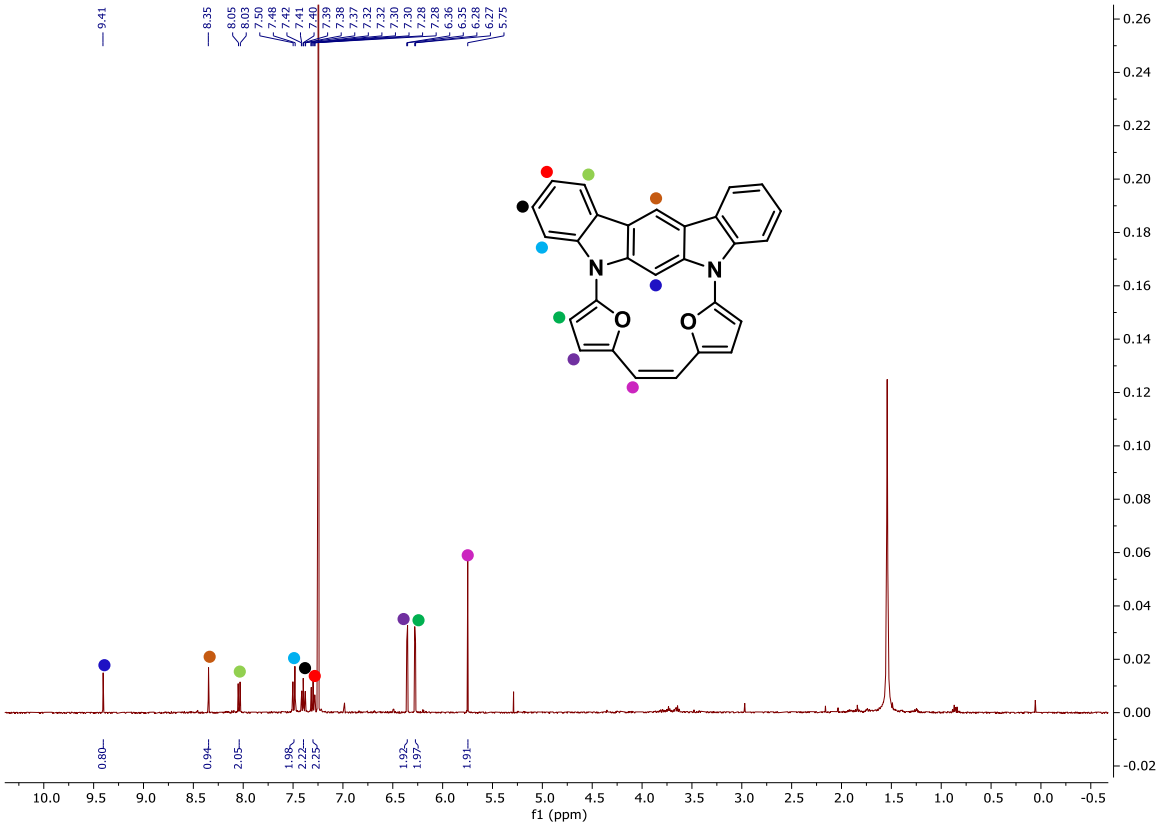


Fig. S24 ^{1}H-NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of **3c**.

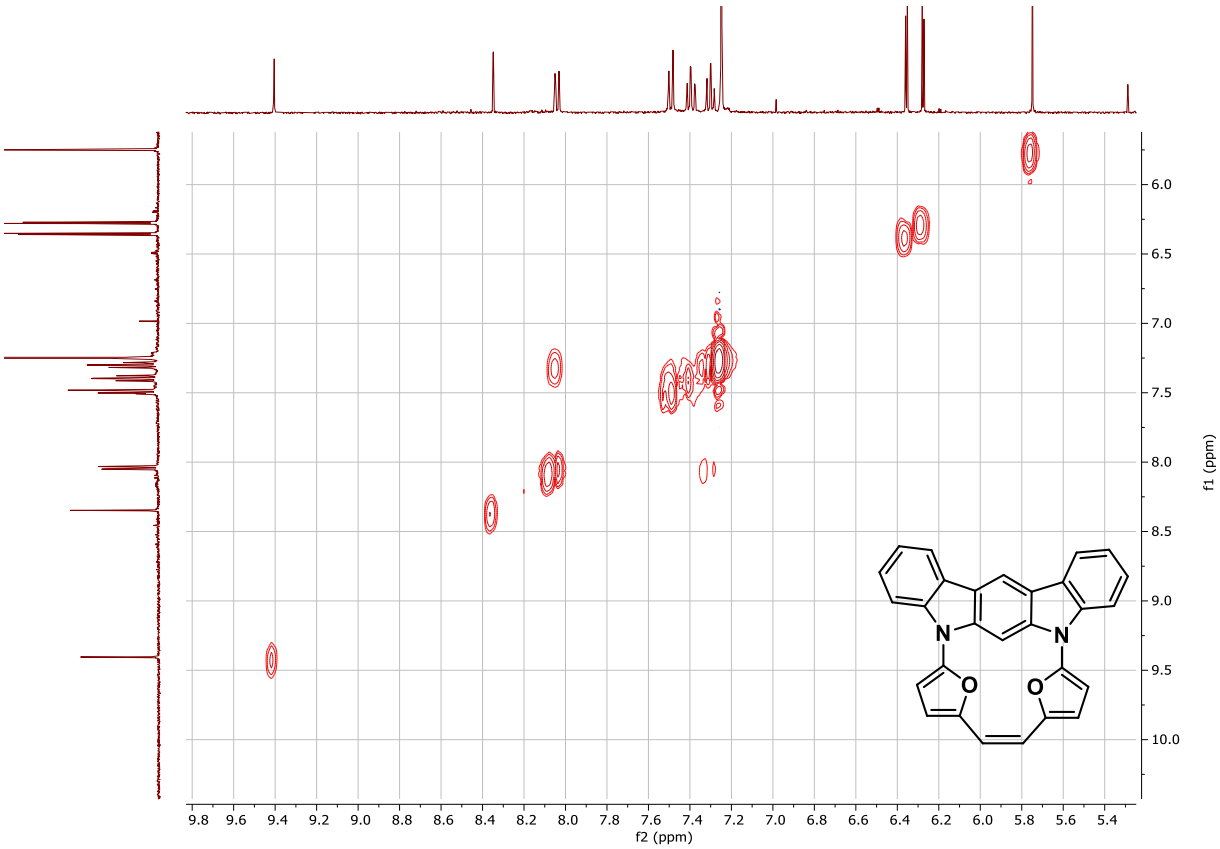


Fig. S25 ^{1}H-^{1}H COSY ($CDCl_3$, 400 MHz, 298 K) spectrum of **3c**.

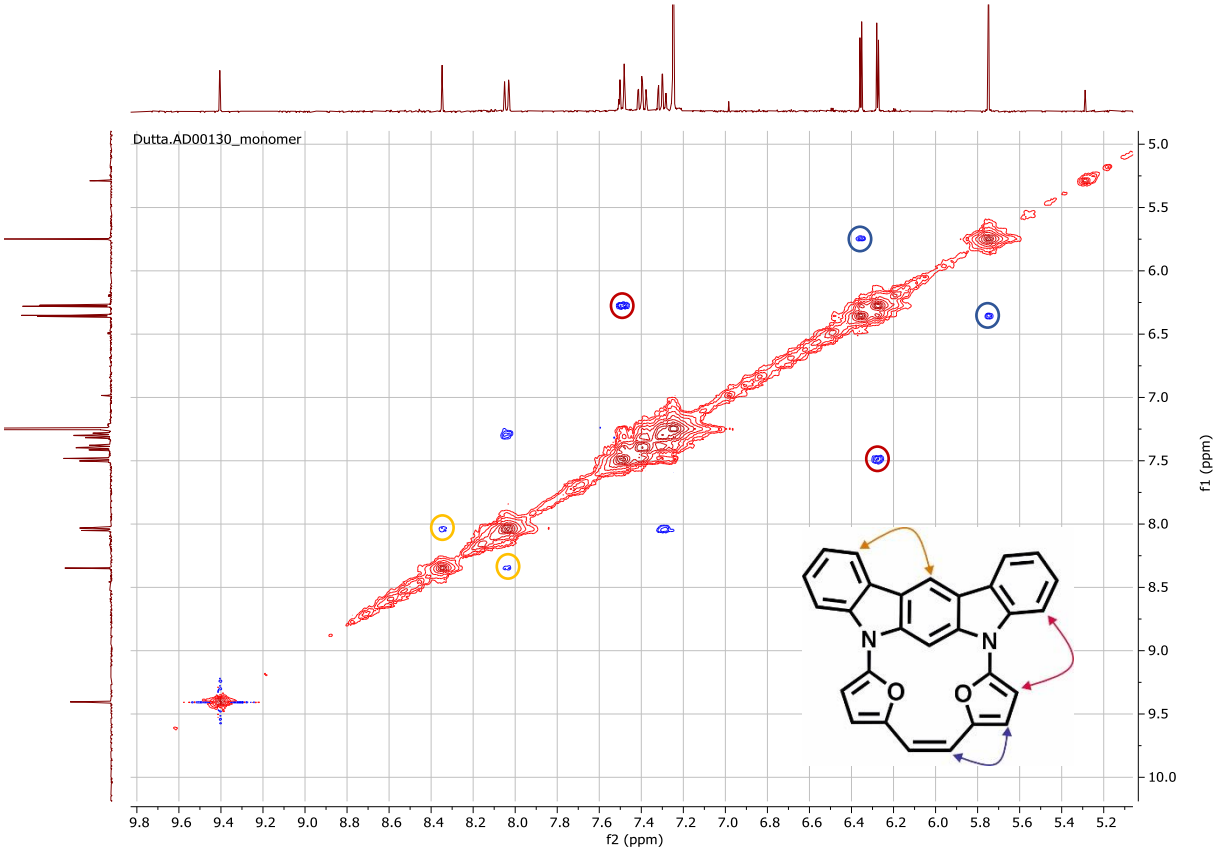


Fig. S26 ^{1}H-^{1}H NOESY ($CDCl_3$, 400 MHz, 298 K) spectrum of **3c**.

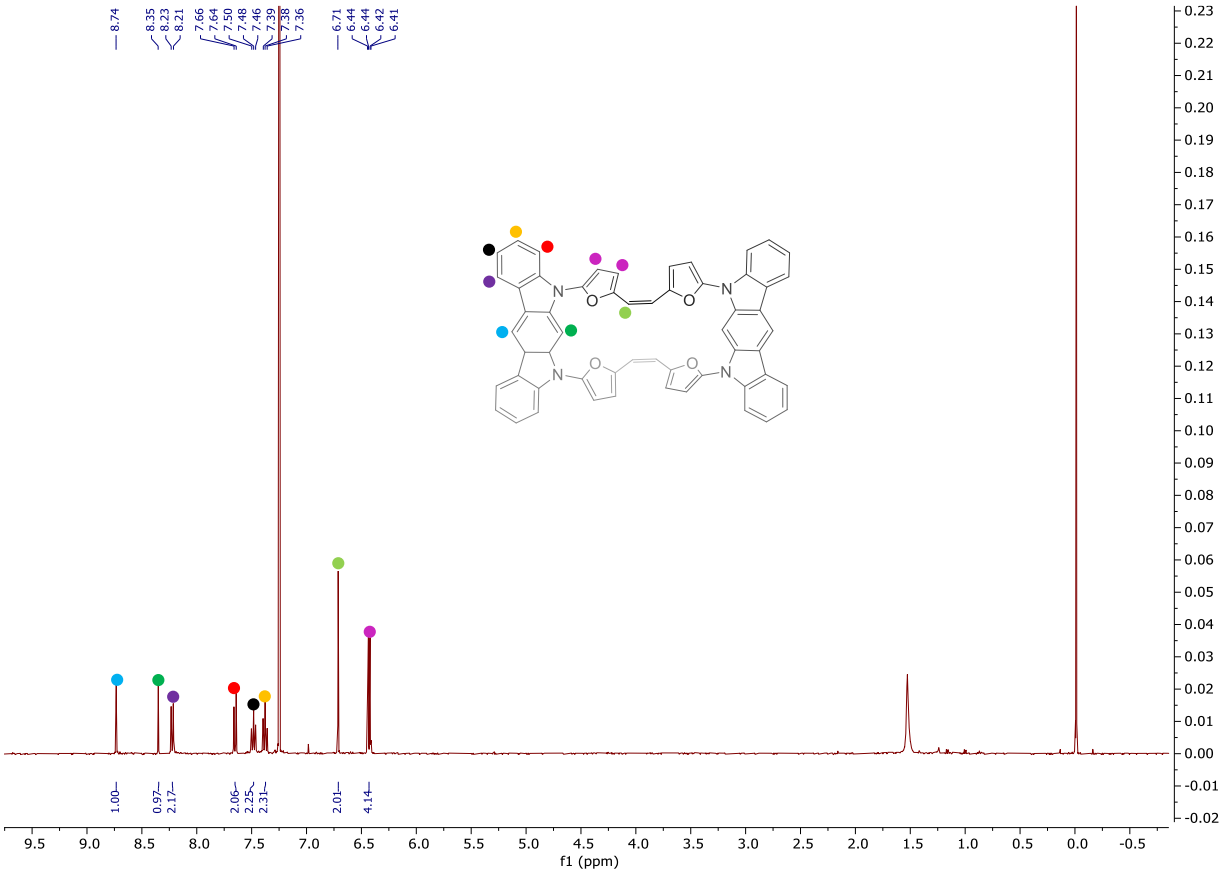


Fig. S27 ^{1}H-NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of **4**.

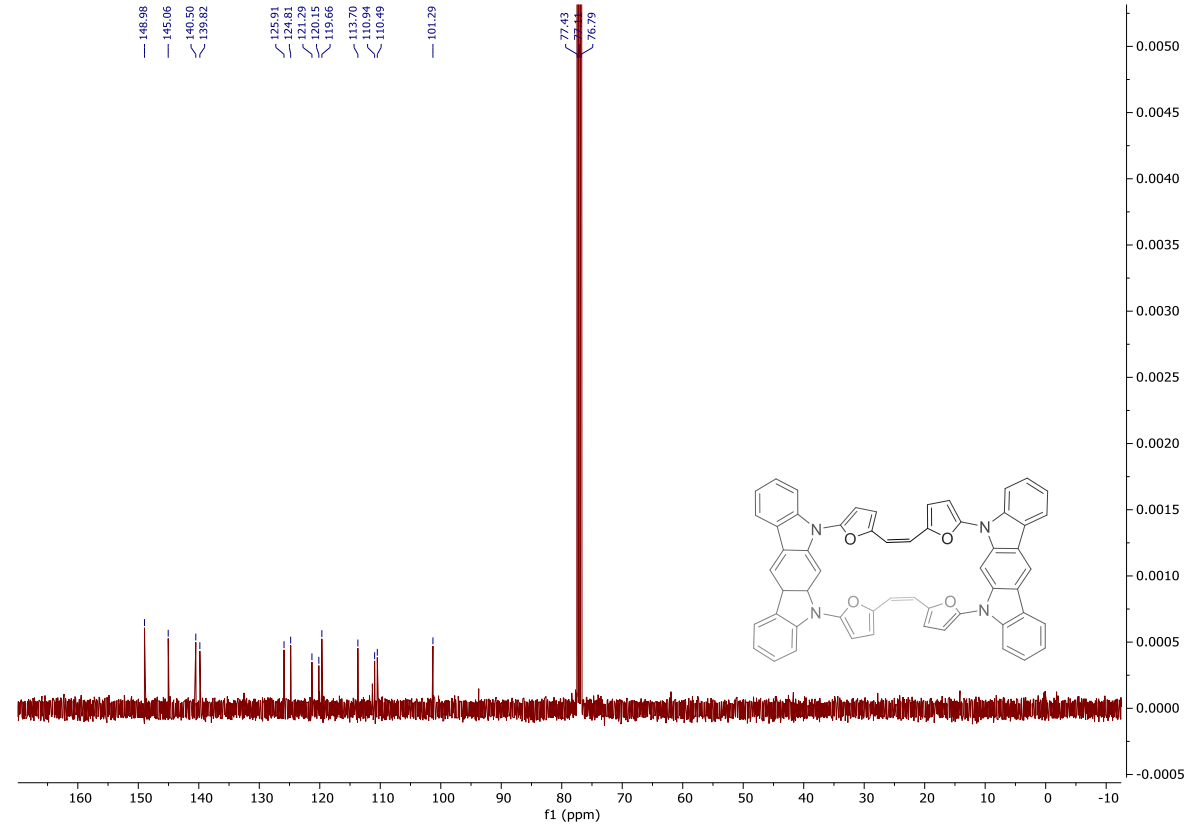


Fig. S28 ^{13}C-NMR ($CDCl_3$, 101 MHz, 298 K) spectrum of **4**.

