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The effects of halogen bonding and molecular design on the self-assembly of coordination polymers of Mn(III)-tetraarylporphyrin with axial bridging ligands

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Two new Mn(III)-porphyrin 1D coordination polymers, $[\text{Mn}^{\text{III}}(\text{TIPP})(\text{L})]_n$ TIPP = dianion of 5,10,15,20-*meso*-tetrakis(4-iodophenyl)-porphyrin, L = isonicotinate (**1**) or pyrimidine-5-carboxylate (**2**), have been prepared through bridging heteroleptic coordination of the polydentate axial ligands. The two bridging ligands differ in the relative disposition and number of the molecular recognition sites. Single crystal X-ray diffraction analysis reveals that directional $\text{O}\cdots\text{I}$ and $\text{N}\cdots\text{I}$ halogen-bonding-type interactions operate between neighboring polymeric chains in **2**, but not in **1**. Correspondingly, the SEM micrographs show completely different self-assembly patterns of the two complexes when deposited on a carbon fiber.

Manganese-porphyrin coordination polymers have been the subject of investigation for last few decades as biomimetic models,¹ and due to their interesting magnetic,²⁻⁴ catalytic,⁵ and diverse structural properties.^{6,7} Two general strategies are primarily followed to achieve these polymers: 1) by direct coordination of the *meso* substituents of one porphyrin unit to the neighbouring manganese (or any other metal ion) center of an adjacent unit; 2) by interporphyrin coordination through a bridging axial ligand that links between the centers of two adjacent metallo-macrocycles. In the latter case, bridging ($\text{N}\cdots\text{O}$)-type ligands that affect heteroleptic coordination are generally rare compared to homoleptic coordination motifs facilitated by ($\text{N}\cdots\text{N}, \text{O}\cdots\text{O}$)-type bidentate linkers.^{2i,6e} Recently, our group has been involved in crystal engineering

efforts to construct supramolecular porphyrin assemblies directed by halogen bonding interactions, demonstrating the effectiveness of $I\cdots N$, $Br\cdots N$ and $I\cdots O$ halogen bonds in directing the self-organization of porphyrin entities (purposely activated with halogen bonding donor and acceptor functions) in crystals.⁸ We have shown that halogen atoms when placed either on the porphyrin periphery or on the axial ligands, readily take part in interactions with complementary electron-rich hetero atom(s) (N, O) of neighboring porphyrin species, giving rise to halogen-bonded network architectures (Figure 1).⁹

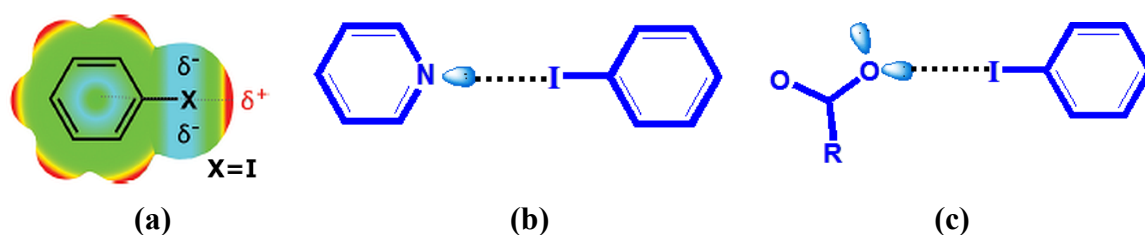


Figure 1, Schematic illustration of (a) the σ -hole at the cap of the C-I bond in iodophenyl, (b) the $I\cdots N$ and (c) the $I\cdots O$ halogen bonding. Note that the electrophilic cap of the C-I bond is directed at the lone electron pairs of the halogen bonding partners for optimal interaction.

As an extension of that project we report here for the first time the occurrence of cooperative halogen bonding between coordination-polymeric multi-porphyrin ensembles. To this end two new coordination polymers of Mn(III)-TIPP, **1** and **2**, have been synthesized through heteroleptic bridging coordination of poly-dentate axial ligands. In **1** the iso-nicotinate linker has two potential coordination sites (one pyridyl-N and one carboxylate-O) *para*-related to one another. The pyrimidine-carboxylate ligand in **2** has three molecular recognition sites at the three *meta*-related positions of the aromatic backbone (two aromatic-N and one carboxylate functions). This report describes the coordination-polymeric structures of the two complexes, and demonstrates how the self-assembly modes of the polymeric chains in the crystalline bulk and in the nano domain is affected by the halogen bonding interactions.

