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Neutral coordination polymers based on a metal—mono(dithiolene) complex: synthesis, crystal structure and supramolecular chemistry of [Zn(dmit)(4,4'-bpy)]<sub>n</sub>, [Zn(dmit)(4,4'-bpe)]<sub>n</sub> and [Zn(dmit)(bix)]<sub>n</sub> (4,4'-bpy = 4,4'-bipyridine, 4,4'-bpe = *trans*-1,2-bis(4-pyridyl)ethene, bix = 1,4-bis(imidazole-1-ylmethyl)-benzene†

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This article describes a unique synthetic route that enables a neutral mono(dithiolene)metal unit,  $\{Zn(dmit)\}$ , to link with three different organic molecules, resulting in the isolation of a new class of neutral coordination polymers. The species  $\{Zn(dmit)\}$  coordinates with 4,4'-bipyridine (4,4'-bpy), *trans*-1,2-bis(4-pyridyl)ethene (4,4'-bpe) and 1,4-bis(imidazole-1-ylmethyl)-benzene (bix) as linkers giving rise to the formation of coordination polymers  $[Zn(dmit)(4,4'-bpy)]_n$  (1),  $[Zn(dmit)(4,4'-bpe)]_n$  (2) and  $[Zn(dmit)(bix)]_n$  (3) respectively. Compounds 1–3 were characterized by elemental analyses, IR, diffuse reflectance and single crystal X-ray diffraction studies. Compounds 1 and 3 crystallize in the monoclinic space group  $P2_1/n$ , whereby compound 2 crystallizes in triclinic space group  $P\overline{1}$ . In the present study, we chose three linkers 4,4'-bpy, 4,4'-bpe and bix (see Schemes 1–3, respectively, for their structural drawings), that differ in terms of their molecular dimensions. The crystal structures of compounds 1–3 are described here in terms of their supramolecular diversities that include  $\pi-\pi$  interactions, not only among aromatic stacking (compounds 1 and 3), but also between an aromatic ring and an ethylenic double bond (compound 2). The electronic absorption spectroscopy of compounds 1–3 support these intermolecular  $\pi-\pi$  interactions.

## Introduction

Investigation of self-assembled coordination polymers containing transition metal complex ions and organic bridging ligands has been carried out by numerous researchers because of their potential applications as functional solid state materials and also their inherent visual appeal.<sup>1</sup> Dithiolene complexes are attractive building blocks for such coordination polymer systems because of their aromaticity and facile reduction propensity. Pickup and coworkers reported on a dithiolene-based conjugated metallopolymer prepared by the electrochemical polymerization of bis[*cis*-1,2-di(2'-thienyl)-1,2-ethenedithiolene]nickel.<sup>2a</sup> Later on, they showed that a complex with one thiophene substituent on each dithiolene ligand[*cis*-1-(2'-thienyl)-2-phenyl-1,2-ethenedithiolene] results in a polymer with electrochemistry characteristic of a coordination polymer.<sup>2b</sup> Wang and Reynolds described a series of coordination

polymers containing nickel bis(dithiolene) complexes that are highly soluble in a number of solvents in the as-made reduced (dianionic) form.<sup>3</sup> A one dimensional coordination polymer, based on a differentiated bischelate-type ligand bearing both 4,5diazafluorene and dithiolene units, has been reported.<sup>4</sup> Duval and co-workers reported a honeycomb network polymer in which the monomeric units, comprising the trigonal nodes, are knitted together by interlocking dative Na-N bonds extended from nitrile groups of bifunctional mnt ligands coordinated through the sulfur atoms to adjacent cerium centers.<sup>5</sup> One dimensional coordination polymers, formed from sodium-crown ether supramolecular cationic complexes and [Ni(*i*-mnt)<sub>2</sub>]<sup>2-</sup> complex anions, have been described by Long, Haung and coworkers.<sup>6</sup> Rovira and co-workers reported an interesting 2D layered coordination polymer based on an unusual mixed valence Cu(III)/Cu(I) bis-1,2-diselenolene complex.<sup>7a</sup> They described a Cu(III) bis-1,2-diselenolene complex with a highly extended 3D framework through Na<sup>+</sup> coordination.<sup>7b</sup> Kuroda-Sowa and coworkers have described a system  $(NBu_{4}^{n})_{2}[M(mnt)_{2}Cu_{4}I_{4}]$  (M = Ni, Pd, Pt), in which a  $Cu_4I_4$  ring is supported by an M(mnt)<sub>2</sub> moiety, two cyano groups out of the four of which coordinate to two Cu(I) ions in neighboring molecules, resulting in the formation of a unique doubly-bridged one-dimensional chain-like