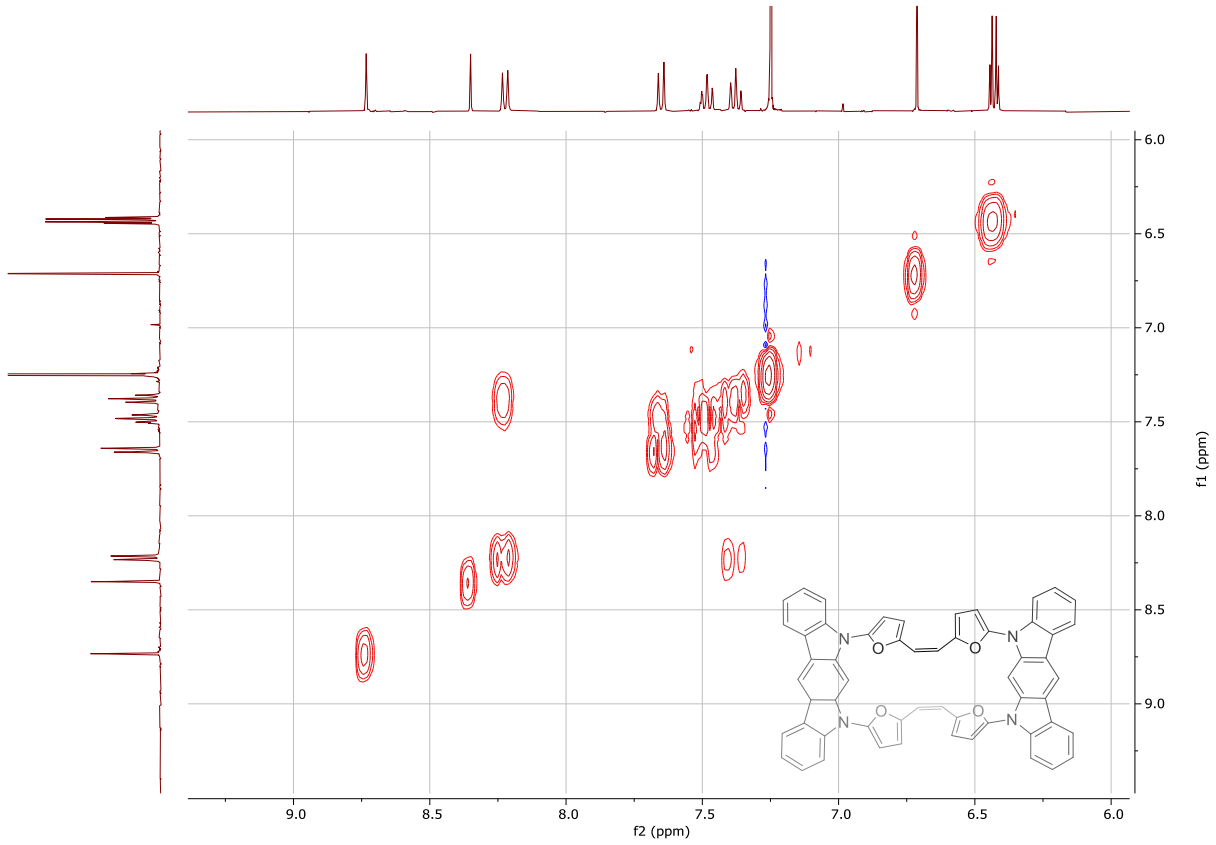


Fig. S29 ^{1}H-^{1}H COSY ($CDCl_3$, 400 MHz, 298 K) spectrum of **4**.

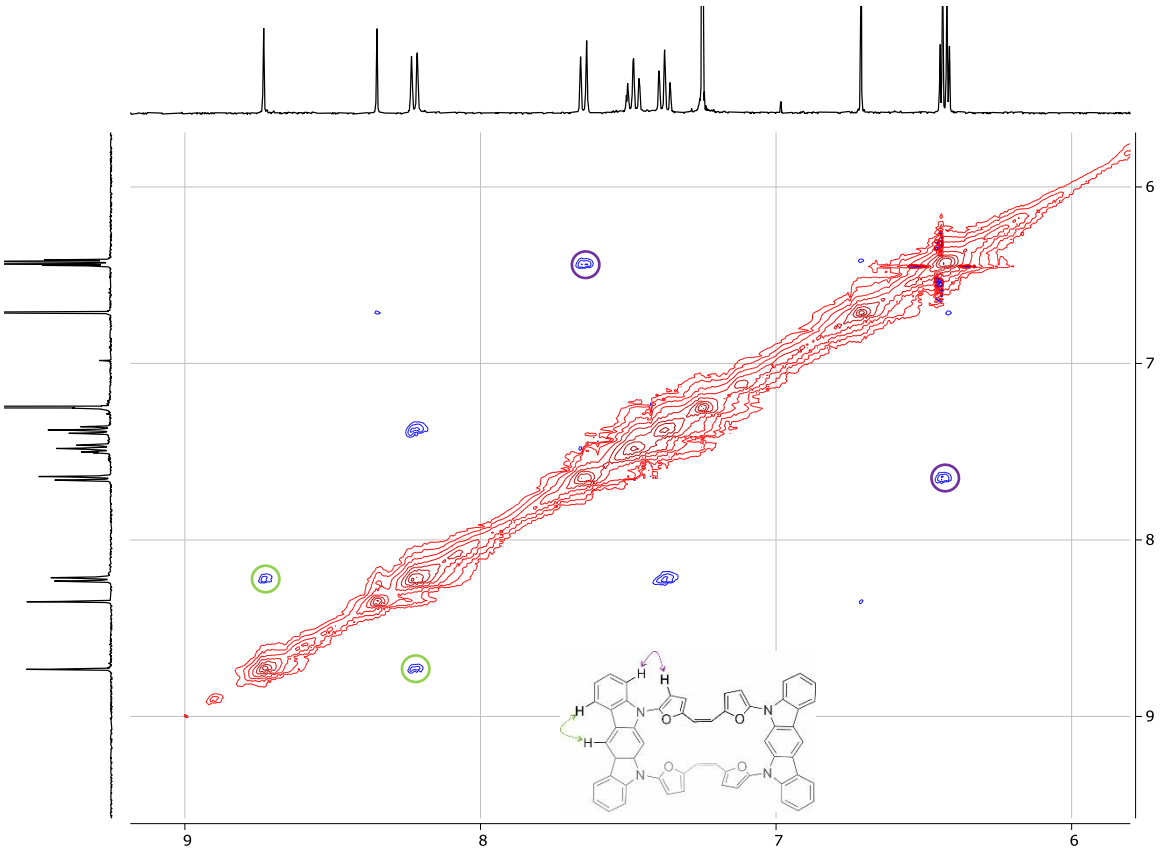


Fig. S30 ^{1}H-^{1}H NOESY ($CDCl_3$, 400 MHz, 298 K) spectrum of **4**.

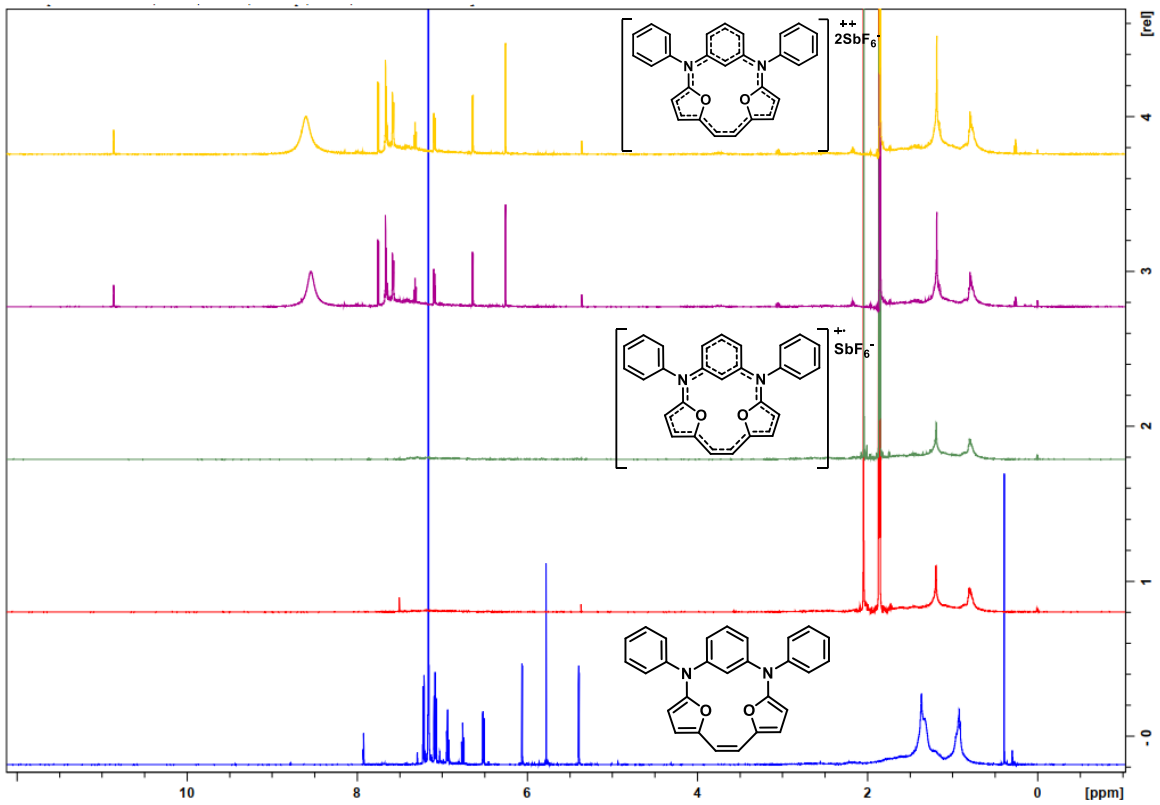


Fig. S31 ^{1}H NMR-monitored titration of **3a** with $NOSbF_6$ (Acetonitrile-d_3, 600 MHz, 233 K); 0 (C_6D_6)– without; 1 – 0.5 eq; 2 – 1.0 eq; 3 – 1.5 eq; 4 – 2.0 eq of $NOSbF_6$.

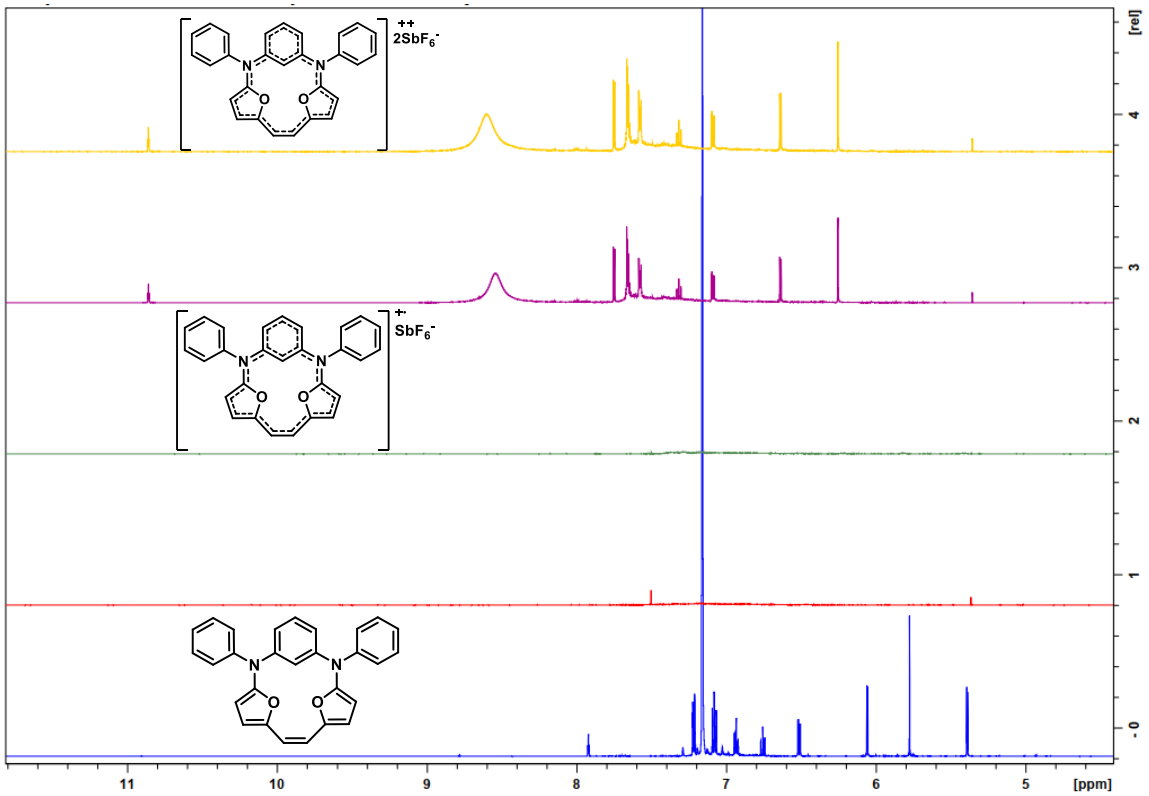


Fig. S32 Zoom on aromatic region of the spectra during ^{1}H NMR-monitored titration of **3a** with $NOSbF_6$ (Acetonitrile-d_3, 600 MHz, 233 K); 0 (C_6D_6)– without; 1 – 0.5 eq; 2 – 1.0 eq; 3 – 1.5 eq; 4 – 2.0 eq of $NOSbF_6$.

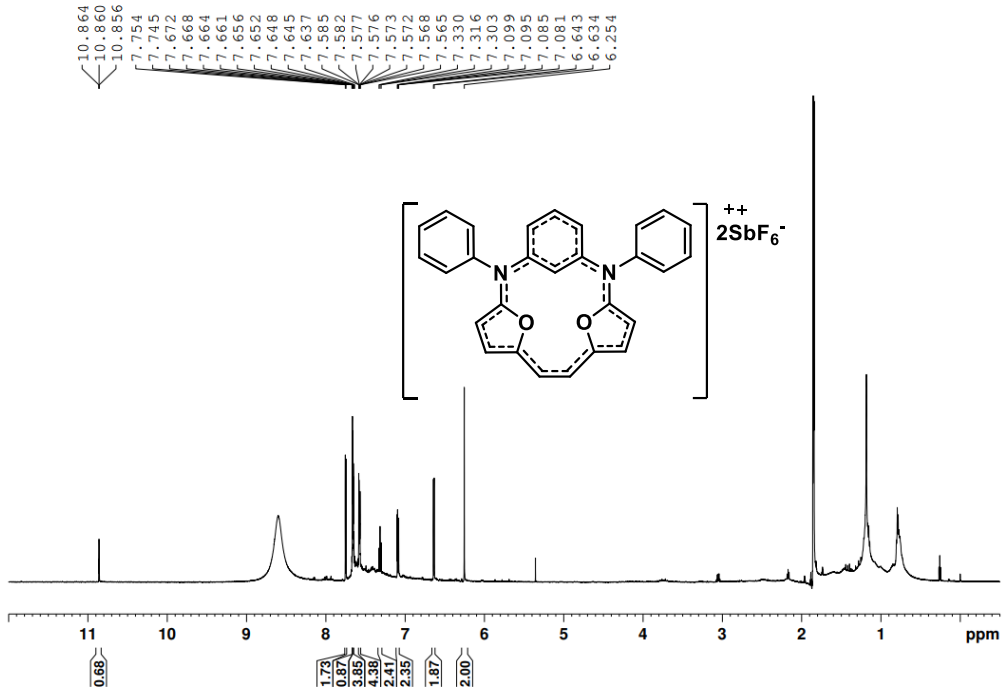


Fig. S33 ^{1}H-NMR (CD_3CN, 600 MHz, 233 K) spectrum of **3a**$^{2+}$.