Considering the capacity of manganese ions within the porphyrin core to coordinate axially both to oxygen and nitrogen ligands it was assumed that coordination polymerization will readily take place with the isonicotinate and pyrimidine-5-carboxylate ligands (de-protonated acid moieties to account for charge balance).^{2i,6e} There is a significant difference, however, between the two organic

linkers. In isonicotinate the N and carboxylate coordination sites of the organic linker are placed in 1 and 4 positions of the aromatic ring, and after coordination to the Mn ions of two different porphyrin entities from both sides they will not be accessible for interaction with other neighboring species. In the second case the sided disposition of the carboxylate group (with respected to the metal-coordinated N on the opposite side) and the presence of an extra N-site in the ring impart to this bridging ligand an electron-rich surface and potential capacity (in addition to metal coordination) to interact in the condensed crystalline phase with complimentary electron-deficient molecular recognition sites of adjacent moieties. Indeed, the iodine substituents located at the periphery of porphyrin scaffold are ideally positioned to be involved in intermolecular interactions with electron-rich sites owing to the presence of a region of positive electrostatic potential, the σ -hole, on their outermost cap/surface (Figure 1). In order to confirm our crystal-engineering considerations we analyzed the crystal structures of coordination the compounds **1** and **2** (Figure 2).

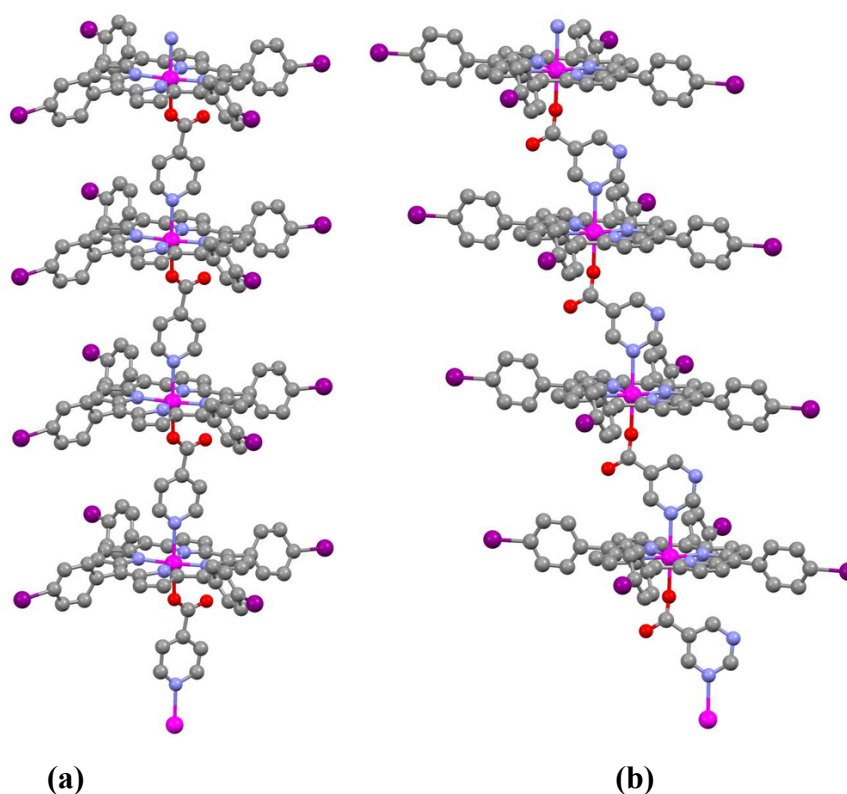


Figure 2. View of the coordination polymers in (a) **1** and (b) **2** (hydrogen atoms are omitted for clarity). Carbon, nitrogen, oxygen, iodine, manganese are presented by gray, light blue, red, purple and magenta colors, respectively. Note the different disposition of the non-coordinated carboxylate-O in the two structures.

