

# A Neutral “Molecular Railroad” Coordination Polymer That Incorporates Polycyclic Aromatic Molecules: Synthesis and Single-Crystal X-Ray Structure of $[\text{Co}(4,4'\text{-bipyridine})_{2.5}(\text{NO}_3)_2] \cdot 2\text{Phenanthrene}$

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The synthesis and crystal structure of  $[\text{Co}(4,4'\text{-bipyridine})_{2.5}(\text{NO}_3)_3] \cdot 2\text{C}_{14}\text{H}_{10}$ ,  $1 \cdot 2\text{C}_{14}\text{H}_{10}$ , are presented and discussed in the context of recent developments in the field of coordination polymers. **1** adapts a “molecular railroad” architecture and is closely related to two previously reported molecular railroads in that it contains both bridging and terminal spacer ligands. However, it differs in two important aspects. First, because **1** is uncharged its crystal packing is dominated by stacking interactions between aromatic moieties rather than hydrogen bonding or interpenetration. Second, the resulting open framework planar architecture of **1** sustains coexistence with two topologically complementary sets of phenanthrene molecules. One of these sets can be regarded as a planar network of (4,4) topology whereas the other is an achiral chain of phenanthrene molecules that fills the channels that are generated by the interpenetration of the two planar networks. © 2000 Academic Press

**Key Words:** coordination polymer compounds; covalent and noncovalent nets; X-ray diffraction; crystal structure.

## INTRODUCTION

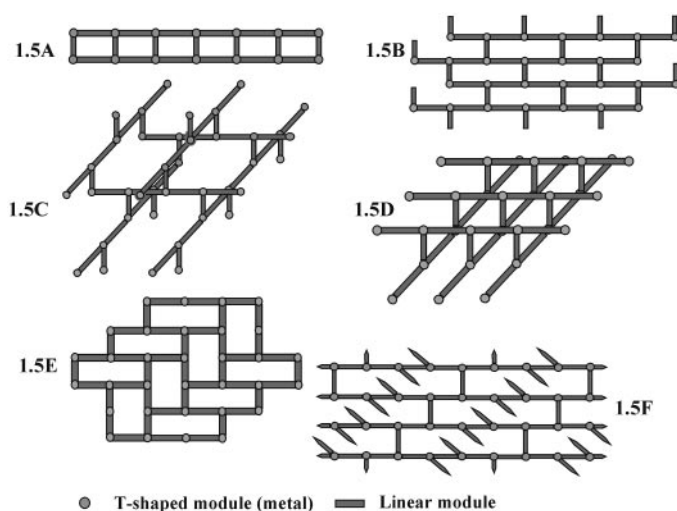
Crystal engineering of coordination polymer networks, metal–organic polymers, is largely based upon the use of exodentate multitopic ligands and represents a growing area of coordination and supramolecular chemistry (1, 2). Thus far, a diverse range of architectures that have no precedent in minerals has resulted in several new classes of open framework compounds that exhibit potentially useful properties including ion exchange and separation of small molecules. The simplest strategy for design and control over polymeric architectures revolves around the use of bifunctional or ditopic ligands (spacers) to propagate known co-

ordination environments (nodes). Prototypical ligands in this context are exemplified by 4,4'-bipyridine or its extended analogues 1,2-bis(4-pyridyl)ethylene and -ethane. They tend to exhibit considerable structural diversity or “structural supramolecular isomerism” (3). For example, if one were to consider only square planar or octahedral transition metal moieties, a metal : ligand ratio of 1 : 1.5 can exhibit any of six very different architectures (Scheme 1): ladder, 1.5A (4); brick wall, 1.5B (4a); 3D frame or “Lincoln Log”, 1.5C (5); “tongue and groove” or bilayer, 1.5D (4d, 4e, 6); herringbone, 1.5E (7); or “3D frame”, 1.5F (8). As would be expected, stoichiometry also critically influences the possible architectures of coordination polymer networks. There have been fewer observed architectures for 1:2 stoichiometry but they are different from those observed for 1:1.5 stoichiometry: square grid (9) and two types of “NbO-type frame” in which adjacent spacer ligands are orthogonal (10). Thus far, only one architecture has been observed for 1:2.5 stoichiometry, the “molecular railroad,” 2.5A (Scheme 2) (11).

