# SUPPORTING INFORMATION

# Bis(vinylenedithio)-tetrathiafulvalene based coordination networks

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# **SUMMARY**

Figure S1.Solid-state CV curves of 1- CdCl<sub>2</sub>, 1-ZnCl<sub>2</sub>, 1-CuCl<sub>2</sub>crystal powder.

Figure S2. (a) PXRD spectra of 1-CuCl<sub>2</sub>(b) Theoretical PXRD spectrum of 1-CuCl<sub>2</sub>.

Figure S3. (a) PXRD spectra of 1-CdCl<sub>2</sub>(b) Theoretical PXRD spectrum of 1-CdCl<sub>2</sub>.

Figure S4. (a) PXRD spectra of 1-HgCl<sub>2</sub>(b) Theoretical PXRD spectrum of 1-HgCl<sub>2</sub>.

**Figure S5**. Raman spectra of  $1^+$ -CdCl<sub>2</sub>-l<sub>3</sub>-measured at room temperature with the 632.8 nm excitation line, in the frequency range of the stretching polyiodide modes.

**Table S1**.Oxidation potential,  $E_{pa}$ , and reduction potential,  $E_{pc}$ , of **1**, **1**-CuCl<sub>2</sub>, **1**-ZnCl<sub>2</sub>,**1**-CdCl<sub>2</sub> and **1**-HgCl<sub>2</sub>. WE : glassy carbon plate, RE: Ag wire, CE: Pt wire.

Table S2. Crystallographic data, details of data collection and structure refinement parameters.

**Table S3.** Experimental polyiodide frequencies in  $cm^{-1}$  observed in Raman spectra of (BVDT-TTF-Py4)(CdCl<sub>2</sub>)(I<sub>3</sub>).

Cyclic voltammograms of 1-CdCl<sub>2</sub>, ZnCl<sub>2</sub>, CuCl<sub>2</sub>



**Figure S1.** CV curve of **1-** CdCl<sub>2</sub>, ZnCl<sub>2</sub>, CuCl<sub>2</sub>crystal powder with Nafion. WE/GCE RE: Ag/AgCl/KCl<sub>sat</sub>,. CE: Pt wire. CV profiles were obtained at 50 mV s<sup>-1</sup> scan rate.

**Table S1.** Oxidation potential, E<sub>pa</sub>, and reduction potential, E<sub>pc</sub>, of **1**, **1**-CuCl<sub>2</sub>, **1**-ZnCl<sub>2</sub>,**1**-CdCl<sub>2</sub> and **1**-HgCl<sub>2</sub>. WE : glassy carbon plate, RE: Ag wire, CE: Pt wire.

	E <sub>pa</sub> (V)	E <sub>pc</sub> (V)
BVDTTF(py)₄ in solution	0.665	0.575
BVDTTF(py) <sub>4</sub> in solid state	0.75	0.61
BVDTTF(py) <sub>4</sub> (CuCl <sub>2</sub> ) in solid state	0.66	0.40
BVDTTF(py) <sub>4</sub> (HgCl <sub>2</sub> ) in solid state	0.74	0.62
BVDTTF(py) <sub>4</sub> (CdCl <sub>2</sub> ) in solid state	0.73	0.62
$BVDTTF(py)_4$ (ZnCl <sub>2</sub> ) in solid state	0.77	0.63

#### X-Ray structure determinations

Details about data collection and solution refinement are given in Table S1. Data collections were performed on a Rigaku Oxford Diffraction SuperNova diffractometer equipped with an Atlas CCD detector and micro-focus Cu-K<sub>a</sub> radiation ( $\lambda = 1.54184$  Å). The structures were solved by intrinsic phasing and refined on F<sup>2</sup> by full matrix least-squares techniques with SHELX programs (SHELXT 2018/2 and SHELXL 2018/3)<sup>1,2</sup> using the ShelXle and the Olex2 graphical user interfaces.<sup>3,4</sup> All non-H atoms were refined anisotropically and absorption was corrected by multiscan empirical absorption using spherical harmonics with CrysAlisPro program for 1-CuCl<sub>2</sub>, 1-ZnCl<sub>2</sub>,1-CdCl<sub>2</sub>and1-HgCl<sub>2</sub>. The H atoms were placed at calculated positions and refined using a riding model. Crystallographic data for the five structures have been deposited with the Cambridge Crystallographic Data Centre, deposition numbers CCDC for 1-CuCl<sub>2</sub> : 2203496; 1-ZnCl<sub>2</sub> : 2203494 ;1-CdCl<sub>2</sub>: 2203493; 1-HgCl<sub>2</sub>: 2203497; 1-CdCl<sub>2</sub>-l<sub>3</sub> : 2203495.These data can be obtained free of charge from CCDC, 12 Union road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

