



A spectroscopic and electrochemical investigation of a tetrathiafulvalene series of metal–organic frameworks

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ABSTRACT

The series of tetrathiafulvalene (TTF)-based metal–organic frameworks (MOFs) $[M_2(\text{TTFTB})(\text{H}_2\text{O})_2]$ ($M = \text{Zn}, \text{Mn}, \text{Co}, \text{Cd}$; TTFTB = tetrathiafulvalene tetrabenzoate), previously reported to have radical character, have been characterised by electrochemical and spectroscopic techniques to elucidate their electronic properties. The intimate columnar arrangement of the TTF ligands coupled with their low oxidation potential gives rise to radical–radical interactions and intervalence charge transfer between mixed-valence pairs of ligands within the framework structures. These interactions are further promoted in $[\text{Zn}_2(\text{TTFTB})(\text{H}_2\text{O})_2]$ (**Zn**) by chemical oxidation with I_2 which lowers the optical band gap from 2.03 eV to 1.23 eV and increases the conductivity from $2.5(2) \times 10^{-10} \text{ S/cm}$ in **Zn** to $1.6(2) \times 10^{-9} \text{ S/cm}$ in its iodine-doped derivative ($\text{I}_2@$ **Zn**). This study highlights the importance of combined electrochemical and spectroscopic interrogations of electroactive MOFs towards understanding the origins of their optical and electronic properties.

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1. Introduction

Tetrathiafulvalene (TTF) has been widely employed as a component of CT complexes such as the highly conductive organic charge transfer complex tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) [1], and more recently, as a building block in coordination polymers and metal–organic frameworks (MOFs) [2–5]. Its non-innocent, π -electron donating nature endows materials with unique magnetic and conducting behaviours, and in numerous cases, the capacity to undergo redox switching [4].

Work by Dincă and coworkers reported the MOF $[\text{Zn}_2(\text{TTFTB})(\text{H}_2\text{O})_2]$ (**Zn**) which incorporated the TTF-based ligand tetrathiafulvalene tetrabenzoate (TTFTB) and demonstrated a charge mobility higher than that of organic conductors such as polyphenylene-vinylenes and polythiophenes ($0.2 \text{ cm}^2/\text{V}\cdot\text{s}$ vs. $0.01\text{--}0.1 \text{ cm}^2/\text{V}\cdot\text{s}$) [2]. A family of isostructural Co, Mn, and Cd analogues demonstrated an important structure–property relationship whereby an increase in metal cation size led to a reduction in the intermolecular S...S stacking distances and, subsequently, higher intrinsic conductivities in the framework [3]. Interestingly, flash photolysis-time-resolved microwave conductivity (FP-TRMC) measurements found these materials to be hole conductors. This was

supported by the detection of the TTFTB radical cation *via* electron paramagnetic resonance (EPR) spectroscopy, despite the frameworks being “charge neutral” (no counterions were found in the structure to accommodate for the TTFTB radical cation). The origins of the ligand radical, however, remained elusive and the redox activity of these materials is still unexplored. A particularly interesting prospect is the possibility of switching the optical and electronic properties through redox-state modulation of either the TTF ligand or the metal components.

To investigate the redox and optical properties of the series of framework materials $[M_2(\text{TTFTB})(\text{H}_2\text{O})_2]$ ($M = \text{Zn}, \text{Mn}, \text{Co}$ and Cd , hereafter abbreviated to **Zn**, **Mn**, **Co** and **Cd**, respectively), the present work probes these properties *via* a suite of solid-state techniques, namely: electrochemistry, vis–NIR spectroelectrochemistry (SEC), Raman and EPR spectroscopy. Electrochemical and spectral studies on the frameworks were compared closely with the H_4 -TTFTB ligand itself both in the solution and solid state. The micro-porous nature of these frameworks, which is afforded by hexagonal channels down the crystallographic *c*-axis, opens up the possibility of host–guest interactions, including oxidation using chemical oxidants. Thus, we set out to investigate the oxidation of **Zn** with I_2 vapour to give $\text{I}_2@$ **Zn**, as a strategy to the enhance conductivity [6–8].

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2. Materials and methods

2.1. Tetrathiafulvalene tetrabenzoic acid (H_4TTFTB)

The ligand H_4TTFTB was synthesised via an adaptation of literature methods [2,9]. A mixture of $Pd(OAc)_2$ (84 mg, 0.38 mmol), P ($t\text{-Bu}$) $_3BF_4$ (326 mg, 1.1 mmol), and $CsCO_3$ (2.44 g, 7.5 mmol) in degassed dioxane (25 mL) was refluxed for 30 min under N_2 . To this mixture, TTF (307 mg, 1.5 mmol) and ethyl-4-bromobenzoate (1.72 g, 7.5 mmol) were added, and refluxed for 18 h under N_2 . The mixture was extracted with CH_2Cl_2 (3×100 mL) and dried over $MgSO_4$. CH_2Cl_2 was removed under reduced pressure to yield a dark red/brown residue. The crude material was purified via flash column chromatography (silica, CH_2Cl_2 and eluted with ethyl acetate) to give the methyl ester as a dark red solid which was used without further purification.

