Two-Dimensional Honeycomb Network Formed by Porphyrinatomanganese(III) and μ4-σ-Dimerized 7,7,8,8-Tetracyano-*p*-quinodimethane Dianion

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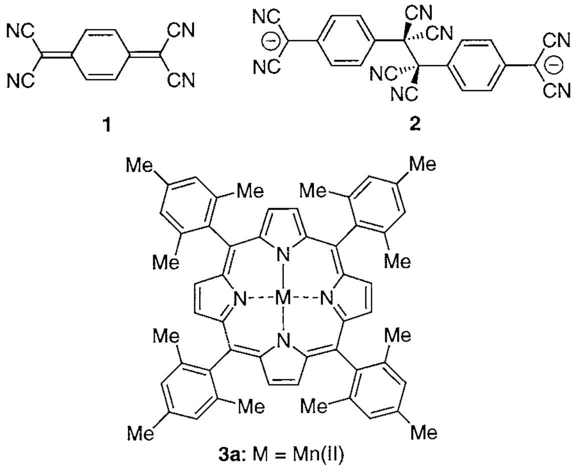
An unprecedented layered (2-D) honeycomb supramolecular structure comprised of μ4-σ-dimerized 7,7,8,8-tetracyano-*p*-quinodimethane dianion bridging four $S = 2$ substituted Mn(III)porphyrins as demonstrated with *meso*-tetrakis(2,4,6-trimethylphenyl)porphyrinato has been structural characterized.

Due to the effects arising from cooperative d-π electron interactions, electron-transfer complexes constructed from transition metals and cyano-substituted acceptors have been studied in detail.[1] The high chemical and redox reactivity of these acceptors sometimes produces unexpected products and interesting architectures using coordination bonds.[1,2] For example, tetracyanoethylene produces $[C_3(CN)_5]^-$,[3] $[(CN)_2C{=}C(CN)O]^-$,[3] $[MeC_6H_4C_5(CN)_6]^-$,[4] and $[C(CN)_3]^-$.[5] While studying the structure-function relationship for the porphyrinatomanganese(III) (MnP) based magnets,[6] we identified the reductive σ-dimerization of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) **1** by *meso*-tetrakis(2,4,6-trimethylphenyl)porphyrinatomanganese(II), Mn^{II}TMesP **3a**, to form an unexpected two-dimensional (2-D) honeycomb structure. Herein, the synthesis, supramolecular crystal structure, and magnetic properties of this unique complex are reported.

The reaction of **1** and **3a**[7,8] in chlorobenzene led to the isolation of $[\mathbf{3b}]_2[\mathbf{2}]\cdot 4PhCl$[9] having ν_{CN} absorptions at 2183 and 2128 cm^{-1} along with $\delta_{C\text{-}H}$ absorption at 805 cm^{-1} characteristic of $[\mathbf{2}]^{-\bullet}$.[10] The single crystal X-ray analysis, however, revealed that $[\mathbf{1}]^{-\bullet}$ is μ4-σ-$[TCNQ]_2^{2-}$ (**2**) bridging four $[\mathbf{3b}]^+$'s (Figure 2).[11] A few σ-$[TCNQ]_2^{2-}$ dimers have been reported.[12] The long central σ-bond of **2**, C(66)-C(66*), is 1.61(1) Å and is comparable to the reported values, including μ4-σ-$[TCNQ]_2^{2-}$-containing 2-D Mn^{II}(TCNQ)$_2$.[10] The bond angles about C(66) are essentially tetrahedral.[11]



1 **2**

3a: M = Mn(II)
3b: M = Mn(III)

Figure 1.

