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Journal:	<i>ChemComm</i>
Manuscript ID	CC-COM-12-2019-009960.R1
Article Type:	Communication

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Manuscripts

COMMUNICATION

Received 00th January
20xx,

Interdigitated conducting tetrathiafulvalene-based coordination networks

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Assembly of a novel ethylenedithio-tetrathiafulvalene (EDT-TTF) derivative bearing two adjacent 4-thiopyridyl groups with M(NCS)₂ nodes (M = Fe, Co) leads to two isostructural 1D coordination polymers showing an enhancement of their electronic conductivity by six orders of magnitude (10⁻⁶ vs 10⁻¹² S/cm), upon surface oxidation by iodine and subsequent generation of EDT-TTF-based radicals.

Owing to their crystallinity and porosity, Metal-Organic Frameworks (MOFs) and Coordination Polymers (CPs)¹ have emerged as an interesting class of hybrid materials with development in diverse fields such as gas sorption and storage,² catalysis³ or sensing,⁴ for example. Interestingly, the well-defined and robust structure of MOFs is, in most cases, constructed by assembly of non-redox-active organic ligands with hard metal cations with a poor orbital overlap and thus no favourable pathway for charge transport. Therefore, the vast majority of MOFs consists of electrically insulating frameworks. The quest for conducting architectures thus represents a current challenge that has triggered intense research,⁵ fuelled by potential electrochemical or energy-related applications.⁶ Three main mechanisms have been identified and promoted to prepare such conducting porous coordination polymers: by introduction of guest molecules/dopants,⁷⁻⁸ by through-bond⁹ or through-space^{10,11} conduction. In the latter case, charge delocalization occurs via an appropriate overlap of the organic components of the network. In this context, the choice of redox-active ligands and the control of their relative arrangement

while retaining porosity of the crystalline material are essential. Recently, a particular emphasis has been put on the use of tetrathiafulvalene (TTF) derivatives for the construction of MOFs,^{12,13} in light of their capacity to reversibly form a stable radical cation and to be readily functionalized by coordinating groups.¹⁴ This has led to the development of some conducting MOFs^{8,10} showing a favourable stacking of the partially oxidized sulfur-rich moieties. However, design strategies to obtain MOFs featuring an organization of the redox-active core akin to the one observed in reported metallic and superconducting TTF-based charge transfer salts,¹⁵ to promote a transport pathway, while forming porous networks, remain to be fully developed and exploited. Whereas interpenetration¹⁶ has been explored to favour a closer packing of organic fragments of MOFs within crystals, interdigitation¹⁷ appears as an appealing alternative approach that has not been pursued in the development of electron conducting systems, to the best of our knowledge. Indeed, one can envision that coordination networks of lower dimensionality (1 or 2D) bearing pendant redox-active fragments known to stack may result in a 3D arrangement in the crystal featuring an organization of the electro-active moieties adequate for conductivity upon oxidation, along with potential porosity. For example, as proposed herein, dissymmetrical ligands comprising, on one hand, coordinating units, and, on the other hand, an extended sulfur-rich core are expected to form 1D coordination networks bearing peripheral TTF cores prone to interdigitation¹⁸ in the crystalline state (Fig. 1). It is foreseen that partial oxidation of the crystalline networks may lead to the promotion of a charge transport pathway and hence to conducting materials.

We report here on the successful application of this strategy using ligand **1** (Fig. 2) and its assembly with M(NCS)₂ (M = Fe, Co) nodes to form interdigitated architectures by stacking of TTFs. The conductivity of these materials has been studied in both their native - as synthesized - form and upon oxidation with iodine, showing a dependence on the doping of the crystals.