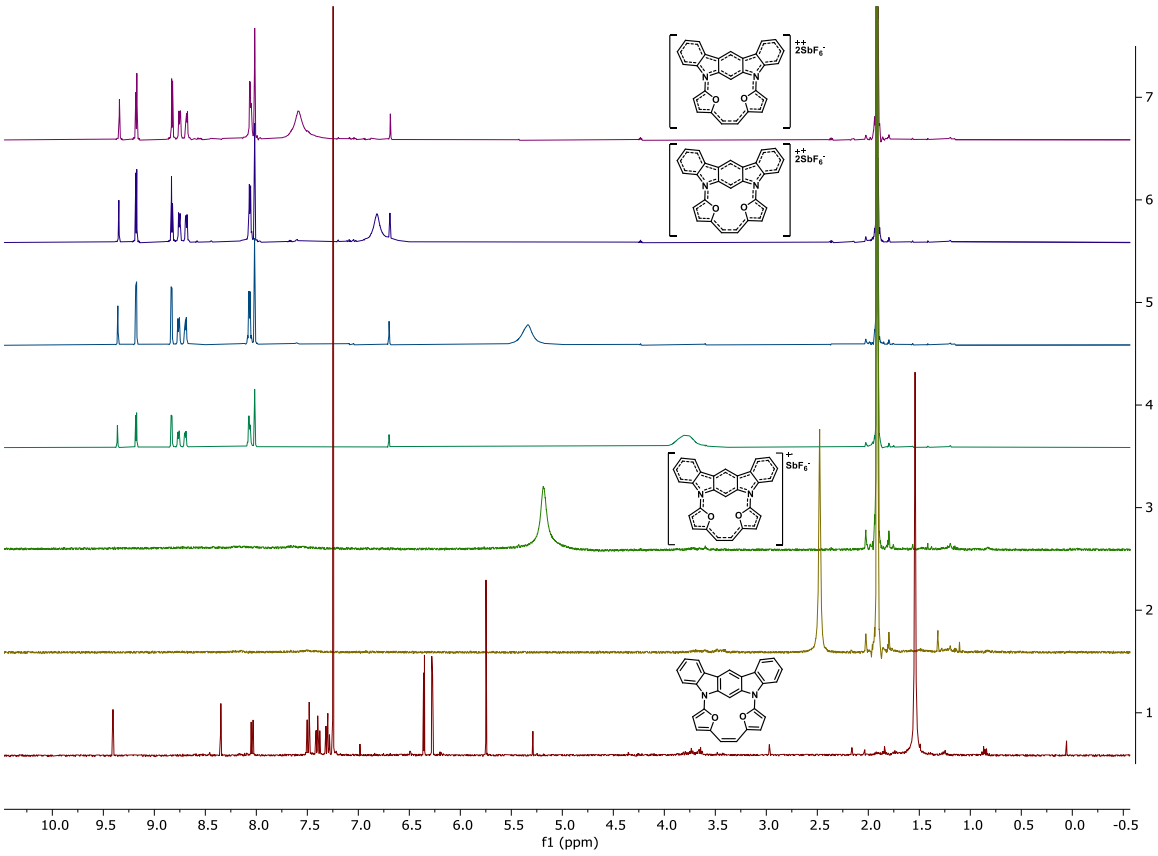


Fig. S34 ^{1}H NMR-monitored titration of **3c** with $NOSbF_6$ (Acetonitrile-d_3, 600 MHz, 233 K); 1 ($CDCl_3$)– without; 2 – 0.5 eq; 3 – 1.0 eq; 4 – 1.5 eq; 5 – 2.0 eq; 6 – 2.5 eq; 7 – 3.0 eq of $NOSbF_6$.

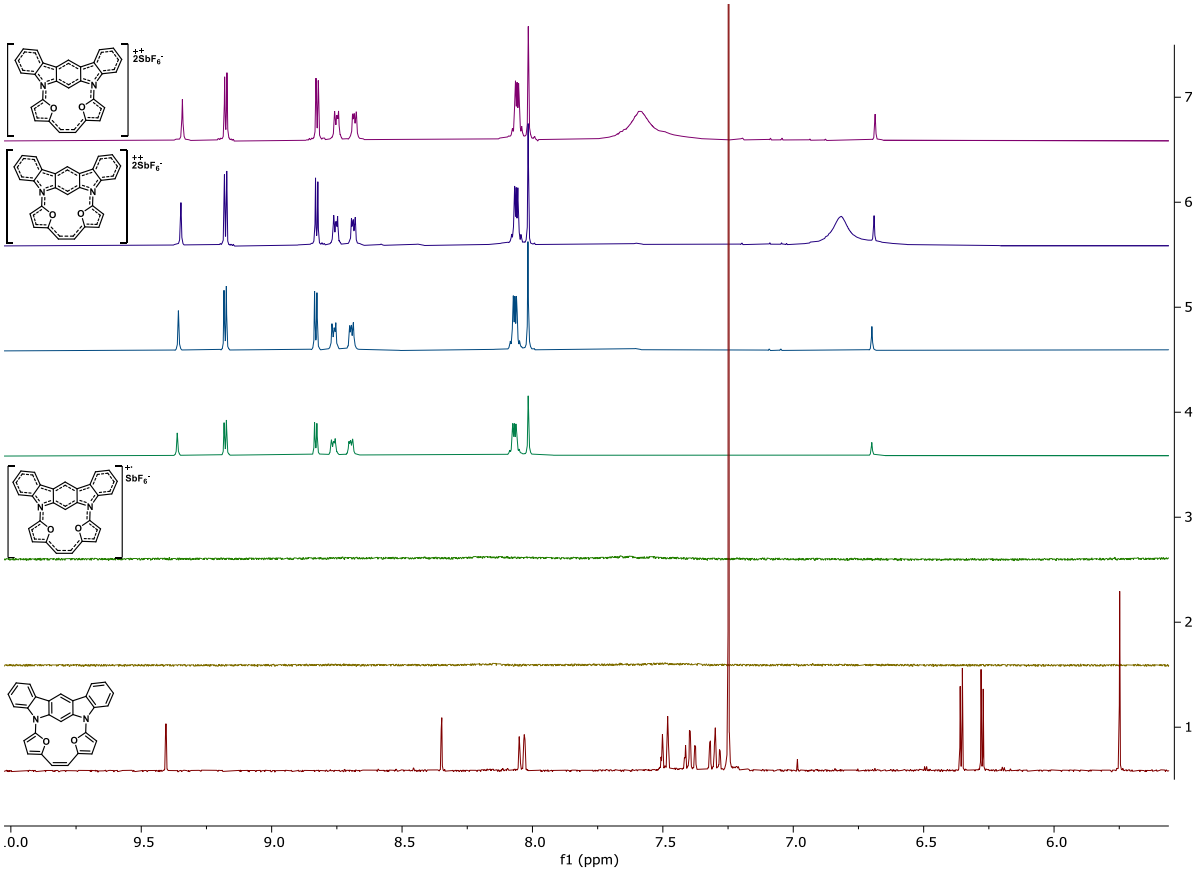


Fig. S35 Zoom on aromatic region of the spectra during ^{1}H NMR-monitored titration of **3c** with $NOSbF_6$ (Acetonitrile-d_3, 600 MHz, 233 K); 1 ($CDCl_3$, 400 MHz, 298 K)– without; 2 – 0.5 eq; 3 – 1.0 eq; 4 – 1.5 eq; 5 – 2.0 eq; 6 – 2.5 eq; 7 – 3.0 eq of $NOSbF_6$.

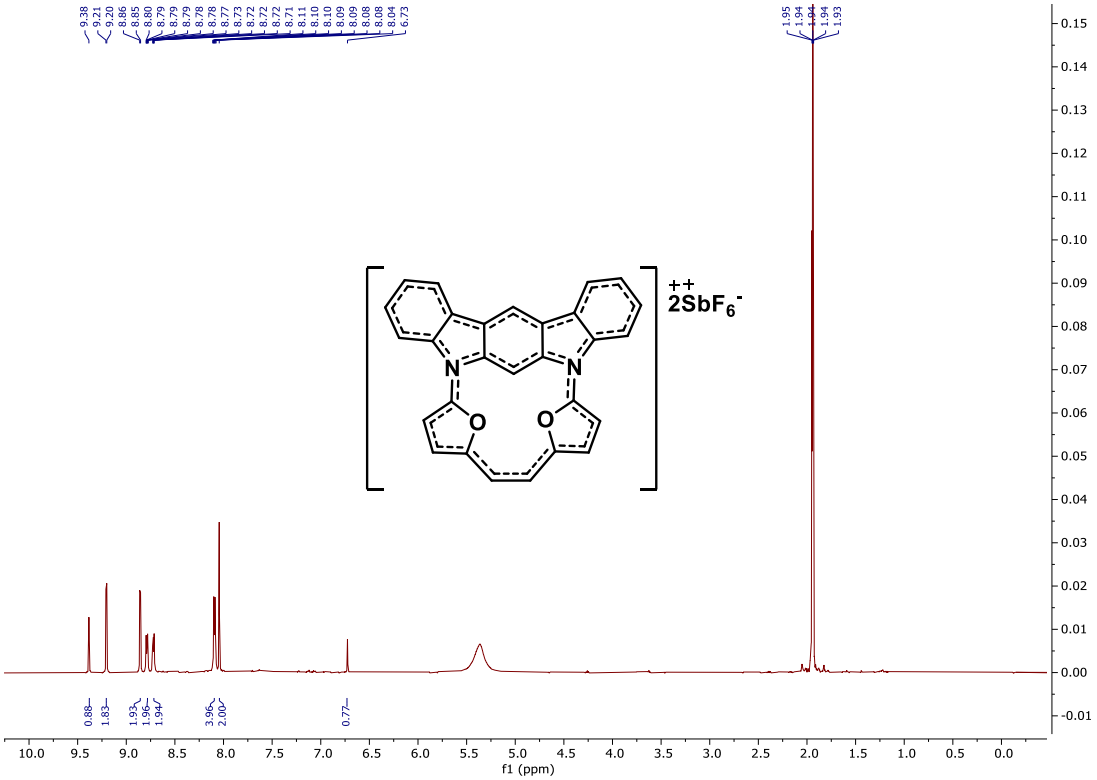


Fig. S36 ^{1}H-NMR (CD_3CN, 600 MHz, 233 K) spectrum of **3c^{2+}**.

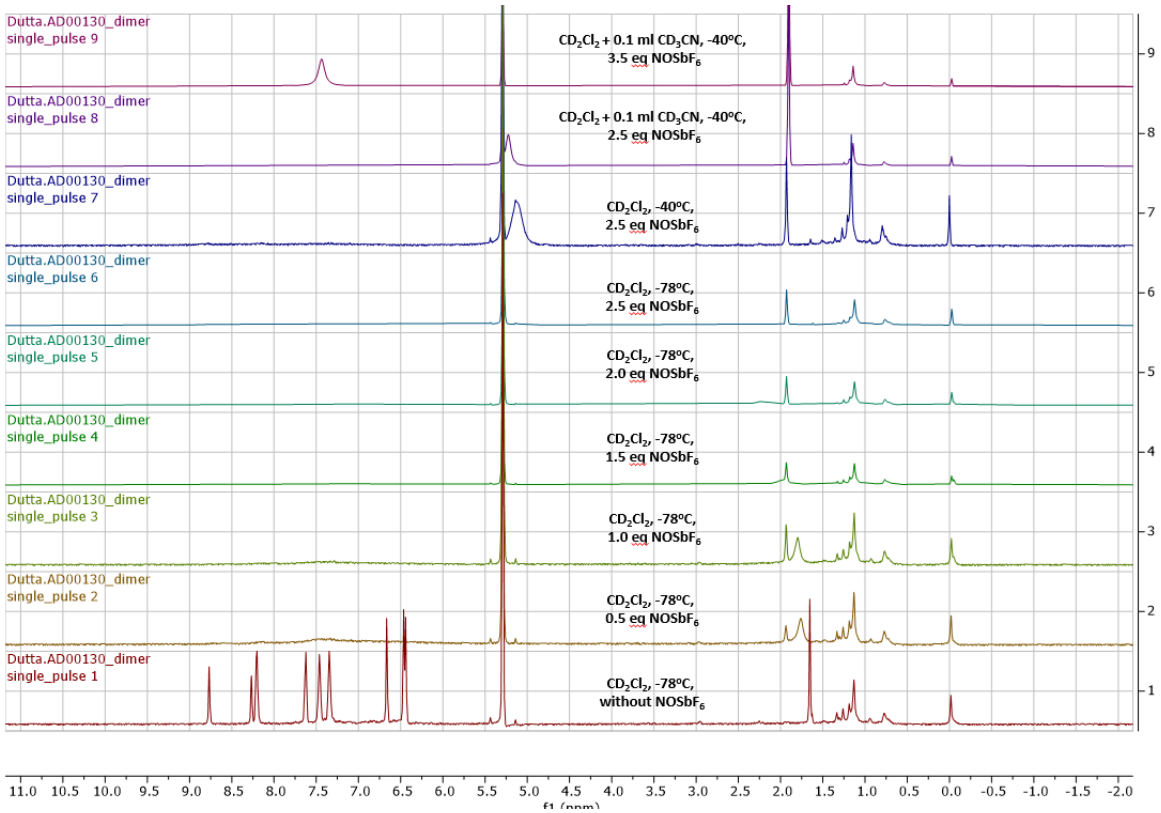


Fig. S37 ^{1}H NMR-monitored titration of **4** with $NOSbF_6$ (CD_2Cl_2, 600 MHz, 195 K).

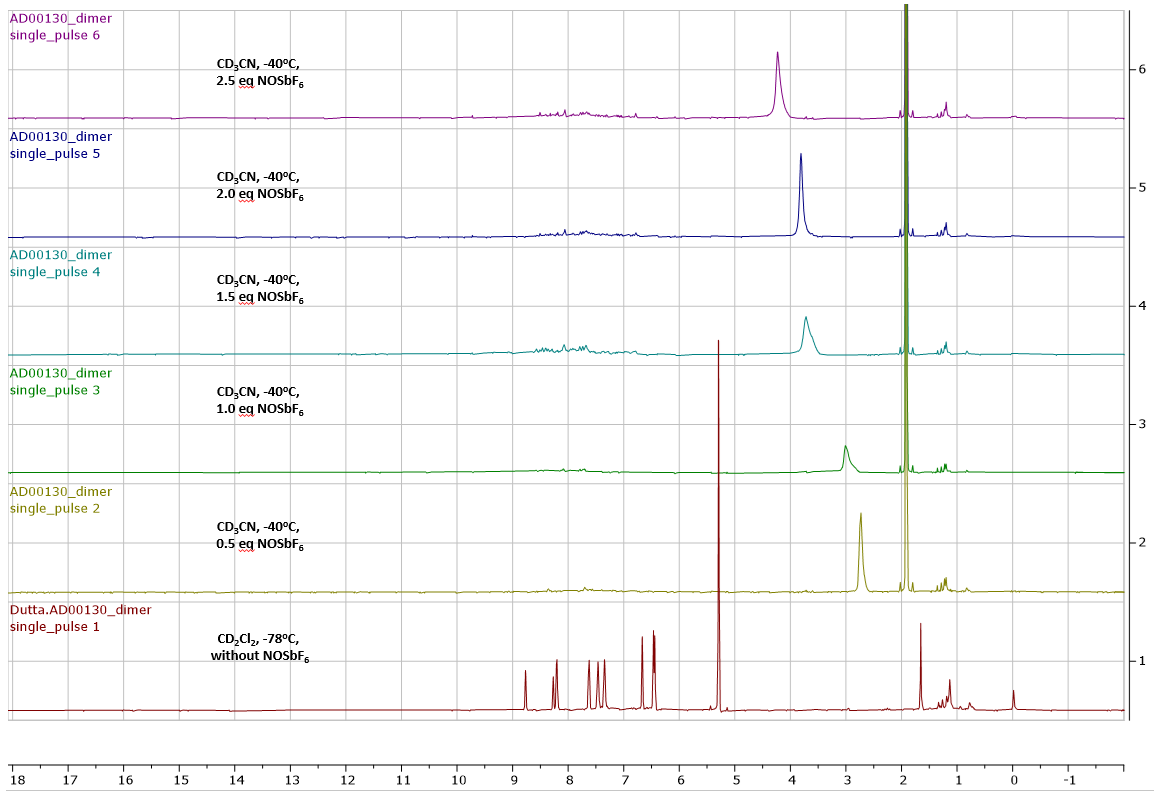


Fig. S3 ^{1}H NMR-monitored titration of **4** with $NOSbF_6$ (Acetonitrile-d_3, 600 MHz, 233 K); 1 (CD_2Cl_2, 600 MHz, 195 K)– without; 2 – 0.5 eq; 3 – 1.0 eq; 4 – 1.5 eq; 5 – 2.0 eq; 6 – 2.5 eq $NOSbF_6$.

