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## COMMUNICATION

**A new type of 3D  $[(M^{II})_2(TCNQ^{II})_3]^{2-}$  coordination network with spacious channels of hexagonal cross-section generated from  $TCNQH_2^\dagger$** 

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The dianion of tetracyanoquinodimethane,  $TCNQ^{2-}$ , is able to act as a ligand capable of binding four metal ions at the corners of a rectangle. When the ligand is combined with divalent metal ions in the presence of appropriate counterions, infinite anionic networks may be formed of composition  $[M_2TCNQ_3]^{2-}$  ( $M = Mn, Zn, Cd$ ). In the structures reported here the cyano groups from six separate  $TCNQ$  dianions provide an octahedral coordination environment around the metal centres. Large hexagonal channels in the anionic network are occupied by highly disordered counterions.

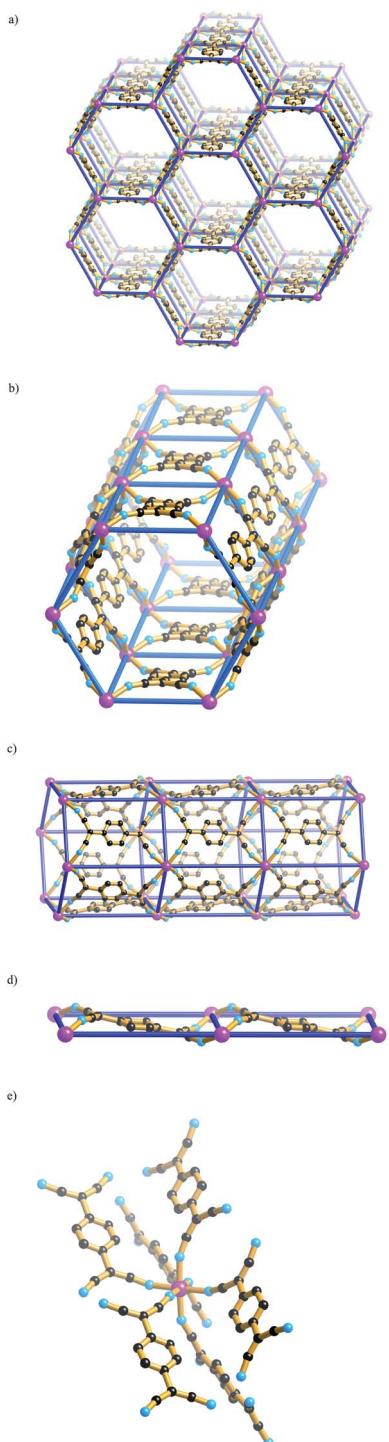
There is continuing interest in the wide range of derivatives, both metal-containing and purely organic, of tetracyanoquinodimethane, **I**, (hereafter  $TCNQ$ ).<sup>1</sup> Much of this research into  $TCNQ$  has been driven by the promise of interesting and possibly useful electronic/magnetic properties arising from the ready accessibility and relative stability of its radical mono-anion,  $TCNQ^{-1,2}$ . We have embarked upon an exploratory synthetic/structural study of the use of  $TCNQH_2$ , **II**, to generate, in a very simple manner, new types of coordination polymers containing  $TCNQ$  in the previously little known minus two oxidation level.<sup>3</sup> Our longer term aim in this sort of exploration is to discover microporous systems amenable to oxidative intercalation, whereby the  $TCNQ^{2-}$  components of the network, in all or in part, may be converted to  $TCNQ^{-}$  with retention of the original network connectivity. Using the  $TCNQH_2$  approach, we have generated an extensive series of coordination polymers containing  $[M^{II}(TCNQ^{II})]^0$  sheets.<sup>3</sup> Above and below the metal centres in the sheets, a range of pyridine derivatives can be attached, some terminal, in which cases the individual neutral sheets interdigitate, and some acting as pillars linking sheet to sheet to generate 3D coordination networks.<sup>3a,4</sup> Kitagawa and co-workers have recently reported similar  $TCNQ^{2-}$ -based coordination polymeric sheet structures obtained from the  $TCNQ^{-}$  radical monoanion in the presence of the reducing agent ascorbic acid.<sup>5</sup> The  $TCNQ^{2-}$  ion in solution was long ago reported to be sensitive to air<sup>6</sup> but our work suggests that when it is attached to appropriate metal centres within

