



Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Functional coordination polymers based on redox-active tetrathiafulvalene and its derivatives

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ARTICLE INFO

Article history:

Received 31 August 2016
 Received in revised form 22 October 2016
 Accepted 28 October 2016
 Available online xxxx

Keywords:

Coordination polymers
 Redox-active
 Tetrathiafulvalenes
 Porous materials
 Molecular conductors

ABSTRACT

This review article focuses on the development of coordination polymers based on tetrathiafulvalene and its derivatives. We aim to demonstrate novel opportunities for these coordination polymers in terms of their architectures and potential applications. The review is presented in five general sections according to the type of coordinating functional group in the organic linkers. Synthetic approaches, structural analyses, as well as physical and chemical properties are presented for each example. Valuable potential applications and perspectives for these novel materials are also discussed.

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Abbreviations: CP, coordination polymer; MOFs, metal-organic frameworks; PCPs, porous coordination polymers; TTF, tetrathiafulvalene; IPCT, ion pair charge-transfer; MV, methyl viologen; DMF, *N,N*-dimethylformamide; H₂trioTTF, 2-(5, 6, 8, 9, 11, 12, 14, 15-octahydro-[1,3]dithiolo[4,5-*h*][1,4,13,7,10]trioxadithiacyclopentadecin-2-ylidene)-1,3-dithiole-4,5-dicarboxylic acid; H₂DMDC-TTF, 4',5'-bis(methylthio)-[2,2'-(1,3-dithiolyldiene)]-4,5-dicarboxylic acid; H₄TTFc, tetrathiafulvalene tetracarboxylic acid; H₄TTFB, tetrathiafulvalene tetrabenzoic acid; HT, high-throughput; SCSC, single-crystal-to-single-crystal; DPNI, *N,N*-di-(4-pyridyl)-1,4,5,8-naphthalenetetracarboxyldiimide; SEC, spectroelectrochemistry; EDT-TTFpy, 4-(4'-pyridylmethylsulfanyl)-4',5'-ethylenedithiotetrathiafulvalene; TTF(py)₂, 2,9-bis(4-pyridyl)tetrathiafulvalene; tta, thenoyltrifluoroacetate; TTF(py)₄, tetra(4-pyridyl)-tetrathiafulvalene; LBT-TTF, bis(TTF-1,2,3-triazole)-lutidine; H₂TTFbp, *N*-(2-(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)-5-(picolinamido)benzo[d][1,3]dithiol-6-yl)picolinamide; TTF-salphen, 2,2'-(2-(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)-1,3-benzodithiole-5,6-diyl)bis(nitrilomethylidene)bis(phenolate); salen, *N,N*-ethylenebis(salicylideneimine) dianion; AF, antiferromagnetic; 2,2'-bpy, 2,2'-bipyridine; 4,4'-bpy, 4,4'-bipyridine; bpe, 1,2-bis(4-pyridine)ethylene; phen, 1,10-phenanthroline; bpa, 1,2-bis(4-pyridine)ethane; AC, 9-anthracenecarboxylate; salphen, *N,N*-1,2-diphenylethylene-bis(salicylideneiminato) dianion; TTC₂-TTF, tetrakis(ethylthio)tetrathiafulvalene; TMT-TTF, tetrakis(methylthio)tetrathiafulvalene; TTC₃-TTF, tetrakis(propylthio)tetrathiafulvalene; BEDT-TTF, bis(ethyleneedithio)tetrathiafulvalene; FP-TRMC, flash photolysis-time-resolved microwave conductivity; VCD, vibrational circular dichroism; SCM, single-chain magnets; SCO, spin-crossover; tces-TTF, 2,3,6,7-tetra(cyanoethylsulfanyl); CM-TTF, 2-[4,5-bis(methylsulfanyl)-1,3-dithiol-2-ylidene]-4,5-bis(2-cyanoethylsulfanyl)-1,3-dithiole; MOS, metalorganic surface; LLCT, ligand-to-ligand charge-transfer.

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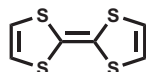
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1. Introduction

Coordination polymers (CPs) are intriguing metal–organic hybrid materials. In CPs, metal ions or metal-containing clusters act as nodes, and organic ligands act as spacers, both of which are linked via coordination bonds to form one-, two- or three-dimensional extended structures [1,2]. When (permanent) porosity is present, CPs are referred to as either metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) [3,4]. The design and study of multifunctional CPs possessing multiple accessible properties has attracted enormous attention owing to their potential applications in a plethora of areas, including sensing, solar energy harvesting, and energy storage, etc. [5–7]. One of the key advantages of CPs is their structural modularity which can be designed according to targeted physical and chemical properties by combining metal ions and organic ligands with appropriate geometries and functionalities [8–10]. Realizing the coexistence or cooperativity between the desired properties is still a major challenge for chemists working in this area.

