

# Ferrimagnetic ordering of a methylthio-substituted planar porphyrin based electron transfer salt, octakis(2,3,7,8,12,13,17,18-methylthio)porphyrinatomanganese(III) tetracyanoethanide

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The direct redox reaction between tetracyanoethylene (TCNE) and a planar porphyrinatomanganese(II), octakis(2,3,7,8,12,13,17,18-methylthio)porphyrinatomanganese(II), Mn<sup>II</sup>OMTP, produced a polymeric electron transfer salt (ETS), that has been structurally and magnetically characterized. The ETS belongs to the orthorhombic *Cmca* space group. The ETS has an extended one-dimensional linear chain coordination polymer motif comprised of  $S=2$  [Mn<sup>III</sup>OMTP]<sup>+</sup> and bridging  $S=1/2$  [TCNE]<sup>-</sup> with an Mn–N<sup>TCNE</sup> distance of 2.330(5) Å, and lacks solvent. The [TCNE]<sup>-</sup> is disordered over two orientations in a 1 : 1 ratio. The interchain Mn···Mn distance, 9.205 Å, is shorter than the intrachain distance, 9.350 Å ( $\equiv a$ -axis). The 2 to 300 K temperature dependence of the magnetic susceptibility can be fit to a Curie–Weiss expression with an effective  $\theta$  value of +40 K. Intrachain coupling was modelled to a Seiden expression ( $H = -2S_a \cdot S_b$ ) with a  $J_{\text{intra}}$  of –125 K, and 10 Hz ac magnetic susceptibility indicates an ordering temperature,  $T_c$ , of 9.6 K. The frequency dependence of the ac susceptibility displays spin glass behaviour.

## Introduction

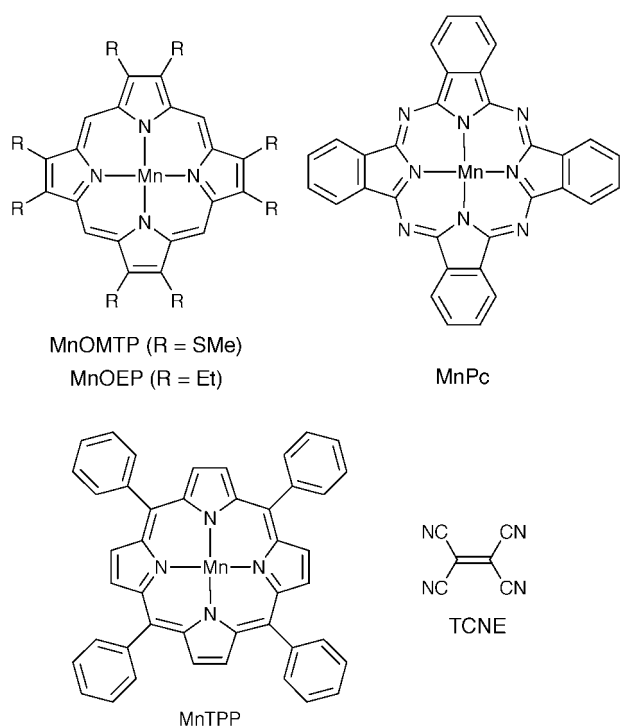
The preparation and characterization of molecule-based magnetic materials is a growing area of contemporary interdisciplinary research.<sup>1</sup> In the past two decades, a variety of ferromagnetically coupled and magnetically ordered materials such as neutral radicals, polycarbenes, and nitrenes, as well as electron transfer salts (ETSs) have been reported. The ETSs, where an organic radical anion is bonded to a paramagnetic transition metal cation, have been attracting special attention, as they have stronger exchange interactions ( $J$ ) through the coordination bond to give higher magnetic ordering temperatures,  $T_c$ . Although there exists an ETS with the highest  $T_c$ , V(TCNE)<sub>*x*</sub>·y(CH<sub>2</sub>Cl<sub>2</sub>) ( $x \sim 2$ ;  $y \sim 1/2$ ) (TCNE = tetracyanoethylene), which has the largest number of bonds between the [TCNE]<sup>-</sup> and the paramagnetic transition metal, the amorphous nature of this room temperature magnet<sup>2</sup> prevents detailed understanding of the structure.

ETSs based on porphyrinatomanganese ([MnP]) and cyanocarbon acceptors such as TCNE have magnetic ordering temperatures as high as 28 K and are frequently well characterized structurally.<sup>2–11</sup> In these complexes, the [MnP]<sup>+</sup> cations are bridged in a *trans*- $\mu$  manner between Mn<sup>III</sup> and a nitrile group of the cyanohydrocarbon acceptor, typically [TCNE]<sup>-</sup>, to form a one-dimensional (1-D) polymeric structure.<sup>12</sup> Further detailed studies on [MnP]<sup>+</sup>[TCNE]<sup>-</sup> complexes are needed to understand the origin of the 3-D magnetic coupling as well as to obtain new magnets with enhanced physical properties, such as a higher  $T_c$ <sup>11</sup> and a higher coercive force,  $H_{cr}$ .<sup>13</sup> We have been carrying out our researches with the following three strategies: first, the development of structure–function relationships as a function of incorporated solvent molecules;<sup>7–10,12,14,15</sup> second, the identification of improved open shelled bridging ligands with respect to [TCNE]<sup>-</sup>, hexacyanobutadiene,<sup>9,14,16–19</sup> chloranil,<sup>20</sup> TCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane),<sup>6,21,22</sup>

and substituted TCNQs,<sup>23</sup> and other cyanocarbons;<sup>21,24–26</sup> and third, the development of additional porphyrinato ligands other than substituted *meso*-tetraphenylporphyrinato (TPP),<sup>7,11–13,17,21,24,25,27–33</sup> and also by replacing the  $\beta$ -hydrogens of porphyrin with groups such as alkyl substituents or by annulation, *e.g.*, 2,3,7,8,12,13,17,18-octaethylporphyrinatomanganese(II) (Mn<sup>II</sup>OEP)<sup>16</sup> and phthalocyaninatomanganese(II) (Mn<sup>II</sup>Pc).<sup>34</sup>

In the course of these studies, we identified an important relationship between the Mn–N<sup>TCNE</sup> angle ( $\angle \text{MnNC}^{\text{TCNE}}$ ) and the magnitude of the intrachain magnetic coupling,  $J_{1D}$ , *i.e.*, the magnitude of the magnetic coupling  $|J_{1D}|$  increases with an increase of  $\angle \text{MnNC}^{\text{TCNE}}$ .<sup>32</sup> This is attributed to the exchange interaction through the  $\sigma$ -type overlap between the Mn<sup>III</sup>  $d_{z^2}$  and [TCNE]<sup>-</sup>  $\pi^*$  orbitals. Although the origin of this phenomenon remains unclear, the replacement of the bulky substituents in TPP ligands with a less bulky group may lead to a smaller value of  $\angle \text{MnNC}^{\text{TCNE}}$  and, hence, to stronger magnetic coupling. Macrocycle complexes such as Mn<sup>II</sup>OEP<sup>16</sup> and Mn<sup>II</sup>Pc<sup>34</sup> are the best candidates. The TCNE ETSs of Mn<sup>II</sup>OEP<sup>16</sup> and Mn<sup>II</sup>Pc<sup>34</sup> showed the expected small  $\angle \text{MnNC}^{\text{TCNE}}$ , however, they have nonuniform chain structures that do not stabilize ferrimagnetic ordering. Recently, we reported a new porphyrin ligand substituted with eight peripheral sulfur atoms, 21*H*,23*H*-2,3,7,8,12,13,17,18-octakis(methylthio)porphyrin, H<sub>2</sub>OMTP (**1**),<sup>35</sup> with the goal of preparing supramolecular architectures constructed by the chalcogen–chalcogen atomic contacts usually seen in tetra-thiafulvalene-based conductors.<sup>36</sup> Since the SMe group is similar in size to the Et group, the possibility of S···S interactions might lead to the stabilization of a uniform chain and magnetic ordering. Furthermore, as the structure of [Mn<sup>III</sup>OEP]<sup>+</sup>[TCNE]<sup>-</sup> lacks solvent and the associated plethora of structure and magnetic behavioural changes that occur on desolvation, it is anticipated that [Mn<sup>III</sup>OMTP]<sup>+</sup>[TCNE]<sup>-</sup> (**2**) would also lack solvent simplify-

ing the interpretation of the magnetic properties. Herein, we report and discuss the first ETS constructed from  $\text{Mn}^{\text{II}}\text{OMTP}$  (**3**) and TCNE,  $[\text{Mn}^{\text{III}}\text{OMTP}]^+[\text{TCNE}]^-$  (**2**).

