[4]Helicene based anions in electrocrystallization with tetrachalcogenafulvalene donors†

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Electrocrystallization is an ubiquitous tool for the assembly of ions formed in situ from electroactive precursors into ordered crystalline macroscopic assemblies. Using tetrachalcogeno-fulvalene derivatives, many conducting and superconducting materials have been developed over the past fifty years, generally referred to as organic molecular conductors. The introduction of chirality in the structure of such molecular materials is triggered by the possible observation of exotic physical effects such as electrical Magneto-Chiral Anisotropy (eMCha). Chirality is more commonly brought by the organic electron donor, rather than the inorganic counter-anion. Herein the synthesis of organic electrolytes based on a [4]helicene scaffold is described. Tetrabutylammonium salts of [4]helicene carboxylate and sulfonate have been synthesized and characterized. Electrocrystallizations with three organic donors, namely tetrathyl-TTF (TMTTF), bis(ethylenedithio)-TFF (BEDT-TTF) and tetramethyl-tetrathiafulvalene (TMTSF) provided crystals whose X-ray analysis on single crystal is reported. While a covalent adduct of TMTTF has been observed with the carboxylate salt as electrolyte, the structures display either discrete organic donor stacks for TMTTF and TMTSF, or chains of laterally connected dimers for BEDTTF when sulfonate salts were used.

Helicenes are a family of ortho-fused aromatics presenting a helicoidal structure, granting them with strong chiroptical properties such as CD or CPL.17,18 Uses in asymmetric catalysis and incorporation in liquid crystals and in receptors for stereoselective molecular recognition have been also explored.19,20 Our team and others dedicated strong efforts to develop chiral emissive or redox-active helicenes, in order to observe the synergistic interaction between chirality and conductivity or luminescence.21-23 In particular, TTF-helicenes have shown redox modulation of their chiroptical properties.24 However, helicene based anions have been never used so far as counter ions in TTF based radical cation salts. Herein, we report on new synthetic strategies to access anionic [4]helicenes, as carboxylate and sulfonate salts, to use them as supporting electrolytes during the electrocrystallization procedure with TTF based electron donors. Although the [4]helicene scaffold is racemizing quickly at room temperature and, therefore, both enantiomers P and M are generally obtained in the structures, the synthetic strategies outlined here can be readily expanded towards more extended, configurationally stable, anionic helicenes.

Results and discussion

Synthesis and electrocrystallization of 3-carboxylate-[4]helicene

As a first approach towards [4]helicene counter anions suitable as electrolytes for electrocrystallization, we selected the tetrabutylammonium (TBA) salt of 3-carboxylate-[4]helicene 3, for its ease of synthesis and availability (Scheme 1). 1 was obtained from 2-bromomethylnaphthalene after...
phosphorylation, Wittig reaction with methyl 4-formylbenzoate and photocyclisation.\textsuperscript{25} Saponification yielded 2 quantitatively.\textsuperscript{26} Deprotonation with one equivalent of tetrabutylammonium hydroxide provided our target compound 3 as an oil.

Compound 2 crystallized in the monoclinic $P2_1/c$ space group by slow evaporation of a CHCl$_3$/MeOH solution (Fig 1a). One molecule is present in the asymmetric unit, with an interplanar angle between the two end aromatic moieties of 28.2° (Fig. 1b). Both $P$ and $M$ forms of the helicene are present in the structure, as expected from their low racemization barrier. A double H-bond involving the carboxylic acids, providing the classical R$^2_2$[8] motif, links two molecules of opposite chirality, with O-O distances of 2.608(5) Å. Homochiral $\pi-\pi$ stacks along the $b$ axis are formed in the crystal.

Compound 3 was readily engaged as electrolyte in electrocrystallization experiments with well-known organic donors of the TTF family: TMTTF, BEDT-TTF and TMTSF in various solvents. While no crystals were observed with BEDT-TTF and TMTSF, dark crystals grew with TMTTF from CH$_3$CN at RT with a 2 $\mu$A current for 2 weeks. Structure resolution revealed that the obtained compound had the unexpected formula C$_{24}$H$_{17}$O$_2$S$_2$ and was actually the neutral compound resulting from the addition of two helicene carboxylates on the dicationic oxidized form of the TMTTF. The compound crystallized in the orthorhombic $Pbcn$ space group with one neutral adduct in the asymmetric unit. One adduct bears two helicene of the same chirality, which optimizes the $\pi$ overlap between the aromatic surfaces (Fig. 2a and b). Due to symmetry operations, the other enantiomer is also found in the structure (Fig. 2c). The double addition on the central bond of a TTF derivative is scarcely reported in the literature, with only two occurrences, to the best of our knowledge, of the formation of a cycloaduct with o-chloranil.\textsuperscript{27,28} Electrocrystallization trials in the same conditions have been performed with aromatic


![Scheme 2. Synthesis of 5-sulfonate-[4]helicene 7.](image)
carboxylates salts obtained from the reaction of TBAOH with benzoic acid, 2-naphthoic acid and 1-pyrene carboxylic acid. However, no crystals nor precipitate were observed. It is hypothesized that the eclipsed conformation around the TMTTF central bond imposes a torsion angle O-C-C-O around 60° that necessitates a flexible aromatic moiety in order to have a favourable π overlap of the aromatic part.

