



HAL
open science

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

Nicolas Zigon, Narcis Avarvari

► To cite this version:

Nicolas Zigon, Narcis Avarvari. [4]Helicene based anions in electrocrystallization with tetrachalcogenafulvalene donors †. CrystEngComm, 2022, 24 (10), pp.1942-1947. 10.1039/D2CE00091A . hal-03855049

HAL Id: hal-03855049

<https://univ-angers.hal.science/hal-03855049v1>

Submitted on 16 Nov 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Nicolas Zigon*^a and Narcis Avarvari *^a

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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 tetramethyl-TTF (TMTTF), bis(ethylenedithio)-TTF (BEDT-TTF) and tetramethyl-tetraselenafulvalene (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.

Introduction

Chiral conducting materials present an increasing interest in the field of molecular conductors. The combination of chirality in a bulk conducting crystalline material may allow the observation of exotic effects such as the electrical Magneto-Chiral Anisotropy (eMChA) effect where the conductivity is influenced by a magnetic field applied parallel to the current direction. This effect was observed, for example, in bismuth helices,¹ carbon nanotubes,² or, more recently, in trigonal tellurium.³ Our team synthesized, by electrocrystallization, bulk crystalline chiral molecular conductors, based on a chiral tetrathiafulvalene (TTF) moiety, that displayed eMChA.⁴ In bulk crystalline conductors, chirality can be brought by the donor,^{5,6} the electrocrystallization solvent^{7,8} or the counter-anion. Concerning the latter, most of the reported examples rely on octahedral metal-based complex anions,^{9,10} where both Δ and Λ forms are present, or on the trisphate anion.^{11,12} This strategy is often prone to chirality inversion between Δ and Λ forms of the tris(chelated) octahedral anions, and the use of chiral ligands is therefore necessary.^{5,13,14} Moreover, Fourmigué *et al.* described the use of *D*-camphorsulfonate in combination with EDT-TTF-I₂,¹⁵ while, very recently, Martin *et al.* reported the electrocrystallization of chiral spiroborate anions with BDH-TTP, yielding a chiral metallic material down to 4.2 K.¹⁶

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.

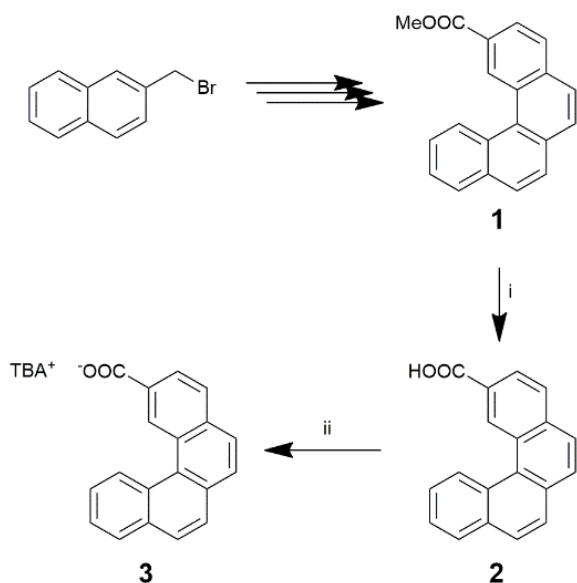
Results and discussion

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

^a Univ Angers, CNRS, MOLTECH-Anjou, SFR MATRIX, F-49000 Angers, France. E-mail: nicolas.zigon@univ-angers.fr ; narcis.avarvari@univ-angers.fr.