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Electronic Supplementary Information (ESI) available: Synthesis and analytical data for the **1**, **4**, **5**, EDX and conductivity measurements of native and oxidized CPs and crystallographic data CCDC 1973791-1973793. See DOI: 10.1039/x0xx00000x

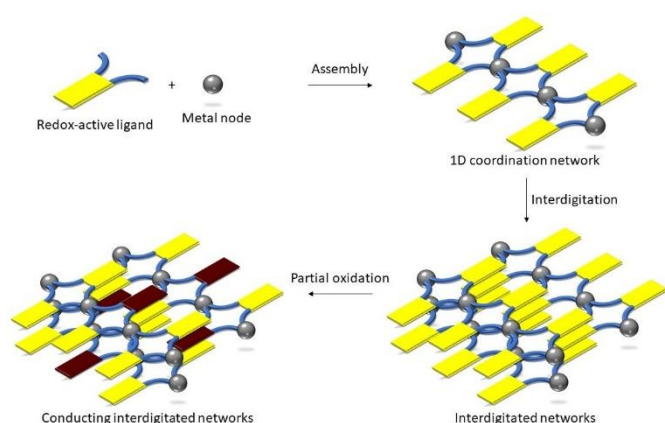


Fig. 1. Schematic representation of the construction strategy proposed for the formation of conducting MOFs by interdigitation of coordination polymers bearing pendant electro-active cores.

Ligand **1** (Fig. 2) has been designed to incorporate an ethylenedithio-tetrathiafulvalene core (EDT-TTF) functionalized by two adjacent 4-thiopyridine groups. The choice of the EDT-TTF moiety and of sulfur-bridged peripheral units was motivated by the enhanced capacity of such species to stack upon increasing the number of sulfur atoms.¹⁸ The two coordinating groups were introduced on the same side of the molecule to favour the formation of coordination networks bearing pendant redox-active fragments, as desired.

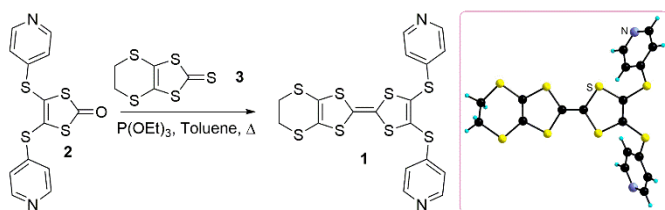


Fig. 2. Synthesis of **1** and its crystal structure determined by X-ray diffraction.

Compound **1** was prepared in 28 % yield by cross coupling with $P(OEt)_3$ of dithiolone **2**¹⁹ with dithiolthione **3**²⁰ (Fig. 2). The compound was characterized in solution by ¹H- and ¹³C-NMR and UV-visible spectroscopies, by high-resolution mass spectrometry and single-crystal X-ray diffraction (Monoclinic, $P2_1/c$) (see ESI for details). The electrochemical properties of **1** were characterized by cyclic voltammetry in CH_2Cl_2 solution (Fig. ESI 4). As expected for such an EDT-TTF derivative, two reversible oxidation processes could be observed ($E_{1/2}^1 = 0.20$ V and $E_{1/2}^2 = 0.55$ V vs Fc/Fc^+).

Upon slow diffusion of an EtOH solution of $M(NCS)_2$ into a $CHCl_3$ solution of **1**, crystals of the two isostructural networks (**1**)₂ $M(NCS)_2(CHCl_3)_3$ ($M = Co, \mathbf{4}; Fe, \mathbf{5}$) were obtained (Monoclinic, space group $C2/c$). The structure of the Co network **4** is presented in Fig. 3. The metal cation is in an octahedral environment, bound to two thiocyanate anions in apical positions ($d_{M-N} = 2.078(3)$ Å for **4**, 2.110(3) Å for **5**) while four pyridine groups belonging to four different bridging molecules of **1** occupy the square base ($d_{M-N} = 2.201(3), 2.205(3)$ Å for **4**, 2.241(3), 2.250(3) Å for **5**). This leads to a one-dimensional coordination network along the c axis, with metal cations