Synthesis and electrocrystallization of 5-sulfonate-[4]helicene

Sulfonate groups are known for their lesser nucleophilic character compared to carboxylates. The synthesis of 5-sulfonate-[4]helicene 7 starts with the Wittig reaction of 2-naphthyl-methyltriphenylphosphonium bromide with 2-formylbenzenesulfonic acid sodium salt to yield 4 quantitatively (Scheme 2). Unfortunately, the photocyclisation of the sodium or tetrabutylammonium salts of 4 yielded an inseparable mixture of [4]helicene and benzo[a]anthracene sulfonate salts. The sulfonate group of 4 was therefore protected with 2,2,2-trifluoroethanol to yield 5 with a 50 % yield after transition through the acid chloride form of the sulfonic acid. Compound 5 was photocyclized in the presence of iodine and propylene oxide to generate the [4]helicene 6 with an 80% yield. Finally, the deprotection and generation of the tetrabutylammonium sulfonate salt 7 occurs smoothly and quantitatively through a saponification with TBAOH.

Electrocrystallizations have been performed with 7 as electrolyte and the TMTDF, TMTSF and BEDTTTF donors. In CH3CN, with a 1 µA current and TMTTF, dark crystals appeared on the anode after 4 days. (TMTTF)2([4]heliceneSO3)2 crystallized in the centrosymmetric P21/n space group, with two TMTTF donors and two helicenes counter-ions in the asymmetric unit (Figure 3). The lengths of the central carbon-carbon bonds of the two donors are 1.393(12) and 1.426(11) Å, which is in the expected range for a donor charge of +I, thus perfectly counterbalancing the two anionic charges. The structure consists in isolated stacks of four TMTTF molecules oriented along the b axis surrounded by [4]helicene moieties. The distances between two adjacent TMTTF are 3.38 and 3.56 Å. Both M and P isomers of the helicene are present in the structure, as expected from their low racemization barrier. The electrocrystallization of TMTSF with [4]heliceneSO3− occurred in a mixture of CH3CN and 1,1,2-trichloroethane at 35 °C with a 0.5 µA current over 11 days and provided dark small blocks along with a microcrystalline powder on the electrode. The structure displays a large P–1 triclinic unit cell of 6920 Å3, with five [4]heliceneSO3− anions and five TMTSF+ in the asymmetric unit, along with 2.5 molecules of CH3CN, a disordered thionyl chloride molecule, most likely generated upon partial decomposition of the sulfonate anion during the electrocrystallization (60% site occupancy), and a water molecule (29% occupancy) (Figure 4). Considering the 1:1 stoichiometry between the anion and the TMTSF, and the central bond length of TMTSF that are in the 1.36-1.39 Å range, a +1 oxidation state of every donor is inferred. Two different stacks of TMTSF+ are observed in the structure (Fig. 4). The first one implies four symmetrically non-equivalent molecules, surrounded by anions. The four molecules are separated by 3.4-3.5 Å for the external pairs, and 3.6 Å for the central pair. The molecular planes are not exactly parallel, with angles for the external pairs of 1.20 and 1.59°, while the two central TMTSF present a 0.53° angle. The second stack implies only two TMTSF+ separated by 3.48 Å that are symmetrically equivalent, and also surrounded by helicenic anions. The anions present both M and P helicities in the structure, with dihedral angles of 25.83, 24.55, 28.37, 29.46 and 24.31/20.00°. The latter angles

Figure 4. Crystal structure of (TMTSF)2([4]heliceneSO3)2, viewed along the a) z axis and b) b axis (red : TMTSF stacked by four ; violet : TMTSF stacked by two ; green : [4]heliceneSO3−, solvent and thionyl chloride molecules and hydrogen atoms have been omitted for the sake of clarity).

