Experimental Supplementary Information

Preparative Details

**Synthesis of PyTIPP.** 1.25g (5.4 mmol) of 4-iodobenzaldehyde, 0.34ml (3.6 mmol) of 4-pyridinecarboxaldehyde were added to 35 ml of hot propionic acid at 120 °C. Then 0.5 ml of distilled pyrrole (7.21 mmol) was added and the resulting solution heated to refluxing for 90 minutes. The solvent was then removed by vacuum distillation and the crude product was digested with hot water to remove traces of propionic acid, filtered, washed with water and dried. The crude porphyrin mixture was dissolved in chloroform and loaded on silica column using chloroform. The desired porphyrin, PyTIPP, was eluted with 3% acetone in chloroform as second fraction. The yield was found to be 0.165 g (9%) based on pyrrole. 1H NMR (CDCl3): 9.00 (dd, 2H, J = 5.9 Hz), 8.80 (m, 8H), 8.10 (asymmetric t, 8H, J = 6 Hz, J = 8.6 Hz), 7.89 (d, 6H, J = 8.2 Hz), -2.93 (s, 2H). UV-Vis in CH2Cl2: \(\lambda_{\text{max}}, \text{nm (log}\ e \text{)}\) 419(5.96), 515(4.60), 549(4.18), 589(4.01), 645(3.72). FAB-mass spectrum (m/z) for C43H26N5I3: found 994, Calcd. 993.43.

**Preparation of metal derivatives.** The free-base porphyrin (0.05g, 5.03 mmol) was dissolved in 25 ml of CHCl3. To this, M(OAc)2 hydrate where M = Cu(II) and Zn(II) (0.09 – 0.125g, 0.05 mol) in 2ml of methanol was added and heated for 10 minutes on water bath at 75 °C and evaporated to dryness. The crude porphyrin was washed with water. The metal complexes were dried under vacuum and their yields were found to be almost quantitative. [Zn-PyTIPP]: 1H NMR (DMSO-d6): 8.98 (d, 2H, J = 5.8 Hz), 8.79 (m, 8H), 8.16 (asymmetric t, 8H, J = 5.76 Hz, J = 8.2 Hz), 7.94 (d, 6H, J = 8.2 Hz). UV-Vis. in CH2Cl2/pyridine mixture: \(\lambda_{\text{max}}, \text{nm (log}\ e \text{)}\) 429(5.69), 562(4.15), 602(3.69). FAB-mass spectrum (m/z) for C43H24N5I3Zn: found 1057, Calcd. 1056.8. [Cu-PyTIPP]: UV-Vis. in CH2Cl2/pyridine mixture: \(\lambda_{\text{max}}, \text{nm (log}\ e \text{)}\) 416(5.82), 540(4.37), 589(4.18). FAB-mass spectrum (m/z) for C43H24N5I3Cu: found 1055, Calcd. 1054.96.

**Supramolecular synthesis.** 4 mg (0.004 mmol) of PyTIPP were dissolved in 2 ml of chloroform followed by few drops of either nitrobenzene or ethyl benzoate, and allowed to evaporate slowly. X-ray quality crystals of the nitrobenzene solvate (structure 1) were obtained after one week. When ~4 mg (0.004 mmol) of [Zn-PyTIPP] and [Cu-PyTIPP] were dissolved in 1.5 ml of 2:1 mixture of DMF/pyridine (v/v) and allowed to evaporate slowly, X-ray quality crystals of the DMF solvate of [Zn(py)-PyTIPP] (structure 2) and pyridine solvate of [Cu-PyTIPP] (structure 3) were obtained after ten days. The uniform identity of the formed crystal lattices in a given reaction was confirmed in each case by repeated measurements of the unit-cell dimensions from different single crystallites.
Summary of the crystallographic details

**Crystal Data: 1**: \( \text{C}_{43}\text{H}_{26}\text{I}_{3}\text{N}_{5} \cdot 2\text{C}_{6}\text{H}_{5}\text{NO}_{2} \), \( \text{M}_{r} = 1239.61 \), triclinic, space group P1, \( a = 10.6814(3) \), \( b = 11.1396(3) \), \( c = 11.4818(4) \) Å, \( \alpha = 103.635(1) \), \( \beta = 93.441(1) \), \( \gamma = 110.096(2) \)°, \( V = 1231.87(6) \) Å\(^3\), \( T = 110 \) K, \( Z = 1 \), \( \mu(\text{MoK} \alpha) = 19.57 \) cm\(^{-1}\), \( \rho_{\text{calcld}} = 1.671 \) g·cm\(^{-3}\), 13768 reflections measured of which 9381 were unique (\( R_{\text{int}} = 0.046 \)) and 7890 with \( I > 2\sigma(I) \). Final \( R_{1} = 0.042 \) and \( wR_{2} = 0.084 \) for the 7890 data above the intensity threshold.