Functional CPs can be rationally designed by using organic ligands with certain desirable properties such as redox activity. A promising candidate is tetrathiafulvalene (TTF, $C_6H_4S_4$, Scheme 1), which has been well studied as a critical component of conductive and optoelectronic materials [11–14]. TTF is a sulfur-rich conjugated molecule with two reversible and easily accessible oxidation processes to its radical cation (TTF^{•+}) and dication (TTF²⁺) states. With TTF derivatives as ligands, redox-active and redox-switchable CPs may be realized [15,16]. Owing to the electron-rich character of TTF, which renders it a good electron donor, numerous organic charge transfer compounds incorporating the TTF core have been investigated for their potential application in electrochromic materials, electrocatalysis and photoconductive switches [17–19]. In addition, TTF moieties can form $\pi \cdots \pi$ stacked columns with relatively short S \cdots S interactions, which have been shown to facilitate efficient pathways for charge transport [20–23]. Recent studies have shown TTF-based CPs to exhibit high electrical conductivity or high charge mobility – properties which are highly desirable in new electronic materials towards applications in semiconductor and/or optoelectronic devices [9,14,24]. If conductivity is combined with the added virtue of porosity of MOFs, TTF-supported CPs could find uses in fields outside traditional areas such as gas storage and separation, including batteries, supercapacitors and electrochemical sensors [25,26]. Moreover, the incorporation of magnetic spins such as paramagnetic ions with electrochemically-active TTF units allows for the development of novel multifunctional materials such as magnetic semiconductors or magnetic conductors that have potential applications in spintronics [27–30]. Taken together, the two highly



Scheme 1. Structure of TTF.

reversible electron oxidation processes, and the well characterized electrochemical and spectral properties make TTF-based complexes attractive motifs for multifunctional materials.

Herein, we provide an overview of TTF-based CPs constructed from the most recurrent transition metals – namely copper, manganese, zinc, cadmium, cobalt, calcium, magnesium silver and iron – that have been prepared and characterized in the past two decades. The review is presented in five sections according to the type of coordinating functional groups in the organic linkers. For each compound, the synthesis, major structural features, and, whenever investigated, its functional properties are presented. Valuable potential applications and perspectives on these novel materials are also discussed. For the sake of legibility, all of the materials described are collected in Table 1.

2. Overview of TTF-based linkers

The important characteristics of TTF-based linkers are rigidity, the number and orientation of binding sites (coordination numbers and coordination geometries), the relative distance(s) between the coordinating functionalities, and the nature of the functionalities present (i.e., the presence of additional heteroatoms, aromatic rings, alkyl chains). In order to promote the construction of materials which have infinite expansion in three dimensional coordination space, the ligands must be multidentate with at least two coordination sites. Finally, the ligands can be symmetric, asymmetric and/or chiral, which give rise to a vast array of coordination modes and topologies. Common TTF-based organic molecules or building blocks which are discussed in this review are shown in Fig. 1, and the auxiliary ligands are shown in Fig. 2.

3. TTF-carboxylates

3.1. TTF-dicarboxylates

Direct coordination of TTF carboxylates to paramagnetic metal ions has proven to be a favorable strategy for constructing new CPs with multiphysical properties. The cobalt coordination polymer containing a TTF-dicarboxylate ligand, $\{[Co_2(trioTTF)_2(H_2O)_6] \cdot 5H_2O\}_n$ (**1**) (trioTTF = 2-(5,6,8,9,11,12,14,15-octahydro-[1,3]dithiol o[4,5-h][1,4,13,7,10]trioxadithiacyclopentadecin-2-ylidene)-1,3-dithiole-4,5-dicarboxylate) was reported and exhibits a 1D structure with interchain S \cdots S interactions between trioTTF units at a distance of 3.565 Å (Fig. 3) [31]. The carboxylate groups bridge Co(1) and Co(2) via a η^2 -COO[−] coordination mode which gives rise to the 1D chain structure. Due to the weak interchain S \cdots S and $\pi \cdots \pi$ interactions between the trioTTF groups, as well as the neutral oxidation state of TTF moieties, the room temperature conductivity of the compound is $2.9 \times 10^{-10} S \cdot cm^{-1}$ which is in the range for insulators. The magnetic properties of compound **1** were indicative of ferromagnetic interactions between the intrachain Co^{II} centers below 16 K, likely facilitated by π -d interactions between the metal ions and trioTTF linkers. Due to limited magnetic ordering in **1** between 300 and 225 K, no appreciable magnetic effect on

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