coordination networks it appears to be significantly stabilised against such oxidation. The  $TCNQ$  components of coordination polymers obtained prior to our  $TCNQH_2$  approach generally carried a formal charge of minus one or less, and generally were involved in close  $\pi-\pi$  contacts. In contrast, the  $TCNQ^{2-}$  components in coordination polymers obtained from  $TCNQH_2$  are free of such  $\pi-\pi$  contacts. In principle these uncluttered  $TCNQ^{2-}$  components are accessible on both sides to incoming reagents, provided the networks contain appropriate channels - as the ones reported below do. Here we consider two major classes of such incoming reagents, *viz.*  $\pi$ -acceptors and oxidants. If  $\pi$ -acceptor species are able to migrate throughout the lattice, they may then be able to form donor-acceptor (DA) charge transfer associations with the  $\pi$ -donor  $TCNQ^{2-}$  components of the network. In support of the feasibility of such DA interactions, we have already reported a number of purely organic combinations in which  $TCNQ^{2-}$  acts as the donor component in association with a variety of acceptors,<sup>7</sup> and we have also described a deep red  $[Zn^{II}(TCNQ^{II})]$  coordination polymer in which 4,4'-bipyridine-di-*N*-oxide, acting as an acceptor, participates in DA association with the framework  $TCNQ^{2-}$   $\pi$ -donor component, giving rise to the intense visible absorption.<sup>3a</sup> Oxidants migrating through the microporous structure may be able to generate networks that retain the original connectivity, but in which all or a fraction of the  $TCNQ$  units have been converted from the minus two oxidation state to the minus one radical state. Both of these types of interactions of the framework  $TCNQ^{II}$  components (ie. either with introduced  $\pi$ -acceptors or with introduced oxidants) are possibilities of major potential significance. We report below the use of the  $TCNQH_2$  approach to generate a new series of 3D coordination polymers of composition  $[(M^{II})_2(TCNQ^{II})_3]^{2-}$  containing spacious channels of hexagonal cross-section in which the roughly planar  $TCNQ^{2-}$  units are potentially accessible at both faces to interaction with  $\pi$ -acceptors or with oxidants.

Reaction between  $Mn(NO_3)_2$  and  $TCNQH_2$  in methanol/DMSO in the presence of acetate ion gives pale yellow hexagonal prismatic crystals, the single crystal X-ray diffraction examination of which reveals an infinite 3D  $[Mn_2(TCNQ)_3]^{2-}$  coordination network with the honeycomb-like structure shown in Fig. 1. Very closely analogous 3D  $[M_2(TCNQ)_3]^{2-}$  coordination networks ( $M = Zn$  and  $Cd$ ) are observed in crystals obtained similarly using  $Zn(NO_3)_2$  or  $Cd(NO_3)_2$  in place of  $Mn(NO_3)_2$  and using triethylamine, in place of acetate, to deprotonate the  $TCNQH_2$ . Fig. 1a shows the extended 3D  $[Mn_2(TCNQ)_3]^{2-}$  coordination network viewed slightly off the