4. UV-VIS spectra

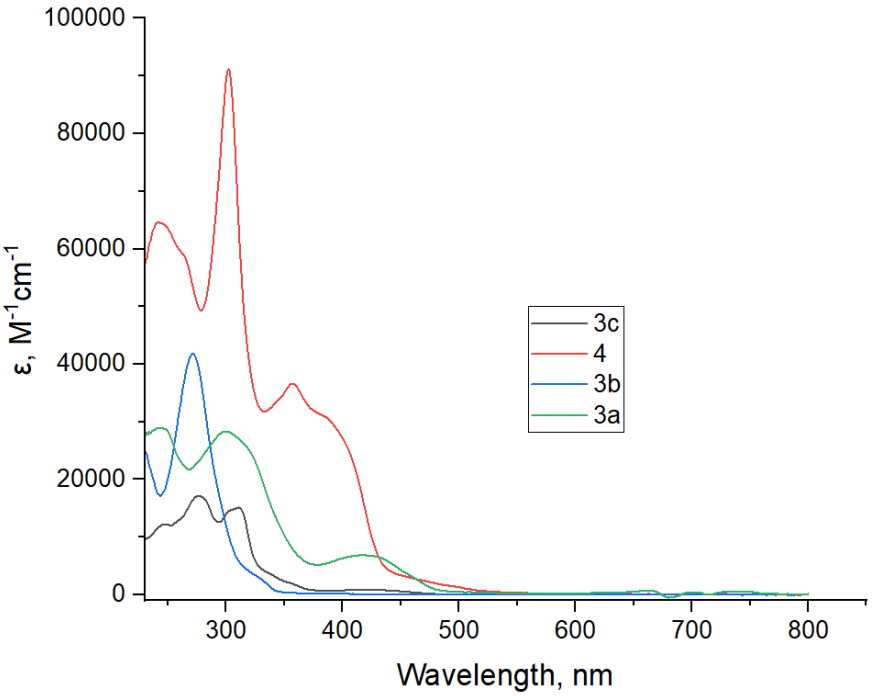


Fig. S39 Extinction spectra of the neutral macrocycle **3a, 3b, 3c, 4** in CH_2Cl_2 at 298 K.

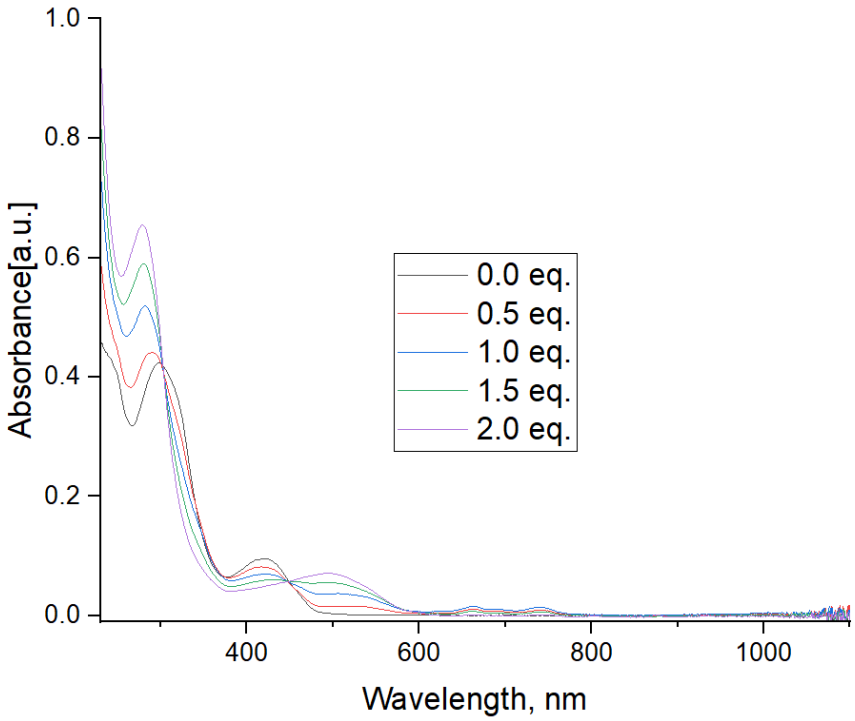


Fig. S40 UV-Vis spectra recorded during titration of **3a** with $NOSbF_6$ in dichloromethane at 279 K.

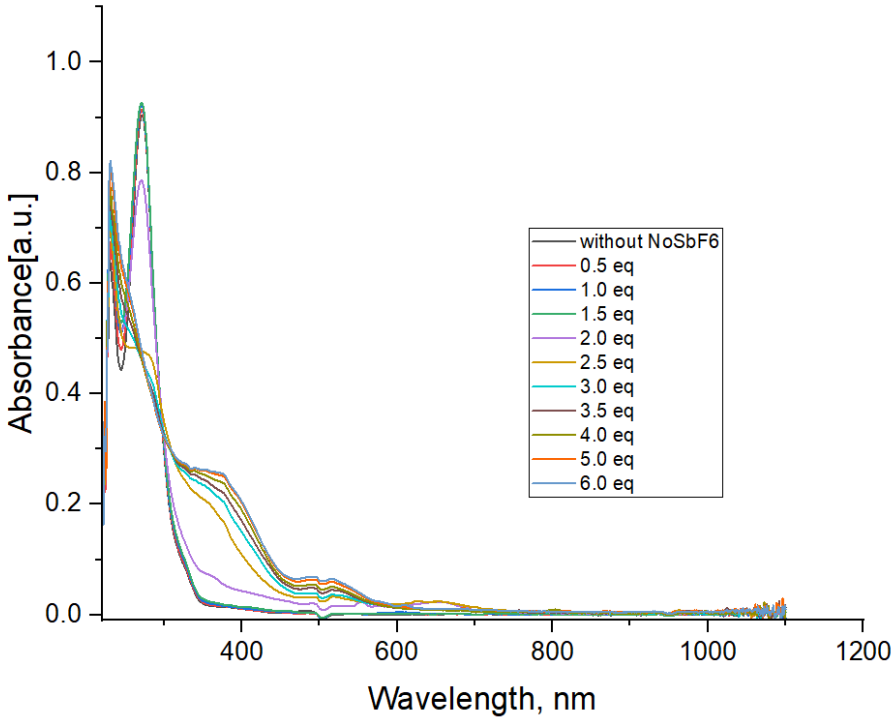


Fig. S4 UV-Vis spectra recorded during titration of **3b** with $NOSbF_6$ in dichloromethane at rt.

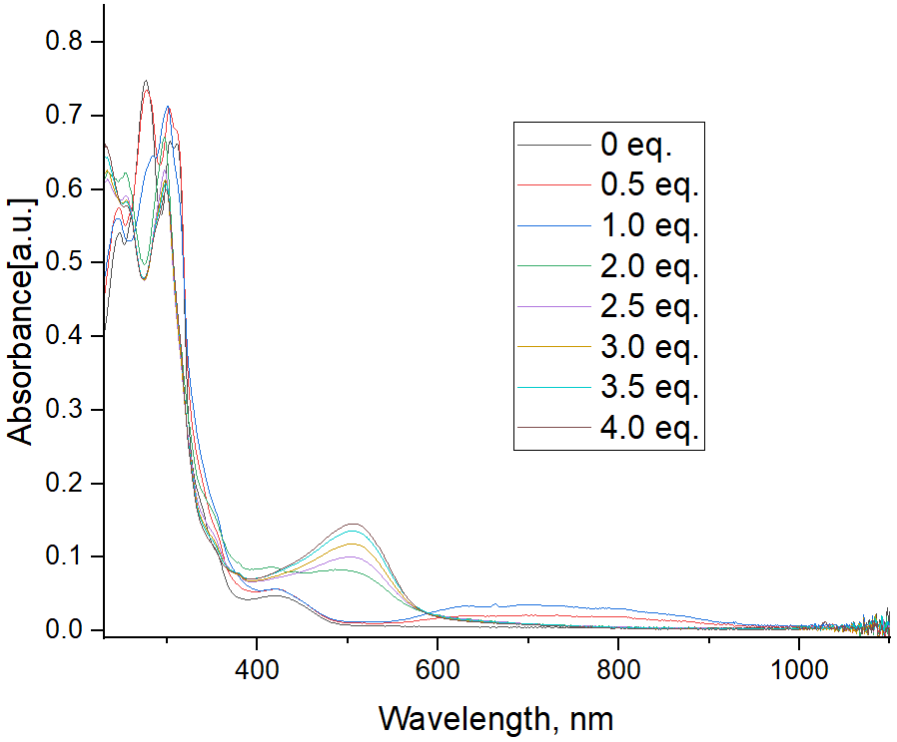


Fig. S5 UV-Vis spectra recorded during titration of **3c** with $NOSbF_6$ in dichloromethane at 276 K.

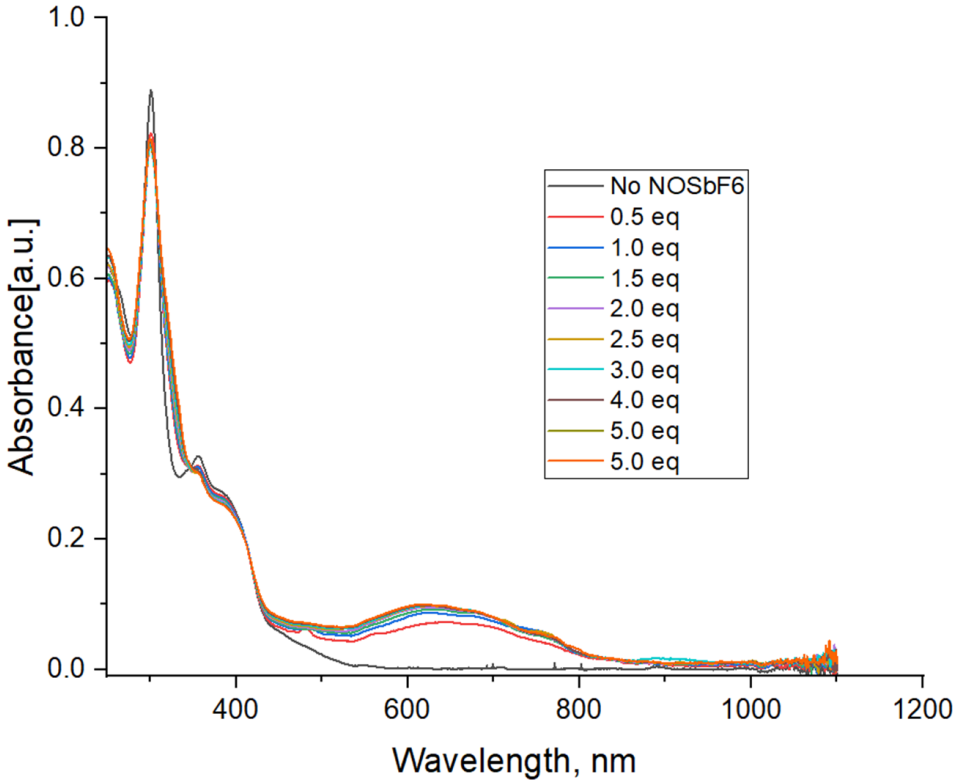


Fig. S43 UV-Vis spectra recorded during titration of **4** with $NOSbF_6$ in dichloromethane at rt.

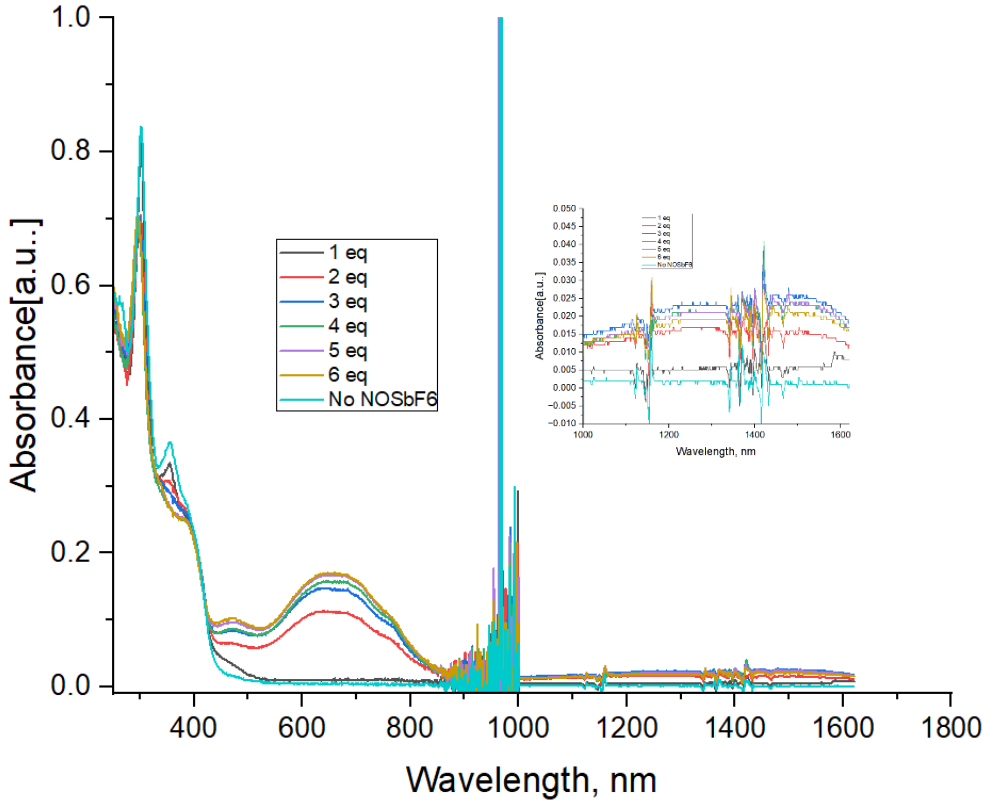


Fig. S44 UV-Vis-NIR spectra recorded during titration of **4** with $NOSbF_6$ in dichloromethane at rt.

5. Emission spectra

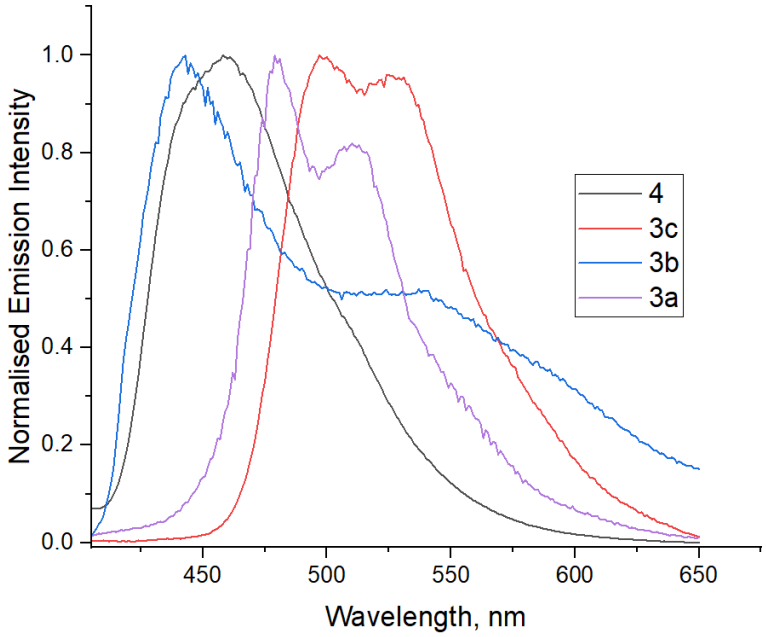


Fig. S45 Normalized emission spectra of the neutral macrocycle **3a, 3b, 3c, 4** in CH_2Cl_2 at 298 K.

Table S1. Emission properties for neutral macrocycle **3a, 3b, 3c and 4.**

Structures	$\lambda_{emission}$[a], nm	$\lambda_{exitation}$[b], nm	Φ[c]
3a	479	350	8 %
3b	363	307	3 %
3c	498	326	3 %
4	459	309	80 %

[a] Emission maxima. [b] Excitation wavelength. [c] Quantum yield.

6. Lifetime Measurement

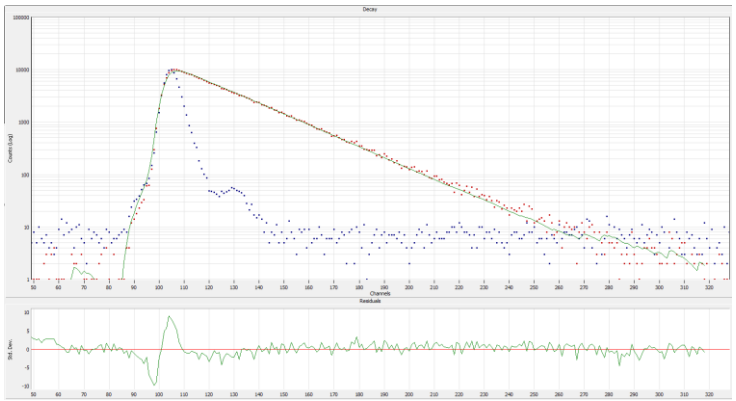


Fig. S46 Fluorescence decay profile of **3a** in CH_2Cl_2 at 298 K.