separated by 10.10 Å within the chain (Fig. 3). The CC and CS bond distances within the central TTF core are similar to the ones observed in the structure of free **1** ($d_{C=C} = 1.345(2)$ for **1**; 1.337(4) for **4**; 1.333(4) Å for **5**) and the EDT moiety is more bent with respect to the central TTF unit in the networks than in the free ligand (12.91° for **1** vs 34.27 and 34.36° for **4** and **5** respectively). This suggests that the electro-active core is neutral in the networks, as confirmed by EPR (*vide infra*). Interestingly, in the crystals, the networks interdigitate by stacking of the sulfur-rich cores along the b axis with $d_{S\dots S}$ varying from 3.513(1) to 3.598(1) Å for **4** and from 3.530(1) to 3.600(1) Å for **5** (Fig. 3). These contacts between consecutive TTFs involve alternatively the sulfur atoms of two central cores or of the thiopyridyl groups and the central unit (Fig. 3). The stacking results in the formation of 1D channels along the b axis, occupied by $CHCl_3$ molecules, thus separating TTF stacks. Our initial attempts at investigating the porosity of the materials have showed a decomposition upon thermal activation at $80^\circ C$, resulting in a small specific surface (6 m²/g, BET).

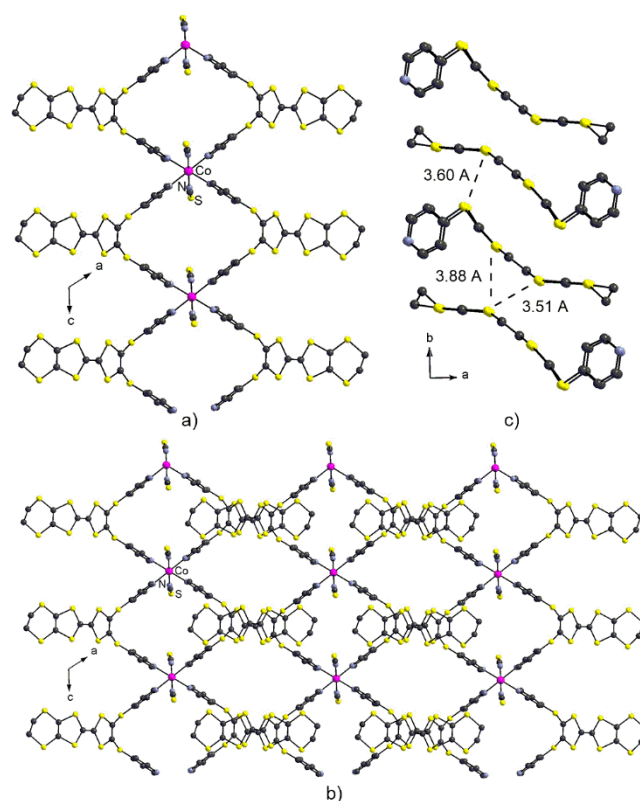


Fig. 3. One-dimensional coordination network in the crystal structure of network **4** (a), view of the interdigitated arrangement (b) and EDT-TTF stack along the b axis (c). Hydrogen atoms and $CHCl_3$ molecules have been omitted for clarity. The positional disorder of the ethylenedithio group is also not shown.

While the organization of the electro-active cores within the crystals for **4** and **5** (Fig. 3c) is analogous to what is observed in TTF-based charge transfer salts,¹⁸ the presence of oxidized TTFs in radical form is also a prerequisite to conductivity in these systems.²¹ The EPR signature of radical cation **1**^{•+} was obtained by exposure of a powder sample of compound **1** to I_2 vapour and consists in a signal centred at 350 mT and with $g_{iso} = 2.006$