Figure 3. Crystal structure of (TMTTF)2([4]heliceneSO3)2, viewed along the a axis (red: TMTTF and green : [4]heliceneSO3−).
are observed on the same [4]helicene presenting a strong disorder arising from the presence of both M and P forms. Finally, electrocrystallization of 7 with BEDT-TTF in 1,1,2-trichloroethane at room temperature with a 1 μA current over one week yielded purple plates. X-ray analysis on single crystals revealed that the salt crystallized in the triclinic P-1 space group (Fig. 5). The asymmetric unit contains one [4]heliceneSO₃⁻ and two symmetrically non-equivalent BEDT-TTF moieties, in addition to a strongly disordered thionyl chloride molecule, and a site partially occupied by a water molecule (31% occupancy). The BEDT-TTF central bond length of 1.355(9) Å (hereafter donor A) and 1.369(8) Å (hereafter donor B) and the global charge of the counter-ion indicates that the +1 charge is quasi-equally shared between the two donors. According to the donors bond lengths, an approximate partial charge of +0.79 and +0.75 is estimated, meaning that both donors have a mixed valence state. Dimers are formed between two donors A and two donors B, separated by 3.614(7) Å and 3.395(7) Å respectively. The dimers A and B are connected laterally along the b axis through S-S interactions, with bond lengths in the 3.39-3.84 Å range. All of these dimer stacks are capped by [4]heliceneSO₃⁻ anions. Both P and M isomers are present and display the classical helicidal structure with a dihedral angle of 29.93°.

Conclusions

In conclusion, the synthesis and characterization of a new [4]helicene-sulfonate anion have been described. Its use as electrolyte in electrocrystallization experiments with various donors demonstrated its propensity to act as counter-ion in TTF based radical cation salts, in opposition to the helicene-carboxylate salts. Three novel radical cation salts have been obtained by electrocrystallization and characterized by X-ray diffraction on single crystals. The packing in the case of TMTTF and TMTSF does not display a long-range orbital overlap of the donors, making these materials very likely insulators, while in the case of BEDTTTF a long-range overlap of the donor molecules occurs. These results pave the way for further improvements when using helicenic anions for electrocrystallizations, along two main trends:

- the use of sulfonate salts over carboxylate as fully organic counter-ions,
- the extension of this method to larger helicenes whose configuration will be stable at room temperature, which is in preparation in our group.

Experimental

General procedures

All the solvents and precursors were commercially available and used without further purification. ¹H, ¹³C, ¹⁹F and 2D-NMR spectra were recorded on a Bruker Advance spectrometer operating at 300 MHz for ¹H, 76 MHz for ¹³C and 283 MHz for ¹⁹F. Chemical shifts are given in ppm relative to residual non-deuterated solvent as an internal standard and coupling constants J in Hz.

Mass spectra were obtained by the MALDI-TOF technique with a Bruker Biflex-IIITM apparatus, equipped with a 337 nm N₂ laser, or by electron impact methods using a Thermo Electron Corporation TRACE-DSQ apparatus. [4]helicene-methyl ester and [4]helicene-COOH were synthetized according to published literature procedures.

General procedure for forming the TBA⁺ salts. [4]helicene (1 mmol, 1eqiv.) is suspended in MeOH. A TBAOH solution (1M/MeOH, 1 equiv.) is added. The mixture turns clear within minutes and is evaporated to dryness after 1 hour at RT.

General procedure for electrocrystallizations.

Galvanostatic oxidation of a solution of the donor (8 μmol, anodic compartment) on a platinum wire electrode was performed in a U shaped cell with two compartments separated by a sintered glass membrane, in the presence of the electrolyte (ca. 25 μmol). ([4]heliceneCOO)₂{TMTTF} : CH₂CN, 20 °C, 1 μA for 6 days, 4 μA for 8 days. ([4]heliceneSO₃)₂{TMTTF} : CH₂CN, 20 °C, 1 μA for 5 days. ([4]heliceneSO₃)₂{TMTSF} : CH₂CN, 1,1,2-trichloroethane 10/1 v/v, 35 °C, 0.5 μA for 11 days. ([4]heliceneSO₃)₂{BEDTTTF} : 1,1,2-trichloroethane, 20 °C, 1 μA for 8 days.

Sodium 2-[(naphthalen-2-yl)vinyl]benzenesulfonate 4. 2-naphthyl-methyltriphenylphosphonium bromide (1.45 g, 3 mmol, 1 equiv.) was suspended in 15 mL of dry THF under an
argon atmosphere. The mixture was cooled down to -78°C and then nBuLi (2.1 mL, 2.5 M in hexane, 3.3 mmol, 1.1 equiv.) was added dropwise. After 30 min at -78°C, it was warmed to room temperature and stirred for one hour. The mixture was cooled down again to -78°C and sodium 2-formylbenzenesulfonate was added (0.62 g, 3 mmol, 1 equiv.). The mixture was stirred 10 minutes at -78°C, then warmed to room temperature and left at RT overnight. After filtration on Celite and concentration under vacuum, column chromatography (SiO₂, DCM : MeOH = 9:1 to 90:1) yielded 4 as an orange powder (quantitative, mixture of Z/E isomers). ¹H NMR (300 MHz, CDCl₃): δ (ppm). 8.23 (d, J = 16.3 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.88 (s, 1H), 7.83 – 7.72 (m, 5H), 7.47 – 7.35 (m, 3H), 7.20 (d, J = 16.3 Hz, 1H). MS (MALDI) m/z = 309.1, theor. calc. 309.1 (M-Na).