† Electronic Supplementary Information (ESI) available. CCDC 2142732–2142736. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x



phosphorylation, Wittig reaction with methyl 4-formylbenzoate and photocyclisation.²⁵ Saponification yielded **2** quantitatively.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 $\text{CHCl}_3/\text{MeOH}$ 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 π - π 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

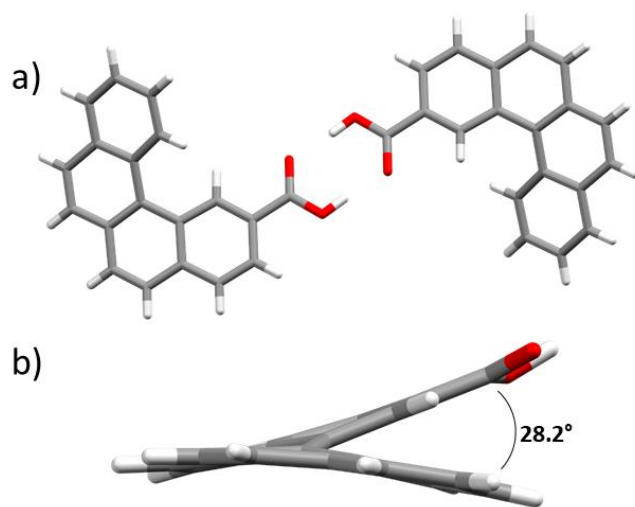


Figure 1. X-Ray structure of compound **2** with a view of a) the H-bonded dimer and b) the interplane angle of the helicenic scaffold (Carbon: grey; Oxygen: red; Hydrogen: white).

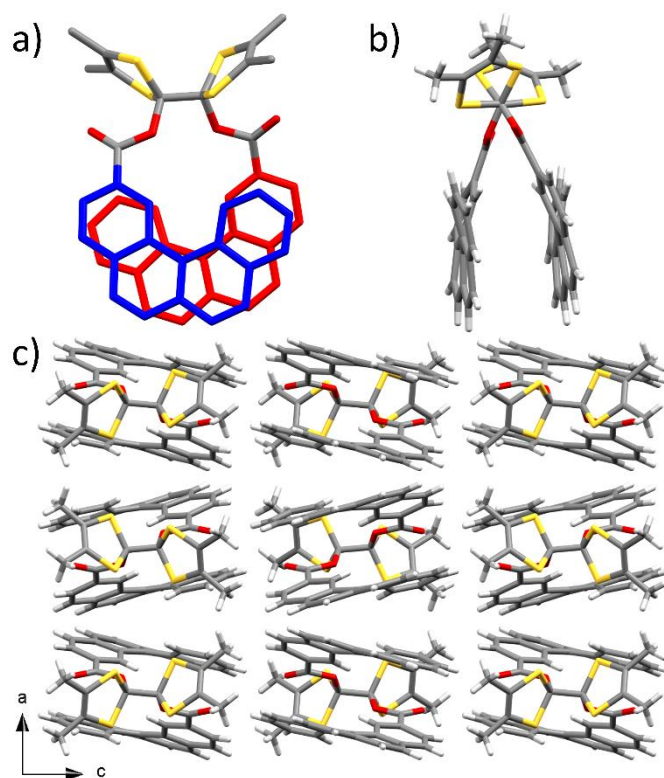
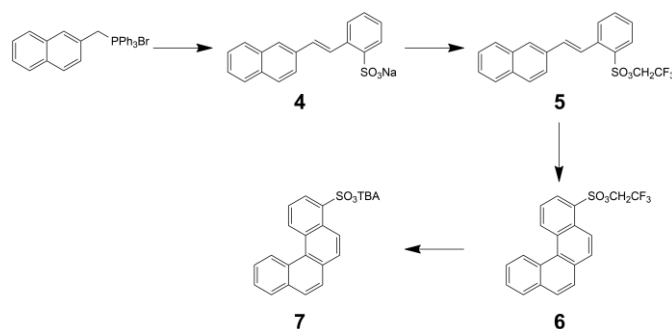


Figure 2. X-Ray structure of the adduct electrocrystallized from TMTTF and **2** with a) a front view of the adduct (the two helicene moieties are highlighted in blue and red), b) a side view of the adduct and c) packing along *b* (Carbon: grey; Oxygen: red; Sulfur: yellow; Hydrogen: white).

various solvents. While no crystals were observed with BEDT-TTF and TMTSF, dark crystals grew with TMTTF from CH_3CN at RT with a 2 μA current for 2 weeks. Structure resolution revealed that the obtained compound had the unexpected formula $\text{C}_{24}\text{H}_{17}\text{O}_2\text{S}_2$ 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 π 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 cycloadduct with *o*-chloranil.^{27,28} Electrocrystallization trials in the same conditions have been performed with aromatic



Scheme 2. Synthesis of 5-sulfonate-[4]helicene **7**.