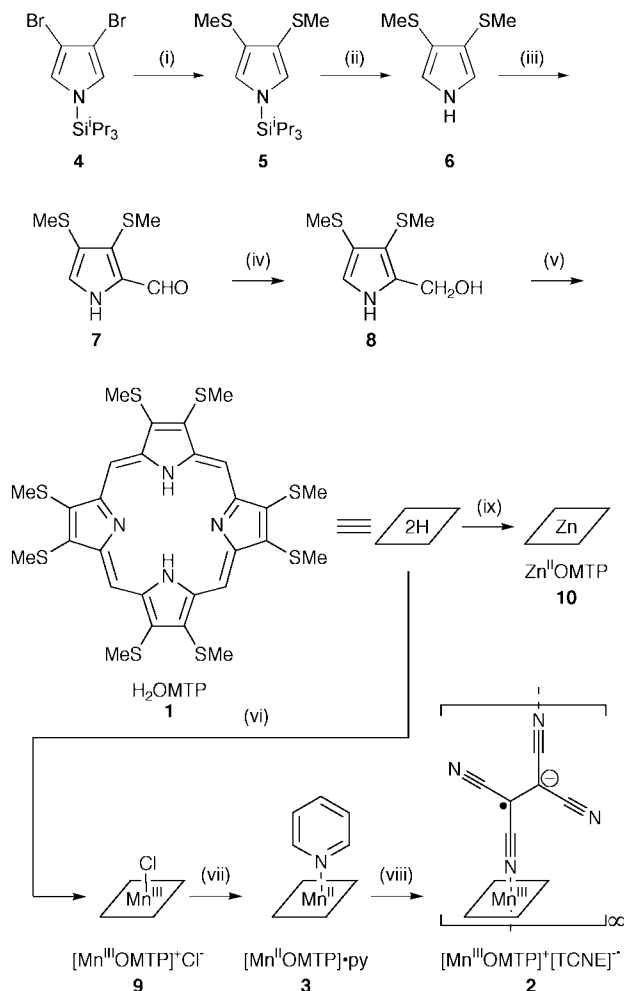


## Results and discussion

### Synthesis

The synthesis of the title complex **2** is summarized in Scheme 1, *i.e.*, the five step synthesis of the free base **1**,<sup>35</sup> metallation (affording **9**), reduction (to give **3**), and the direct redox reactions (providing **2**). Pyrrole **5** was synthesized by treatment of **4**<sup>37</sup> with <sup>n</sup>BuLi followed with dimethyl disulfide. Deprotection of **5** was carried out by treatment with <sup>n</sup>Bu<sub>4</sub>NF to give an important intermediate, 3,4-bis(methylthio)pyrrole (**6**). According to the standard reaction conditions for porphyrin synthesis, **6** was treated with formaldehyde in pyridine.<sup>38</sup> However, the desired H<sub>2</sub>OMTP **1** was not obtained. Presumably, the weak electron withdrawing property of methylthio groups deactivates the pyrrole. We employed another tetramerization reaction using 2-hydroxymethylpyrrole, as reported by Ogoshi and coworkers<sup>39</sup> and Ono and coworkers<sup>40</sup> for the synthesis of porphyrins with electron withdrawing groups such as  $-\text{C}_n\text{F}_{2n+1}$ . The corresponding pyrrole derivative **8** was prepared by application of the Vilsmeier–Haack formylation reaction to **6** and subsequent reduction with NaBH<sub>4</sub>. This pyrrole **8** was cyclized in the presence of dimethoxymethane with a catalytic amount of *p*-TsOH to give H<sub>2</sub>OMTP **1** in acceptable yield, 30%. The intermediates, **4–8**, were used for the subsequent reactions as soon as possible because of their instabilities.

The metallation and reduction reactions were achieved by similar procedures<sup>41</sup> to give  $\text{Mn}^{\text{III}}$  (**9**) and  $\text{Mn}^{\text{II}}$  (**3**) complexes, respectively. The first reversible oxidation potential of **3**, attributable to the  $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}$  couple, was observed at +0.07 V (*vs.* Ag/AgCl, in PhCN), which is comparable to that of  $[\text{Mn}^{\text{II}}\text{TPP}][\text{pyridine}]$  (−0.08 V). The direct redox reaction between **3** and TCNE ( $E_{1/2}^{\text{red}} = +0.28$  V) was performed under an inert atmosphere and led to the formation of ferrimagnetic black-green crystals **2**. The stoichiometry of the complex **2** was determined to be 1:1 on the basis of



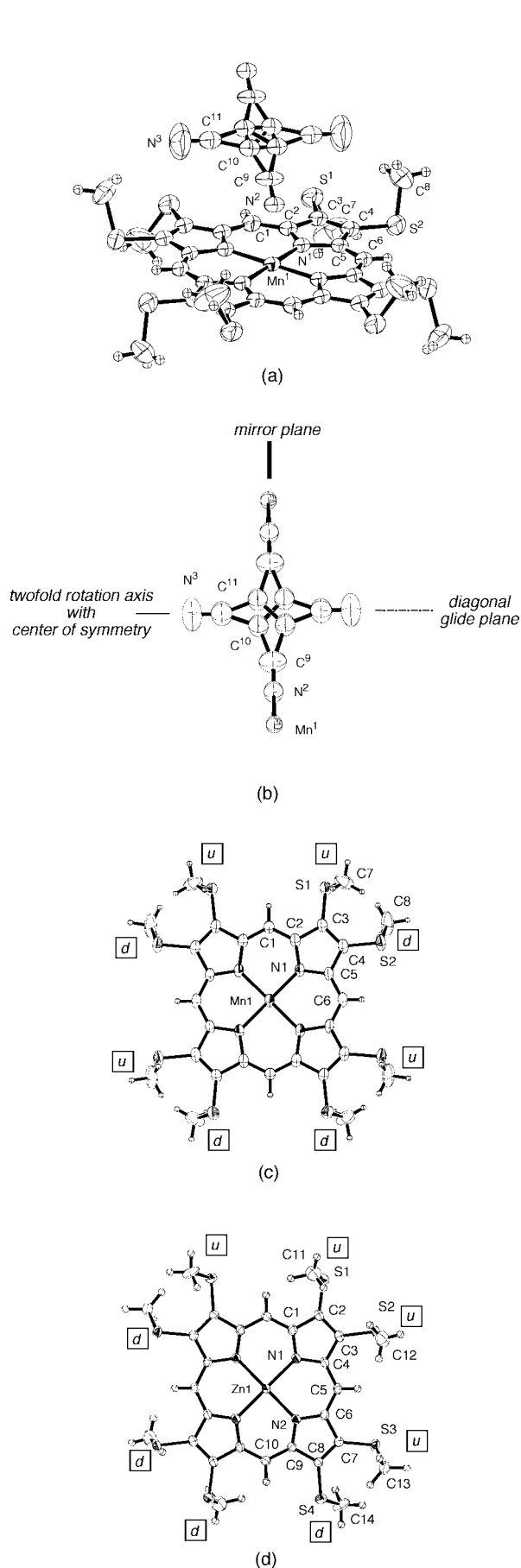
**Scheme 1** Reagents and conditions. (i) <sup>n</sup>BuLi, THF, −78 °C, then MeSSMe. (ii) <sup>n</sup>Bu<sub>4</sub>NF, THF. (iii) Vilsmeier reagent (POCl<sub>3</sub>–DMF), (CH<sub>2</sub>Cl)<sub>2</sub>, then AcONa aq. (iv) NaBH<sub>4</sub>, diethyl ether–MeOH. (v) CH<sub>2</sub>(OMe)<sub>2</sub>, *p*-TsOH·H<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, then DDQ. (vi)  $\text{Mn}^{\text{II}}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ , DMF, then HCl aq. (vii) NaBH<sub>4</sub>, pyridine–MeOH. (viii) TCNE, *p*-xylene. (ix)  $\text{Zn}^{\text{II}}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ , CHCl<sub>3</sub>.