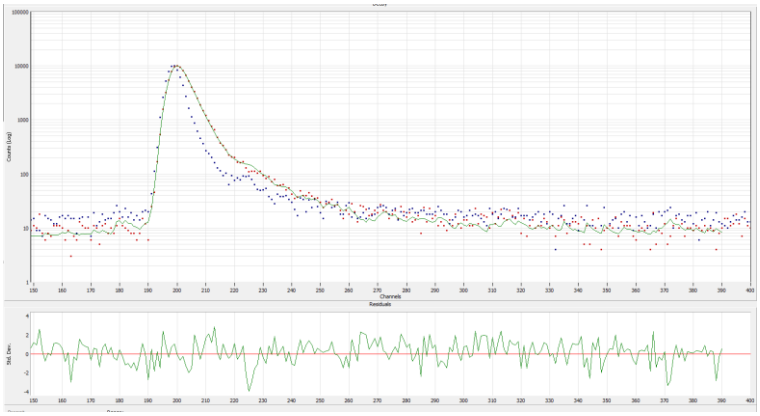


Fig. S47 Fluorescence decay profile of **3b** in CH_2Cl_2 at 298 K.

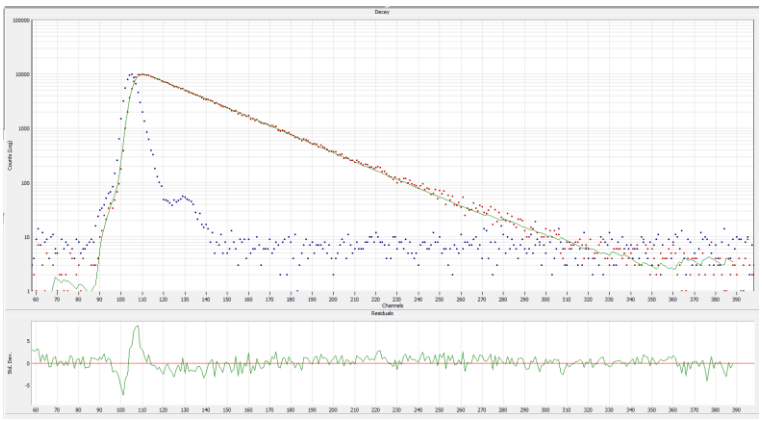


Fig. S48 Fluorescence decay profile of **3c** in CH_2Cl_2 at 298 K.

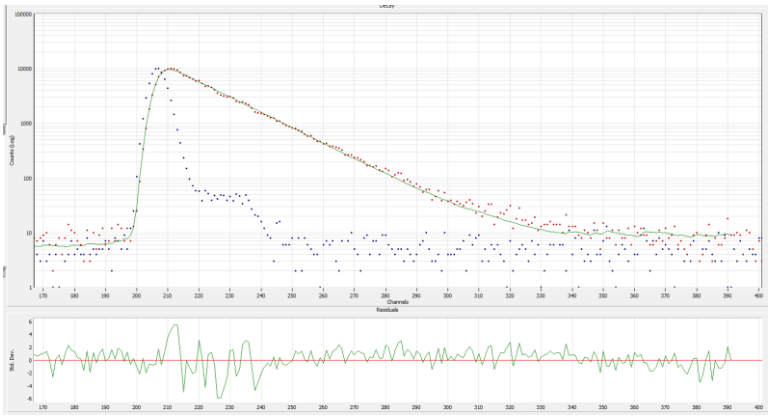


Fig. S49 Fluorescence decay profile of **4** in CH_2Cl_2 at 298 K.

7. Cyclic voltammograms

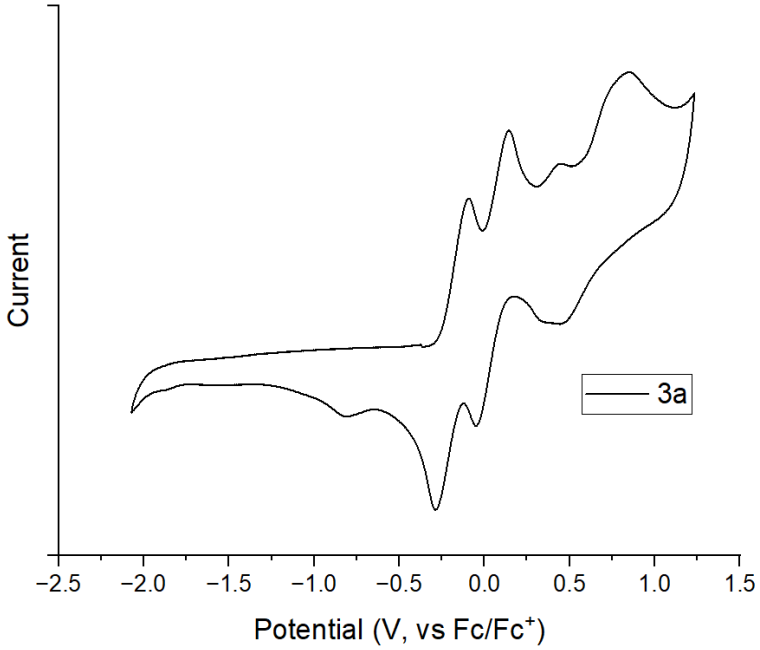


Fig. S50a Cyclic voltammogram recorded for the oxidation waves of **3a** in CH_2Cl_2, vs Fc/Fc^+ with n-Bu_4NPF_6 as electrolyte, v = 100 mV/s.

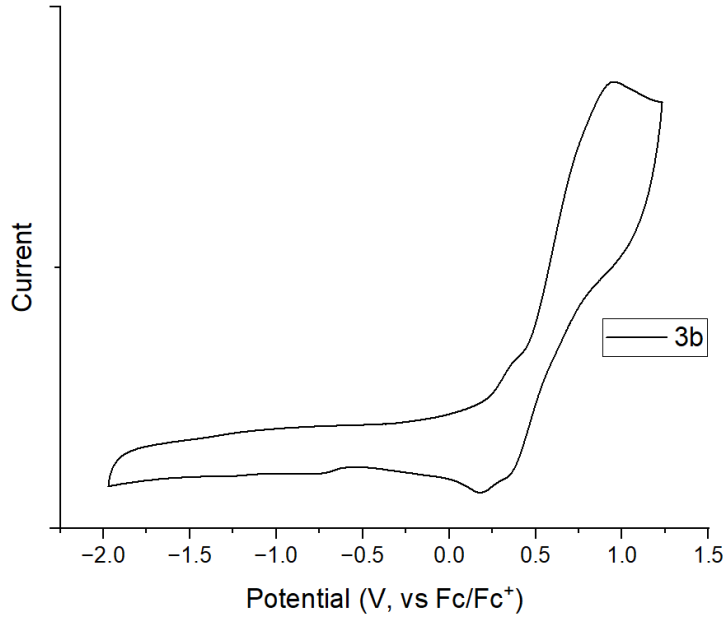


Fig. S50b Cyclic voltammogram recorded for the oxidation waves of **3b** in CH_2Cl_2, vs Fc/Fc^+ with n-Bu_4NPF_6 as electrolyte, v = 100 mV/s.

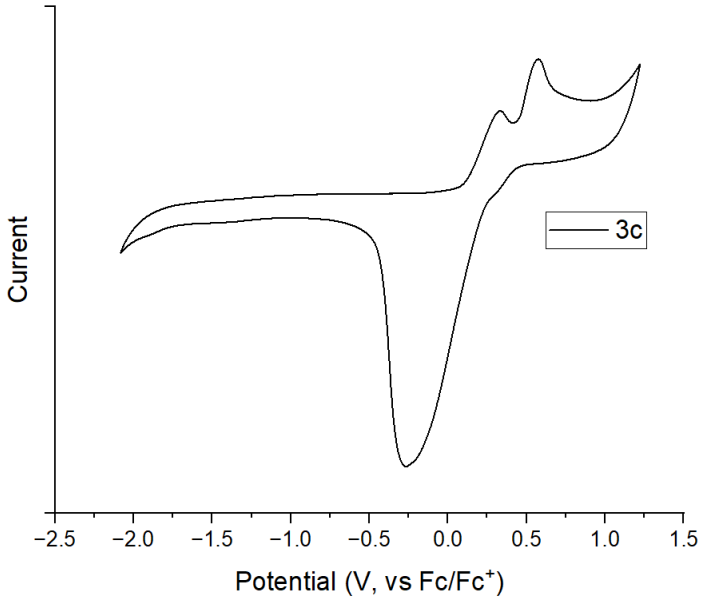


Fig. S50c Cyclic voltammogram recorded for the oxidation waves of **3c** in CH_2Cl_2, vs Fc/Fc^+ with n-Bu_4NPF_6 as electrolyte, v = 100 mV/s.

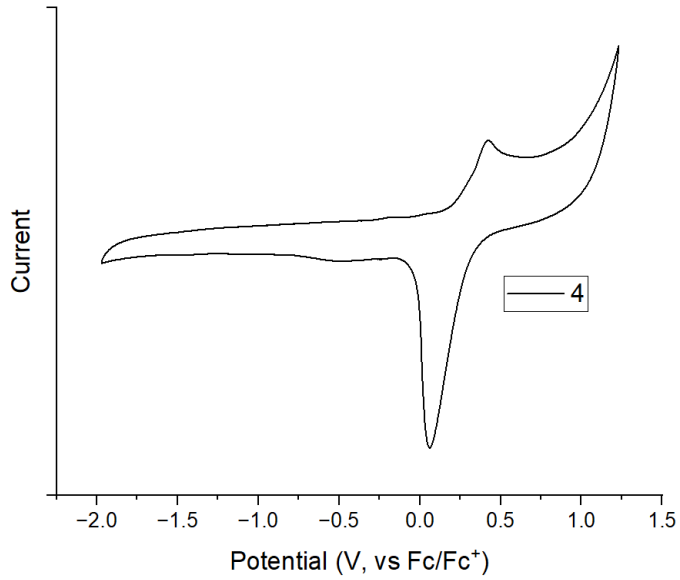


Fig. S50d Cyclic voltammogram recorded for the oxidation waves of **4** in CH_2Cl_2, vs Fc/Fc^+ with n-Bu_4NPF_6 as electrolyte, v = 100 mV/s.

8. ESI-MS spectra

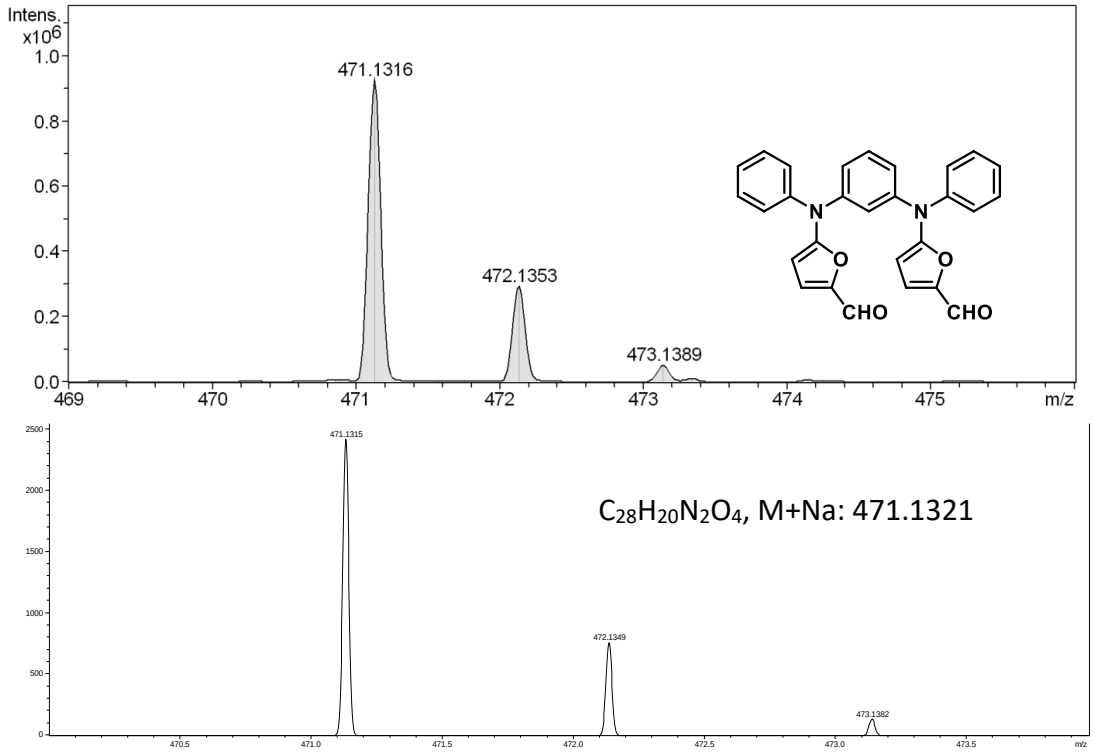


Fig. S51 ESI-MS spectrum of **1a** with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).

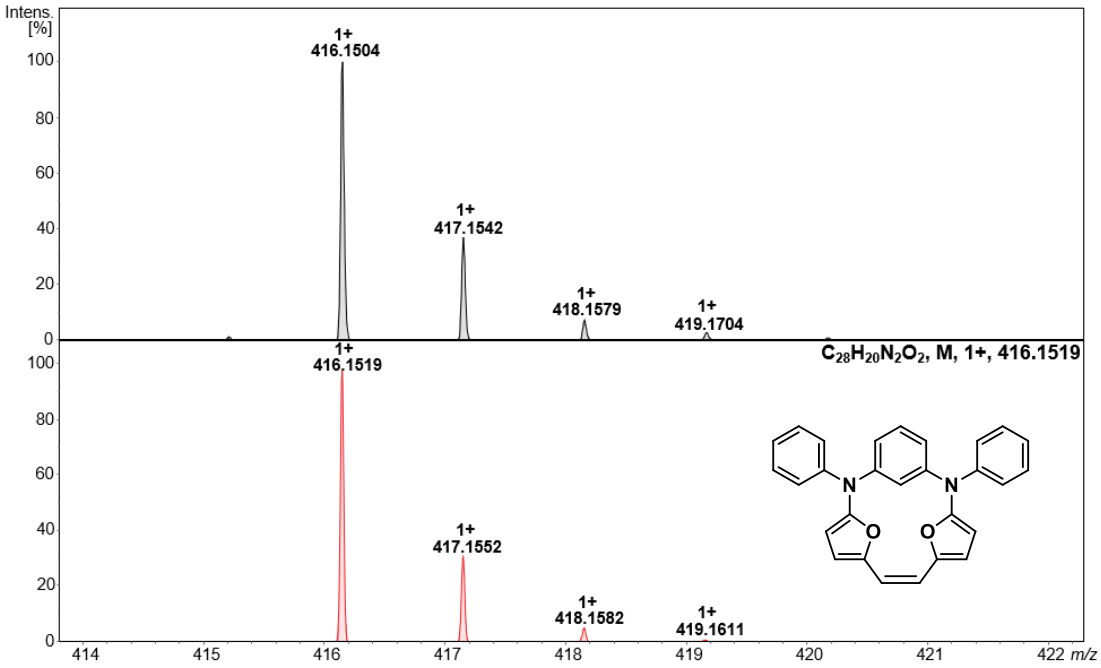


Fig. S52 ESI-MS spectrum of **3a** with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).