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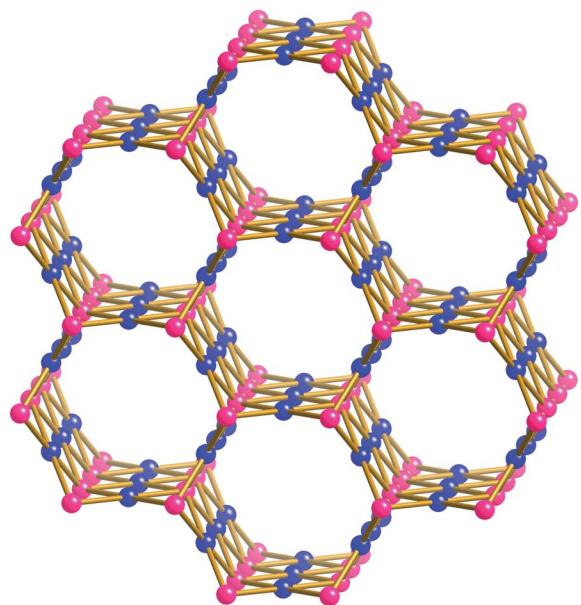
† Electronic supplementary information (ESI) available: Powder diffraction and thermogravimetric data. CCDC reference numbers 842123–842126. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ce06104f



**Fig. 1** a) The honeycomb-like structure of the  $[\text{Mn}_2(\text{TCNQ})_3]^{2-}$  coordination network. The blue rods, representing imaginary  $\text{Mn}\cdots\text{Mn}$  connections, highlight the channels of hexagonal cross-section. b) A single hexagonal channel viewed somewhat off the channel axis. c) A single channel viewed perpendicular to the channel axis. d) Each  $\text{TCNQ}^{2-}$  ligand is inclined to the plane of the four metal centres to which it is attached. e) The octahedral environment of the metal centre.

hexagonal axis. Fig. 1b and 1c show a single hexagonal channel viewed slightly off the hexagonal axis and roughly perpendicular to the axis respectively. The channels are spacious, the atom-to-atom

separation across them being at least  $14.9\text{ \AA}$ . The  $\text{TCNQ}^{2-}$  ligand is inclined to the plane of the four metal centres to which it is attached as shown in Fig. 1d. All  $\text{TCNQ}$  units within a single wall of the hexagonal channel are inclined in the same direction while all the  $\text{TCNQ}$  units in adjacent walls are inclined in the opposite direction, as can be seen in Fig. 1a and b. The metal coordination geometry, shown in Fig. 1e, is close to octahedral. The metal ion acts as a 6-connecting node and the  $\text{TCNQ}^{2-}$  unit as a roughly square planar 4-connecting node to generate a net with the underlying connectivity shown in Fig. 2 [point symbol  $(4^6)2(4^46^2)_3$ .<sup>8</sup> In its geometrically most symmetrical form this pleasingly simple, archetypal net consists of 6-connecting nodes, that are required to have the trigonal prismatic geometry, and 4-connecting nodes with the square planar geometry. This network topology was first seen in 1999 in the structure of  $(\text{R}_2\text{Sn})_3[\text{Co}(\text{CN})_6]_2$ .<sup>9,10</sup> A few years later we discovered accidentally that lanthanum muate possesses this topology,<sup>11</sup> at a time when we had been deliberately (but unsuccessfully) targeting just this net by the use of the tetraanion of  $4,4',4'',4'''$ - (21*H*,23*H*-porphine-5,10,15,20-tetrayl)-tetrakis(benzoic acid) (and a number of its metal derivatives), intended to serve as the 4-connecting square node, and the trinuclear  $\text{Cr}_3\text{O}(\text{carboxylate})_6$  cluster (as seen in basic chromium acetate) intended to provide the 6-connecting trigonal prismatic node. Since our isolation of the lanthanum muate structures a number of other lanthanide-based networks involving dicarboxylate ligands with the same topology have been identified.<sup>10,12-17</sup> A purely inorganic example of the network is provided by  $\text{Sc}_2(\text{SeO}_3)_3$ .<sup>10,18</sup> The  $[\text{Mn}_2(\text{TCNQ})_3]^{2-}$  network reported here is able to adopt the  $(4^6)2(4^46^2)_3$  topology despite the fact that the metal coordination geometry is octahedral not trigonal prismatic, because of the considerable flexibility inherent in the four C-CN-M connections of each  $\text{TCNQ}^{2-}$  unit, only minor deviations at each ideally linear C and N centre being required to achieve this. Similar structural features are apparent in  $(\text{R}_2\text{Sn})_3[\text{Co}(\text{CN})_6]_2$  where octahedral  $\text{Co}(\text{III})$  centres are