Structure **1** can be best described in the monoclinic $C2/c$ space group, with the polymeric entities located on axes of twofold symmetry. This is associated with a twofold disorder of the axial ligand, and alternating coordination of the manganese ion to each of the carboxylate O-atoms at 2.122(3) Å. On the opposite side of the porphyrin ring the Mn(III) ion coordinates to the N-site of another ligand at 2.392(3) Å. In the equatorial plane the distorted octahedral coordination sphere around Mn is completed by Mn-N(pyrrole) bonds of 2.011(2) and 2.020(2) Å. The carboxylate-Os and the pyridyl-N of the isonicotinate ligand coordinate in opposite direction to two different metalloporphyrin rings, thus forming a 1D coordination polymer that propagates along the b -axis of the crystal (Figure 2a). Adjacent polymeric chains in the crystal structure are directed alternatively in opposite directions, \mathbf{b} and $-\mathbf{b}$. The two O-sites of the Mn-coordinated carboxylate lie in close proximity to the nearby porphyrin framework and due to this steric hindrance cannot be approached by the iodine electrophiles from neighboring polymeric chains. Crystal packing of the polymers is thus stabilized by common dispersion (isotropic) forces. Adjacent polymeric entities are offset one with respect to the other along the b -direction so that the axial ligands of one polymer are placed between the iodophenyl arms of adjacent units. Their arrangement is associated with apparent $I \cdots \pi$ interactions (at ~ 3.5 Å) between the iodophenyl arms of one chain and the perpendicularly oriented aryl residues of an adjacent polymer. The same structural model (apart from the ligand disorder) is obtained when the structure is described and refined in space group Cc as a 1:1 merohedral twin.

Structure **2** crystallizes in triclinic space group $P1$. It consists of 1D coordination polymers (as in **1**) with alternating disposition of the metalloporphyrin and the pyrimidine carboxylate entities along the chain. The manganese ion reveals a distorted octahedral coordination to the four pyrrole N-atoms at 2.004(7)-2.043(7) Å, the carboxylate-O (from one side of the porphyrin) at 2.138(5) Å and the pyrimidine-N (from the other side of the porphyrin) at 2.393(6) Å. This heteroleptic coordination motif of the ligand to adjacent porphyrin macrocycles leads to 1D coordination polymerization as in the former example (Figure 2b). The *meta*-disposition of the coordination sites on the ligand in **2**, as opposed to the *para*-disposition of the corresponding ligation sites in **1**, accounts for the shorter intra-chain Mn \cdots Mn distance of 8.916 Å in **2** than of 9.528 Å in **1** (Figure 2). In spite of the smaller

separation distance between the porphyrin rings along polymer **2**, inspection of its outer molecular surface reveals that the electron-rich non-coordinated carboxylate-O and pyrimidine-N sites are now exposed to possible interactions with nearby entities. Correspondingly, inter-digitation of adjacent polymeric chains in the crystalline phase optimizes electrostatic attraction between them by short contacts between the iodophenyl residue from one polymer and the O and N sites of the other (Figure 3). The I \cdots O distance is 2.998 Å, shorter by about 0.5 Å than the sum of the van der Waals radii of I and O.¹⁰ The angular characteristics of this interaction, C-I \cdots O of 175.8° and C-O \cdots I of 111.5°, confirm that the lone electron pair of the O-donor is directed at the σ -hole of the iodine acceptor. The non-coordinated pyrimidine-N is also involved in a halogen-bonding-type interaction with an I-atom from another neighbouring polymeric entity. The observed N \cdots I distance is 3.215 Å (and C-I \cdots N angle 176.3°) which is \sim 0.3 Å shorter than the sum of the corresponding van der Waals radii of N and I atoms.¹⁰ In another direction perpendicular to the polymeric chains the intermolecular arrangement reveals also I \cdots I halogen bonds of type II at 3.809 and 3.993 Å.¹¹ As the approaching C-I bond is oriented roughly perpendicular to the corresponding electron-rich pyrimidine ring, this contact can be better classified as an I \cdots π interaction (Figure 3a). In a given halogen-bonded layer the coordination polymeric moieties are oriented in the same direction, imparting to it a chiral nature. This effects also the non-centrosymmetric space symmetry of the entire structures, in similarity with earlier observations.^{8a}