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Tables of complete bond distances and angles for compounds **1–3** and X-ray crystallographic files in CIF format for compounds **1–3**. CCDC reference numbers 824385–824387. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10814j

structure.<sup>8</sup> Very recently, Takaishi and co-workers have reported an electroconductive coordination polymer Cu[Cu(pdt)<sub>2</sub>] (pdt = 2,3-pyrizinedithiolate) composed of donor and acceptor building units.<sup>9</sup> Fourmigué and team have demonstrated the attractive ability of the CN moieties in the [Ni(tfadt)<sub>2</sub>]<sup>2-,•-</sup> (tfadt = 2-(trifluoromethyl)acrylonitrile-1,2-dithiolate) complexes to coordinate metallic cationic centers resulting in heterobimetallic chainlike structure.<sup>10</sup> The coordination polymers, based on zinc-triad 1,1-dithiolates {ZnN<sub>2</sub>S<sub>2</sub>}, are known; in this context, it worth mentioning that unlike the compounds of 1,1-dithiolate ligands, 1,2-dithiolene-ligated complexes are more conjugated than 1,1dithiolates.<sup>11</sup>

The above described dithiolene-based polymers are mostly ionic coordination polymers that are synthesized by chemical synthesis, except the electrochemical polymerization of bis[cis-1,2-di(2'-thienyl)-1,2-ethenedithiolene]nickel.<sup>2</sup> We are interested to synthesize neutral coordination polymers (based on metaldithiolene coordination complexes) because neutral coordination polymers offer possibilities to develop new functional materials.<sup>12</sup> In order to synthesize metal-dithiolene-based neutral coordination polymers, we chose dmit<sup>2-</sup> dithiolate, 1,3-dithiole-2-thione-4,5-dithiolate, which has been used extensively in metal coordination chemistry.<sup>13</sup> To the best of our knowledge, there is no report of a coordination polymer that is constructed from a metal mono(dmit) complex [M<sup>II</sup>(dmit)], which is basically a neutral species. There are two reports of ionic coordination polymers based on [M<sup>II</sup>(dmit)<sub>2</sub>]<sup>2-</sup> complexes.<sup>14</sup> Keeping in mind the fact that  $[M^{II}(dmit)]$  is a neutral species, we have chosen three neutral organic linkers, namely three diimine molecules, 4,4'-bipyridine (4,4'-bpy), trans-1,2-bis(4-pyridyl)ethene (4,4'-bpe) and 1,4-bis(imidazole-1-ylmethyl)-benzene (bix). Even though this class of compounds [M(diimine)(dithiolate)] has largely been investigated based on their electronic structures and photoluminescence studies,15-17 they have never been obtained/isolated as coordination polymers  $[M(diimine)(dithiolate)]_{\alpha}$ . We report here neutral coordination polymers  $[Zn(dmit)(4,4'-bpy)]_n$  (1),  $[Zn(dmit)(4,4'-bpe)]_n$  (2) and  $[Zn(dmit)(bix)]_n$  (3) (4,4'-bpy = 4,4'bipyridine, 4,4'-bpe = trans-1,2-bis(4-pyridyl)ethane, bix = 1,4bis(imidazole-1-ylmethyl)-benzene)), that are formed by neutral building block  $[M^{II}(dmit)]$  and neutral linker to obtain diverse architectures ranging from a zig-zag-type chain to curved-type (concavo-convex) chain depending on the choice and shape of the linker. We describe the crystal structures of 1–3 in detail, stressing their supramolecular diversities based on  $\pi$ - $\pi$  intermolecular interactions.

## Experimental

**General considerations.** The coordination complex  $[Bu_4N]_2[Zn(dmit)_2]$  was synthesized according to a reported method.<sup>18</sup> The 1,4-bis(imidazol-1-ylmethyl)benzene (bix) ligand was prepared by a known procedure.<sup>19</sup> All other chemicals were purchased from commercial sources and used without further purification. Microanalytical (C, H, N, S) data were obtained with a FLASH EA 1112 Series CHNS Analyzer. The IR spectra (with KBr pellets) were recorded in the range 400–4000 cm<sup>-1</sup> on a JASCO FT/IR-5300 spectrometer. UV-vis-NIR spectra were recorded using a 3101 PC/UV/vis-NIR Philips spectrometer equipped with a diffuse reflectance accessory.

Synthesis of  $[Zn(dmit)(4,4'-bpy)]_n$  (1). 80 mg (0.51 mmol) of 4,4'-bipyridine was dissolved in 5 mL of acetonitrile. To this solution was added Cu(BF<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O (60 mg, 0.25 mmol) in 5 mL of water. The color of the reaction mixture became blue. It was then filtered and the resulting filtrate was taken in a 20 mL roundbottomed flask. The [Bu<sub>4</sub>N]<sub>2</sub>[Zn(dmit)<sub>2</sub>] (230 mg, 0.24 mmol) was dissolved in 10 mL of acetonitrile in a 20 mL round-bottomed flask. Then, these two different reaction (round-bottomed) flasks, with copper salt and dmit complex, were connected to the two different terminals of the  $\lambda$ -shaped glass tube. Finally, the empty part of the tube was slowly filled with MeCN (on the top) and sealed. The tube was then allowed to stand undisturbed at room temperature for 15-20 days, yielding dark red crystals that were identified as 1. These, crystals were suitable for a single crystal X-ray structure determination. Yield 30 mg (24%). Anal. calcd (%) for C<sub>13</sub>H<sub>8</sub>N<sub>2</sub>S<sub>5</sub>Zn: C, 37.36; H, 1.93; N, 6.70; S, 38.36; Zn, 15.65. Found: C, 36.67; H, 2.06; N, 6.89; S, 40.18; Zn (ICP), 15.23. IR (KBr pellet):  $(v/cm^{-1}) = 1604, 1529, 1485, 1412, 1215, 1055$ (-C=S), 1032, 885, 806, 636, 461.