elemental analysis and the crystal structure analysis (*vide infra*). In marked contrast to  $[\text{MnTPP}]^+[\text{TCNE}]^-$ 's, which behave as *solvent sponges*,<sup>42</sup> the  $[\text{OMTP}]^{2-}$  ligand produced a non-solvated structure similar to  $[\text{Mn}^{\text{II}}\text{OEP}]^+[\text{TCNE}]^-$ <sup>16</sup> and  $[\text{Mn}^{\text{III}}\text{Pc}]^+[\text{TCNE}]^-$ <sup>34</sup> and achieved the objective of preparing a solvent-free system. The reference complex,  $\text{Zn}^{\text{II}}\text{OMTP}$  (**10**), was prepared under the usual metallation reaction conditions using  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  from H<sub>2</sub>OMTP **1** in quantitative yield.

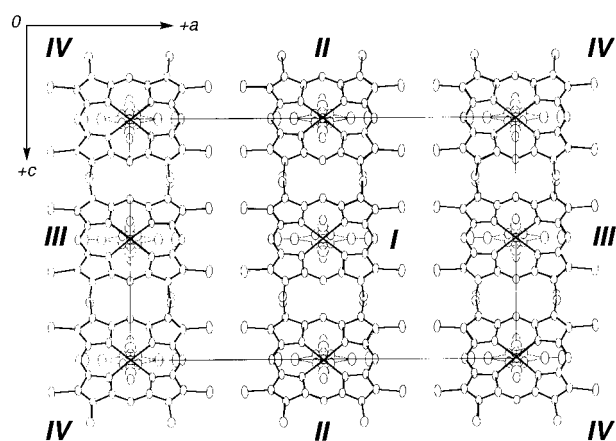
The  $\nu_{\text{CN}}$  absorptions of **2** at 2193 (m) and 2126 (s) cm<sup>−1</sup> indicate the presence of coordinated  $[\text{TCNE}]^-$  species and the non-presence of  $[\text{TCNE}]^n$  ( $n = 0, -2$ ).<sup>43</sup> Heating these samples does not lead to a change in the  $\nu_{\text{CN}}$  absorption as occurs for the  $[\text{MnTCIPP}]^+[\text{TCNE}]^-$  system (TCIPP = *meso*-tetrakis(4-chlorophenyl)porphyrinato).<sup>30</sup> The absorption at 2193 cm<sup>−1</sup> is shifted to higher frequency compared with those of non-coordinated  $[\text{TCNE}]^-$  (2184 and 2144 cm<sup>−1</sup>). The result suggests that the lone pair  $\sigma$ -donations has little metal-to-ligand back-bonding arising from the Mn–N<sup>TCNE</sup> coordination bond and is consistent with the crystallographic study (*vide infra*).<sup>44</sup>

### Structure

Single crystal X-ray analyses were performed for  $[\text{Mn}^{\text{III}}\text{OMTP}]^+[\text{TCNE}]^-$  **2** and the reference compound,  $\text{Zn}^{\text{II}}\text{OMTP}$  **10** (Fig. 1).  $[\text{Mn}^{\text{III}}\text{OMTP}]^+[\text{TCNE}]^-$  **2** forms uniform one-dimensional (1-D) chains comprised of alternat-

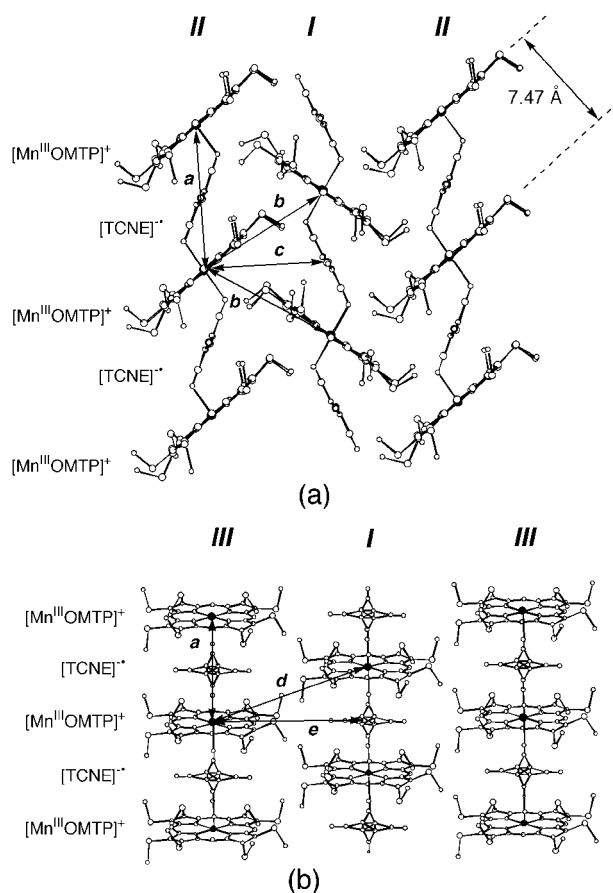


**Fig. 1** ORTEP (50%) drawings of  $[\text{Mn}^{\text{III}}\text{OMTP}][\text{TCNE}]$  (a, b, and c) and  $\text{Zn}^{\text{II}}\text{OMTP}$  (d). Crystallographically independent atoms are labelled. The notations *u* and *d* in (c) and (d) are the conformations of methylthio groups, up directions toward the porphyrin mean plane and down directions, respectively.