(Fig. 4a) as expected for such species.²² EPR spectra collected on native networks **4** or **5** showed only the EPR signature of the Co and Fe coordination polymers (see Fig. ESI 6 and 7), thus emphasizing the absence of the EPR signal of the cation radical **1^{•+}**. This contrasts with reports on TTF-based MOFs for which the solvothermal conditions used for the synthesis induced a partial oxidation of the ligands and hence the presence of organic radicals.¹⁰ It may be explained by the softer crystallization conditions employed here (liquid-liquid diffusion at room temperature) as well as by the nature of the TTF derivative itself; EDT-TTFs are harder to oxidize than tetraphenyl-appended TTF species.²³

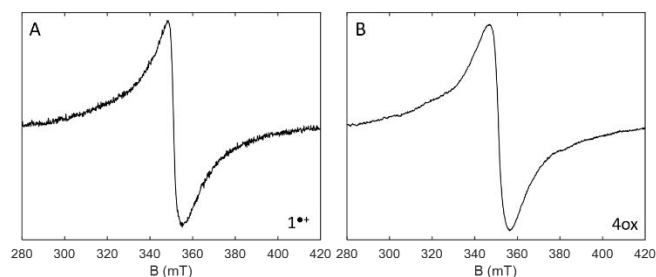


Fig. 4. Room temperature X-band EPR spectra : a) polycrystalline powder of **1** upon exposure to I_2 vapor showing the **1^{•+}** signature b) signal associated to **1^{•+}** observed at room temperature, upon leaving polycrystalline powder of **4** in a $CHCl_3$ solution of I_2 (0.05 M) for 3 hours (right).

The post-synthetic formation of radicals in the materials was then explored. As for the free ligand, iodine was considered as oxidant, since it is compatible with the redox characteristics of **1** and it has been used in the literature for the oxidation of other TTF- and dithiolene-based MOFs.⁸ While exposure of crystals of **4** and **5** to I_2 vapour led to the appearance of the EPR signature of radical **1^{•+}**, a loss of crystallinity of the materials could be observed. Oxidation in solution was therefore considered as an alternative. Crystals of **4** and **5** were left to stand in a $CHCl_3$ solution of I_2 [0.05 M] for several hours leading to a darkening of the crystal faces (see Fig. ESI 5 for photographs of the crystals throughout the oxidation process). Once again, partial oxidation was confirmed by the presence of the EPR signature of **1^{•+}** (Fig. 4b for **4** and Fig. ESI 7b for **5**).

Powder X-ray diffraction indicated that the samples remained crystalline with retention of the original structure throughout the oxidation process (Fig. 5). Data collection on single crystals of network **4** exposed to I_2 [0.05 M] for 3 hours could be performed, allowing the structure determination of the oxidized samples. Interestingly, in the channels formed by stacking of the coordination polymers, the presence of $CHCl_3$ was observed but residues associated with iodide-based anions could not be clearly identified. A similar phenomenon has been recently reported for a TTF/TCNQ based MOF where no inclusion of iodine could be observed.^{13h} This suggests that formation of radicals is taking place solely at the surface of the materials. This has been confirmed by EDX analysis with a SEM demonstrating the presence of iodine in a uniform fashion at the surface of oxidized crystals of **4** and **5** (Fig. ESI 8 and 9).

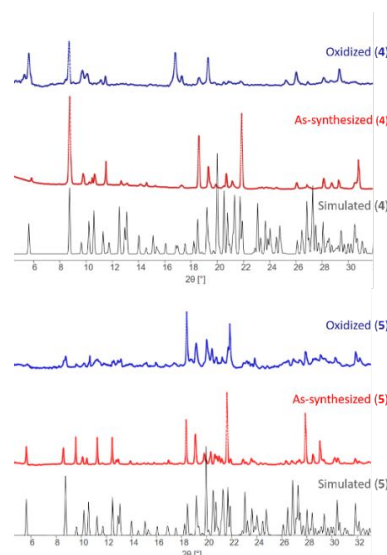


Fig. 5. X-Ray powder patterns of **4** (top) and **5** (bottom): simulated from single-crystal data (in black), obtained from as-synthesized material (in red) and upon treatment with a 0.05 M of I_2 solution in $CHCl_3$ (in blue). Difference in peak intensity result from preferential orientation.