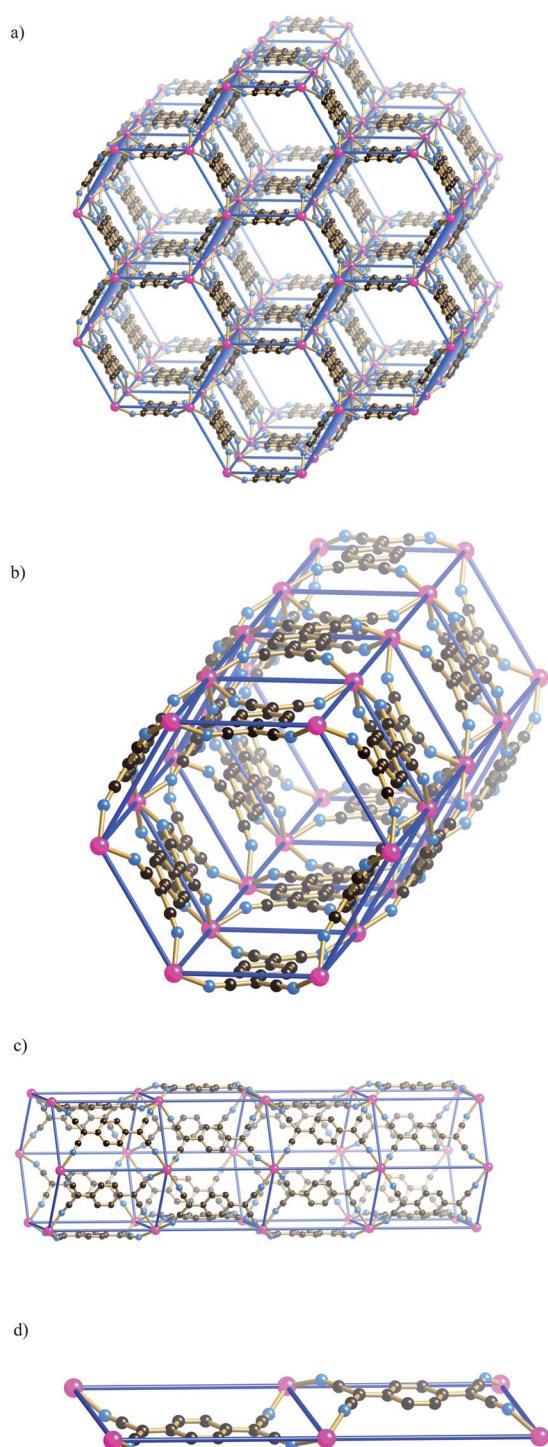
**Fig. 2** A representation of the  $(4^6)2(4^46^2)_3$  net composed of square planar 4-connecting nodes and trigonal prismatic 6-connecting nodes, each node connected to the appropriate number of nodes (four or six) of the other type.

bound through cyanide groups to six  $(R_2Sn)^{2+}$  units that act as 4-connecting planar units.<sup>9</sup>

The anionic framework represents only ~45% of the crystal volume.<sup>19</sup> The negative charge on the  $[Mn_2(TCNQ)_3]^{2-}$  network is balanced by disordered  $[Mn(DMSO)_4(H_2O)_2]^{2+}$  cations<sup>‡</sup> located within the large hexagonal channels. The Mn centre of each of these cations is positionally disordered along the 3-fold channel axis over three sites, one of which is located on the origin (a site of symmetry,  $-3m$ ); the other two sites are symmetry related to each other and lie ~2.2 Å either side of the Mn center at the origin. The Mn centre at the origin is located within the planes of framework Mn centres lying perpendicular to the channel axis, that can be discerned in Fig. 1a, b and c. In addition to the disorder associated with the location of the Mn centres of the cations, the coordinated solvent molecules bound to the manganese are orientationally disordered.<sup>§</sup>