**Fig. 2** ORTEP (20%) views of interchain interactions between the unique chains: chains *I*, *II*, *III*, and *IV* for  $[\text{Mn}^{\text{III}}\text{OMTP}][\text{TCNE}]$  (the methyl groups are omitted for clarity).

ing  $[\text{Mn}^{\text{III}}\text{OMTP}]^+$  and  $[\text{TCNE}]^-$  with hexacoordinate *trans*- $\mu$ -*N*-bonds between  $\text{Mn}^{\text{III}}$  and two  $[\text{TCNE}]^-$ 's (Fig. 1–3). The crystal belongs to the orthorhombic crystal system, which possesses the highest symmetry among  $[\text{Mn}^{\text{III}}\text{P}][\text{TCNE}]^-$ 's reported to date.<sup>12,13</sup> The Mn and  $[\text{TCNE}]^-$  are located on special positions and, hence, the 1-D chain is uniform as typical for  $[\text{Mn}^{\text{III}}\text{TPP}][\text{TCNE}]^-$ 's.<sup>12,13</sup> This is in marked contrast to  $[\text{Mn}^{\text{III}}\text{OEP}][\text{TCNE}]^-$ <sup>16</sup> and  $[\text{Mn}^{\text{III}}\text{Pc}][\text{TCNE}]^-$ ,<sup>34</sup> which have nonuniform chains. The symmetry operation for this space group requires the  $[\text{TCNE}]^-$  to be disordered with a 1 : 1 probability, *i.e.*,  $[\text{TCNE}]^-$  has a mirror plane perpendicular to the  $\text{Mn1-N2-C9-C9}^*-\text{N2}^*-\text{Mn1}^*$  axis, a diagonal glide plane



**Fig. 3** Views of interchain interactions between the unique chains: (a) chain *I* and chain *II*, (b) chain *I* and chain *III* (all hydrogen atoms are omitted for clarity). The important interactions are the followings:  $a=9.350$ ,  $b=9.205$ ,  $c=9.64$ ,  $d=13.577$ , and  $e=12.76$  Å.

**Table 1** Interatomic distances for [Mn<sup>III</sup>OMTP][TCNE]

Distance/Å		Distance/Å	
Mn(1)–N(1)	2.008(3)	Mn(1)–N(2)	2.330(5)
N(1)–C(2)	1.389(5)	N(1)–C(5)	1.383(4)
C(1)–C(2)	1.378(5)	C(2)–C(3)	1.442(5)
C(3)–C(4)	1.369(6)	C(4)–C(5)	1.452(6)
C(5)–C(6)	1.370(5)		
S(1)–C(3)	1.745(5)	S(1)–C(7)	1.773(7)
S(2)–C(4)	1.754(4)	S(2)–C(8)	1.763(7)
S(1)–C(2)	3.602(2)		
N(2)–C(9)	1.132(9)	C(9)–C(10)	1.46(1)
C(10)–C(10)	0.99(2)	C(10)–C(10)	1.41(2)
C(10)–C(10)	1.41(2)	C(10)–C(11)	1.46(1)
N(3)–C(11)	1.121(9)		

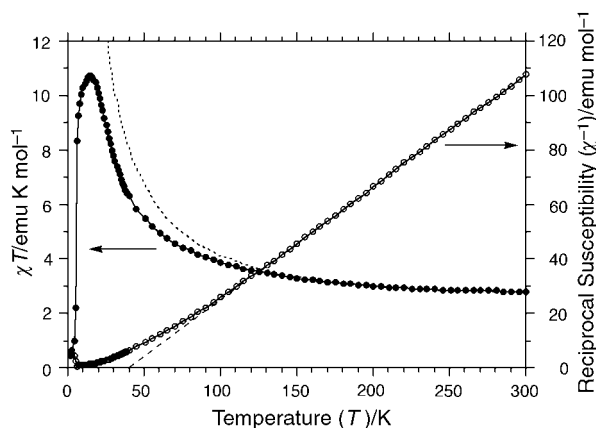
perpendicular to the N3–C11–C11\*–N3\* axis, and a twofold rotational axis with a center of symmetry identical to the N3–C11–C11\*–N3\* axis (Fig. 1(b)). This kind of disorder is proposed as one of the main reasons for the spin glass phenomenon, but previously has only been present in small percentages.<sup>15,45</sup> The central C–C bond distance of [TCNE]<sup>2-</sup> is 1.41(2) Å as expected for its 1.5 bond order.<sup>43</sup> In addition to the above-mentioned IR  $\nu_{\text{CN}}$  data, this is further evidence for the presence of [TCNE]<sup>2-</sup>.

The structure of the [OMTP]<sup>2-</sup> ligand was determined for the first time as the Mn<sup>III</sup> complex (Fig. 1(a)–(c)) and the Zn<sup>II</sup> complex (Fig. 1(d)). Both porphyrin cores are planar within  $\pm 0.02$  Å. The intramolecular bond distances of [Mn<sup>III</sup>OMTP]<sup>+</sup>[TCNE]<sup>2-</sup> **2** are in the range of the standard values for usual porphyrinatomanganese(III), *e.g.*, Mn–N<sup>OMTP</sup> is 2.008(3) Å (Table 1). The distances between the non-bonded vicinal sulfur atoms are 3.602(2) Å for [Mn<sup>III</sup>OMTP]<sup>+</sup> and 3.530(2) and 3.633(2) Å for Zn<sup>II</sup>OMTP, respectively, and are comparable to the sum of the van der Waals radius (3.60 Å)<sup>46</sup> or the corresponding values of the structurally similar 2,3,7,8,12,13,17,18-octakis(alkylthio)porphyrazine complexes ([ORSPz]<sup>2-</sup>), *e.g.*, 3.53 Å for the Mg<sup>II</sup> complex.<sup>47</sup> The conformation of the vicinal methylthio groups for [Mn<sup>III</sup>OMTP]<sup>+</sup>[TCNE]<sup>2-</sup> **2** is *anti*, *i.e.*, two methyl groups are directed in opposite directions and take *u-d-u-d-u-d-u* orientations (*u*: up, *d*: down). This conformation seems to be achieved by the crystal packing requirement, because ZnOMTP, *u-d-d-d-u-u-u* orientation, and ORSPz as well as the ethyl groups of [Mn<sup>III</sup>OEP]<sup>+</sup>[TCNE]<sup>2-</sup> and [Mn<sup>III</sup>OEP]<sup>+</sup>[HCBd]<sup>2-</sup> take different orientations.<sup>16,47</sup>

For [Mn<sup>III</sup>OMTP]<sup>+</sup>[TCNE]<sup>2-</sup> **2**, the Mn–N<sup>TCNE</sup> distance ( $d_{\text{Mn-N}^{\text{TCNE}}}$ ) is 2.330(5) Å, in the range of the reported [MnP]<sup>+</sup>[TCNE]<sup>2-</sup>s, 2.269–2.519 Å (Table 2).<sup>12–14</sup> However, [OMTP]<sup>2-</sup> produced a predicted closer interchain packing than that of [Mn<sup>III</sup>TPP]<sup>+</sup>[TCNE]<sup>2-</sup>s. The four key parameters best describing the structure of the 1-D chain, *i.e.*, intrachain Mn···Mn distance ( $d_{\text{Mn-Mn}}$ ),  $\angle \text{MnNC}^{\text{TCNE}}$ , dihedral angle between the porphyrin ligand and [TCNE]<sup>2-</sup> ( $\angle \text{P-TCNE}$ ), and the intrachain interplanar porphyrin–porphyrin distance ( $d_{\text{P-P}}$ ) are the smallest observed when compared to those of uniform [MnTPP]<sup>+</sup>[TCNE]<sup>2-</sup>s (Table 2). The  $d_{\text{Mn-Mn}}$  of 9.3495(7) Å is shorter by 0.766 Å than the distance reported

**Table 2** Comparison of geometries of [MnOMTP][TCNE] with related ETSS

Compound		$d_{\text{Mn-N}^{\text{TCNE}}}$ / Å	$d_{\text{Mn-Mn}}$ / Å	$\angle \text{MnNC}^{\text{TCNE}}$ / degrees	$\angle \text{P-TCNE}$ / degrees	$d_{\text{P-P}}$ / Å	Reference
[MnOMTP][TCNE]	Uniform	2.330	9.350	124.8	28.2	7.47	This work
[MnTPP][TCNE]·2PhMe	Uniform	2.305	10.116	148.1	55.3	9.28	4
[MnOEP][TCNE]	Nonuniform, Type I	2.519	9.361	117.6	18.2	7.04	16
	Orientation II	2.361	9.794	132.4	35.9	8.16	
$\beta$ -[MnTF4OMePP]	Nonuniform, Type II	2.283	9.301	124.1	34.7	7.87	29
	Orientation II	2.291	9.301	121.5	31.2	7.87	