Conductivity measurements were performed on pressed-pellets and single-crystals of networks **4** and **5**, in both their native and oxidized forms (Fig. ESI 10-12). For both as-synthesized materials, a room-temperature conductivity below 10^{-13} S/cm indicating an insulating behaviour was measured in either form (single-crystal and pressed pellets). Upon exposure to I_2 , the conductivity measured on single-crystals reached 10^{-6} - 10^{-7} S/cm highlighting the positive effect of the formation of radicals. Surprisingly, no orientation effect could be observed. The value of conductivity was indeed similar, when measured along the stacking direction of the TTF cores or perpendicularly. Slightly higher conductivities were measured on pressed pellet samples ($\sigma_{\text{average}} = 1.1 \times 10^{-5}$ S/cm for **4**). This may be explained by the larger surface area/volume ratio of the samples used for the pellet measurements. Indeed, since the pellets are composed of smaller particles on average than for the single-crystal studies, there may be more iodine incorporation and a higher doping level with a doping limited to the surface. In conclusion, the assembly of a novel EDT-TTF derivative bearing two adjacent 4-thiopyridyl groups with $M(NCS)_2$ nodes ($M = Fe, Co$) has led to two isostructural 1D coordination polymers featuring a stacking of the pendant sulfur-rich cores. While the as-synthesized materials include neutral TTFs as demonstrated by EPR measurements and are insulating, treatment with iodine in solution resulted in surface oxidation and hence appearance of organic radicals inducing an enhancement of the electronic conductivity by six orders of magnitude (10^{-6} vs 10^{-12} S/cm). The foregoing results show that interdigitation/stacking of coordination of networks of lower dimensionality followed by post-synthetic oxidation is an effective approach for the elaboration of conducting systems. Future work will aim at exploring other TTF derivatives, modulating their acceptor character and stacking by modification of the EDT moiety, as well as the elaboration of porous materials.

Conflicts of interest

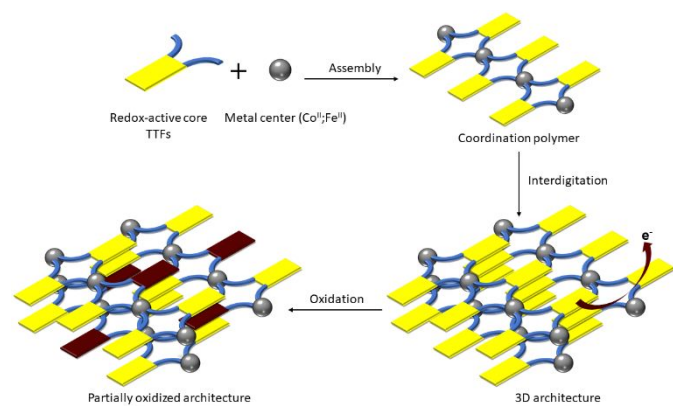
There are no conflicts to declare.

Acknowledgements

We thank the Université de Strasbourg, the C.N.R.S., the International centre for Frontier Research in Chemistry (icFRC), the Labex CSC within the Investissement d'Avenir program ANR-10-IDEX-0002-02 (Ph. D. fellowship to D. B.) and the Ministère de l'Enseignement Supérieur, de la Recherche et de l'Innovation for financial support, E. Devaux for EDX analysis and B. Louis and R. Amaral for BET analysis. Work in the Dincă lab (L. S. X. and M. D.) was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (DE-SC0018235). L. S. X. thanks the National Science Foundation for support through the Graduate Research Fellowship Program (1122374).

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Graphical abstract The electronic conductivity of two isostructural interdigitated coordination polymers based on a novel tetrathiafulvalene derivative and M(NCS)₂ nodes (M = Fe, Co) is enhanced upon surface oxidation by iodine.