We estimated that the channel seen in the compounds above was approximately the correct size to house a  $[M^{II}(bipy)]^{2+}$  cation (bipy = 2,2'-bipyridine), which itself would possess a 3-fold axis that we imagined might nicely complement the 3-fold channel axis. We hoped that if we could obtain crystals containing  $[M^{II}(bipy)]^{2+}$  cations in the channels these might be better defined crystallographically than those described above – unfortunately this latter hope was not fulfilled. Reaction of  $Mn(NO_3)_2$ ,  $TCNQH_2$  and 2,2'-bipyridine in MeOH/DMSO yields large, bright red, hexagonal prismatic, solvated crystals of composition  $[Mn(bipy)]_3[Mn_2(TCNQ)_3]$ . Single crystal X-ray diffraction analysis reveals a 3D  $[Mn_2(TCNQ)_3]^{2-}$  coordination network with the same connectivity as that described above, but with a geometry that differs in a significant and interesting way (see Fig. 3). The “long” 2-fold axis of each  $TCNQ^{2-}$  unit (ie. the methine carbon-to-methine carbon axis) is now parallel to the channel axis (see Fig. 3c and d), in contrast to the structure depicted in Fig. 1 where this long ligand axis is inclined to the channel axis (in particular compare with Fig. 1d). As can be seen in Fig. 3b, c and d the  $TCNQ^{2-}$  units are displaced from the plane of the four metal centres to which they are attached; if one proceeds along a wall of a particular channel one ligand unit is displaced away from the channel centre and the next is displaced towards it. We propose that these alternating displacements of the  $TCNQ^{2-}$  units arise to allow the  $[Mn(bipy)]^{2+}$  cation to be incorporated with its outermost CH bonds (those most remote from the metal) all pointing towards the outwardly displaced  $TCNQ^{2-}$  units, but unfortunately the disorder in the  $[Mn(bipy)]^{2+}$  cations prevents confirmation of this. This structure, with the alternation of the  $TCNQ$  dianions along the length of the channel (away from the channel centre and towards the channel centre) closely resembles the arrangement in  $(R_2Sn)_3[Co(CN)_6]_2$ ; in fact both structures have the same hexagonal space group,  $P6_3/mcm$ .<sup>9</sup>

The deep red colour of the crystals containing  $[Mn(bipy)]^{2+}$  cations in the channels, in contrast to the pale yellow colour of the crystals containing  $Mn(DMSO)_4(H_2O)_2^{2+}$ , is indicative of charge transfer interaction between the  $TCNQ^{2-}$  units, acting as  $\pi$ -donors, and the  $[Mn(bipy)]^{2+}$  cations, acting as  $\pi$ -acceptors. Recently we reported a series of  $TCNQ^{2-}$  “salts” in which the dianionic units existed as discrete entities, not as a component of a coordination polymer network.<sup>7</sup> Some of these, with “innocent”, non- $\pi$ -donor cations were colourless, showing that the  $TCNQ^{2-}$  unit itself does not absorb in the visible region, whereas in others charge transfer interactions between the discrete  $TCNQ^{2-}$  unit, which acted as the  $\pi$ -donor, and a range of  $\pi$ -acceptors led to strong visible absorption and intense colouration.<sup>7</sup> One compound in this group was the



**Fig. 3** a) A view of the  $[Mn_2(TCNQ)_3]^{2-}$  coordination network in  $[Mn(bipy)]_3[Mn_2(TCNQ)_3]$ . The blue rods, as in Fig. 1, represent imaginary  $Mn \cdots Mn$  connections and highlight the channels of hexagonal cross-section. b) A view along a single channel. c) A single channel viewed almost perpendicular to the channel axis. d) The disposition of the  $TCNQ^{2-}$  units “parallel” to the channel axis, adjacent ones being on opposite sides of the plane of the metal centres to which they are attached, a disposition which is to be contrasted with that in Fig. 1d.

almost black  $[Pt(bipy)]^{2+} [TCNQ^{2-}]$ , in which the cation played the role of  $\pi$ -acceptor. The parallel between black  $[Pt(bipy)]^{2+} [TCNQ^{2-}]$  and deep red  $[Mn(bipy)]_3[Mn_2(TCNQ)_3]$  is clear, strongly supporting

the charge transfer origin of the visible absorption in the latter, in which the  $\text{TCNQ}^{2-}$  unit, now part of a coordination network, acts as the  $\pi$ -donor.