Synthesis of  $[Zn(dmit)(4,4'-bpe)]_n$  (2). 104 mg (0.57 mmol) of 4,4'-bpe (trans-1,2-Bis(4-pyridyl)ethane) was dissolved in 5mL of acetonitrile. To this solution was added  $Cu(BF_4)_2 \cdot xH_2O$  (60 mg, 0.25 mmol) in 5 mL of water. The reaction mixture color turned to blue. The filtrate of this was taken in a 20 mL round-bottomed flask. The [Bu<sub>4</sub>N]<sub>2</sub>[Zn(dmit)<sub>2</sub>] (230 mg, 0.24 mmol) was then dissolved in 10 mL of acetonitrile and the resulting solution was taken in another 20 mL round-bottomed flask. Single crystals, suitable for an X-ray structure determination, were grown based on the same procedure as that described in the case of compound of 1. In this case, the  $\lambda$ -tube was allowed to stand undisturbed at room temperature for 20-25 days, yielding dark red crystals of 2 in the  $\lambda$ -shaped glass tube. The resulting crystals were identified as compound 2. Yield 20 mg (20%). Anal. calcd (%) for C60 H42 N8 O2 S20 Zn4: C, 39.82; H, 2.34; N, 6.19; S, 35.43; Zn, 14.45. Found: C, 40.05; H, 2.28; N, 5.87; S, 36.05; Zn (ICP), 14.72. IR (KBr pellet):  $(v/cm^{-1}) = 1614, 1530, 1475, 1403, 1215, 1055$ (-C=S), 1008, 885, 807, 636, 461.

#### Synthesis of [Zn(dmit)(bix)]<sub>n</sub> (3)

**Preparation of benzoyl protected dmit.** 600 mg of  $(Bu_4N)_2[Zn(dmit)_2]$  was dissolved in 10 mL of dry acetone under  $N_2$  atm. To this solution was added 2 mL of benzoyl chloride in 10 mL of dry acetone drop-wise by using an additional funnel. While adding the benzoyl chloride solution, the reaction mixture color turned from red to yellow. The reaction mixture was continuously stirred overnight. Then, the solvent was evaporated using a rotary evaporator and the yellow colour compound was separated. The compound was crystallized from the CH<sub>2</sub>Cl<sub>2</sub>:MeOH (1:1) mixture. The spectroscopic data of (dmit)(COPh)<sub>2</sub>, obtained in this process, is identical to those for reported (dmit)(COPh)<sub>2</sub>.<sup>20</sup>

Synthesis of 3. 136 mg (0.334 mmol) of benzoylated dmit was suspended in a 10 mL of MeOH under dry  $N_2$  atm. To this mixture, 40 mg of sodium (washed with hexane) was added and continuously stirred for 20 min. This reaction mixture was treated with imidazole solution, which was prepared *in situ* by suspending 150 mg (0.63 mmol) of imidazole based ligand, **bix**,

in 20 mL of MeOH. The resulting reaction mixture was then treated with anhydrous ZnCl<sub>2</sub> (46 mg, 0.338 mmol), whereby the white methanolic turbidity was formed. Subsequently, it was stirred for 10 min at room temperature. The resulting orange solution was filtered and kept at room temperature. After 10 days, orange needle-shaped crystals separated out. These crystals are not soluble in any common organic solvents. Yield 58 mg (34%). Anal. calcd (%) for  $C_{17}H_{14}N_4S_5Zn$ : C, 40.83; H, 2.82; N, 11.20; S, 32.06; Zn, 13.08. Found: C, 41.53; H, 2.38; N, 10.20; S, 33.21; Zn (ICP), 12.89. IR (KBr pellet): ( $\nu/cm^{-1}$ ) = 1521, 1423, 1350, 1278, 1236, 1111, 1089, 1022, 947, 823, 713, 653, 617, 513, 459.

#### Single crystal structure determination

Data were measured at room temperature for compounds 1–3 on a Bruker SMART APEX CCD area detector system [ $\lambda$ (Mo-K $\alpha$ ) = 0.7103 Å], graphite monochromator; 2400 frames were recorded with an  $\omega$  scan width of 0.3°, each for 8 s, crystal-detector distance 60 mm, collimator 0.5 mm. Data reduction was performed with the SAINTPLUS software,<sup>21</sup> absorption correction using an empirical method SADABS,<sup>22</sup> structure solution using the SHELXS-97 program<sup>23</sup> and this was refined using the SHELXL-97 program.<sup>24</sup> Hydrogen atoms on the aromatic rings were introduced on the calculated positions and included in the refinement riding on their respective parent atoms. It has to be mentioned that the value of  $R_{(int)}$  is high (0.26) for compound 2. We could not improve the  $R_{(int)}$ value for compound 2, even after several attempts from different syntheses. The crystals of this compound do not diffract well.