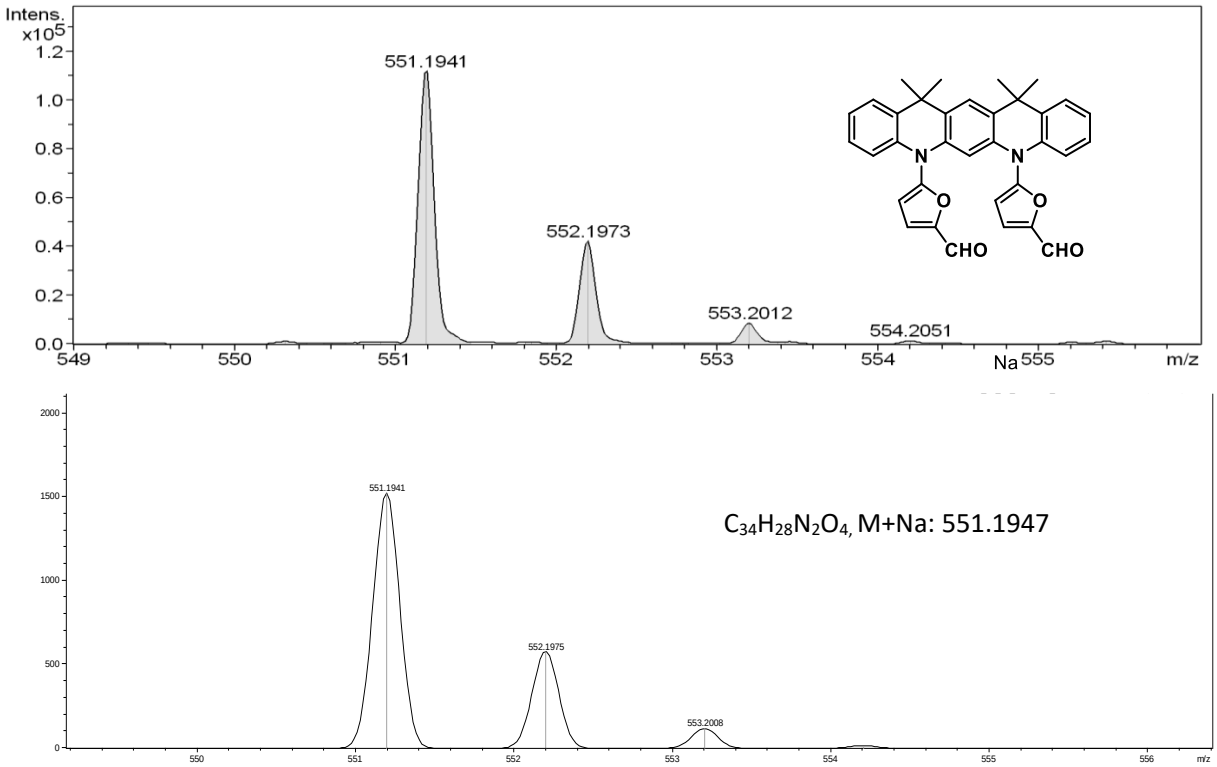


Fig. S53 ESI-MS spectrum of **1b** with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).

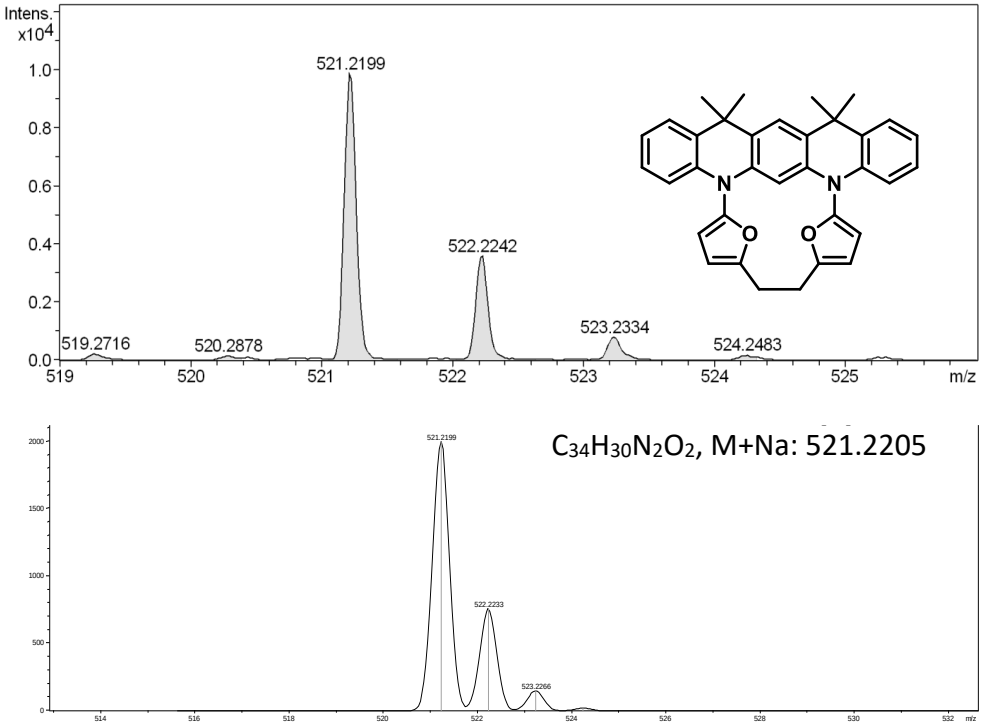


Fig. S54 ESI-MS spectrum of **3b** with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).

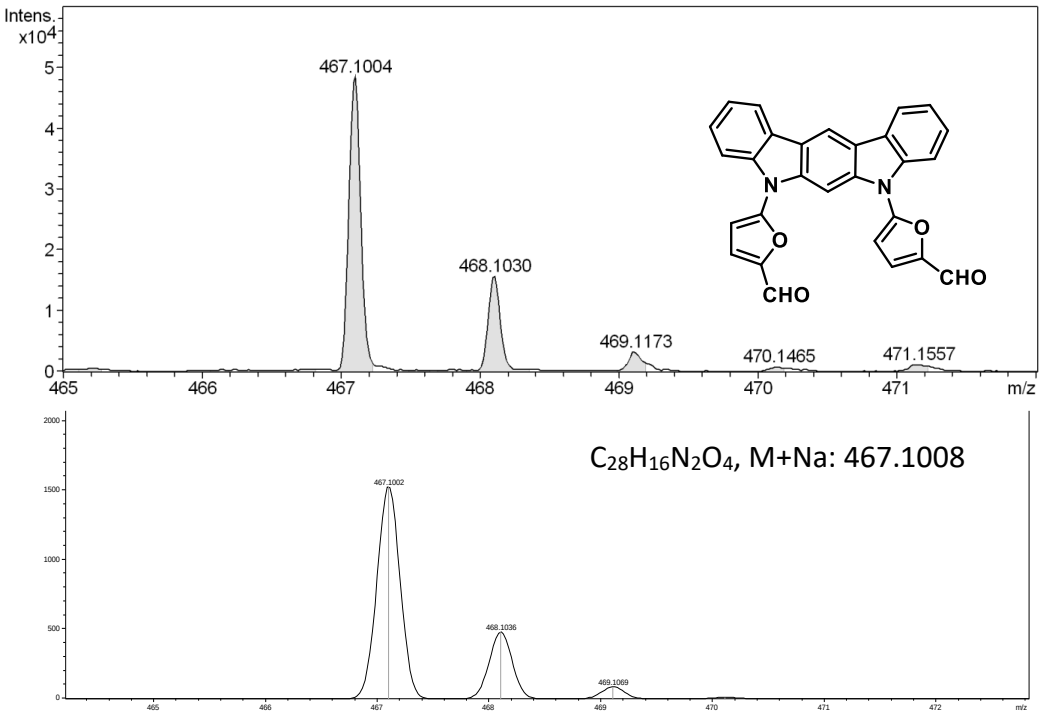


Fig. S55 ESI-MS spectrum of **1c** with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).

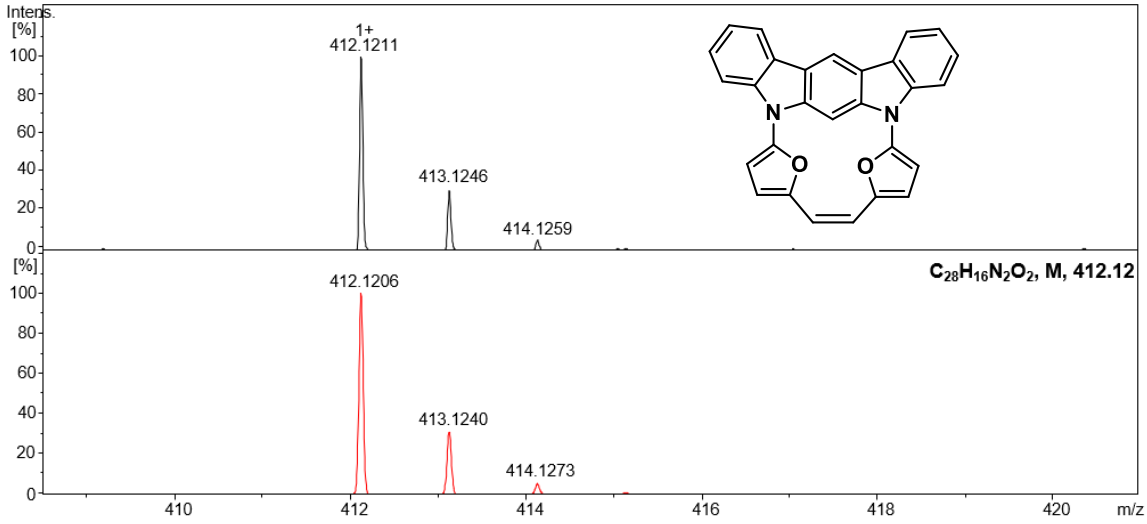


Fig. S56 ESI-MS spectrum of **3c** with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).

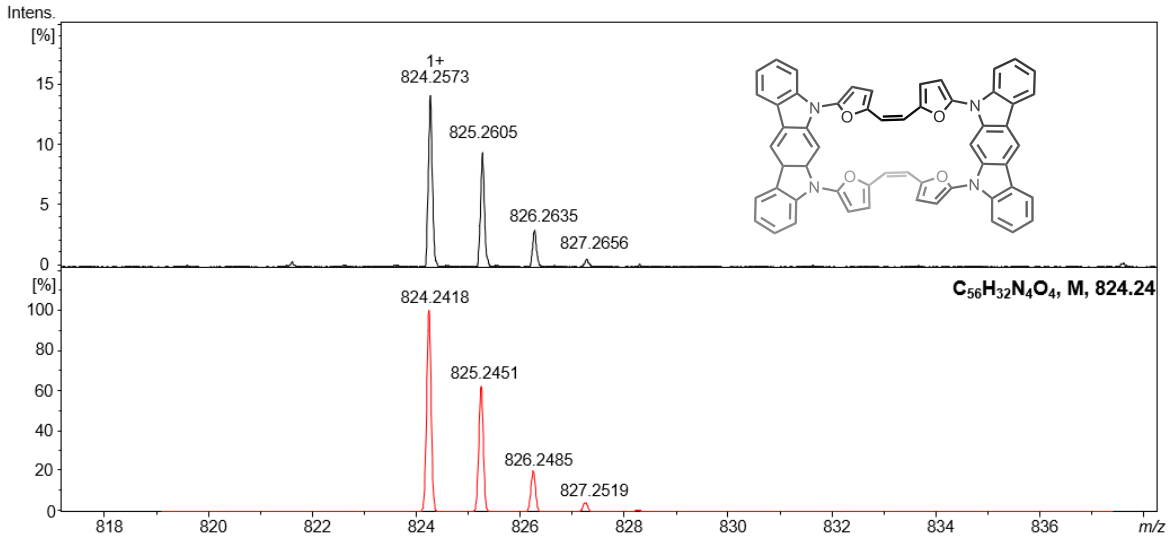


Fig. S57 ESI-MS spectrum of **4** with simulated spectrum (bottom panel - simulated isotopic patterns for molecular formula of investigated compounds).

9. Theoretical calculations

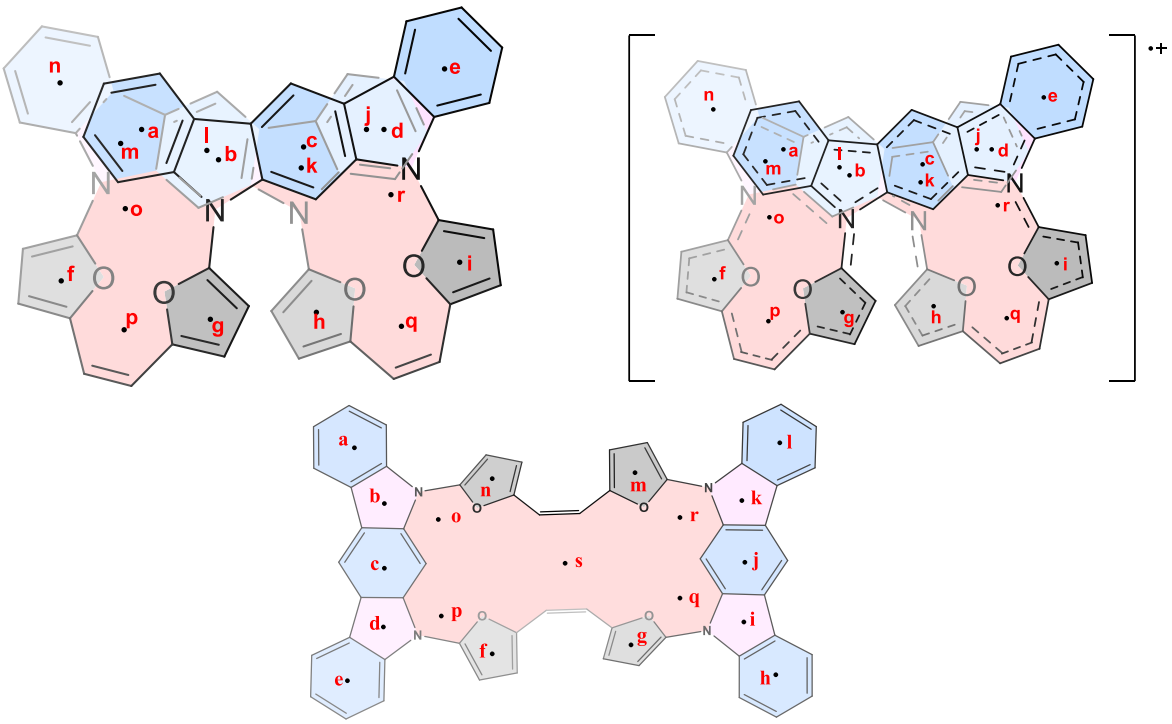
9.1 NICS and GIAO calculations

Table S2. Comparison of ^{1}H chemical shifts recorded and predicted with GIAO calculations.

	3a		**3b**		**3c**		**4 (Open variant)**	
	Obs.	Theory	Obs.	Theory	Obs.	Theory	Obs.	Theory
	Neutral							
3	6.75	7.05	7.39		8.36	8.38	8.75	8.93
2,4	6.51	6.33				----		----
2^2,4^2					8.04	7.42	8.25	8.38
2^3,4^3					7.31	7.33	7.51	7.58
6^2,17^2					7.51	8.07	7.67	7.65
6^3,17^3					7.41	7.36	7.39	7.58
8,15	5.39	5.31	6.23		6.29	6.16	6.43-6.46	6.91
9,14	6.05	6.17	6.16		6.37	6.23	6.43-6.46	7.34
11,12	5.77	5.46	3.09		5.76	5.35	6.73	6.24
18	7.92	7.61	4.43		9.42	9.74	8.36	7.81
	Oxidized							
3	7.43	7.72			9.36	10.29		9.51
2,4		7.74				----		----
2^2,4^2						9.57		8.77
2^3,4^3						9.00		8.18
6^2,17^2						9.40		8.41
6^3,17^3						8.93		8.10
8,15	6.75	6.51			8.84	9.80		7.37 7.30
9,14	7.78	7.49			9.18	9.53		6.85 6.74
11,12	6.37	5.90			8.02	8.94		5.84 5.64
18	10.98	12.62			6.70	4.28		4.92 4.62
	NICS(0)iso							
	Neutral	Oxidized			Neutral	Oxidized	Neutral	Oxidized
a	-0.13	+5.21			+3.23	-5.99	+0.78	-2.48
b	-10.83	-1.78			-9.76	-9.40	-10.10	-10.17
c	-2.50	+2.81			+1.19	-9.56	----	----
d	-10.83	-9.65			-10.92	-12.32	-11.70	-9.25
e	----	----			-5.88	-7.92	-7.73	-6.38
f	----	----			-10.22	-11.10	-10.76	-9.32
g	----	----			----	----	-0.39	-5.16
	NICS(0)zz							
	Neutral	Oxidized			Neutral	Oxidized	Neutral	Oxidized
a	+17.41	+31.63			+24.24	-4.43	+5.61	-0.95
b	+4.11	+23.75			+7.31	+2.21	-20.95	+4.13
c	+23.57	+36.85			+35.88	+1.71	----	----
d	-8.83	-5.14			-7.99	-17.44	-11.75	-2.01
e	----	----			+15.55	+7.92	+0.16	+10.10
f	----	----			-9.60	-15.38	-11.34	-4.98
g	----	----			----	----	+5.73	-11.84

Table S3. Comparison NICS(0)iso and NICS(0)zz for compound 4 and its cation radical .