The very simple synthetic approach reported here using  $\text{TCNQH}_2$  as the starting material generates a new type of open 3D structure containing spacious channels whose walls consist of potentially readily accessible and oxidisable  $\text{TCNQ}^{2-}$  units. The structure appears ideally suited to undergo oxidative intercalation to generate networks with unchanged connectivity but in which some or all of the  $\text{TCNQ}$  components have been oxidised to the radical monoanion state. The compounds described are the first examples of a potentially very large class of new redox-active solids.

## Notes and references

‡ Synthetic details: Synthesis of  $[\text{Mn}(\text{DMSO})_4(\text{H}_2\text{O})_2][\text{Mn}_2\text{TCNQ}_3]$ : A solution of  $\text{M}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (27.8 mg, 0.097 mmol),  $\text{K}(\text{OAc})$  (15.9 mg, 0.16 mmol), in  $\text{MeOH}$  (6.0 mL) was allowed to diffuse into a solution of  $\text{TCNQH}_2$  (20 mg, 0.097 mmol) in  $\text{DMSO}$  (1.0 mL) under nitrogen. Pale yellow hexagonal prismatic crystals suitable for X-ray diffraction were formed from this mixture. Yield 19.4 mg. Anal. Calcd for  $\text{Mn}_3(\text{C}_{12}\text{H}_4\text{N}_4)_3[(\text{CH}_3)_2\text{SO}]_{3.5}(\text{H}_2\text{O})_{1.5}$ : C, 47.92; H, 3.37; N, 15.59; S 10.41% Found: C, 48.11; H, 3.22; N, 15.82; S, 10.44%. X-ray powder diffraction indicated that the bulk products are identical to the single crystals (see supporting information). Synthesis of  $[\text{M}(\text{DMSO})_4(\text{H}_2\text{O})_2][\text{M}_2\text{TCNQ}_3]$  ( $\text{M} = \text{Zn, Cd}$ ): A solution of  $\text{M}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.097 mmol) in  $\text{MeOH}$  (6 mL) was allowed to diffuse into a solution of  $\text{TCNQH}_2$  (20 mg, 0.097 mmol) and triethylamine (0.10 mL, 1.5 mmol) in  $\text{DMSO}$  (1.0 mL) under nitrogen. The precipitate formed consisted of a mixture of pale yellow hexagonal prismatic crystals along with an amorphous powder. The crystals were suitable for X-ray structural analysis. X-ray powder diffraction indicated that the bulk products are identical to the single crystals (see supporting information). Synthesis of  $[\text{Mn}(2,2'\text{-bipyridine})_3][\text{Mn}_2\text{TCNQ}_3]$  solvate: A solution of  $\text{M}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (27.8 mg, 0.097 mmol),  $\text{Li}(\text{OAc}) \cdot 2\text{H}_2\text{O}$  (16.5 mg, 0.16 mmol), and 2,2'-bipyridine (15.1 mg, 0.097 mmol) in  $\text{MeOH}$  (6.0 mL) was allowed to diffuse into a solution of  $\text{TCNQH}_2$  (20 mg, 0.097 mmol) in  $\text{DMSO}$  (1.0 mL) under nitrogen. Bright red hexagonal prismatic crystals suitable for X-ray diffraction were obtained from this mixture. Yield 12.5 mg. Anal. Calcd for  $\text{Mn}_3(\text{C}_{12}\text{H}_4\text{N}_4)_3(\text{C}_{10}\text{H}_8\text{N}_2)_3 \cdot \text{CH}_3\text{OH} \cdot 10\text{H}_2\text{O}$ : C, 55.2; H, 4.1; N, 17.3%. Found: C, 55.2; H, 3.40; N, 17.1%. X-ray powder diffraction indicated that the bulk products are identical to the single crystals (see supporting information).