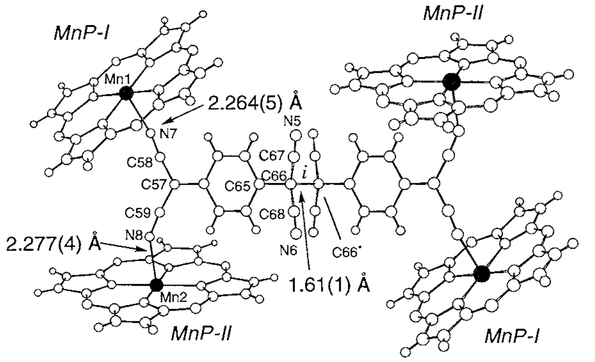


Figure 2. Labeled drawing of $[\mathbf{3b}]_2[\mathbf{2}]\cdot 4PhCl$. For clarity, aryl groups of **3b** were removed.

The terminal N's bond to Mn^{III}'s with Mn-N distances of 2.264(5) and 2.277(4) Å averaging 2.271 Å, and Mn-N-C angles 136.8(5)° and 147.1(4)° averaging 137.0°. Each dicyanomethylene moiety connects two $[\mathbf{3b}]^+$ cations, *MnP-I* and *MnP-II*, along the *a*-axis, and the dihedral angle between the two adjacent porphyrin rings is 64.1°. This canting of nearest MnP planes in a chain albeit less pronounced has been observed for $[MnP][MeC_6H_4C_5(CN)_6]$ (46.0°),[4] $[MnP][C_3(CN)_5]$ (50.3°),[13] [MnP][imidazole] (28.5°),[14] and $[MnP][HCO_2]$ (34.9°),[15] is not observed for [MnP][TCNE] magnets.[6]

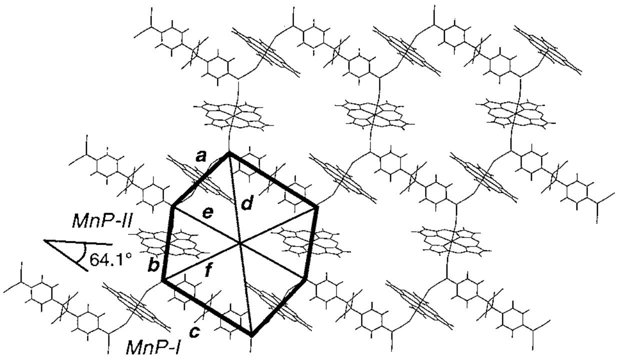


Figure 3. A segment of 2-D honeycomb structure of $[\mathbf{3b}]_2[\mathbf{2}]\cdot 4PhCl$. The size of the hexagon are the followings: *a*: 9.26, *b*: 8.97, *c*: 12.20, *d*: 21.83, *e*: 18.19, and *f*: 20.30 Å.

Due to **2**'s four external nitrile groups, it bonds to four Mn^{III}'s forming a 2-D honeycomb structure (Figure 3). This alignment is quite different from parallel stacked structure seen in [MnP][TCNE] structures.[6] The lengths of the edges of the honeycomb hexagon are 8.97, 9.25, and 12.20 Å, and diagonals are 18.19, 20.30, and 21.83 Å. The cavity of the hexagon is permeated by the aryl groups introduced in the porphyrin ligand. The honeycomb layers lie the *bc*-plane in about 14.4 Å .

The magnetic susceptibility (χ) can be fitted to the Curie-Weiss expression, $\chi \propto (T - \theta)^{-1}$ (θ = -8 K) above 20 K. The observed room-temperature effective moment was 6.95 μB, consistent with the expectation for isolated two $S = 2$ spin system (6.93 μB) and the presence of diamagnetic σ-$[\mathrm{TCNQ}]_2^{2-}$. In contrast to magnetically ordered [MnP][TCNE] magnets, the similar magnetic ordering was not observed in this system because the paramagnetic bridging ligand **2** prevents $\mathrm{Mn^{III}}\cdots\mathrm{Mn^{III}}$ spin coupling.[13-15] Considering that the central σ-bond of **2** is weak, the bond should be easily broken to produce two $[\mathrm{TCNQ}]^{-\bullet}$ in the solid state, *i. e.*, μ4-σ-$[\mathrm{TCNQ}]_2^{2-} \rightarrow 2$ *cis*-μ-$[\mathrm{TCNQ}]^{-\bullet}$.[12] The formed $S = 1/2$ *cis*-μ-$[\mathrm{TCNQ}]^{-\bullet}$ should couple with the $S = 2$ **3b**$^+$'s leading to magnetic ordering. Hence, [**3b**]$_2$[**2**] may be induced to switch from a paramagnetic state to an ordered ferrimagnet[16] by external conditions such as light, heat, and pressure, *etc.*, and studies are in progress.