### **Results and discussion**

## Synthesis

The syntheses of compounds 1 and 2 are described in Schemes 1 and 2 respectively. In both syntheses,  $Cu(BF_4)_2 \cdot xH_2O$  was used, even though copper is not present in the final products, 1 and 2. Compounds 1 and 2 could not be isolated without using  $Cu(BF_4)_2 \cdot xH_2O$ . We believe that copper ion, in these syntheses, plays important role by dragging a dmit ligand from  $[Zn(dmit)_2]^{2-}$ , resulting in the formation of neutral Zn(dmit) species. The copper species, formed in these syntheses, could not be isolated/identified; the copper species, once formed, remain soluble in the present synthesis conditions. Compound 3, which is stabilized with a more flexible ligand (bix), could not be synthesized in a straightforward manner, as shown in Schemes 1 and 2. Compound 3 has been synthesized by using a benzoyl



Scheme 1





protected dmit and  $[Bu_4N]_2[Zn(dmit)_2]$ , as shown in Scheme 3. As shown in Scheme 3, the compound 3 is actually synthesized from Na<sub>2</sub>dmit, prepared *in situ* from benzyol protected dmit and Na/MeOH, and anhydrous zinc chloride. The reason why the direct reaction between  $[Bu_4N]_2[Zn(dmit)_2]$  and bix does not afford compound 3, as in the case of the syntheses of compounds 1 and 2, is not clear to us. Probably, the flexible nature of the bix linker makes this difference to the synthetic routes for compounds 1–3. Thus, we have shown two different synthetic routes (Schemes 1–3) that lead to the isolation of 1–3.



#### Description of the crystal structures

Crystal structure description of compound 1. The coordination polymer  $[Zn(dmit)(4,4'-bpy)]_n$  (1) was synthesized as red colored crystals from [Bu<sub>4</sub>N]<sub>2</sub>[Zn(dmit)<sub>2</sub>] and 4,4'-bpy in the presence of  $[Cu(BF_4)_2] \cdot xH_2O$  based on the ligand exchange reaction in acetonitrile solvent (vide supra). The single crystal X-ray structure analysis shows that the crystals belong to the monoclinic system with space group  $P2_1/n$ . The asymmetric unit of crystal structure of 1 consists of two half 4,4'-bpy units and one dmit unit of zinc complex, as shown in Fig. 1. The basic crystallographic data for compound 1 is presented in Table 1. As shown in Fig. 1, the Zn(II) ion is in a distorted tetrahedral geometry, coordinated to the two sulfur atoms of the dmit<sup>2-</sup> ligand and two pyridine nitrogen atoms from two different 4,4'-bipyridine molecules, leading to the formation of a zig-zag chain-like coordination polymer (Fig. 2). The selected bond lengths and bondangles for compound 1 are described in Table 2. In compound 1, the Zn(1)-S(1) and

 Table 1
 Crystal data and structural refinement parameters for compounds 1–3

	1	2	3
	1	2	
Empirical formula	$C_{13}H_8N_2S_5Zn$	$C_{60}H_{42}N_8O_2S_{20}Zn_4$	$C_{17}H_{14}N_4S_5Zn$
Formula weight	417.88	1809.70	499.99
T/K	100(2)	298(2)	298(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\overline{1}$	$P2_1/n$
a/Å	9.1288(16)	9.211(2)	10.0567(6)
b/Å	14.655(3)	19.641(4)	16.1864(10)
c/Å	11.670(2)	20.970(5)	13.0716(8)
α (°)	90	105.288(3)	90
β(°)	101.561(3)	97.714(4)	99.3920(10)
$\gamma$ (°)	90	94.959(4)	90
$V/Å^3$	1529.6(5)	3596.7(14)	2099.3(2)
Ζ	4	2	4
$D_{\rm c}/{\rm Mg}~{\rm m}^{-3}$	1.815	1.671	1.582
$\mu/\mathrm{mm}^{-1}$	2.279	1.947	1.677
F[000]	840	1828	1016
Crystal size/mm	$0.23 \times 0.08 \times 0.03$	$0.34 \times 0.10 \times 0.07$	0.18  imes 0.08  imes 0.06
$\theta$ range for data collection [deg]	2.26 to 25.00	1.08 to 25.00	2.02 to 25.00
Reflections collected/unique	14442/2687	33824/12619	19854/3689
$R_{(int)}$	0.0472	0.2600	0.0646
Refinement method			Full-matrix least-squares on $F^2$
Data/restraints/parameters	2687/0/190	12619/0/847	3689/0/244
Goodness-of-fit on F <sup>2</sup>	1.062	0.935	0.953
$R_{1/W}R_2\left[I>2\sigma(I)\right]$	0.0376/0.0884	0.0873/0.1813	0.0422/0.0821
$R_1$ , w $R_2$ (all data)	0.0501/0.0946	0.2231/0.2424	0.0639/0.0883
Largest diff. Peak/hole/e Å <sup>-3</sup>	0.775/- 0.339	0.736/-0.694	0.588/-0.301