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 TMTTF, TMTSF and BEDTTTF donors.

In CH_3CN , with a $1 \mu\text{A}$ current and TMTTF, dark crystals appeared on the anode after 4 days. $(\text{TMTTF})_2([\text{4]heliceneSO}_3)_2$ crystallized in the centrosymmetric $P2_1/n$ 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 +1, thus

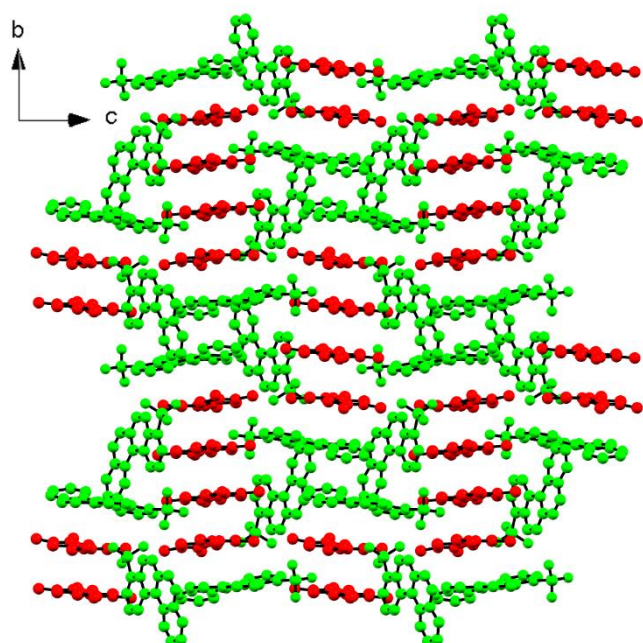


Figure 3. Crystal structure of $(\text{TMTTF})_2([\text{4]heliceneSO}_3)_2$ viewed along the a axis (red: TMTTF and green: [4]helicene SO_3).

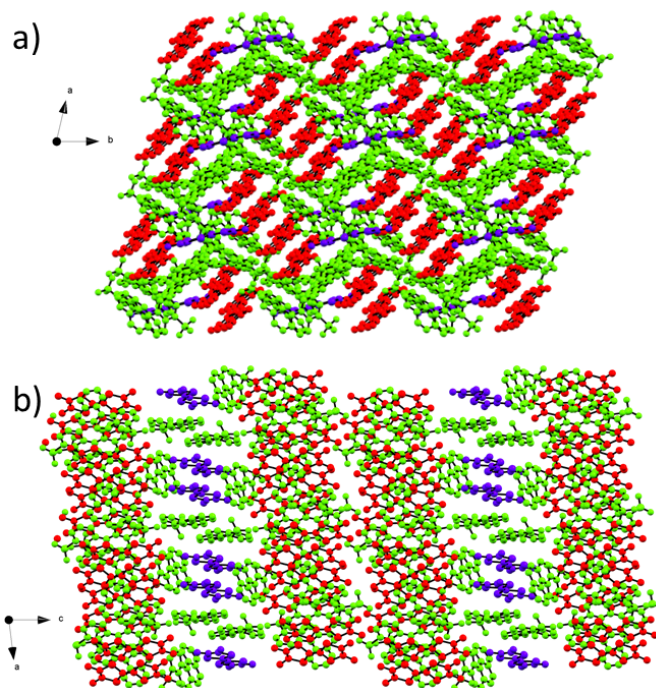


Figure 4. Crystal structure of $(\text{TMTSF})_5([\text{4]heliceneSO}_3)_5$ viewed along the a) c axis and b) b axis (red: TMTSF stacked by four; violet: TMTSF stacked by two; green: [4]helicene SO_3 , solvent and thionyl chloride molecules and hydrogen atoms have been omitted for the sake of clarity).