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9 Complex formation reactions were carried out in a glove box with less than 1 ppm oxygen. A filtered hot solution of **3a** (33.0 mg, 36.0 mmol) dissolved in 12.5 mL of boiling chlorobenzene (PhCl) was added to **1** (7.5 mg, 37.0 mmol) dissolved in 12.5 mL of hot PhCl. After standing for overnight, black-green crystals formed and were harvested by vacuum filtration and dried under vacuum for 3 h, 15.0 mg (40%). Even after a vacuum drying, elemental analysis indicates that the sample incorporates four PhCl molecules. Anal. Found: C, 76.13; H, 5.08; Cl, 5.57; N, 9.11 %. Calcd for $\mathrm{C_{160}H_{132}Cl_4Mn_2N_{16}}$: C, 75.93; H, 5.38; Cl, 5.57; N, 8.80 %. This composition was used for the diamagnetic correction.

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11 Crystal data for $\mathrm{C_{80}H_{66}Cl_2MnN_8}$ {[**3b**]$_2$[**2**]•4PhCl}, Z = 1, M = 2530.60, triclinic $P\bar{1}$ (#2) space group: a = 17.1603(5) Å, b = 17.4730(5) Å, c = 14.3585(4) Å, α = 112.728(1)°, β = 102.849(2)°, γ = 110.721(2)°,V = 3377.1(3) Å^3, ρ_c = 1.244 g cm^{-3}, λ = 0.71070 Å, T = -100±1 °C, $2\theta_{\max}$ = 55.0°, R (Rw) = 0.074 (0.113), Goodness-of-Fit = 1.96, reflection-parameter ratio = 11.43 based on 9062 unique reflections with $I > 3\sigma(I)$. Data were collected on a Rigaku R-AXIS IV imaging plate area detector system with a graphite monochromated Mo-Kα radiation (60 KV X 300 mA), and the structure was solved by a teXsan crystallographic software package from Rigaku. A total of 40 oscillation images with 4.50° oscillation angles were collected, each being exposed for 45.0 min. 12872 reflections were collected. Importanet structural parameters for the dianion are the followings; Mn(1)-N(7): 2.264(5), Mn(2)-N(8): 2.277(4), N(5)-C(67): 1.143(7), N(6)-C(68): 1.152(9), N(7)-C(58): 1.158(8), N(8)-C(59): 1.156(6), C(57)-C(58): 1.405(8), C(57)-C(59): 1.391(6), C(57)-C(60): 1.449(5), C(60)-C(61): 1.406(5), C(60)-C(62): 1.402(7), C(61)-C(63): 1.377(6), C(62)-C(64): 1.376(5), C(63)-C(65): 1.397(8), C(64)-C(65): 1.379(5), C(65)-C(66): 1.529(5), C(66)-C(66*): 1.61(1), C(66)-C(67): 1.471(7), C(66)-C(68): 1.477(9) Å, Mn(1)-N(7)-C(58): 136.8(5)°, Mn(2)-N(8)-C(59): 147.1(4)°, C(65)-C(66)-C(66): 111.8(5)°, C(65)-C(66)-C(67): 111.0(4)°, C(65)-C(66)-C(68): 111.0(3)°, C(66)-C(66)-C(67): 107.9(4)°, C(66)-C(66)-C(68): 107.2(5)°, C(67)-C(66)-C(68): 107.7(5)°.

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