The methyl ester was dissolved in a 1:1 solution of methanol and THF degassed under N_2 , and to this solution NaOH (717 mg, 18.0 mmol) was added. The mixture was refluxed under N_2 for 12 h, and a precipitate of Na_4TTFTB was obtained as an orange solid. The solid was filtered, washed with methanol and redissolved in H_2O (10 mL). To this solution, concentrated HCl was added dropwise with vigorous stirring to precipitate H_4TTFTB as a dark purple solid. The product was isolated via vacuum filtration and washed with water to yield a dark purple powder. Yield: 0.51 g, 50%. 1H NMR (200 MHz, d_6 -DMSO): 7.35 (d, $J = 0.042$, 8H), 7.87 (d, $J = 0.042$, 8H), 13.15 (br, 4H).

2.2. $[M_2(TTFTB)(H_2O)_2]$ ($M = Zn, Mn, Co, Cd$)

Crystals of $[M_2(TTFTB)(H_2O)_2]$ were synthesised via an adaptation of literature methods [2]. The appropriate metal salt (0.19 mmol) and H_4TTFTB were separately dissolved in 1:1 H_2O /ethanol (2.8 mL) and 3:1 DMF/ethanol (2.8 mL) mixtures, respectively. The solutions of H_4TTFTB and metal salt were combined and the mixture was heated in a sealed screw capped vial at 65 °C for 72 h. Dark red/orange tablet-shaped crystals formed from the dark red solution. Metal salts employed were $Zn(NO_3)_2 \cdot 6H_2O$, $MnCl_2 \cdot 2H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $Cd(NO_3)_2 \cdot 4H_2O$.

2.3. Oxidation of $[Zn_2(TTFTB)(H_2O)_2]$ with I_2

As-synthesised $[Zn_2(TTFTB)(H_2O)_2]$ (50 mg) was placed into a small 2 mL uncapped vial which was subsequently placed within a larger vial containing a few crystals of iodine. The larger vial was sealed and the crystals of $[Zn_2(TTFTB)(H_2O)_2]$ were allowed to oxidise over 5 days, yielding a black powder $I_2@Zn$. The small vial was removed from the iodine chamber and allowed to sit uncapped to allow the evaporation of crystallised I_2 .

2.4. Powder X-ray diffraction (PXRD)

Powder X-ray diffraction data were obtained using a PANalytical X'Pert PRO Diffractometer employing non-monochromated $Cu\text{-}K\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation and equipped with a solid-state PIXcel detector. Diffraction patterns from dry powdered samples were collected on a rotating stage over the range $2\theta = 5\text{--}50^\circ$ using a step size of 0.013° and scan speed of $0.033^\circ/s$.

2.5. Thermogravimetric analysis (TGA)

TGA experiments were performed on a TA Instruments Discovery TGA. Approximately 3–5 mg of material was loaded into a platinum pan and heated from room temperature to 600 °C at a ramp

rate of $2^\circ/\text{min}$. Analyses were performed under a constant flow of N_2 at a rate of 10 mL/min.

2.6. Inductively-coupled plasma–mass spectrometry (ICP–MS)/optical emission spectrometry (ICP–OES)

MOFs were analysed by ICP–MS and ICP–OES at the Solid State & Elemental Analysis Unit at the Mark Wainwright Analytical Centre, University of New South Wales, Sydney, Australia. For I determination, samples were digested with tetramethylammonium hydroxide and analysed by ICP–MS whilst, for the determination of Zn, samples were digested with HNO_3 and HCl and analysed by ICP–OES.

2.7. Solid state UV–vis–NIR spectroscopy

Solid state UV–vis–NIR spectroscopy was performed on a CARY5000 spectrophotometer equipped with a Harrick Praying Mantis attachment. Samples were prepared in a dry $BaSO_4$ matrix and spectra were collected in the range $5000\text{--}40\,000\text{ cm}^{-1}$ at a scan rate of $6000\text{ cm}^{-1}/\text{min}$.

2.8. Diffuse reflectance infrared Fourier transform (DRIFTS) spectroscopy

IR spectra were collected using a Bruker Tensor 27 FTIR spectrometer. Samples were ground in a dry KBr matrix and spectra were measured over the range $4000\text{--}400\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} and averaged over 16 accumulations.

2.9. Confocal Raman spectroscopy

Raman spectra were obtained using a Renishaw Raman inVia Reflex Spectrometer equipped with a Leica DMLM microscope. Excitation lasers of wavelength 785 and 514 nm were employed. Data were processed using the *wiRE*TM software.

2.10. Electron paramagnetic resonance (EPR) spectroscopy

Continuous wave (CW) X-band EPR measurements were collected on a Bruker EMXnano bench-top spectrometer. Samples were loaded into quartz tubes and spectra were obtained at room temperature. The general parameters utilised were: microwave frequency, 9.645 GHz; modulation frequency, 100 kHz; modulation amplitude, 1.0 G; gain, 47–60 dB resolution, 1024 points. Attenuation was adjusted for each sample to minimise saturation. Spectra were simulated using the EasySpin [10] package in MATLAB.

2.11. Electrochemistry

DC cyclic voltammetry (CV) was performed using a BASi Epsilon Electrochemical Analyser potentiostat in a three-electrode cell setup. The electrodes employed were a glassy carbon working electrode, a Pt wire auxiliary electrode, and an Ag/Ag^+ quasi-reference electrode. The electrolyte was degassed under a flow of high purity Ar for 5 min prior to measurements. Solution state CV of H_4TTFTB was performed by dissolving the ligand into 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$)/DMF electrolyte. Solid MOF samples were mechanically immobilised onto the surface of the glassy carbon working electrode and CVs were collected in 0.1 M $TBAPF_6/CH_3CN$ electrolyte. Ferrocene was added as an internal reference at the conclusion of each experiment, and potentials were referenced to the ferrocene/ferrocenium (Fc/Fc^+) couple.

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