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]helicene SO_3^- occurred in a mixture of CH_3CN and 1,1,2-trichloroethane at 35°C with a $0.5 \mu\text{A}$ 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 \AA^3 , with five [4]helicene SO_3^- anions and five TMTSF^{2+} in the asymmetric unit, along with 2.5 molecules of CH_3CN , 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^{2+} 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^{2+} 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 $24.31/20.00^\circ$. The latter angles

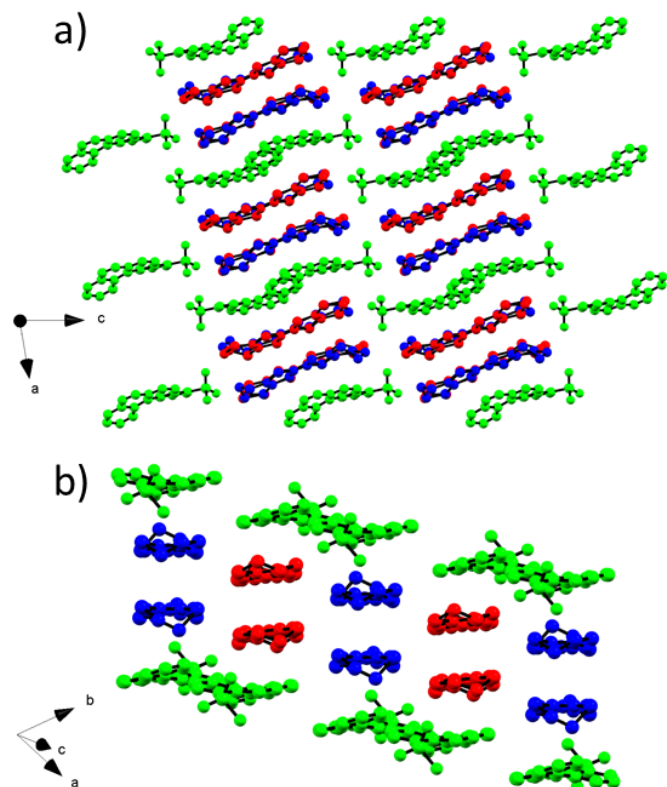


Figure 5. Crystal structure of $(\text{BEDT-TTF})_2([\text{4}]\text{heliceneSO}_3)$ viewed a) along the b axis and b) perpendicularly to the dimer stacks (red : BEDTTF B ; blue : BEDTTF A ; green : [4]heliceneSO₃; solvent molecules and hydrogen atoms have been omitted for the sake of clarity).

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 $P\bar{1}$ 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 lengths 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.²⁹ 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 helical 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 BEDTTF 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 Avance 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-IIIITM apparatus, equipped with a 337 nm N₂ laser, or by electron impact methods using a Thermo Electron Corporation TRACE-DSQ apparatus.

[4]helicene-methyl ester²⁵ and [4]helicene-COOH²⁶ were synthesized according to published literature procedures.

General procedure for forming the TBA⁺ salts. [4]helicene (1 mmol, 1equiv.) 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).

$([\text{4}]\text{heliceneCOO})_2\text{TMTTF}$: CH₃CN, 20 °C, 1 μA for 6 days, 4 μA for 8 days. $([\text{4}]\text{heliceneSO}_3)_2(\text{TMTTF})_2$: CH₃CN, 20 °C, 1 μA for 5 days. $([\text{4}]\text{heliceneSO}_3)_2(\text{TMTSF})_2$: CH₃CN/1,1,2-trichloroethane 10/1 v/v, 35 °C, 0.5 μA for 11 days. $([\text{4}]\text{heliceneSO}_3)(\text{BEDTTF})_2$: 1,1,2-trichloroethane, 20 °C, 1 μA for 8 days.

Sodium 2-(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 $n\text{BuLi}$ (2.1 mL, 2.5M 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 (SiO_2 , DCM : MeOH = 99:1 to 90:10) yielded **4** as an orange powder (quantitative, mixture of Z/E isomers). ^1H NMR (300 MHz, CDCl_3): 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).