**Fig. 1** The structure of  $[Zn(dmit)(4,4'-bpy)]_n$  (1) in the asymmetric unit with atom labeling, showing 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Zn(1)-S(2) bond distances are 2.2772(11) Å and 2.3117(11) Å, respectively, with a S(1)-Zn(1)-S(2) bond angle of 98.87(1)°. Along the chain axis, each bipyridine ligand coordinates to two  $\{Zn(dmit)\}\$  complex species (from opposite sides). In each complex unit, the N(1)–Zn(1)–N(2) bond angle is  $105.20(1)^{\circ}$ , which considerably deviates from the ideal tetrahedral situation (109°). Although, the two Zn-S bond distances are not equal (which is consistent with different bond angles of C(1)-S(1)- $Zn(1) 93.38(13)^{\circ}$  and  $C(2)-S(2)-Zn(1) 92.70(13)^{\circ}$ , the two Zn(1)-N bond distances are virtually identical. The polymer structure of  $[Zn(dmit)(4,4'-bpy)]_n$  (1) has a  $\{ZnN_2S_2\}$  core that resembles the  $[Zn(S_2P(OR)_2)_2(4,4'-bpe)]_n$  coordination polymer,<sup>11</sup> but the important difference lies in the fact that this reported coordination polymer is prepared by using 1,1-dithiolate type of ligand. Obviously, the properties of 1,2-dithiolene system (compound 1 in the present study) would be much different from 1,1-dithiolate



Fig. 2 (a) A segment of the zig-zag coordination polymer 1 and (b) a packing diagram of compound 1 viewed down the crystallographic a axis. The hydrogen atoms are omitted for clarity.

analogue  $[Zn(S_2P(OR)_2)_2(4,4'-bpe)]_n$  in terms of conjugation. One segment of the zig-zag coordination polymer of compound 1 is described in Fig. 2(a). In the crystal, these chains pack/arrange in an interesting manner (Fig. 2(b)). The 4,4'-bypiridine regions of each chain are used as inter-crossing zones, which exploit their  $\pi$ - $\pi$ stacking interactions, leading to the formation of a 3-dimensional grid-type framework (Fig. 3). The  $\pi$ - $\pi$  stacking parameters are characterized by a centroid-centroid (Cg-Cg) distance of 4.13(2) Å and a mean plane separation (MPS) of 3.79 Å. Interestingly, when a chain crosses over another chain, they interact roughly in a perpendicular fashion and it proceeds above and below with respect to the bipyridine rings (see the inter-crossing region in Fig. 3) to its inter-crossing chains. Thus, the  $\pi$ - $\pi$  interactions between the {N1-C4-C5-C6-C7-C8} and {N2-C9-C10-C11-C12-C13} rings can be considered as an incentive for the formation of such a three-dimensional arrangement, which is very similar to the intertwining/weaving situation in making a cloth sheet (Fig. 3(b)).

Table 2 Selected bond lengths [Å] and angles [°] for compound  $[Zn(dmit)(4,4'bpy)]_{_{\it P}}(1)$ 

Zn(1)–N(1)	2.052(3)	Zn(1)–N(2)	2.063(3)
Zn(1)-S(1)	2.2772(11)	Zn(1)-S(2)	2.3117(11)
S(5)–C(3)	1.660(4)	N(2)–C(9)	1.335(5)
C(11)-C(10)	1.401(5)	$C(11)-C(11)^{a}$	1.479(7)
C(6)–C(7)	1.393(5)	$C(6) - C(6)^{b}$	1.488(7)
N(1)-Zn(1)-N(2)	105.19(12)	N(1)-Zn(1)-S(1)	113.01(9)
N(2)-Zn(1)-S(1)	119.15(9)	N(1)-Zn(1)-S(2)	114.97(9)
C(3)-S(4)-C(1)	98.47(18)	C(2)-S(2)-Zn(1)	92.70(13)
C(9)-N(2)-C(13)	117.9(3)	C(9)-N(2)-Zn(1)	122.6(3)
C(13)-N(2)-Zn(1)	118.7(2)	C(12)-C(11)-C(10)	116.6(3)
$C(12)-C(11)-C(11)^{a}$	121.3(4)	$C(10)-C(11)-C(11)^a$	122.1(4)
S(5)-C(3)-S(3)	124.5(2)	N(2)-C(9)-C(10)	123.0(4)

Symmetry transformations used to generate equivalent atoms:<sup>*a*</sup> -x,-y,-z; <sup>*b*</sup> -x,-y+1, z+1.



**Fig. 3** (a) A view of the  $\pi$ - $\pi$  interaction between the adjacent perpendicular polymer chains (the middle (red) chain is interacting with two different chains (cyan)). (b) A schematic representation of the 2D-networks in compound 1, the independent polymer chains are distinguished by different colors (side view).