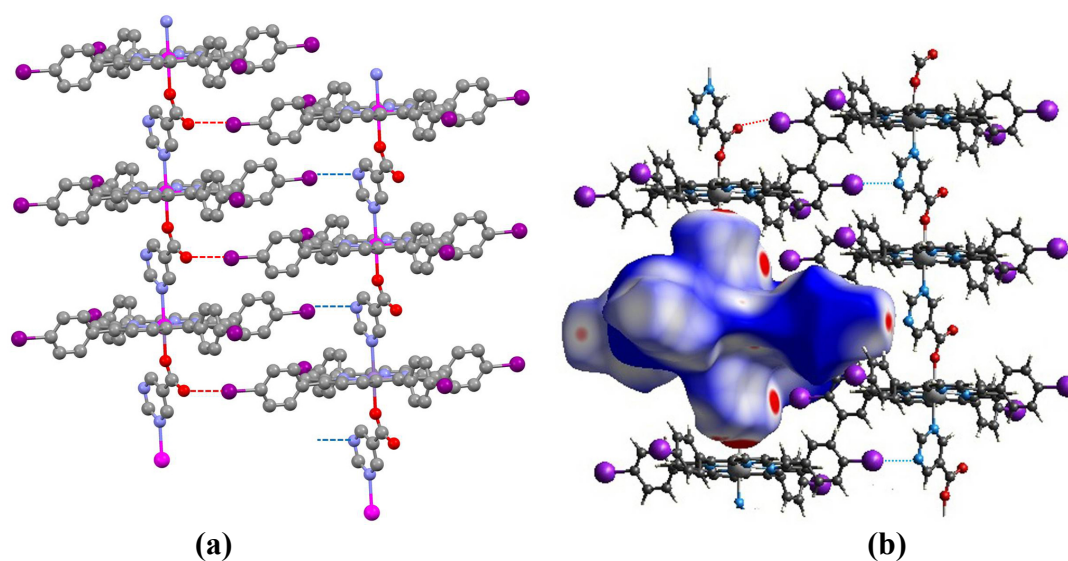


Figure 3. Crystal packing of two adjacent interdigitating polymeric chains in **2**, showing the halogen-bonding type interactions between them. (a) The red and blue dotted lines represent $O \cdots I$ halogen bonds and $N/\pi \cdots I$ interactions, respectively. (b) Calculated Hirshfeld surface for a fragment of **2**. The halogen-bonding sites (tips of the C-I and C-O bonds on the right side of the surface) can be seen as large red spots.

The Hirshfeld surface is an illustration of the three-dimensional electron density of a molecule in a crystal.^{12,13} Mapping the Hirshfeld surface (by using CrystalExplorer)¹⁴ is a useful tool for understanding and visualization of intermolecular interactions. Figure 3b depicts the Hirshfeld surface of a single fragment within the coordination polymer of **2**. The red spots on the Hirshfeld surface evidence the appearance of close intermolecular interactions, such as halogen bonds, whereas areas without close contacts are shown as blue spots, in perfect agreement with the earlier discussion.