(2,2,2-trifluoroethyl) 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 SOCl_2 (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), H_2O (100 mL) and finally HCl 10% (100 mL) were successively added to the reaction media, which was extracted with 200 mL of CH_2Cl_2 . The organic phase was washed with H_2O (100 mL), brine (100 mL) and dried over MgSO_4 before being evaporated to dryness to yield the acid chloride intermediate as a yellow oily compound. It was poured back in CH_2Cl_2 (20 mL) at 0°C under inert atmosphere and 2,2,2-trifluoroethanol (240 μL , 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. CH_2Cl_2 (100 mL) was added and the mixture was washed with H_2O (2 x 150 mL), dried over MgSO_4 and evaporated to dryness. Column chromatography (SiO_2 , DCM) afforded **5** as an oily white compound (0.6 g, 51%, mixture of Z/E isomers).

^1H NMR (300 MHz, CDCl_3): 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.q., $J = 10.2$ Hz, 0.9 Hz, 0.9H), 4.36 (d.q., $J = 10.2$ Hz, 1.1H). ^{13}C NMR (76 MHz, CDCl_3) 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. ^{19}F NMR (283 MHz, CDCl_3) 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 (SiO_2 , PE : CH_2Cl_2 9:1 to 0:1) compound **6** was obtained as a yellow oil (0.60 g, quant.).

^1H NMR (300 MHz, CDCl_3): 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). ^{13}C NMR (76

MHz, CDCl_3) 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). ^{19}F NMR (283 MHz, CDCl_3) δ (ppm) -73.56 (t, $J = 7.9$ Hz). HRMS (MALDI) $m/z = 390.0528$, theor. calc. 390.05320 (M+).

4-sulfonate-[4]helicene tetrabutylammonium salt 7. This compound was synthesized according to the general procedure. ^1H NMR (300 MHz, CDCl_3): δ (ppm). ^{13}C NMR (76 MHz, CDCl_3) δ (ppm) 143.85, 133.43, 130.75, 130.41, 130.23, 129.99, 129.63, 128.54, 127.99, 127.47, 127.19, 126.83, 126.79, 126.64, 126.06, 125.72, 125.50, 124.34, 58.42, 23.82, 19.57, 13.61. HRMS (MALDI) $m/z = 307.0429$, theor. calc. 307.04344 (M-TBA⁻).

Author Contributions

N.Z. synthesized the compounds, performed the electrocrystallization of the materials and the X-Ray measurements, N.Z. and N.A. supervised the project and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The CNRS and the University of Angers are acknowledged for their financial support. Magali Allain (Moltech-Anjou) is warmly acknowledged for helpful discussions and comments on the X-ray structures and Clara Pasgrimaud (Moltech-Anjou) and Cécile Mézière (Moltech-Anjou) for their assistance in the synthesis.

Notes and references

- G. L. J. A. Rikken, J. Fölling and P. Wyder, *Phys. Rev. Lett.*, 2001, **87**, 236602.
- V. Krstić, S. Roth, M. Burghard, K. Kern, and G. L. J. A. Rikken, *J. Chem. Phys.*, 2002, **117**, 11315–11319.
- G. L. J. A. Rikken and N. Avarvari, *Phys. Rev. B*, 2019, **99**, 245153.
- F. Pop, P. Auban-Senzier, E. Canadell, G. L. J. A. Rikken and N. Avarvari, *Nat Commun*, 2014, **5**, 3757.
- N. Avarvari and J. D. Wallis, *J Mater Chem*, 2009, **19**, 4061–4076.
- F. Pop, N. Zigon and N. Avarvari, *Chem. Rev.*, 2019, **119**, 8435–8478.
- L. Martin, H. Akutsu, P. N. Horton and M. B. Hursthouse, *CrystEngComm*, 2015, **17**, 2783–2790.
- L. Martin, H. Akutsu, P. N. Horton, M. B. Hursthouse, R. W. Harrington and W. Clegg, *Eur. J. Inorg. Chem.*, 2015, **2015**, 1865–1870.
- P. Day and M. Kurmoo, *J. Mater. Chem.*, 1997, **7**, 1291–1295.
- C. J. Gómez-García, E. Coronado, S. Curreli, C. Giménez-Saiz, P. Deplano, M. L. Mercuri, L. Pilia, A. Serpe, C. Faulmann and E. Canadell, *Chem. Commun.*, 2006, 4931–4933.
- M. Clemente-León, E. Coronado, C. J. Gómez-García, A. Soriano-Portillo, S. Constant, R. Frantz and J. Lacour, *Inorg. Chim. Acta*, 2007, **360**, 955–960.