Positions	$NICS(0)_{iso}$			$NICS(0)_{zz}$		
	4 (closed variant)	4 (open variant)	$4^{+\cdot}$ (closed variant)	4 (closed variant)	4 (open variant)	$4^{+\cdot}$ (closed variant)
a	-12.01	-10.79	-9.99	-16.67	-11.55	-9.88
b	-9.15	-8.35	-6.12	5.27	9.79	13.57
c	-12.53	-11.69	-9.21	-14.07	-9.89	-3.74
d	-8.81	-7.97	-4.32	6.98	12.03	18.94
e	-11.00	-10.71	-8.81	-11.84	-11.28	-5.39
f	-10.58	-10.72	-10.06	-1.04	-3.87	3.12
g	-10.89	-10.64	-9.13	-3.15	-10.21	4.53
h	-10.89	-10.79	-7.87	-3.15	-11.55	7.95
i	-10.58	-8.35	-8.75	-1.04	9.8	6.03
j	-12.01	-11.69	-9.36	-16.68	-9.89	-8.23
k	-9.15	-7.97	-4.50	5.27	12.01	18.06
l	-12.53	-10.72	-9.46	-14.07	-11.29	-4.37
m	-8.81	-10.71	-6.02	6.98	-3.87	14.45
n	-11.00	-10.64	-9.35	-11.84	-10.21	-6.80
o	-3.12	-3.71	-2.66	21.47	23.98	20.96
p	0.52	-2.25	0.44	12.41	26.89	16.33
q	0.52	-3.71	0.86	12.41	23.98	17.56
r	-3.12	-2.25	-2.33	21.47	26.89	21.54
s		-0.36			5.75	



9.2. AICD plots.

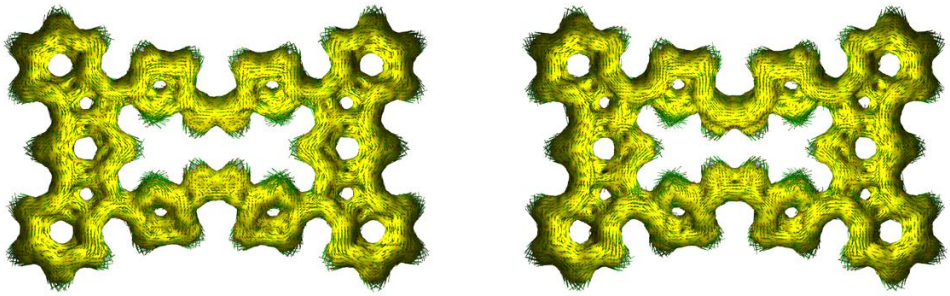


Figure S58. AICD Plot for **4** and $\mathbf{4}^{2+}$ (open variant).

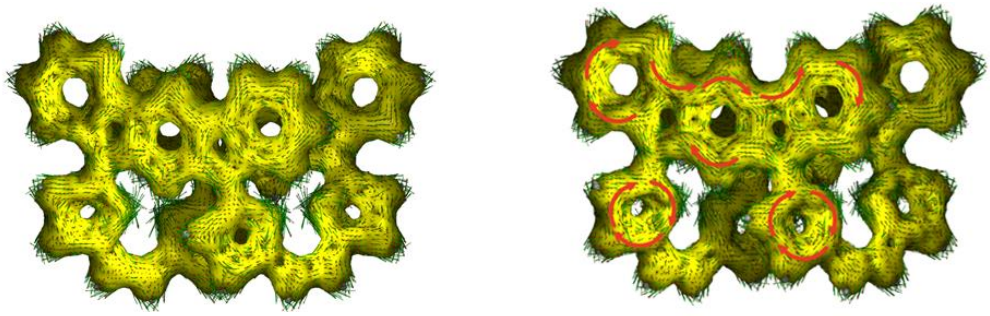


Figure S59. AICD Plot for **4** and $\mathbf{4}^{\cdot+}$ (closed variant).

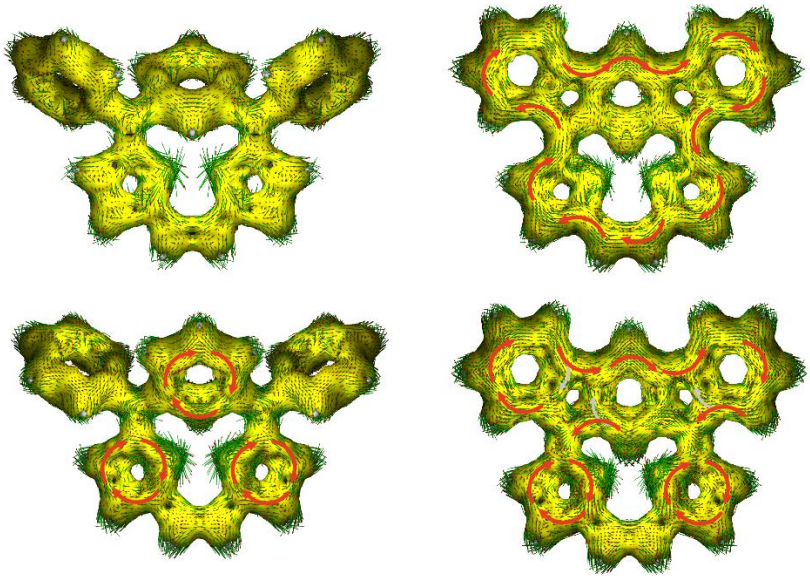


Figure S60. AICD Plot for **3a** (bottom left), $\mathbf{3a}^{2+}$ (top left) **, 3c** (bottom right) and $\mathbf{3c}^{2+}$ (open variant).

9.3. Energy profile diagram

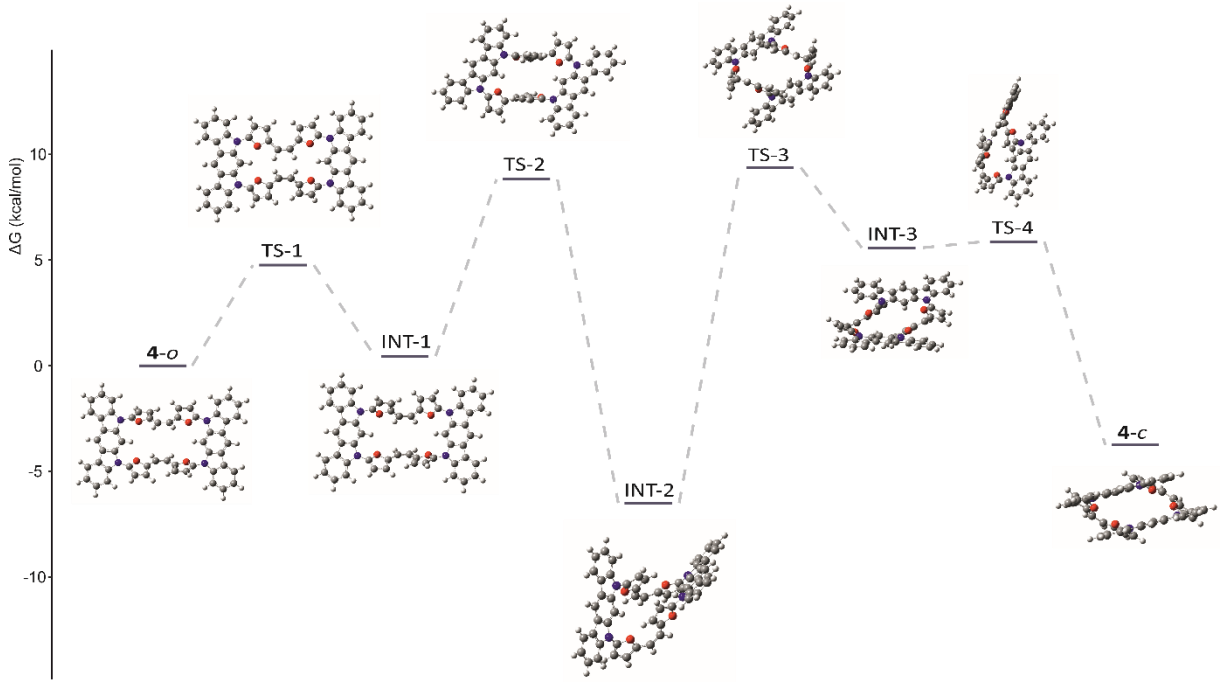


Figure S61. Energy profile diagram of structural conversion between 4(open) to 4(close) variants.

9.4. Cartesian Coordinates.

4 (open variant)				**4** (closed variant)			
C	1.19865	-1.6181	-1.86772	C	-4.68438	3.064266	-0.09332
C	6.54253	0.46247	0.93308	C	-0.50687	-1.7035	1.987822
C	5.17993	-0.77435	-1.07015	C	-2.93579	-0.55629	1.319101
C	3.30371	1.44104	2.31026	C	0.777358	1.684512	2.284691
C	3.30814	-1.53943	-2.41068	C	-4.76484	1.032892	0.771053
C	5.1649	0.61963	0.84839	C	-0.6681	-0.29081	1.894957
C	1.11686	1.87913	2.25068	C	1.919849	3.543628	1.941709
C	6.54409	-0.58895	-1.17885	C	-2.81967	-1.9715	1.4267
C	6.92285	0.93257	2.32703	C	0.885116	-1.94868	2.316271
C	2.68785	0.52154	3.09708	C	0.055489	2.684232	2.882412
H	3.16752	-0.26377	3.64468	H	-0.86441	2.565255	3.434206
C	0.17337	-1.87741	-0.96275	C	3.002471	4.386239	1.522219
C	6.90044	-1.05274	-2.58631	C	-4.12996	-2.5263	1.141706
C	5.7505	-1.58835	-3.13764	C	-4.99306	-1.43957	0.862117
C	5.77946	1.45419	2.90052	C	1.520513	-0.68865	2.420059
C	2.67255	-0.66323	-3.22861	C	-5.91036	1.661008	1.182699
H	3.12003	-0.04155	-3.97778	H	-6.66992	1.246046	1.827674
C	-0.04352	2.54025	1.7859	C	-4.1341	4.190081	-0.79109
C	1.3078	-0.71248	-2.87683	C	-5.86239	2.965662	0.616739
H	0.51615	-0.13566	-3.30689	H	-6.5946	3.752026	0.732336
C	1.29598	0.78574	3.04509	C	0.787988	3.880764	2.653575
H	0.52546	0.22596	3.53561	H	0.52895	4.875652	2.986821
H	0.34359	-2.6836	-0.27937	H	-4.7728	5.063843	-0.68812
H	0.14058	3.44849	1.25002	H	-1.97302	1.387755	1.444191
H	3.35094	-0.10533	-0.09873	C	4.684382	3.064251	0.093325
C	-1.92203	1.04371	2.44673	C	0.506868	-1.7035	-1.98787
C	-6.55574	0.41832	-1.24013	C	2.935779	-0.5563	-1.3191
C	-5.21043	-0.53277	0.95058	C	-0.77734	1.684517	-2.28471
C	-3.28491	0.91299	-2.36652	C	4.764819	1.032877	-0.77105
C	-3.44326	-0.53378	2.55691	C	0.668108	-0.29082	-1.895
C	-5.20522	0.63877	-1.09086	C	-1.91981	3.543638	-1.94168
C	-1.5931	-0.30667	-1.68781	C	2.819663	-1.97152	-1.4267
C	-6.59366	-0.55385	0.94177	C	-0.88512	-1.94868	-2.31631
C	-6.86171	0.83987	-2.67876	C	-0.05544	2.68425	-2.88237
C	-2.45335	0.77878	-3.43341	H	0.864467	2.565281	-3.43417
H	-2.60846	1.1628	-4.42057	C	4.134136	4.190068	0.791117
C	-0.98967	-1.21858	-0.82077	C	4.129941	-2.52632	-1.14169
C	-6.98998	-1.07077	2.32833	C	4.993039	-1.43959	-0.86208
C	-5.80948	-1.35889	3.01632	C	-1.52051	-0.68864	-2.4201
C	-5.6664	1.28801	-3.24216	C	5.910296	1.661012	-1.18278
C	-2.30918	-1.03878	3.09908	H	6.669821	1.246058	-1.82781
H	-2.17895	-2.0243	3.49411	C	-3.00243	4.386247	-1.52218
C	-1.35992	2.2092	1.91517	C	5.862341	2.965668	-0.61682
C	-1.33118	-0.03461	3.01267				
H	-0.30729	-0.1145	3.31558				
C	-1.34876	0.01359	-2.98796				
H	-0.49546	-0.27781	-3.56813				
H	-3.42148	0.22738	0.03555				

O	2.37321	2.42265	1.85687
O	2.38152	-2.37946	-1.74419
O	-3.34464	0.8791	2.40937
O	-2.67788	0.43598	-1.1814
N	4.71486	-1.74285	-2.09047
N	4.70564	1.59647	1.87927
C	7.30614	-0.05408	-0.1284
C	4.42159	-0.08946	-0.10506
C	5.67829	-1.92331	-4.48043
C	6.85695	-1.80634	-5.24434
C	8.06901	-1.3632	-4.64352
C	5.74238	1.79621	4.25106
C	6.94562	1.7023	4.98821
H	6.9528	1.96434	6.02685
C	8.14627	1.26584	4.35773
H	9.05814	1.23033	4.91467
C	8.13738	0.87268	3.00113
H	9.02882	0.53424	2.51259
C	8.09366	-0.97681	-3.28685
H	4.76368	-2.26564	-4.9171
H	6.84064	-2.05691	-6.28195
H	8.96557	-1.3188	-5.22613
H	8.9911	-0.63081	-2.82064
H	8.37384	-0.0387	-0.13619
H	4.83554	2.12818	4.71208
C	-7.34395	-0.12542	-0.19
C	-5.82398	-1.68907	4.36729
C	-7.0809	-1.81896	5.00152
H	-7.12798	-2.07862	6.03815
C	-8.28592	-1.61434	4.27232
H	-9.2305	-1.74928	4.76362
C	-8.2447	-1.22886	2.90931
H	-9.14236	-1.05776	2.34875
C	-5.56058	1.54537	-4.60004
C	-6.74079	1.47141	-5.37135
H	-6.69952	1.68015	-6.41846
C	-7.98379	1.12853	-4.76595
H	-8.87532	1.11746	-5.35624
C	-8.04733	0.79576	-3.39547
H	-8.96851	0.51552	-2.92891
H	-8.40993	-0.20842	-0.24777
H	-4.62069	1.79962	-5.04472
H	-4.91294	-1.84725	4.9065
C	-4.48475	0.12543	-0.02612
N	-4.63572	1.42806	-2.18493
N	-4.63755	-1.25777	2.09907
H	-2.05826	2.92948	1.54441
H	-1.52675	-1.41985	0.08252

H	6.594533	3.752049	-0.73247
C	-0.78793	3.880782	-2.65352
H	-0.52887	4.87568	-2.98671
H	4.772844	5.063822	0.688142
H	-2.86427	5.400985	-1.88761
H	1.973029	1.387742	-1.44422
O	1.902686	2.186844	1.700553
O	-4.01622	1.863911	-0.01044
O	4.016249	1.863882	0.01051
O	-1.90266	2.186842	-1.70057
N	-4.26154	-0.24219	0.973807
N	0.568414	0.319416	2.165721
C	-1.5927	-2.54868	1.756607
C	-1.87472	0.316632	1.553648
C	-6.3323	-1.62854	0.522914
C	-6.80824	-2.93962	0.476793
C	-5.97111	-4.0305	0.760875
C	2.872586	-0.56673	2.74036
C	3.592202	-1.74314	2.953033
H	4.648094	-1.6788	3.197336
C	2.982021	-3.0034	2.847841
H	3.57212	-3.8996	3.012086
C	1.629866	-3.11364	2.530368
H	1.159149	-4.08939	2.452458
C	-4.6315	-3.83126	1.090377
H	-6.98027	-0.78945	0.296533
H	-7.84743	-3.11523	0.215394
H	-6.37194	-5.03862	0.720623
H	-3.98428	-4.67746	1.301703
H	-1.48495	-3.6267	1.828559
H	3.351081	0.402829	2.80177
C	1.592689	-2.54869	-1.75663
C	6.332278	-1.62856	-0.52285
C	6.808215	-2.93963	-0.47672
H	7.847405	-3.11525	-0.21531
C	5.971085	-4.03051	-0.76082
H	6.371921	-5.03864	-0.72056
C	4.631483	-3.83128	-1.09035
H	3.984268	-4.67748	-1.30168
C	-2.87258	-0.56672	-2.74039
C	-3.59221	-1.74313	-2.95305
H	-4.6481	-1.67878	-3.19735
C	-2.98203	-3.00339	-2.84786
H	-3.57214	-3.89958	-3.0121
C	-1.62988	-3.11363	-2.5304
H	-1.15917	-4.08938	-2.45249

H	1.484928	-3.62671	-1.82858
H	-3.35107	0.402846	-2.80181
H	6.980238	-0.78947	-0.29646
C	1.874727	0.31662	-1.55367
N	-0.5684	0.319416	-2.16577
N	4.261521	-0.24221	-0.97378
H	2.864334	5.40097	1.887677