**Fig. 4** Reciprocal molar magnetic susceptibility,  $\chi^{-1}(T)$  and  $\chi T(T)$  as a function of temperature for polycrystalline [Mn<sup>III</sup>OMTP][TCNE]. The dotted line along  $\chi T(T)$  is a fit to the Seiden expression,  $J = -125$  K.

for [MnTPP]<sup>+</sup>[TCNE]<sup>2-</sup>·2PhMe (10.116(1) Å), while  $\angle \text{MnNC}^{\text{TCNE}}$  (124.8(6)°) and  $\angle \text{P-TCNE}$  (28.2(1)°) are smaller than those reported for [MnTPP]<sup>+</sup>[TCNE]<sup>2-</sup>·2PhMe, 148.1(4)° and 55.3(1)°, respectively. The  $d_{\text{P-P}}$  (7.47 Å) also expresses the closer molecular packing of [Mn<sup>III</sup>OMTP]<sup>+</sup>[TCNE]<sup>2-</sup> **2**, this value is 1.81 Å shorter than that of [Mn<sup>III</sup>TPP]<sup>+</sup>[TCNE]<sup>2-</sup>·2PhMe (9.28 Å).

This 1-D chain (Chain *I*; Fig. 2 and 3) is surrounded by the two nearest neighbouring chains (Chain *II*) in the [001] direction and by the next neighbouring two chains (Chain *III*) in the [100] direction. These chains are *out-of-registry* (Fig. 3).<sup>48</sup> Surprisingly, the interchain Mn···Mn distance (9.205 Å) between Chain *I* and Chain *II* is 0.145 Å shorter than that for the intrachain  $d_{\text{Mn-Mn}}$  (9.350 Å). The shortest distance between Mn and the centre of [TCNE]<sup>2-</sup> is 9.64 Å, which is also shorter than those for [MnTPP]<sup>+</sup>[TCNE]<sup>2-</sup>s (> 10 Å). Interactions between Chain *I* and Chain *III* are weaker, with interchain Mn···Mn and Mn–TCNE distances of 13.577 and 12.761 Å, respectively. This 2-D character is reflected in the magnetic properties (*vide infra*). Such marked structural characteristics are achieved by the planar shape of [MnOMTP]<sup>+</sup>, where the introduced bulky and rigid phenyl groups of TPP separate the neighbouring chains by more than 10 Å.

Unfortunately, sulfur–sulfur contacts less than the sum of van der Waals radius (3.6 Å)<sup>46</sup> were not observed in the crystal structure.

### Magnetic behaviour

The susceptibility ( $\chi$ ) of [Mn<sup>III</sup>OMTP]<sup>+</sup>[TCNE]<sup>2-</sup> **2** was measured from 2 to 300 K and can be fit to the Curie–Weiss equation,  $\chi \propto 1/(T - \theta)$ , with  $\theta$  of  $+40 \pm 1$  K (Fig. 4). This  $\theta$  value is within the reported values for the uniform chain systems of [MnP]<sup>+</sup>[TCNE]<sup>2-</sup> in the range of 12 to > 100 K.<sup>12–14</sup> The room temperature effective moment value,  $\mu_{\text{eff}} [\equiv (8\chi T)^{1/2}]$ , is 4.81  $\mu_{\text{B}}$  which is lower than the predicted value for independent isotropic  $g=2$ ,  $S=2$  of Mn<sup>III</sup> and  $S=1/2$  of

[TCNE]<sup>-</sup> spin systems (5.20  $\mu_B$ ). A minimum in  $\chi T(T)$  characteristic of 1-D antiferromagnetic coupling<sup>49</sup> was not observed below 300 K. Presumably, it occurs above room temperature.<sup>33</sup> Because of the proximity of this minimum to room temperature, the room temperature  $\chi T$  and  $\mu_{\text{eff}}$  values are lower than the calculated values. With decreasing temperature,  $\chi T(T)$  reaches a maximum of 10.7 emu K mol<sup>-1</sup> at 14 K due to saturation and then decreases rapidly.

Above 150 K,  $\chi T(T)$  can be fitted to the Seiden model<sup>50</sup> for noninteracting chains comprised of alternating  $g=2$  quantum, and  $S=2$  and classical  $S=1/2$  spins, with  $J/k_B = -125$  K, for  $H = -2JS_i \cdot S_j$  (Fig. 4). The  $J$  value reflects the strong intrachain antiferromagnetic coupling. However, the minimum was predicted from the best fit of data to the Seiden expression and was then extended beyond the experimental temperature range to give a value of 375 K. Below a temperature of 130 K the data deviated from the predicted value for a purely 1-D system indicating that the ferromagnetic coupling between chains begins to dominate as observed for other [mangano-porphyrin][TCNE] magnets. This temperature exceeds that for [MnP][TCNE], which is attributed to the short interchain interaction in the [001] direction. For the tetraphenylporphyrinmanganese(II) ETSs with cyanohydrocarbon acceptors,  $\chi T(T)$  exceeds the expectation from the Seiden expression due to ferromagnetic coupling attributed to dipolar interactions between the chains.<sup>13,14</sup> [Mn<sup>III</sup>OMTP]<sup>+</sup>[TCNE]<sup>-</sup> type  $\chi T(T)$  behaviour has been observed for [MnOEP]<sup>+</sup>[HCBd]<sup>-</sup>, where this antiferromagnetic coupling was attributed to closer interchain interactions enabling antiferromagnetic  $\pi-\pi$  interaction between the Mn<sup>III</sup>porphyrin moieties between chains.<sup>14,16,18,19</sup> In contrast, the bulkier Ph and substituted Ph groups minimize this interaction, enabling the weaker, albeit ferromagnetic, interchain dipolar interactions to dominate. This is attributed to the short interchain interaction in *out-of-registry* manner.

Antiferromagnetic behaviour is also evident from the saturation magnetization. The 2 K isothermal magnetization increases rapidly with the application of a small field, quickly rising to near saturation (Fig. 5). At 2 K, the magnetization is 14 900 emu Oe mol<sup>-1</sup> or 89% of 16 755 emu Oe mol<sup>-1</sup> expected for  $S_{\text{Tot}} = 2 - 1/2 = 3/2$  system. This is substantially lower than that expected from ferromagnetic coupling, *i.e.*, 27 925 emu Oe mol<sup>-1</sup> for  $S_{\text{Tot}} = 2 + 1/2 = 5/2$  system, but consistent with the lack of saturation observed for related compounds.<sup>1a</sup> At 2 K metamagnetic behaviour, *i.e.*, field-induced change from an antiferromagnetic ground state to a ferromagnetic ground state, was observed with a critical field of *ca.* 28 kOe. Similar field dependence was observed for many [MnTPP]<sup>+</sup>[TCNE]<sup>-</sup>s, which exhibit large coercive and critical fields of *ca.* 28 kOe at 2 K.<sup>13</sup> Hysteresis with a large coercive

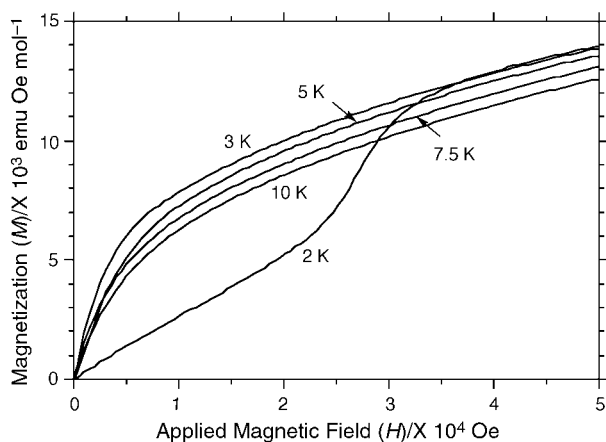


Fig. 5 Variable temperature saturation magnetization for a polycrystalline sample of [Mn<sup>III</sup>OMTP][TCNE] at 2, 3, 5, 7.5 and 10 K.