Besides these  $\pi$ - $\pi$  interactions, we found fascinating interchain S...S contacts (Fig. S1, Supporting Information†). More specifically, this contact includes the interaction of S(2) of Znchelate five-member ring with S(5) of C=S and vice versa. The relevant S...S separation is 3.5819(16) Å (Figure S1(a), Supporting Information†), which is less than the sum of their van der Waals radii (3.70 Å). Usually, the S...S contacts are a very important requirement for developing conducting and even superconducting materials; for example, most of the [Ni(dmit)<sub>2</sub>]<sup>-</sup> and tetrathiafulvalene derivatives show high conductivity due to the presence of S...S contacts in relevant solids.<sup>25</sup>

Crystal structure description of compound 2. Compound 2 crystallizes in triclinic space group  $P\overline{1}$ . The relevant asymmetric unit consists of two full 4,4'-bpe units (bridged), four halves of 4,4'-bpe units and four  $\{dmit\}^{2-}$  units that are coordinated with four zinc metals, as depicted in Fig. 4. The basic crystallographic data for compound 2 is described in Table 1. The geometry around the Zn(II) ion is distorted tetrahedral, with two sulfur atoms of the dmit<sup>2-</sup> ligand and two pyridine nitrogen atoms from two different trans-1,2-bis(4-pyridyl)ethene (4,4'-bpe) molecules. In the crystal, both terminal nitrogen atoms of the (4,4'-bpe) ligand are involved in coordination (to two different zinc complexes), thereby leading to the formation of a one-dimensional chain-like coordination polymer (Fig. 5(a)). The selected bond lengths and bond angles for compound 2 are presented in Table 3. The average Zn-S and Zn-N bond distances are 2.287 Å and 2.037 Å, respectively, which are consistent with those of compound 1 and the corresponding S-Zn-S and N-Zn-N bond angles are 99.13(14)° and 99.07°,

**Table 3** Selected bond lengths [Å] and angles  $[\circ]$  for  $[Zn(dmit)(4,4'-bpe)]_n$ (2)

Zn(1)-N(2)	2.032(10)	Zn(1)-N(1)	2.040(10)
Zn(1)-S(1)	2.271(4)	Zn(1)-S(2)	2.299(4)
Zn(2) - S(7)	2.260(4)	Zn(4) - S(17)	2.268(4)
S(8)-C(22)	1.730(14)	N(7)-C(45)	1.295(17)
$C(21) - C(28)^a$	1.288(18)	$C(51)-C(60)^{b}$	1.328(16)
$C(60)-C(51)^{c}$	1.328(16)	$C(28) - C(21)^d$	1.287(18)
N(2)-Zn(1)-N(1)	97.8(4)	N(2)-Zn(1)-S(1)	113.1(3)
N(2)-Zn(1)-S(2)	122.0(3)	N(1)-Zn(1)-S(2)	107.6(3)
S(1)-Zn(1)-S(2)	99.02(13)	N(4)-Zn(2)-N(3)	100.0(4)

Symmetry transformations used to generate equivalent atoms:<sup>*a*</sup> x, y, z - 1; <sup>*b*</sup> x, y - 1, z; <sup>*c*</sup> x, y + 1, z; <sup>*d*</sup> x, y, z + 1.



**Fig. 4** The structural unit of  $[Zn(dmit)(4,4'-bpe)]_n$  (2) with atom labeling. The non-hydrogen atoms are drawn as 50% probability thermal ellipsoids.



Fig. 5 (a) A segment of the zig-zag coordination polymer 2 and (b) a packing diagram of compound 2 viewed down the a axis. The hydrogen atoms are omitted for clarity.

respectively. The coordination polymer in compound **2** also exists in a zig-zag manner, as found in the crystals of compound **1**. The packing diagram of  $[Zn(dmit)(4,4'-bpe)]_n$  (**2**) is shown in Fig. 5(b).

It is to be noted that even though the organic spacer length is relatively larger in compound 2 than that in compound 1 (the length is exceeded by a -C=C- group in 2), the overall packing of the chains in the crystal of 2 is very much comparable to that in the crystals of compound 1. Nevertheless, in the case of compound 2, the inter-crossing zig-zag chains are assembled by the influence of  $\pi-\pi$  interactions that involve the C=C bond (from one chain) and the aromatic ring of the 4,4'-bpe (of the other chain) per intercrossing region. This situation of  $\pi-\pi$  interactions is shown in Fig. 6.



Fig. 6 A view of the inter-crossing of the perpendicular chains for compound 2 and the  $\pi$ - $\pi$  interaction shown in green shadow (left), the origin of interaction between C=C bond (red) and pyridine ring (green) shown in middle and a side view of the packing representation of independent polymer chains are distinguished by different colors (right).