4$^{+\cdot}$ (closed variant)				**4**$^{++}$ (closed variant)			
C	-4.50143	3.160034	-0.07455	C	-4.80814	2.886603	-0.51999
C	0.003974	-1.52895	2.35369	C	-0.79755	-1.58367	2.218186
C	-2.37272	-0.26417	1.701474	C	-3.16921	-0.58935	1.195238
C	1.522495	1.671272	2.243691	C	0.5121	1.770162	1.921176
C	-4.24471	1.351087	1.153257	C	-4.98622	0.846808	0.30511
C	-0.02698	-0.16623	1.951155	C	-0.93518	-0.22325	1.842547
C	2.661413	3.538412	2.120466	C	1.744467	3.573156	1.602453
C	-2.34987	-1.66232	1.975084	C	-3.08461	-1.94179	1.616153
C	1.376845	-1.83954	2.708241	C	0.579058	-1.77744	2.623508
C	1.128565	2.427066	3.319899	C	-0.33651	2.85663	2.115047
H	0.429433	2.112592	4.079019	H	-1.36739	2.813723	2.426955
C	3.68898	4.38019	1.652992	C	2.889228	4.351778	1.374652
C	-3.70855	-2.15573	1.848748	C	-4.38346	-2.54433	1.394575
C	-4.5255	-1.04744	1.576892	C	-5.22549	-1.55437	0.840477
C	2.14623	-0.69388	2.436871	C	1.24614	-0.53595	2.492639
C	-5.14634	2.152676	1.812973	C	-6.27289	1.384026	0.318352
H	-5.58914	1.915906	2.767614	H	-7.16003	0.915948	0.711915
C	-4.2807	4.171162	-1.04313	C	-4.19132	4.046747	-1.00827
C	-5.3274	3.299096	1.027385	C	-6.15349	2.674129	-0.19909
H	-5.94552	4.159707	1.23138	H	-6.9416	3.403471	-0.32004
C	1.853832	3.635506	3.237363	C	0.44597	3.995209	1.913806
H	1.83398	4.470481	3.921007	H	0.137311	5.025419	2.015411
H	-4.87847	5.055919	-0.8551	H	-4.88888	4.876968	-1.06846
H	-1.22808	1.563574	1.406535	H	-2.17232	1.31834	0.941913
C	4.555621	3.030537	-0.30801	C	4.8077	2.887107	0.519739
C	-0.03661	-1.93335	-2.13571	C	0.797686	-1.58396	-2.21764
C	2.331596	-0.58291	-1.6348	C	3.169092	-0.5895	-1.19413
C	-1.54955	1.252436	-2.4756	C	-0.51228	1.769794	-1.92114
C	4.204624	1.103053	-1.30749	C	4.98604	0.847054	-0.30466
C	-0.01156	-0.52757	-1.92555	C	0.935133	-0.22356	-1.84178
C	-2.5636	3.187891	-2.53571	C	-1.74499	3.572655	-1.60296
C	2.316211	-2.00534	-1.72339	C	3.084701	-1.94185	-1.61533
C	-1.40701	-2.29359	-2.45592	C	-0.57871	-1.7777	-2.62368
C	-1.0927	1.87851	-3.60894	C	0.33625	2.856393	-2.11488
H	-0.43054	1.439636	-4.33844	H	1.36718	2.813576	-2.42662
C	4.505274	4.128364	0.594883	C	4.190697	4.047385	1.007566

C	3.677917	-2.46838	-1.53233	C	4.383602	-2.54427	-1.39382
C	4.487761	-1.32742	-1.41012	C	5.225539	-1.55425	-0.83966
C	-2.17963	-1.1224	-2.36048	C	-1.24587	-0.53623	-2.49307
C	5.079422	1.802942	-2.09879	C	6.272569	1.384537	-0.31836
H	5.440112	1.46397	-3.05671	H	7.159735	0.916602	-0.71203
C	-3.43702	4.207524	-2.11293	C	-2.88983	4.351174	-1.3754
C	5.323936	3.023798	-1.45634	C	6.153007	2.6748	0.198709
H	5.932032	3.847628	-1.79626	H	6.941004	3.404326	0.31928
C	-1.74111	3.128234	-3.64789	C	-0.44643	3.994861	-1.91399
H	-1.67727	3.886068	-4.41375	H	-0.13792	5.025117	-2.01561
H	5.227504	4.895062	0.336052	H	4.888171	4.877702	1.067453
H	-3.43731	5.093548	-2.73766	H	-2.70167	5.405131	-1.55898
H	1.182181	1.264465	-1.6085	H	2.171936	1.31802	-0.94054
O	2.398144	2.360734	1.463641	O	1.763706	2.191945	1.60434
O	-3.88114	1.924935	-0.05336	O	-4.10272	1.739728	-0.20444
O	3.867006	1.835647	-0.18072	O	4.102431	1.739972	0.204745
O	-2.41984	2.0406	-1.79885	O	-1.76403	2.191442	-1.6047
N	-3.72467	0.145474	1.615334	N	-4.48588	-0.34794	0.72536
N	1.304973	0.330092	1.87173	N	0.310864	0.42649	2.035368
C	-1.16159	-2.29276	2.339043	C	-1.88693	-2.44958	2.116989
C	-1.21292	0.5115	1.660664	C	-2.10201	0.302883	1.296317
C	-5.90093	-1.16336	1.399452	C	-6.53394	-1.83696	0.445062
C	-6.45671	-2.44244	1.503515	C	-7.00249	-3.13205	0.657497
C	-5.65974	-3.56057	1.798092	C	-6.18821	-4.12009	1.235184
C	3.505164	-0.62334	2.725791	C	2.591674	-0.37861	2.835439
C	4.100922	-1.7565	3.286941	C	3.266041	-1.50389	3.302628
H	5.15601	-1.73056	3.535519	H	4.311943	-1.41423	3.576947
C	3.358547	-2.92375	3.533272	C	2.622768	-2.74775	3.428038
H	3.853166	-3.79246	3.952956	H	3.181183	-3.60284	3.794235
C	1.996762	-2.97709	3.240719	C	1.280099	-2.8927	3.094246
H	1.425076	-3.87817	3.433779	H	0.783318	-3.85161	3.200738
C	-4.28381	-3.4244	1.979393	C	-4.87416	-3.83754	1.597192
H	-6.51957	-0.30407	1.17202	H	-7.16673	-1.10216	-0.03414
H	-7.52358	-2.56812	1.355754	H	-8.01628	-3.3791	0.360729
H	-6.12145	-4.53659	1.895321	H	-6.58609	-5.11764	1.388636
H	-3.67016	-4.2862	2.217762	H	-4.239	-4.60687	2.024014
H	-1.14739	-3.3444	2.602445	H	-1.80497	-3.48961	2.414333
H	4.081131	0.273315	2.534589	H	3.097045	0.572565	2.743052
C	1.131358	-2.68322	-2.0075	C	1.887122	-2.44976	-2.1163
C	5.864266	-1.41292	-1.22257	C	6.534079	-1.83677	-0.44444
C	6.427205	-2.69135	-1.15741	C	7.00278	-3.13174	-0.65719
H	7.495006	-2.78985	-0.99627	H	8.016648	-3.37869	-0.36061
C	5.637453	-3.84374	-1.30076	C	6.188602	-4.11978	-1.23506
H	6.104992	-4.82132	-1.26782	H	6.586647	-5.11721	-1.38885
C	4.260891	-3.74022	-1.49779	C	4.874481	-3.83734	-1.59685
H	3.652513	-4.62888	-1.62491	H	4.239407	-4.60662	-2.02389

C	-3.53417	-1.09247	-2.67356	C	-2.59119	-0.37885	-2.83672
C	-4.12646	-2.29595	-3.06886	C	-3.26525	-1.50408	-3.30446
H	-5.17886	-2.30674	-3.33006	H	-4.31098	-1.4144	-3.57944
C	-3.38314	-3.48617	-3.1331	C	-2.62191	-2.74792	-3.4296
H	-3.87484	-4.4071	-3.42554	H	-3.18009	-3.60297	-3.79625
C	-2.02332	-3.49606	-2.82405	C	-1.27946	-2.89291	-3.09497
H	-1.45058	-4.41514	-2.88028	H	-0.78261	-3.85182	-3.20129
H	1.123143	-3.75977	-2.13644	H	1.805368	-3.48978	-2.41375
H	-4.10766	-0.17492	-2.6243	H	-3.09671	0.572284	-2.74457
H	6.47895	-0.528	-1.11487	H	7.166842	-1.10201	0.034865
C	1.169363	0.187222	-1.71123	C	2.10178	0.30262	-1.29513
N	-1.34541	-0.02991	-1.93468	N	-0.31086	0.426169	-2.03518
N	3.67725	-0.15599	-1.59923	N	4.485793	-0.3479	-0.72453
H	3.841693	5.289432	2.222849	H	2.700979	5.405756	1.558028

10. X-Ray Analysis

Identification code	**3b**	**1b**
CCDC	**2373300**	**2373298**
Empirical formula	$C_{34}H_{30}N_2O_2$	$C_{34}H_{28}N_2O_4$
Formula weight	498.629	528.612
Temperature [K]	100(1)	100(1)
Wavelength [Å]	0.71073	0.71073
Crystal system, space group	orthorhombic, Pbca	Triclinic, P-1
Unit cell dimensions [Å] and [°]	a = 9.7988(3) α = 90 b = 22.1962(7) β = 90 c = 23.7615(7) γ = 90	a = 10.0198(3) α = 94.415(1) b = 11.0048(3) β = 94.158(1) c = 12.9519(4) γ = 113.090(1)
Volume [Å^3]	5168.0(3)	1301.61(7)
Z, Calculated density [Mg·m^{-3}]	8, 1.282	2, 1.349
Absorption coefficient [mm^{-1}]	0.080	0.089
F(000)	2113.2	556.4
Crystal size [mm]	0.25 × 0.2 × 0.2	0.4 × 0.25 × 0.25
2Θ range for data collection [°]	4.86 to 56.56	5.42 to 66.28
Limiting indices	-13 ≤ h ≤ 12 -29 ≤ k ≤ 29 -31 ≤ l ≤ 30	-15 ≤ h ≤ 15 -16 ≤ k ≤ 16 -19 ≤ l ≤ 19
Reflections collected/unique	71596/6340 (R_{int} = 0.0531)	48454/9800 (R_{int} = 0.0198)
Completeness [%] to theta [°]	98.8 to 28.28	99.0 to 33.14
Absorption correction	multi-scan	multi-scan
Max. and min. transmission	0.746/0.698	0.650/0.609
Refinement method	Gauss-Newton	Gauss-Newton with non-spherical form factors
Data/restraints/parameters	6340/10/366	9800/0/445
Goodness-of-fit on F^2	1.050	1.091
Final R indices [I>2σ(I)]	R_1 = 0.0839, wR_2 = 0.1573	R_1 = 0.0190, wR_2 = 0.0410
R indices (all data)	R_1 = 0.0956, wR_2 = 0.1628	R_1 = 0.0219, wR_2 = 0.0421
Largest diff. peak and hole [eÅ^{-3}]	0.52/-0.49	0.19/-0.19

Identification code	**3c**	**1c**
CCDC	**2373296**	**2373295**
Empirical formula	$C_{28}H_{16}N_2O_2$	$C_{28}H_{16}N_2O_4$
Formula weight	412.43	444.43
Temperature [K]	100(1)	100(1)
Wavelength [Å]	0.71073	0.71073
Crystal system, space group	orthorhombic, $Cmc2_1$	monoclinic, $P2_1/c$
Unit cell dimensions [Å] and [°]	a = 23.5151(6) α = 90 b = 10.1202(2) β = 90 c = 7.7223(2) γ = 90	a = 7.6584(3) α = 90 b = 16.7506(6) β = 102.8020(10) c = 16.0779(6) γ = 90
Volume [Å^3]	1837.73(8)	2011.25(13)
Z, Calculated density [Mg·m^{-3}]	4, 1.491	4, 1.468
Absorption coefficient [mm^{-1}]	0.095	0.100
F(000)	856.0	920.0
Crystal size [mm]	0.25 × 0.17 × 0.07	0.2 × 0.2 × 0.15
2Θ range for data collection [°]	6.574 to 56.556	5.196 to 54.204
Limiting indices	-31 ≤ h ≤ 30 -12 ≤ k ≤ 13 -9 ≤ l ≤ 10	-6 ≤ h ≤ 9 -20 ≤ k ≤ 20 -20 ≤ l ≤ 15
Reflections collected/unique	18575/ 2239 (R_{int} = 0.0302)	9321/4272 (R_{int} = 0.0224)
Completeness [%] to theta [°]	96.0 to 28.28	96.3 to 27.10
Absorption correction	multi-scan	multi-scan
Max. and min. transmission	0.746/0.709	0.746/0.626
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2239/1/148	4272/0/311
Goodness-of-fit on F^2	1.129	1.117
Final R indices [I>2σ(I)]	R_1 = 0.0434, wR_2 = 0.0955	R_1 = 0.0529, wR_2 = 0.1162
R indices (all data)	R_1 = 0.0445, wR_2 = 0.0960	R_1 = 0.0665, wR_2 = 0.1222
Largest diff. peak and hole [eÅ^{-3}]	0.31/-0.28	0.41/-0.33

Identification code	**4**	**3a**
CCDC	**2373301**	**2373299**
Empirical formula	$C_{56}H_{32}N_4O_4$	$C_{28}H_{20}O_2N_2$
Formula weight	824.85	416.46
Temperature [K]	99.99(10)	100(1)
Wavelength [Å]	1.54184	1.54184
Crystal system, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$
Unit cell dimensions [Å] and [°]	a = 11.55069(18) α = 90 b = 28.1034(4) β = 107.3208(17) c = 12.47602(19) γ = 90	a = 8.20060(10) α = 90 b = 25.6429(3) β = 94.6740(10) c = 9.61100(10) γ = 90
Volume [Å^3]	3866.23(11)	2014.35(4)
Z, Calculated density [Mg·m^{-3}]	4, 1.417	4, 1.373
Absorption coefficient [mm^{-1}]	0.720	0.692
F(000)	1712.0	872.0
Crystal size [mm]	0.10 × 0.05 × 0.02	0.52 × 0.27 × 0.22
2Θ range for data collection [°]	6.29 to 151.334	6.894 to 155.682
Limiting indices	-13 ≤ h ≤ 14 -35 ≤ k ≤ 33 -15 ≤ l ≤ 15	-10 ≤ h ≤ 9 -31 ≤ k ≤ 32 -10 ≤ l ≤ 12
Reflections collected/unique	52809/7927 (R_{int} = 0.0408)	9406/4210 (R_{int} = 0.0400)
Completeness [%] to theta [°]	98.6 to 75.68	97.7 to 77.84
Absorption correction	multi-scan	analytical
Max. and min. transmission	1.000/0.765	0.954/0.915
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7927/0/577	4210/0/369
Goodness-of-fit on F^2	1.010	1.046
Final R indices [I>2σ(I)]	R_1 = 0.0427, wR_2 = 0.0979	R_1 = 0.0654, wR_2 = 0.1723
R indices (all data)	R_1 = 0.0739, wR_2 = 0.1116	R_1 = 0.0705, wR_2 = 0.1800
Largest diff. peak and hole [eÅ^{-3}]	0.24/-0.19	0.38/-0.43

Identification code	**1a**	
CCDC	**2373297**	
Empirical formula	$C_{28}H_{20}N_2O_4$	
Formula weight	448.46	
Temperature [K]	100(1)	
Wavelength [Å]	0.71073	
Crystal system, space group	triclinic, P-1	
Unit cell dimensions [Å] and [°]	a = 10.0117(3) α = 91.5050(18) b = 14.9714(4) β = 105.123(2) c = 15.3960(3) γ = 95.377(2)	
Volume [Å^3]	2214.88(9)	
Z, Calculated density [Mg·m^{-3}]	4, 1.345	
Absorption coefficient [mm^{-1}]	0.091	
F(000)	936.0	
Crystal size [mm]	0.38 × 0.22 × 0.19	
2Θ range for data collection [°]	5.626 to 54.998	
Limiting indices	$-13 \le h \le 12$ $-19 \le k \le 19$ $-19 \le l \le 18$	
Reflections collected/unique	22636/10060 (R_{int} = 0.0409)	
Completeness [%] to theta [°]	99.0 to 27.50	
Absorption correction	multi-scan	
Max. and min. transmission	1.000/0.686	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	10060/0/613	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2σ(I)]	R_1 = 0.0556, wR_2 = 0.1433	
R indices (all data)	R_1 = 0.0698, wR_2 = 0.1584	
Largest diff. peak and hole [eÅ^{-3}]	0.30/-0.34	