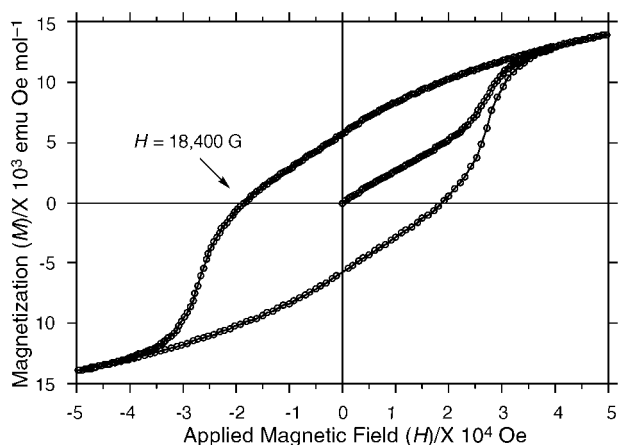


Fig. 6 Hysteretic behavior at 2 K for [Mn<sup>III</sup>OMTP][TCNE].

field of 18.4 kOe was observed at 2 K (Fig. 6), but is not observed at 5 K. The 2 K remanent magnetization is 5720 emu Oe mol<sup>-1</sup>. The field induced crossover from an antiferromagnetic state to a ferrimagnetic ground state is not observed above 3 K.

In addition to dc measurements, the ac susceptibility was determined in an applied ac field of 1000 Oe (<0.05 dc field) at several frequencies and the data are consistent with long-range ferromagnetic order (Fig. 7). A peak in the real part of the 10 Hz ac susceptibility,  $\chi'(T)$ , at 9.6 K is a better measure of the ordering temperature,  $T_c$ ; the value is used for comparison with similar systems. When the value is compared with the similar systems [Mn<sup>III</sup>TPP]<sup>+</sup>[TCNE]<sup>-</sup>·2PhMe ( $T_c = 14$  K) and [MnTCIPP]<sup>+</sup>[TCNE]<sup>-</sup>·2PhMe ( $T_c = 8.8$  K), it is located between the two values. An out-of-phase component,  $\chi''(T)$ , characteristic of a noncompensated moment is present with a peak at 8.3 K. There are also large frequency dependences of both  $\chi'(T)$  and  $\chi''(T)$ . The frequency dependence of  $\chi'(T)$ ,  $\phi = (T_{1000\text{Hz}} - T_{10\text{Hz}}) / \{T_{10\text{Hz}} [\log(100/1)]\}$ , is 0.17 which is sufficiently large to be characteristic for the materials being in a spin glass or superparamagnetic state.<sup>51</sup> The broad nature of the  $\chi'(T)$  and  $\chi''(T)$  peaks suggests the presence of more than one transition.

## Conclusion

The structure of [Mn<sup>III</sup>OMTP]<sup>+</sup> was structurally characterized. This structure may help the further understanding of the widely used [ORSPz]<sup>2-</sup><sup>47</sup> and related macrocycles.<sup>52</sup> Additionally the first non-tetraphenylporphyrinatomanganese(III)

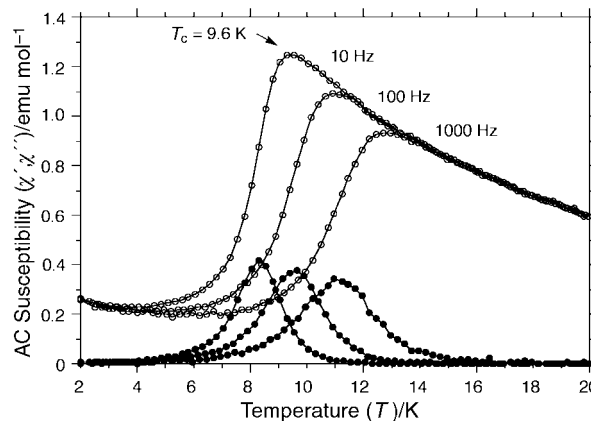


Fig. 7 The dispersive,  $\chi'$  (○), and absorptive,  $\chi''$  (●), components of the ac susceptibility measured at 10, 100 and 1000 Hz. The 9.6 K absorption in the 10 Hz frequency data is defined as  $T_c$ . The sample was cooled to 2 K in zero field and data were taken upon warming.

based ETS exhibiting magnetic ordering was prepared and structurally characterized. In marked contrast to other ETSs based on other planar ligand such as  $[\text{Mn}^{\text{III}}\text{OEP}]^+[\text{TCNE}]^{-\cdot 16}$  and  $[\text{Mn}^{\text{III}}\text{Pc}]^+[\text{TCNE}]^{-\cdot 34}$  which possess nonuniform structure and weak magnetic couplings,  $[\text{Mn}^{\text{III}}\text{OMTP}]^+[\text{TCNE}]^{-\cdot 2}$  is a 1-D uniform structure that stabilizes ferrimagnetic coupling.

## Experimental

### General

TCNE (TCI Co., Ltd) was purified by vacuum sublimation. *p*-Xylene (Nacalai Tesque, Inc.; >98%) and THF (Wako Pure Chemical Ind., Ltd.; >98%) were distilled under nitrogen over sodium.  $\text{CH}_2\text{Cl}_2$  (Nacalai Tesque, Inc.; >98%),  $(\text{CH}_2\text{Cl})_2$  (Wako Pure Chemical Ind., Ltd.; >98%), and DMF (Wako Pure Chemical Ind., Ltd.; >99%) were distilled under nitrogen over  $\text{CaH}_2$ . Dry pyridine (Aldrich) used for the synthesis and UV-vis studies was used without further purification. Other reagents and solvents were used as received. All manipulations for  $\text{Mn}^{\text{II}}$  (**3**) and  $\text{Mn}^{\text{III}}$  (**2** and **9**) complexes were performed in a glove box with less than 1 ppm oxygen. Melting points (mp) were measured with a Yanako hot stage apparatus without correction. The  $^1\text{H}$  NMR spectra were recorded on a JEOL EX-270 (270 MHz and 67.5 MHz) spectrometer in  $\text{CDCl}_3$  with TMS as the internal standard. The elemental analysis was performed using a Perkin-Elmer 2400 apparatus. The FAB mass spectra were recorded on a JEOL JMS-600 spectrometer using 3-nitrobenzyl alcohol as a matrix. Infrared spectra were recorded on a Perkin-Elmer System-2000 FTIR in the range of 650 to 4000  $\text{cm}^{-1}$  on NaCl discs as a mineral oil mull. Absorption spectra were obtained with a Shimadzu UV-PC3100 spectrometer. Cyclic voltammetry was performed with a BAS CV-50 set-up using glassy carbon working, Pt counter, and Ag/AgCl reference electrodes in the  $\text{PhCN}/^n\text{Bu}_4\text{N}^+\text{PF}_6^-$  system.