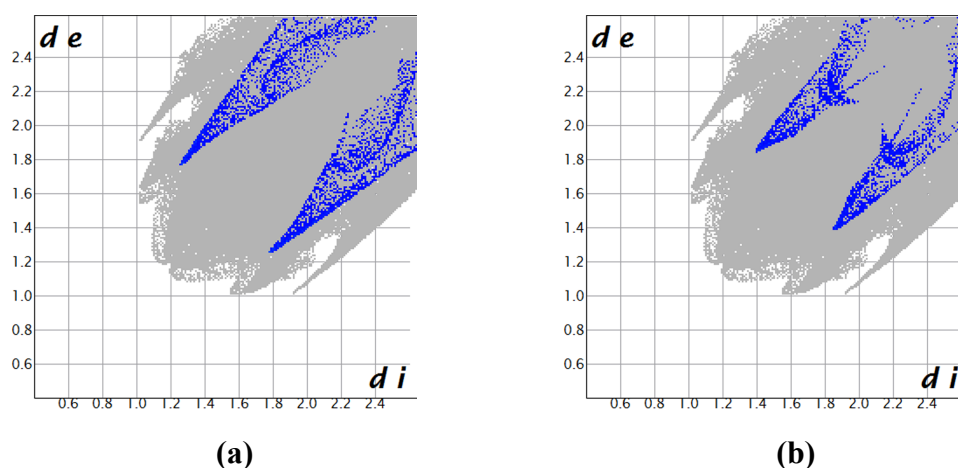


Figure 4. Hirshfeld analysis of intermolecular interactions in **2**. The fingerprints plots of the specific (a) $I \cdots O$ and (b) $I \cdots N$ interactions.

These interactions can be analyzed by 2D fingerprint plots that exhibit the contributions of the specific $I \cdots O$ and $I \cdots N$ interactions (on the background of all intermolecular interactions, Figure 4). The tips of the spikes in Figure 4a are located at $d_i=1.80 \text{ \AA}$ and $d_e=1.20 \text{ \AA}$ or $d_i=1.20 \text{ \AA}$ and $d_e=1.80 \text{ \AA}$, where d_i+d_e represents the shortest distance between atoms inside the molecular surface and outside the surface, correspondingly. Thus, the shortest calculated interaction of about 3.0 \AA is in perfect agreement with the shortest $I \cdots O$ observed in **2**. The minimal d_e+d_i calculated distance between the tips of the spikes in Figure 4b is near 3.23 \AA , in consent with the observed 3.215 \AA in the crystal structure. In the above context, one should keep in

mind that the I \cdots O and I \cdots N halogen-type-bonds contribute respectively only 2.43 % and 1.76 % to the total intermolecular surface-contact interactions responsible for the cohesive energy in **2**. The halogen bonds of the type described here belong to the regime of weak interactions and they provide only a secondary contribution to the cohesive free energy of molecular solids. Their expression in crystals should be accommodated favourably by the more dominant crystal packing forces in the condensed crystalline phase (as it is illustrated e.g. by inter-digitating of the shish-kebab-shaped coordination polymer in **2**), and thus requires an appropriate molecular design of the assembling molecular components to bear accessible 'donor' and 'acceptor' sites. In a related coordination polymeric structure of MnTIPP with tetracyanoethene as the bridging ligand only I \cdots π halogen bonds at 3.6 Å have been observed.^{2h}

A histogram of percentage contribution of the different intermolecular interactions involving the peripheral iodine sites to the Hirshfeld surface area in **1** and **2** is shown in Figure 5. As expected, the I \cdots C (including I \cdots π) and I \cdots H contacts provide the largest share. In **1** weak I \cdots I interactions contribute only about 0.5% (no other halogen bonds are present), while in **2** the share of the I \cdots N (including I \cdots π), I \cdots O and I \cdots I halogen bonds is about tenfold larger. Evidently, the I \cdots π (phenyl) interactions in **1** (at 3.5 Å) are considerably weaker than the I \cdots π (pyrimidine) ones (at 3.2 Å) in **2**. The major significance of the halogen bonding in **2** is also reflected in the fact that the halogen substituents contribute only 26.5% (in **1**), but nearly 32% (in **2**) to the total intermolecular surface-contact interaction.