	<b>1-</b> CuCl <sub>2</sub>	1-ZnCl <sub>2</sub>	1-CdCl <sub>2</sub>	<b>1-</b> HgCl <sub>2</sub>	1-CdCl <sub>2</sub> -I <sub>3</sub>
Formula	0.5 (C <sub>30</sub> H <sub>16</sub> CuCl <sub>2</sub> N <sub>4</sub> S <sub>8</sub> ), CHCl <sub>3</sub>	0.5 (C <sub>30</sub> H <sub>16</sub> ZnCl <sub>2</sub> N <sub>4</sub> S <sub>8</sub> ), CH <sub>2</sub> Cl <sub>2</sub> , 0.5(CH <sub>3</sub> OH)	0.5 (C <sub>30</sub> H <sub>16</sub> CdCl <sub>2</sub> N <sub>4</sub> S <sub>8</sub> ), CH <sub>2</sub> Cl <sub>2</sub>	0.5 (C <sub>30</sub> H <sub>16</sub> CdCl <sub>2</sub> N <sub>4</sub> S <sub>8</sub> ), CH <sub>2</sub> Cl <sub>2</sub> , 0.35(CH <sub>3</sub> OH)	0.5 (C <sub>30</sub> H <sub>16</sub> CdCl <sub>2</sub> N <sub>4</sub> S <sub>8</sub> , I <sub>3</sub> )
Formula weight	531.06	505.29	521.05	575.91	626.47
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P21/c	P21/c	P21/c	P21/c	<i>C</i> 2/m
a/Å	12.7692(6)	12.8519(2)	13.1301(15)	13.0601(3)	16.216(6)
b/Å	9.5235(5)	9.6095(2)	9.5611(10)	9.7826(2)	9.725(3)
c/Å	16.6155(8)	15.9424(3)	16.1205(12)	16.0640(3)	12.885(5)
α/°	90	90	90	90	90
β/°	90.673(4)	94.469(2)	94.781(8)	95.873(2)	94.80(3)
γ/°	90	90	90	90	90
V/ų	2020.43(17)	1962.91(6)	2016.7(3)	2041.59(7)	2024.9(13)
Z	4	4	4	4	4
D <sub>c</sub> /g cm <sup>-3</sup>	1.746	1.710	1.716	1.874	2.055
т/к	288(14)	150.00(10)	200.00(10)	150.00(10)	150.01(10)
µ/mm⁻¹	9.773	8.892	12.127	14.485	27.581
Reflectionscollected	8362	8295	6561	9841	1934
Independent reflection	3819[R <sub>int</sub> = 0.0359]	3780[R <sub>int</sub> = 0.0287]	3501[R <sub>int</sub> = 0.0888]	4192[R <sub>int</sub> = 0.0.0324]	1124[R <sub>int</sub> = 0.1519]
final $R_1^a$ , $wR_2^b [l > 2\sigma(l)]$	0.0435/0.1108	0.0440/0.1149	0.1091/0.2851	0.0354/0.0936	0.2114/0.5038
$R_1^a$ , $wR_2^b$ (all data)	0.0631/0.1240	0.0486/0.1188	0.1647/0.3488	0.0391/0.0985	0.2265/0.5198
goodness-of-fit on F <sup>2</sup>	1.026	1.045	1.065	1.029	1.738
$\Delta ho_{ extsf{min}}/\Delta ho_{ extsf{max}}$ (eÅ-3)	-0.474/0.619	-1.658/2.130	-1.298/3.624	-2.302/0.934	-1.941/5.536
Completeness (%)	98.5	99.9	96.7	99.9	97.3
CCDC numbers	2203496	2203494	2203493	2203497	2203495