### *N*-(Triisopropylsilyl)-3,4-bis(methylthio)pyrrole (**5**)

A solution of  $^n\text{BuLi}$  in hexane (99 mL of a 1.6 M solution, 158 mmol; Nacalai Tesque, Inc.) was added to a stirred solution of *N*-(triisopropylsilyl)-3,5-dibromopyrrole **4** (7.50 g, 19.7 mmol)<sup>37</sup> in anhydrous THF (200 mL) at  $-78^\circ\text{C}$  in a nitrogen atmosphere. The solution was stirred at this temperature for 8 h, and then  $\text{Me}_2\text{S}_2$  (14 mL, *ca.* 14.64 g, 155 mmol; Wako Pure Chemical Ind., Ltd.) was added and the reaction mixture was left to reach room temperature and stirred for 20 min. The mixture was poured into water and was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic phases was combined and washed with water and brine, dried over  $\text{Na}_2\text{SO}_4$ . The crude oily product was purified by silica-gel chromatography to give 4.71 g of **5** (76%). This compound was unstable under ambient conditions. Without further purification, **5** was used for the following reaction as soon as possible.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta=6.76$  (s, 2H), 2.37 (s, 6H), 1.48 (septet,  $J=7.6$  Hz, 3H), and 1.08 (d,  $J=7.6$  Hz, 18H); MS ( $m/z$ ) 316 ( $\text{M}^+$ ); calcd. for  $\text{C}_{15}\text{H}_{29}\text{NS}_2\text{Si}$  315.62.

### 3,4-Bis(methylthio)pyrrole (**6**)

A 1.0 M solution of  $^n\text{Bu}_4\text{NF}$  in THF (1.1 mL, 1.1 mmol; Aldrich) was added to a stirred solution of **5** (1.00 g, 3.2 mmol) in THF. After 10 min, the solvent was removed under vacuum and the residue was subjected to column chromatographic purification on florisil<sup>®</sup> (Wako Pure Chemical Ind., Ltd.) using  $\text{CH}_2\text{Cl}_2$  as the eluent to give 0.50 g of **6** (quant.). This compound was quite unstable under ambient conditions. Without further purification, the product was used for the following reaction as soon as possible.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ,

270 MHz):  $\delta=8.91$  (bs, 2H), 6.75 (d,  $J=2.0$  Hz, 2H), and 2.30 (s, 6H); MS ( $m/z$ ) 159 ( $\text{M}^+$ ); calcd. for  $\text{C}_6\text{H}_9\text{NS}_2$  159.27.

### 2-Formyl-3,4-bis(methylthio)pyrrole (**7**)

$\text{POCl}_3$  (0.32 mL, *ca.* 0.53 g, 3.4 mmol; Wako Pure Chemical Ind., Ltd.) was added to stirred anhydrous DMF (0.27 mL) at  $0^\circ\text{C}$ . The solution was stirred at this temperature for 15 min and then at room temperature for another 15 min, then anhydrous  $(\text{CH}_2\text{Cl})_2$  (5 mL) was added to the solution. A solution of crude **6** (0.50 g, 3.1 mmol) in anhydrous  $(\text{CH}_2\text{Cl})_2$  (50 mL) was added dropwise over 30 min at  $0^\circ\text{C}$ . The solution was refluxed for 15 min, then cooled to room temperature. A solution of  $\text{AcONa}$  (20.10 g, 245 mmol; Wako Pure Chemical Ind., Ltd.) in 100 mL water was added to the mixture which was then refluxed for a further 15 min. The cooled reaction mixture was extracted with three portions of 50 mL of  $\text{CH}_2\text{Cl}_2$ . The combined organic phases were washed with brine and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was removed *in vacuo* and the residue was purified by silica-gel chromatography using  $\text{CH}_2\text{Cl}_2$  as the eluent to give 0.50 g of **7** (84%); mp 115.0–116.0  $^\circ\text{C}$  (from  $\text{CH}_2\text{Cl}_2$ –hexane).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta=9.33$  (bs, 2H), 7.10 (d,  $J=2.0$  Hz, 1H), 2.47 (s, 3H), and 2.41 (s, 3H); MS ( $m/z$ ) 188 ( $\text{M}+\text{H}$ ); calcd. for  $\text{C}_7\text{H}_9\text{NOS}_2$  187.28.

### 2-Hydroxymethyl-3,4-bis(methylthio)pyrrole (**8**)

A mixture of 250.0 mg of **7** (1.3 mmol), 203.0 mg  $\text{NaBH}_4$  (6.7 mmol; Wako Pure Chemical Ind., Ltd.), 100 mL of diethyl ether, and 100 mL of MeOH was stirred for 10 min at room temperature. The mixture was diluted with 200 mL of water and the product was extracted with ether. The organic phases were combined and washed with water and brine, dried over  $\text{Na}_2\text{SO}_4$ . The solvent was removed *in vacuo* to give 230 mg of **8** as a pale brown viscous oil (91%). This compound was extremely unstable at room temperature even in an inert atmosphere, the product was used for the next reaction as soon as possible without further purification.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta=8.55$  (bs, 2H), 6.80 (d,  $J=3.0$  Hz, 1H), 4.76 (s, 2H), 2.38 (s, 3H), and 2.29 (s, 3H).

### 21*H*,23*H*-2,3,7,8,12,13,17,18-Octakis(methylthio)porphyrin ( $\text{H}_2\text{OMTP}$ ) (**1**)

A mixture of 230 mg of crude **8** (1.2 mmol), 0.33 mL of dimethoxymethane (284 mmol; TCI Co., Ltd.), and 200 mL of anhydrous  $\text{CH}_2\text{Cl}_2$  was purged with nitrogen for 5 min. 708.0 mg of *p*-TsOH· $\text{H}_2\text{O}$  (3.7 mmol; Wako Pure Chemical Ind., Ltd.) was added to the solution and stirred under a nitrogen atmosphere for 14 h avoiding the light. 310.0 mg of DDQ (1.4 mmol; TCI Co., Ltd.) was added to the solution and refluxed for 1 h. The reaction mixture was subjected to column chromatography on silica gel using  $\text{CH}_2\text{Cl}_2$  to elute the product. The crude product was recrystallized from  $\text{CH}_2\text{Cl}_2$ –MeOH to give 67.6 mg of **1** (30%).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta=10.78$  (s, 4H), 3.13 (s, 24 H), and  $-3.16$  (bs, 2H); MS ( $m/z$ ) 678 ( $\text{M}-\text{H}$ ); calcd. for  $\text{C}_{28}\text{H}_{30}\text{N}_4\text{S}_8$  679.09. UV-vis  $\lambda_{\text{abs}}$  (PhMe) 659 (log  $\epsilon=3.90$ ), 599.0 (390), 570.0 (4.16), 531.0 (4.14), and 433 (5.19) nm.

### $[\text{Mn}^{\text{III}}\text{OMTP}]^+\text{Cl}^-$ (**9**)

A mixture of 1.00 g of  $\text{H}_2\text{OMTP}$  (1.47 mmol)<sup>35</sup> and 7.23 g of  $\text{Mn}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$  (14.7 mmol; Wako Pure Chemical, Inc.; >99%) was dissolved in 100 mL of freshly distilled reagent grade DMF (Wako Pure Chemical, Inc.) and refluxed under ambient atmosphere for 1 h. The mixture was cooled to room temperature and poured into 1 L of water. The precipitated crude product was collected, dissolved in 500 mL of  $\text{CHCl}_3$ , and stirred vigorously with 500 mL of 50% v/v HCl aq. overnight. The organic phase was separated and poured on the

top of a silica gel column. The first band eluted with  $\text{CHCl}_3$  contained unreacted  $\text{H}_2\text{OMTP}$ . The main second band, which was eluted with 1:1  $\text{CHCl}_3$ :ethyl acetate, yielded 860.3 mg (54%) of  $[\text{Mn}^{\text{III}}\text{OMTP}]^+\text{Cl}^-$ . UV-vis ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$  630, 594, 500, and 391 nm. Without further purification, the product was used for the following reaction.