§ Crystal data for  $[\text{Mn}(\text{DMSO})_4(\text{H}_2\text{O})_2][\text{Mn}_2(\text{TCNQ})_3]$   $\text{C}_{44}\text{H}_{40}\text{Mn}_3\text{N}_{12}\text{O}_6\text{S}_4$ ,  $M = 1125.94$ , trigonal,  $P-31m$ ,  $a = 13.0158(9)$ ,  $c = 10.8532(4)$  Å,  $V = 1592.3(2)$  Å $^3$ ,  $T = 130$  K,  $R_{\text{int}} = 0.0452$ ,  $Z = 1$ , 3473 measured reflections, 1136 independent reflections,  $wR_2 = 0.2809$  (all data),  $R_1 = 0.0821$  ( $I > 2\sigma(I)$ ).<sup>20,21</sup> Crystal data for  $[\text{Zn}(\text{DMSO})_4(\text{H}_2\text{O})_2][\text{Zn}_2(\text{TCNQ})_3]$   $\text{C}_{44}\text{H}_{40}\text{N}_{12}\text{O}_6\text{S}_4\text{Zn}_3$ ,  $M = 1157.23$ , trigonal,  $P-31m$ ,  $a = 12.7447(4)$ ,  $c = 10.7107(3)$  Å,  $V = 1506.63(8)$  Å $^3$ ,  $T = 130$  K,  $R_{\text{int}} = 0.0190$ ,  $Z = 1$ , 3576 measured reflections, 1098 independent reflections,  $wR_2 = 0.2859$  (all data),  $R_1 = 0.00827$  ( $I > 2\sigma(I)$ ).<sup>20,21</sup> Crystal data for  $[\text{Cd}(\text{DMSO})_4(\text{H}_2\text{O})_2][\text{Cd}_2(\text{TCNQ})_3]$   $\text{C}_{44}\text{H}_{40}\text{Cd}_3\text{N}_{12}\text{O}_6\text{S}_4$ ,  $M = 1298.32$ , trigonal,  $P-31m$ ,  $a = 12.9515(4)$ ,  $c = 10.8818(2)$  Å,  $V = 1580.78(7)$  Å $^3$ ,  $T = 130$  K,  $R_{\text{int}} = 0.0185$ ,  $Z = 1$ , 3620 measured reflections, 1155 independent reflections,  $wR_2 = 0.1181$  (all data),  $R_1 = 0.0390$  ( $I > 2\sigma(I)$ ).<sup>20,21</sup> Crystal data for  $[\text{Mn}(\text{bipy})_3][\text{Mn}_2(\text{TCNQ})_3] \cdot 2\text{CH}_3\text{OH}$   $\text{C}_{68}\text{H}_{44}\text{Mn}_3\text{N}_{18}\text{O}_2$ ,  $M = 1310.03$ , hexagonal,  $P6_3/mcm$ ,  $a = 12.8814(3)$ ,  $c = 22.0591(4)$  Å,  $V = 3169.89(12)$  Å $^3$ ,  $T = 130$  K,  $R_{\text{int}} = 0.0243$ ,  $Z = 2$ , 7375 measured reflections, 1202 independent reflections,  $wR_2 = 0.3385$  (all data),  $R_1 = 0.0990$  ( $I > 2\sigma(I)$ ).<sup>20,21</sup> The ligands of the cationic complexes located in the hexagonal channels of each of the anionic networks could not be satisfactorily resolved because of severe disorder.

The SQUEEZE routine within the crystallographic program PLATON was employed in the treatment of the disordered regions of the crystal.<sup>19</sup>

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