The  $\pi$ - $\pi$  interactions among aromatic rings are common, but we did not come across such interactions between an aromatic ring and a C=C double bond in the literature. Unlike compound 1, compound 2 does not exhibit any considerable  $S \cdots S$  intermolecular contact. This may be due to the relatively longer length of the organic spacer (4,4'-bpe). In the case of the compound 1, the N-N distance of 4,4'-bpy is 7.105(8) Å (spacer length), whereas in the crystal structure of compound 2, the N–N distance of 4,4'-bpe is 9.368(23) Å (spacer length). We believe that free rotation between two aromatic rings in the linker 4,4'-bpe is restricted due to the presence of C=C double bond between them and consequently we observed similar chain type and packing arrangement in compounds 1 and 2. Even though, polymers 1 and 2 have similar kind of packing arrangement, their structures exhibit sufficient diversities due to the little difference (particularly the spacer length) between 4,4'-bpy and 4,4'-bpe. Thus, the supramolecular structures of coordination polymers can be altered/tuned by a slight change of the spacer/linker molecules.

**Crystal structure description of compound 3.** The coordination polymer  $[Zn(dmit)(bix)]_n$  (3) was synthesized as orange crystals from sodium salt of  $\{dmit\}^{2^-}$  and **bix** ligand in the presence of anhydrous  $ZnCl_2$  in EtOH solvent. The crystals belong to the monoclinic system with space group  $P2_1/n$ . The asymmetric unit of the crystal structure of 3 consists of two halves of bix units and one  $\{dmit\}^{2^-}$  unit coordinated to the zinc ion, as shown in Fig. 7. In the molecular structure, the Zn(II) ion is



Fig. 7 The molecular structure of the asymmetric unit in  $[Zn(dmit)(bix)]_n$ (3) with atom labeling, showing 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

**Table 4** Selected bond lengths [Å] and angles  $[\circ]$  for  $[Zn(dit)(bix)]_n$  (3)

Zn(1) - N(3)	2.014(3)	Zn(1)-N(1)	2.021(3)
Zn(1)-S(2)	2.2963(11)	Zn(1)-S(1)	2.3329(11)
S(3) - C(3)	1.714(4)	S(3) - C(1)	1.747(3)
N(3) - C(11)	1.355(5)	N(1)-C(4)	1.307(4)
$C(16) - C(10)^a$	1.373(6)	$C(9) - C(17)^{b}$	1.378(5)
$C(10) - C(16)^{b}$	1.373(6)	$C(17)-C(9)^{a}$	1.378(5)
N(3) - Zn(1) - N(1)	108.28(12)	N(3)-Zn(1)-S(2)	116.45(9)
N(1)-Zn(1)-S(2)	119.28(9)	N(3)-Zn(1)-S(1)	107.51(10)
S(2) - Zn(1) - S(1)	96.50(4)	C(1)-S(1)-Zn(1)	93.81(12)
$C(15)-C(16)-C(10)^{a}$	120.9(4)	$C(8)-C(9)-C(17)^{b}$	121.9(4)
$C(8) - C(10) - C(16)^{b}$	121.4(4)	$C(15)-C(17)-C(9)^{a}$	120.4(4)

Symmetry transformations used to generate equivalent atoms:<sup>*a*</sup> -x + 1/2, y - 1/2, -z + 1/2;  $^{b}-x + 1/2$ , y + 1/2, -z + 1/2.

tetrahedrally coordinated to two sulfur atoms of the dmit<sup>2–</sup> ligand and two imidazole nitrogens from two different bix molecules, leading to the formation of a one-dimensional concavo–convextype coordination polymer (Fig. 8). The selected bond lengths and bond angles for compound **3** are described in Table 4. In compound **3**, the Zn(1)–S(1) and Zn(1)–S(2) bond distances are 2.332(11) Å and 2.296(11) Å, respectively, with a S(2)–Zn(1)– S(1) bond angle of 96.50(4)°. The two Zn(1)–N bond distances are virtually same. That two Zn–S bond distances are not equal, which is consistent with the bond angle of C–S–Zn being 93.8(12)°. Along the concavo–convex chain, the Zn–Zn distance is 16.186(1) Å (Fig. 8).



**Fig. 8** A segment of the concavo–convex-type coordination polymer **3**. The hydrogen atoms are omitted for clarity.

Numerous coordination polymers, known in literature, exhibit helical chain-like arrangements, double strand chains, and ladder-like chain structures, *etc.* Amazingly, the coordination polymer **3** (in the present work) provides the addition of a new type of chain, *i.e.*, the concavo–convex chain structure. We have succeeded in constructing this concavo–convex chain in compound **3** because we chose a much more flexible and larger linker **bix** (see Scheme 3 for its structural representation) in the case of compound **3**.