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. {}^{b}wR_{2} = [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}]^{1/2}; w = 1 / [\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP] where P = [max(F_{o}^{2}, 0) + 2F_{c}^{2}] / 3.$ 

PXRD



Figure S2. (a) PXRD spectra of 1-CuCl<sub>2</sub>(b) Theoretical PXRD spectrum of 1-CuCl<sub>2</sub>



Figure S3.(a) PXRD spectra of 1-CdCl<sub>2</sub>(b) Theoretical PXRD spectrum of 1- CdCl<sub>2</sub>



Figure S4. (a) PXRD spectra of 1-HgCl<sub>2</sub>(b) Theoretical PXRD spectrum of 1- HgCl<sub>2</sub>

## **Raman Setup**

Theoretical calculations of normal vibrational modes for **1** as an isolated molecule were performed with Gaussian 0323 using the standard 6-31++G(d,p) basis set and the hybrid density functional (B3LYP). The initial geometry used in calculations was prepared based on the experimental X-ray data. The result of the structure optimization corresponds to energy minima since no imaginary frequencies were found.On the basis of optimized structure, vibrational frequencies as well as Raman scattering activities were calculated. The frequencies computed with a quantum harmonic oscillator approximation tend to be higher than experimental ones. So that the scaling factor 0.9614 has been applied.[5]

Crystalline samples selected for Raman measurements were between 0.1 and 0.2 mm in length. Raman spectra in the range 1100 – 1700 cm<sup>-1</sup> were measured at room temperature using Renishaw inVia Raman microscope equipped with a thermoelectrically (TE)-cooled CCD detector and semiconductor laser emitting light in near-infrared region at 785 nm wavelength. Low-frequency Raman spectra were measured at room temperature in a backward scattering geometry with a LABRAM HR800 Raman spectrometer equipped with a microscope and a He-Ne  $\lambda$ =632.8 nm laser line. The spectral resolution of Raman measurements was better than 2 cm<sup>-1</sup>, and the power was reduced to about 0.3 mW to avoid sample overheating.

**Figure S5** displays Raman spectra of coordination polymer that contain triiodide ions, **1**-(CdCl<sub>2</sub>)(I<sub>3</sub>) in the frequency range of the stretching polyiodide modes. The spectra is characterized by three distinct features (**Table S3**). The band centred at 111 cm<sup>-1</sup> is attributed to the Raman-active symmetric stretching  $v_s(I_3^-)$  mode of the centrosymmetric triiodide anion with the symmetry  $D_{ih}$ . The middle feature at ~144 cm<sup>-1</sup> assigned to asymmetric stretch  $v_a(I_3^-)$  mode, reveals the presence of the asymmetric triiodide with the symmetry lower than  $D_{ih}$ .[6] On the other hand, the highest-frequency band at 167 cm<sup>-1</sup>, is most probably related with the presence of iodine I<sub>2</sub> weakly coordinated to triiodide, resulting in an appearance of L-shaped pentaiodide in the structure. Therefore, we attribute the 167 cm<sup>-1</sup> band to a symmetric stretching  $v_s(I_5^-)$  mode of pentaiodide.[6,7]



**Figure S5.** Raman spectra of  $1^+$ -CdCl<sub>2</sub>-l<sub>3</sub>-measured at room temperature with the 632.8 nm excitation line, in the frequency range of the stretching polyiodide modes; the spectra are offset for clarity.

**Table S3.** Experimental polyiodide frequencies in  $cm^{-1}$  observed in Raman spectra of (BVDT-TTF-Py4)(CdCl<sub>2</sub>)(I<sub>3</sub>).

	(BVDT-TTF-Py4) (CdCl <sub>2</sub> )(l <sub>3</sub> )
$\nu_{s}(I_{3})$	111
$\nu_a(I_3)$	~144
$\nu_{s}(I_{5})$	~167

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