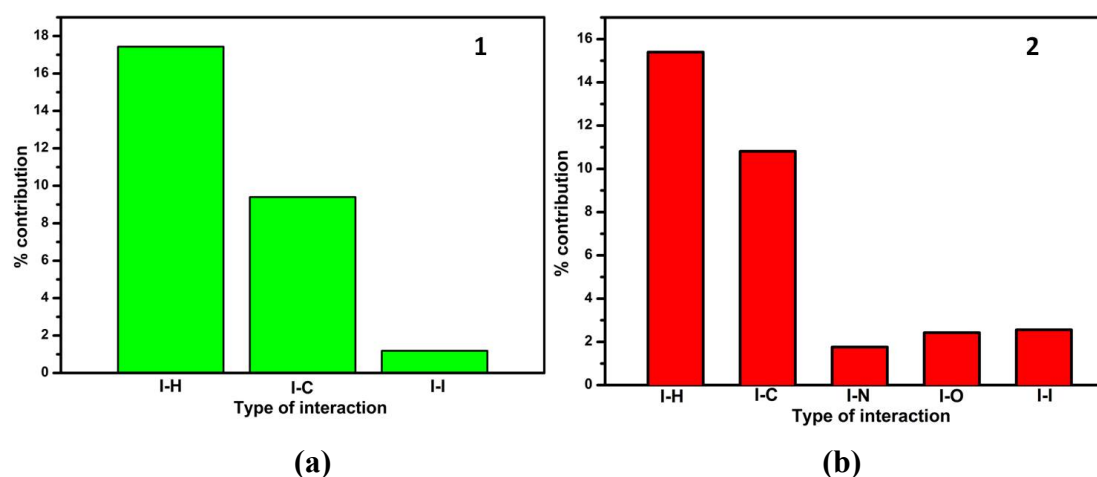


Figure 5. The percentage contribution of the various intermolecular contacts involving I-atoms to the total surface-contact interaction in (a) **1** and (b) **2**.

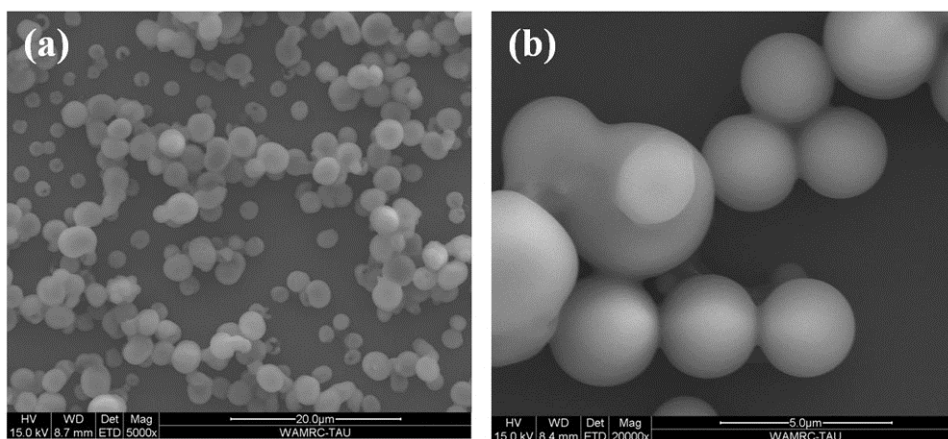


Figure 6. SEM micrographs of **1** on carbon fibre surface at (a) low resolution and (b) high resolution.

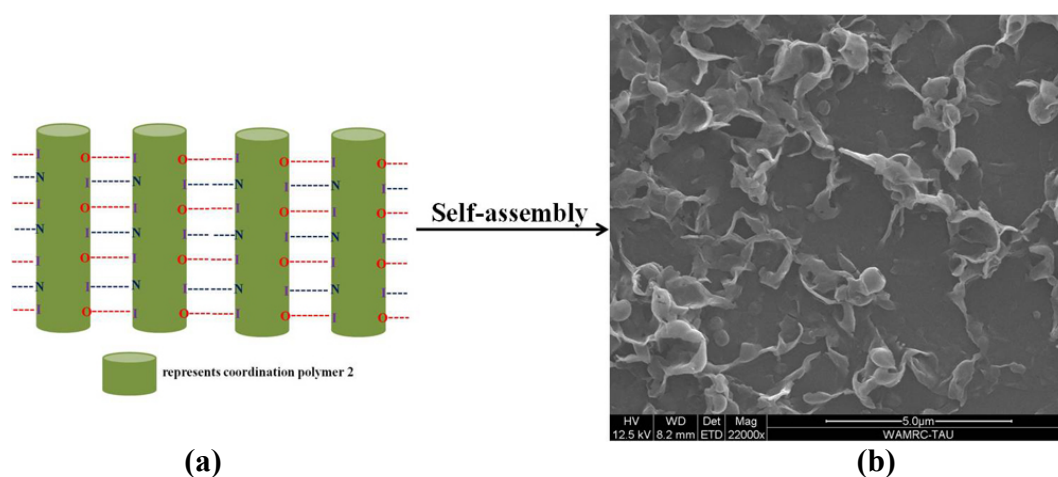


Figure 7. Compound **2**. (a) Pictorial presentation of the halogen bonding interactions between the adjacent coordination polymer in the crystal structure. (b) SEM micrograph of the sheet-like assembled material on graphite surface.