**Crystal Data: 2**: \( \text{C}_{48}\text{H}_{29}\text{I}_{3}\text{N}_{6}\text{Zn} \cdot \text{C}_{3}\text{H}_{7}\text{NO} \), \( \text{M}_{r} = 1208.94 \), triclinic, space group P1, \( a = 15.9721(4) \), \( b = 17.4838(4) \), \( c = 18.8968(5) \) Å, \( \alpha = 66.985(1) \), \( \beta = 86.963(1) \), \( \gamma = 75.270(1) \)°, \( V = 4690.9(2) \) Å\(^3\), \( T = 110 \) K, \( Z = 4 \), \( \mu(\text{MoK} \alpha) = 25.44 \) cm\(^{-1}\), \( \rho_{\text{calcld}} = 1.712 \) g·cm\(^{-3}\), 39597 reflections measured of which 29624 were unique (\( R_{\text{int}} = 0.066 \)) and 20744 with \( I > 2\sigma(I) \). Final \( R_{1} = 0.067 \) and \( wR_{2} = 0.159 \) for the 20744 data above the intensity threshold.

**Crystal Data: 3**: \( \text{C}_{43}\text{H}_{24}\text{CuI}_{3}\text{N}_{5} \) (excluding disordered solvent), \( \text{M}_{r} = 1054.91 \), monoclinic, space group C2, \( a = 24.2489(13) \), \( b = 20.5698(11) \), \( c = 9.1014(5) \) Å, \( \alpha = 94.477(4) \)°, \( V = 4525.9(4) \) Å\(^3\), \( T = 110 \) K, \( Z = 4 \), \( \mu(\text{MoK} \alpha) = 25.61 \) cm\(^{-1}\), \( \rho_{\text{calcld}} = 1.548 \) g·cm\(^{-3}\), 20122 reflections measured of which 10024 were unique (\( R_{\text{int}} = 0.066 \)) and 7222 with \( I > 2\sigma(I) \). Final \( R_{1} = 0.060 \) and \( wR_{2} = 0.149 \) for the 7222 data above the intensity threshold. In structure 3 the contribution of the disordered solvent was subtracted from the diffraction pattern (A. L. Spek, *J. Appl. Crystallogr.* 2003, 36, 7-13). All the three analysed crystals were found to be twins of varying composition of inter-grown domains of opposing chirality: 1:1 (1), 1:9 (2) and ~1:2.5 (3).

CCDC reference numbers 662252 (1), 662254 (2) and 662255 (3).

All three crystal structures are pseudo-centrosymmetric and the molecular frameworks in them arrange nearly in a centrosymmetric manner (including pseudo-inverted arrangements of the 5-coordinate [Zn(py)-PyTIPP] entities, but not quite. It is the asymmetric disposition of the iodine atom between the halogen-bonded pyridyl and iodophenyl groups that makes the difference; the iodine is distanced 2.8-3.0 Å from the N-site it points at, but only ~2.1 Å from the C(phenyl)-atom it covalently binds to.
(a) Supramolecular layered assembly of PyTIPP in 1. The dashed I···N contact indicates the directional halogen bond, while the I'···N and I''···C dashed lines represent the I···π interactions.

(b) Unidirectional arrangement of two successive layers in space group P1; only the N···I halogen bonds are indicated by dashed lines. (The crystal packing diagrams in all figures exclude the H-atoms and crystallization solvent.)

(a) Assembly in one of the supramolecular layers in 2. The I···N lines indicate the unidirectional halogen bonds, while the I'···N and I''···I dashed contacts represent the I···π and I···I interactions. The asymmetric unit of this structure contains four crystallographically independent porphyrin molecules displaced with respect to one another along the c-axis of the unit-cell. Each one of them is part of a different unidirectional- layered assembly of the 5-coordinate metalloporphyrin species, composed of linear head-to-tail porphyrin chains sustained by N···I halogen bonds. The four molecules of the asymmetric unit have slightly different orientations. As a result, the corresponding halogen-bonded chains within the individual layer are differently shifted with respect to one another, interacting sideways via secondary intermolecular I···π and I···I contacts in a varied manner. The molecular organization in two of the layers is similar to that found in 1. That in the two other layers exhibit significant I···I interactions at 3.68 and 3.73 Å (these distances are considerably shorter than the sum of the van der Waals radii; commonly assumed to be within 4.0-4.3 Å), as well the I···π contacts (3.45-3.57 Å). The former provide strong halogen-halogen attractions, and offer an additional option for the stabilization of the layered arrangement.

(b) Unidirectional arrangement of the four crystallographically independent layers in the crystal in space group P1; only the N···I halogen bonds are indicated by dashed lines. Note the pseudo-centrosymmetric arrangement of the 5-coordinate metalloporphyrin species.
(a) Supramolecular layered assembly of [Cu-PyTIPP] in 3. The I···N dashed contact indicates the halogen bond, while the I′···N and I′′···C contacts represent the perpendicular I···π interactions. Optimization of these interactions and formation of the layered molecular grids is associated in this structure with severe saddle-type deformation of the porphyrin core from planarity into a chiral form. The porphyrin molecules are located on the axes of twofold rotation, and the asymmetric unit comprises two crystallographically independent halves of the porphyrin species.

(b) Unidirectional arrangement of successive layers in the crystal structure 3 in space group C2; only the N···I halogen bonds are marked by dashed lines.