### $[\text{Mn}^{\text{II}}\text{OMTP}]$ -pyridine (3)

$\text{NaBH}_4$  (248.5 mg; 6.57 mmol) was added in three portions to a solution of  $[\text{Mn}^{\text{III}}\text{OMTP}]^+\text{Cl}^-$  (500.0 mg; 0.65 mmol) in pyridine (10 mL) and methanol (10 mL). The solution was heated to reflux for 30 min prior to cooling to room temperature. To the solution was added MeOH (100 mL) purged with nitrogen. The precipitate was collected using Schlenk techniques to yield 395 mg (83%) of the desired product as dark green-purple crystals. UV-vis (pyridine)  $\lambda_{\text{max}}$  619, 583, and 463 nm. This product was used for further reaction without additional purification. CV (PhCN, vs. Ag/AgCl)  $[\text{Mn}^{\text{III}}\text{OMTP}^{\cdot+}]^{2+}/[\text{Mn}^{\text{III}}\text{OMTP}^{2-}]^+ = +1.30$  (irr.),  $[\text{Mn}^{\text{III}}\text{OMTP}^{2-}]^+ / [\text{Mn}^{\text{II}}\text{OMTP}^{2-}]^0 = +0.07$ ,  $[\text{Mn}^{\text{II}}\text{OMTP}^{2-}]^0 / [\text{Mn}^{\text{II}}\text{OMTP}^{3-}]^- = -0.92$ , and  $[\text{Mn}^{\text{II}}\text{OMTP}^{3-}]^- / [\text{Mn}^{\text{II}}\text{OMTP}^{4-}]^{2-} = -1.23$  V.

### $[\text{Mn}^{\text{III}}\text{OMTP}]^+[\text{TCNE}]^-$ (2)

A filtered hot solution of  $[\text{Mn}^{\text{II}}\text{OMTP}]$ -pyridine (80.0 mg, 98.6  $\mu\text{mol}$ ) in 50 mL of boiling *p*-xylene was added to TCNE (65.0 mg, 507  $\mu\text{mol}$ ) in 40 mL of hot *p*-xylene. The solution was left to stand overnight, to form black-green crystals, which were collected by vacuum filtration and dried under vacuum for 3 h (yield: 23.1 mg, 27%). Anal. Calc. for  $\text{C}_{34}\text{H}_{28}\text{MnN}_8\text{S}_8$ : C, 47.48; H, 3.28; N, 13.03; S, 29.82%. Found: C, 47.20; H, 3.08; N, 13.22; S, 29.77%.

### Zn(II)OMTP (10)

A mixture of 50 mg of **1** (0.07 mmol), 162 mg of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.74 mmol; Wako Pure Chemical, Inc.; >98%), and 20 mL of  $\text{CHCl}_3$  was stirred under reflux for 30 min. The reaction mixture was subjected to column chromatography on silica gel using  $\text{CHCl}_3$  to elute the product. The crude product was recrystallized from toluene–MeOH to give 50.0 mg of **10** (91%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 270 MHz):  $\delta = 10.48$  (s, 4H), and 3.10 (s, 24 H); MS (*m/z*) 742 ( $\text{M}^+$ ); calcd. for  $\text{C}_{28}\text{H}_{28}\text{N}_4\text{S}_8\text{Zn}$  742.47.

### Crystallographic study

The crystal data of the complexes are summarized in Table 3. The temperature was calibrated with an Anritsu HFT-50 thermometer. Data for  $[\text{Mn}^{\text{III}}\text{OMTP}][\text{TCNE}]$  (**2**) were col-

**Table 3** Crystallographic data for  $[\text{Mn}^{\text{III}}\text{OMTP}][\text{TCNE}]$  and  $\text{Zn}^{\text{II}}\text{OMTP}$

	$[\text{Mn}^{\text{III}}\text{OMTP}][\text{TCNE}]$	$\text{Zn}^{\text{II}}\text{OMTP}$
Formula	$\text{C}_{34}\text{H}_{28}\text{N}_8\text{MnS}_8$	$\text{C}_{28}\text{H}_{28}\text{N}_4\text{S}_8\text{Zn}$
$M_r/\text{Da}$	860.07	742.42
Crystal system	orthorhombic	monoclinic
Space group	$C_{mca}$ (#64)	$P2_1/n$ (#14)
$\mu(\text{MoK}\alpha)/\text{cm}^{-1}$	8.30	13.92
$R$	0.064	0.050
$a/\text{\AA}$	25.495(2)	5.058(4)
$b/\text{\AA}$	9.3495(7)	19.804(7)
$c/\text{\AA}$	15.859(1)	15.190(4)
$\beta/\text{degrees}$		95.75(4)
Volume/ $\text{\AA}^3$	3780(1)	1513(1)
$T/\text{K}$	198.0(4)	223.0(4)
$Z$	4	2
Measured/independent Reflections	2077/1397	4805/2693
$R(\text{int})$	0.063	0.071

lected on a Rigaku RAXIS-IV imaging plate area detector system with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71070 \text{ \AA}$ , 60 kV, 300 mA) equipped with a Rigaku low temperature device. The crystal-to-detector distance was 105.00 mm with the detector at the zero swing position, *i.e.*, a maximum  $2\theta$  value of  $55.0^\circ$ . A total of 15 oscillation images with  $6.0^\circ$  oscillation angles were collected, each being exposed for 180.0 min. Data for  $\text{Zn}^{\text{II}}\text{OMTP}$  (**10**) were collected on a Rigaku AFC7R four circle diffractometer system with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71070 \text{ \AA}$ , 60 kV, 300 mA) equipped with a Rigaku low temperature device. The data were collected using  $\omega$ - $2\theta$  scan techniques to a maximum  $2\theta$  value of  $60^\circ$ .

CCDC 1145/237. See <http://www.rsc.org/suppdata/jm/b0/b006261h/> for crystallographic files in .cif format.

### Physical methods

The magnetic susceptibility with range of 2 to 300 K was determined on a Quantum Design MPMS-5XL 5 T SQUID (sensitivity =  $10^{-8}$  emu or  $10^{-12}$  emu Oe $^{-1}$  at 1 T) magnetometer with an ultra-low field ( $\sim 0.005$  Oe), and ac options using a reciprocating sample measurement system, and continuous low temperature control with enhanced thermometry features. The ac magnetic susceptibility ( $\chi'$  and  $\chi''$ ) was studied in the range of 10 to 1000 Hz. Samples were loaded in an airtight Delrin<sup>®</sup> holder and packed with oven-dried quartz wool (to prevent movement of the sample in the holder) or in a gelatin capsule. For isofield dc measurements, the samples were zero-field cooled (following oscillation of the dc field), and data collected upon warming. For dc isothermal and ac measurements, remanent fluxes were minimized by oscillation of the dc field, followed by quenching of the magnet. Remaining fluxes were detected using a flux gate gaussmeter and further minimized by application of an opposing field, to bring the dc field to  $< 0.5$  Oe. The diamagnetic correction of  $-622 \times 10^{-6}$  emu mol $^{-1}$  was used for  $[\text{Mn}^{\text{III}}\text{OMTP}][\text{TCNE}]$ .

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