As the two compounds are characterized by similar coordination connectivity into 1D polymeric architectures, it was of further interest to examine how they self-assemble in the nano-domain given their different architectures in the crystalline bulk. Correspondingly, 4×10^{-5} M solutions of **1** and **2** in 1:1 DCM and petroleum ether mixture were drop-casted on a carbon fibre, and after immediate evaporation were subjected to scanning electron microscopy (SEM). The SEM micrographs of **1** show nanospherical shapes. The nanospheres are poly-dispersed in nature and are in the diameter range of 700 nm to 4.5 μm (Figure 6). In the nucleation stage at this concentration low diffusion flux may induce an equi-directional growth of the

nanocrystals, thus yielding nanospheres. A similar type of 0D growth of Zn- and Mg-porphyrins is known.¹⁵ The self-organized and well-defined structures result spontaneously from the components of the analyzed system at room temperature. Such assembly appears to be of general interest for macromolecular and polymer chemistry where the spherical shape is achieved based on the principle of minimizing the surface area. The native chlorophyll-*a* is also known to assemble in a spherical manner.¹⁶ SEM analysis of **2** in the same experimental conditions showed curved sheet like shapes (rather than spherical) in the nano domain (Figure 7).¹⁷ This could be related to the chiral inter-molecular organization in **2** and the directional/anisotropic O \cdots I and N \cdots I halogen bonding interactions which hold together adjacent polymeric chains.

In conclusion, we have synthesized two new 1D coordination polymers of Mn(III)-porphyrin through heteroleptic bridging coordination of the axial ligand (isonicotinate in **1** and pyrimidine-5-carboxylate in **2**), to continue our exploration of supramolecular self-assembly of tetraarylporphyrins by halogen bonding. The two structures revealed similarly shaped 1D coordination polymers, but a striking difference in the supramolecular self-assembly in the crystalline bulk and in the nano-domain. In the absence of effective halogen bonding in **1** the resulting crystalline architecture is centrosymmetric and this material assembles from its solution as nanospheres on graphite fiber. On the other hand, in **2**, the observed O \cdots I and N \cdots I halogen bonding interactions have a pronounced effect in the self-assembly of the polymeric complex. The halogen-bond-directed layered self-organization of **2** is characterized by the P1 space symmetry in the crystal and irregularly shaped nano-domains on the graphite-fiber surface. The above observations support our earlier findings that directional supramolecular halogen bonding among porphyrin moieties may be effective in the formation of chiral/asymmetric architectures from achiral constituents.^{8a} They also provide the first example of supramolecular porphyrin assembly via a concerted utilization of coordination and halogen bonding.

Halogen bonding has emerged in recent years as a particularly interesting non-covalent interaction for crystal engineering and supramolecular assembly of organic, coordination as well as polymeric compounds.¹⁸ It plays also a continuously increasing role in the design of functional supramolecular materials in solid and

liquid-crystalline phases, and the ability to tune their mechanical, optical, conducting and magnetic properties.¹⁹ Activities in this area are expected to continue aiming to harness the halogen bonding in the development of new materials and applications.

Experimental section

All reagents, starting materials for the porphyrin synthesis, and solvents were commercially available. Solvents were distilled prior to use by standard procedures. Free-base H₂TIPP was prepared by condensing pyrrole and *p*-iodobenzaldehyde, following the Adler method.²⁰ {[Mn(TIPP)]₂(OH)}ClO₄ was prepared by following the procedure as employed for {[Mn(TPP)]₂(OH)}ClO₄ and {[Mn(OEP)]₂(OH)}ClO₄, using MnCl₂·4H₂O as the metallating agent.²¹