Furthermore, the adjacent concavo-convex coordination polymers/chains of **3** interact with each other by  $\pi$ - $\pi$  interactions that involve imidazole rings of the **bix** ligand, as well as the aromatic ring of the **bix** ligand and the five-member ring of the dmit ligand, giving rise to a kind of infinite zipper structure (Fig. 9). The relevant  $\pi$ - $\pi$  interactions (between the inter-planar distances) are in the range 3.5-4.1 Å. The molecular packing diagram of [Zn(dmit)(bix)]<sub>n</sub> (**3**) in the crystallographic *ab* plane is shown in Fig. S2 (Supporting Information†). In the crystal structure of compound **3**, the central aromatic ring in the **bix** linker is connected to two pyrazine rings by C-CH<sub>2</sub>-C bonds that make the **bix** linker more flexible. As a result, the coordination polymers in compound **3** acquire the shape of a concavo-convex curved chain or puckered ribbon. The explanation for this type



**Fig. 9** The crystal packing diagram of  $[Zn(dmit)(bix)]_n$  (3). The solid blue lines indicate the  $\pi$ - $\pi$  interactions between the imidazole five-member rings and the solid red line indicates the  $\pi$ - $\pi$  interaction between the aromatic ring of the **bix** ligand and five-member ring of the dmit ligand.

of shape can be rationalized by the zipper-like arrangement of these concavo-convex chains that are sustained by  $\pi$ - $\pi$  inter-chain supramolecular interactions, as shown in Fig. 9.

#### Spectroscopy

The solid state (diffuse reflectance) electronic absorption spectra of  $[Zn(dmit)(4,4'-bpy)]_n$  (1) and  $[Zn(dmit)(4,4'-bpe)]_n$  (2), which are identical, exhibit two absorption bands in the 270-700 nm region, as shown in Fig. 10(a). The corresponding solution absorption spectra (in DMF) are also comparable (not shown here). Both bands are assigned to dmit ligand transitions; the absorption band at 320 nm is assigned to a  $\pi$ - $\pi$ \* transition and the absorption band at 498 nm to an n- $\pi^*$  transition of the dmit ligand. However, a careful investigation of the 500 nm region in the absorption spectrum of [NBu<sub>4</sub>]<sub>2</sub>[Zn(dmit)<sub>2</sub>] by resonance Raman spectroscopy showed vibrational bands at 1429, 530 and 345 cm<sup>-1</sup> with enhanced intensities, out of which the band at 345 cm<sup>-1</sup> was assigned to Zn-S stretching. The other two bands, located at 1429 and 530 cm<sup>-1</sup> were assigned to C=C stretching and dmit ligand deformation, respectively.26 Thus, the combined UV-vis and resonance Raman spectroscopic studies recommend that the absorption band at 498 nm (for both compounds 1 and 2) is a MLCT charge transfer band. Both bands (at 320 and 498 nm) show blue shifts relative to those in [Na<sub>2</sub>(dmit)] (316, 514 nm in MeOH),<sup>1</sup> [NBu<sub>4</sub>]<sub>2</sub>[Zn(dmit)<sub>2</sub>] (300, 530 nm in MeCN)<sup>27</sup> and [NMe<sub>4</sub>]<sub>2</sub>[Zn(dmit)(Sph)<sub>2</sub>] (327, 512 nm).<sup>28</sup> The electronic spectrum of compound  $[Zn(dmit)(bix)]_n$  (3) exhibits, in the solid state, two absorption bands at 305 nm and 487 nm (Fig. 10(b)). We could not record the absorption spectra of compound 3 in the solution state because of its insolubility. The assignment feature for these bands (305 and 487 nm) of compound 3 should be comparable to that of compounds 1 and 2.

## Conclusion

While most of the supramolecular coordination polymers (a special class of metallosupramolecular entities) are generally cationic<sup>29</sup> or anionic,<sup>3–9</sup> it would be of great interest to assemble a neutral metal coordination complex unit and neutral organic linkers to generate neutral coordination polymers of diverse morphology, which could eventually be used to blend into conventional neutral polymers. We demonstrated that a neutral zinc coordination complex unit/species, [Zn(dmit)], can be assembled with three different neutral organic linkers/spacers to generate a new class of three neutral coordination polymers [Zn(dmit)(4,4'-



**Fig. 10** (a) The diffuse reflactance electronic absorption spectra of compounds  $[Zn(dmit)(N-N)]_n$  (N-N = 4,4'-bpy (1) and N-N = 4,4'-bpe (2)) in the solid state; (b) the absorption spectrum of compound  $[Zn(dmit)(bix)]_n$  (3) in the solid state.

byy)]<sub>n</sub> (1),  $[Zn(dmit)(4,4'-bpe)]_n$  (2) and  $[Zn(dmit)(bix)]_n$  (3). The isolated coordination compounds include one dimensional polymeric species {Zn(diimine)(dithiolate)}<sub>n</sub> that are formed by coordinate covalent bonds (in 1–3), leading to the formation of an intriguing variety of architectures and topologies. We have demonstrated a potential approach for the design of various supramolecular architectures based on a neutral metal–dithiolene unit, in which metal centers, as well as the 1,2-dithiolene ligand with various substituents can be varied. The importance of the present synthetic routes lies in the fact that even though the coordination polymers of  $ZnCl_2$  exist with bridging ligands, the substitution of two anions by the dmit ligand is not so easy; it is difficult to take place by a normal chemical synthetic method. Hence, we have shown a unique synthetic approach to synthesize this class of Zn coordination polymers.

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