2-(2-(naphthalen-2-yl)vinyl) benzenesulfonate 5. Compound 4 (1 g, 3.01 mmol, 1 equiv.) was introduced in a Schlenk flask under inert atmosphere at 0°C and SOCl₂ (11 mL, 150 mmol, 50 equiv.) then DMF (5 mL) were added dropwise. After 30 minutes at 0°C the mixture was allowed to warm to room temperature and stirred for 4 hours. Ice (100 g), H₂O (100 mL) and finally HCl 10% (100 mL) were successively added to the reaction media, which was extracted with 200 mL of CH₂Cl₂. The organic phase was washed with H₂O (100 mL), brine (100 mL) and dried over MgSO₄ before being evaporated to dryness to yield the acid chloride intermediate as a yellow oily compound. It was poured back in CH₂Cl₂ (20 mL) at 0°C under inert atmosphere and 2,2,2-trifluoroethanol (240 mL, 330 mg, 3.3 mmol, 1.1 equiv.) followed by triethylamine (0.45 mL, 335 mg, 3.3 mmol, 1.1 equiv.) were added. The flask was kept at 0°C for 30 minutes and then stirred at room temperature for 18 hours. CH₂Cl₂ (100 mL) was added and the mixture was washed with H₂O (2 x 150 mL), dried over MgSO₄ and evaporated to dryness. Column chromatography (SiO₂, DCM) afforded 5 as an oily white compound (0.6 g, 51%, mixture of Z/E isomers).

¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.06 (m, 1H), 8.01-7.81 (m, 4H), 7.80 – 7.63 (m, 2H), 7.63 – 7.31 (m, 5H), 7.27 (s, 0.6H), 7.11 (m, 0.8H), 7.00 (d, J = 12.2 Hz, 0.5H), 4.46 (d, J = 10.0 Hz, 0.9 Hz, 0.9H), 4.36 (d,q., J = 10.0 Hz, 1.1H). ¹³C NMR (76 MHz, CDCl₃) δ (ppm) 138.47, 138.29, 134.84, 134.62, 134.33, 134.09, 133.71, 133.68, 133.55, 133.47, 133.44, 132.86, 132.70, 131.98, 130.45, 130.16, 128.97, 128.78, 128.39, 128.18, 128.05, 127.93, 127.81, 127.74, 127.57, 126.71, 126.65, 126.48, 126.43, 126.40, 124.00, 123.77, 65.03. ¹⁹F NMR (283 MHz, CDCl₃) δ (ppm) -73.60 (t, J = 8.5 Hz). MS (MALDI) m/z = 392.2, theor. calc. 392.1 (M+).

2-(2,2-trifluoroethyl) 4-sulfonate-[4]helicene 6. Compound 5 (0.60 g, 1.53 mmol, 1 equiv.) was dissolved in 700 mL of degassed toluene in a photoreactor. Iodine (0.43 g, 1.68 mmol, 1.1 equiv.) and propylene oxide (5.2 mL) were added and the mixture was irradiated with an immersion lamp (150 W) for 20 hours. After evaporation of the solvent and column chromatography (SiO₂, PE : CH₂Cl₂ : 9:1 to 0:1) compound 6 was obtained as a yellow oil (0.60 g, quant.).

¹H NMR (300 MHz, CDCl₃): δ (ppm) 9.47 (d, J = 8.6 Hz, 1H), 8.93 (d, J = 8.4 Hz, 1H), 8.72 (d, J = 9.0 Hz, 1H), 8.46 (d, J = 7.5 Hz, 1H), 8.19 – 8.08 (m, 2H), 8.05 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.5 Hz, 1H), 7.87 – 7.67 (m, 3H), 4.43 (q, J = 7.9 Hz, 2H). ¹³C NMR (76 MHz, CDCl₃) δ (ppm) 135.59, 133.90, 131.57, 130.91, 130.46, 130.15, 129.82, 129.66, 129.11, 129.08, 128.87, 127.91, 127.35, 126.87, 126.70, 126.36, 124.03, 122.61, 64.89 (q., J = 38.3 Hz).

Conflict of interest
There are no conflicts to declare.

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Notes and references