Synthesis of 1: 25 mg (0.01 mmol) of {[Mn(TIPP)]₂(OH)}ClO₄ was taken in 10 mL DMF in a 50 mL round bottom flask and 2.5 mg (0.02 mmol) isonicotinic acid was added to it. The solution was stirred for 2h and the solvent was then evaporated in a rotary evaporator to give a dark green solid. The solid was recrystallized from DCM and petroleum ether (60–80 °C) to yield dark-green, block shaped, diffraction-quality crystals of **1**. Yield: 96%. Elem. anal. Calcd (found) for C₉₄H₅₂N₉O₂I₈Mn₂: C, 45.81 (45.62); H, 2.13 (2.22); N, 5.11 (5.21); FTIR (cm⁻¹): 1639, 1584, 1485, 1468, 1390, 1321, 1204, 1097, 1072, 1005, 884, 760, 665.

Synthesis of 2: This complex was prepared by similar methodology as described for **1** using pyrimidine-5-carboxylic acid instead of isonicotinic acid in similar stoichiometric ratio. Yield: 93%. Elem. anal. Calcd (found) for C₉₃H₅₁I₈N₁₀O₂Mn₂: C, 45.30 (45.22); H, 2.08 (2.11); N, 5.68 (5.71); FTIR (cm⁻¹): 1648, 1580, 1486, 1469, 1391, 1321, 1205, 1177, 1072, 1007, 801, 721, 667.

The X-ray measurements (Bruker-ApexDuo diffractometer, MoK α I μ micro-focus X-ray source) were carried out at ca. 110(2) K on crystals coated with a thin layer of amorphous oil. These structures were solved by direct methods and refined by full-matrix least squares (SIR-97, SHELXTL-2013 and SHELXL-97).^{22,23} All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in idealized/calculated positions and were refined using a riding model. Compounds **1** and **2** were found to contain also severely disordered crystallization solvent in the lattice which could not be modeled by discrete atoms. Contribution of the disordered

DCM solvent was subtracted from the diffraction data by the Squeeze technique in PLATON software.²⁴

Crystal Data: **1**, C₅₀H₂₈I₄MnN₅O₂: formula weight 1293.31, monoclinic, space group C2/c, $a = 34.108(2)$, $b = 9.5282(6)$, $c = 19.5702(13)$ Å, $\beta = 116.626(2)^\circ$, $V = 5685.6(6)$ Å³, $Z = 4$, $T = 110(2)$ K, $D_{\text{calc}} = 1.511$ g.cm⁻³, $\mu(\text{MoK}\alpha) = 0.24$ mm⁻¹, 27103 collected data and 7061 unique reflections ($\theta_{\text{max}} = 28.33^\circ$), $R_{\text{int}} = 0.022$. The final $R1=0.033$ for 6230 observations with $F_o > 4\sigma(F_o)$, $R1=0.037$ ($wR2 = 0.104$) for all unique data, $|\Delta\rho| \leq 1.80$ e/Å³. CCDC 1005893. **2**, C₄₉H₂₇I₄MnN₆O₂: formula weight 1294.31, triclinic, space group *P1*, $a = 8.9158(3)$, $b = 11.1440(4)$, $c = 14.0968(6)$ Å, $\alpha = 83.256(2)$, $\beta = 72.321(2)$, $\gamma = 84.057(2)^\circ$, $V = 1321.83(9)$ Å³, $Z = 1$, $T = 110(2)$ K, $D_{\text{calc}} = 1.626$ g.cm⁻³, $\mu(\text{MoK}\alpha) = 0.26$ mm⁻¹. 22514 collected data and 10572 unique reflections ($\theta_{\text{max}} = 28.54^\circ$), $R_{\text{int}} = 0.027$. The final $R1=0.039$ for 8954 observations with $F_o > 4\sigma(F_o)$, $R1=0.050$ ($wR2 = 0.102$) for all unique data, $|\Delta\rho| \leq 1.15$ e/Å³. CCDC 1005892.

Acknowledgements

This research was supported by the Israel Science Foundation (Grant No. 108/12).

* Electronic supplementary information (ESI) available: X-ray crystallographic details in CIF format. CCDC 1005893 (**1**) and 1005892 (**2**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/xxxxxxxxxx.

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