- 12 F. Riobé, F. Piron, C. Réthoré, A. M. Madalan, C. J. Gómez-García, J. Lacour, J. D. Wallis and N. Avarvari, *New J. Chem.*, 2011, **35**, 2279–2286.
- 13 E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García, A. Murcia-Martínez and E. Canadell, *Inorg. Chem.*, 2004, **43**, 8072–8077.
- 14 N. P. Chmel, L. E. N. Allan, J. M. Becker, G. J. Clarkson, S. S. Turner and P. Scott, *Dalton Trans.*, 2011, **40**, 1722–1731.
- 15 M. Brezgunova, K.-S. Shin, P. Auban-Senzier, O. Jeannin and M. Fourmigué, *Chem. Commun.*, 2010, **46**, 3926–3928.
- 16 T. J. Blundell, M. Brannan, H. Nishimoto, T. Kadoya, J. Yamada, H. Akutsu, Y. Nakazawa and L. Martin, *Chem. Commun.*, 2021, **57**, 5406–5409.
- 17 K. Dhbaibi, L. Favereau, M. Srebro-Hooper, C. Quinton, N. Vanthuyne, L. Arrico, T. Roisnel, B. Jamoussi, C. Poriel, C. Cabanetos, J. Autschbach and J. Crassous, *Chem. Sci.*, 2020, **11**, 567–576.
- 18 C. Maeda, K. Nagahata, T. Shirakawa and T. Ema, *Angew. Chem. Int. Ed.*, 2020, **59**, 7813–7817.
- 19 Y. Shen and C.-F. Chen, *Chem. Rev.*, 2012, **112**, 1463–1535.
- 20 M. Gingras, *Chem. Soc. Rev.*, 2013, **42**, 1051–1095.
- 21 T. Biet, T. Cauchy, Q. Sun, J. Ding, A. Hauser, P. Oulevey, T. Burgi, D. Jacquemin, N. Vanthuyne, J. Crassous and N. Avarvari, *Chem. Commun.*, 2017, **53**, 9210–9213.
- 22 A. Abhervé, K. Martin, A. Hauser and N. Avarvari, *Eur. J. Inorg. Chem.*, 2019, **2019**, 4807–4814.
- 23 M. Savchuk, S. Vertueux, T. Cauchy, M. Loumaigne, F. Zinna, L. D. Bari, N. Zigon and N. Avarvari, *Dalton Trans.*, 2021, **50**, 10533–10539.
- 24 T. Biet, A. Fihey, T. Cauchy, N. Vanthuyne, C. Roussel, J. Crassous and N. Avarvari, *Chem. – Eur. J.*, 2013, **19**, 13160–13167.
- 25 H. Guédouar, B. Ben Hassine and F. Aloui, *C R Chim.*, 2019, **22**, 310–315.
- 26 Y. Zhang, J. L. Petersen and K. K. Wang, *Tetrahedron*, 2008, **64**, 1285–1293.
- 27 C. Kwang-Fu Shen, H. M. Duong, G. Sonmez and F. Wudl, *J. Am. Chem. Soc.*, 2003, **125**, 16206–16207.
- 28 F. Pop, J. Lacour and N. Avarvari, *Rev. Roum. Chim.*, 2012, 457–462.
- 29 P. Guionneau, C. J. Kepert, G. Bravic, D. Chasseau, M. R. Truter, M. Kurmoo and P. Day, *Synth. Met.*, 1997, **86**, 1973–1974.