There remains the possibility of packing diversity within each of these architectures. Indeed, all nine of the architectures inherently possess cavities and several have been shown to exhibit interpenetration, which can be regarded as being another form of supramolecular isomerism. Indeed, the first two examples of molecular railroads are open framework (11a) and interpenetrated (11b), respectively. In this contribution we present what is to our knowledge only the third example of a “molecular railroad” architecture that has been structurally characterized,  $[\text{Co}(4,4'\text{-bipyridine})_{2.5}(\text{NO}_3)_2] \cdot 2\text{C}_{14}\text{H}_{10}$ ,  $1 \cdot 2\text{C}_{14}\text{H}_{10}$ ,  $1 \cdot 2\text{C}_{14}\text{H}_{10}$  is discussed in the context of its differences from the earlier examples of “molecular railroads” and is interpreted and rationalized on the basis of the assumption that noncovalent nets form by interactions between phenanthrene molecules. The concept of nets and interpenetration was presented in detail by A. F. Wells over 20 years ago (12) and again in 1998, in a comprehensive review in the context of

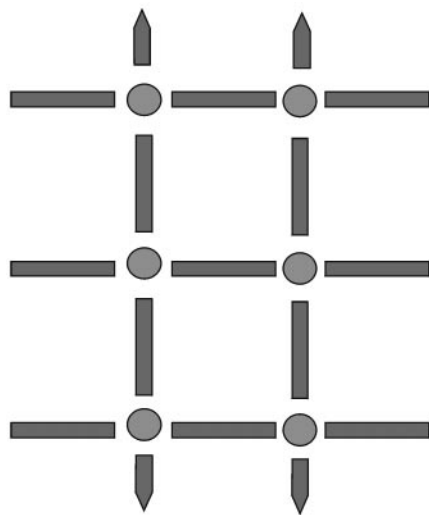
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**SCHEME 1.** Diversity of frameworks that have been observed for coordination polymers based upon octahedral or square planar transition metal moieties and 1.5 equivalents of linear bifunctional ligands.

coordination polymers by Batten and Robson (13). However, these reports addressed only homotopologic interpenetration, and in particular interpenetration of identical networks, or self-inclusion. Indeed, Batten and Robson found only one example (13) of chemically different interpenetrating nets (differing by only one ligand) and both nets are topologically equivalent (4,4). A present interest of ours concerns the rational design of host-guest complexes based upon topologically complementary planar nets that are of very different chemical compositions. We have reported that 2D networks of aromatic molecules can be complementary



**SCHEME 2.** Schematic representation of the "molecular railroad" motif.

**TABLE 1**  
Crystal Data and Structure Refinement for  
 $[\text{Co}(4,4'\text{-bipyridine})_{2.5}(\text{NO}_3)_2] \cdot 2\text{C}_{14}\text{H}_{10}$

Identification code	dk41
Empirical formula	$\text{C}_{106} \text{H}_{80} \text{Co}_2 \text{N}_{14} \text{O}_{12}$
Formula weight	1859.70
Temperature	173(2) K
Wavelength	0.70930 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	$a = 9.4892(8) \text{ \AA}$ $\alpha = 81.026(3)^\circ$ $b = 10.3662(9) \text{ \AA}$ $\beta = 82.053(3)^\circ$ $c = 23.9721(16) \text{ \AA}$ $\gamma = 70.161(3)^\circ$
Volume	$2181.7(3) \text{ \AA}^3$
Z, Calculated density	1, 1.415 $\text{Mg/m}^3$
Absorption coefficient	$0.456 \text{ mm}^{-1}$
$F(000)$	964
Crystal size	$0.12 \times 0.10 \times 0.08 \text{ mm}$
$\theta$ range for data collection	$12.05$ to $25.00^\circ$
Limiting indices	$-11 \leq h \leq 11,$ $-12 \leq k \leq 11,$ $-28 \leq l \leq 28$
Reflections collected/unique	14207/6805 [ $R(\text{int}) = 0.1041$ ]
Completeness to $\theta = 25.00$	87.8%
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	6805/9/692
Goodness-of-fit on $F^2$	1.008
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0829, wR2 = 0.1587$
R indices (all data)	$R1 = 0.1518, wR2 = 0.1750$
Extinction coefficient	0.100 (11)
Largest diff. peak and hole	0.367 and $-0.372 \text{ e \AA}^{-3}$

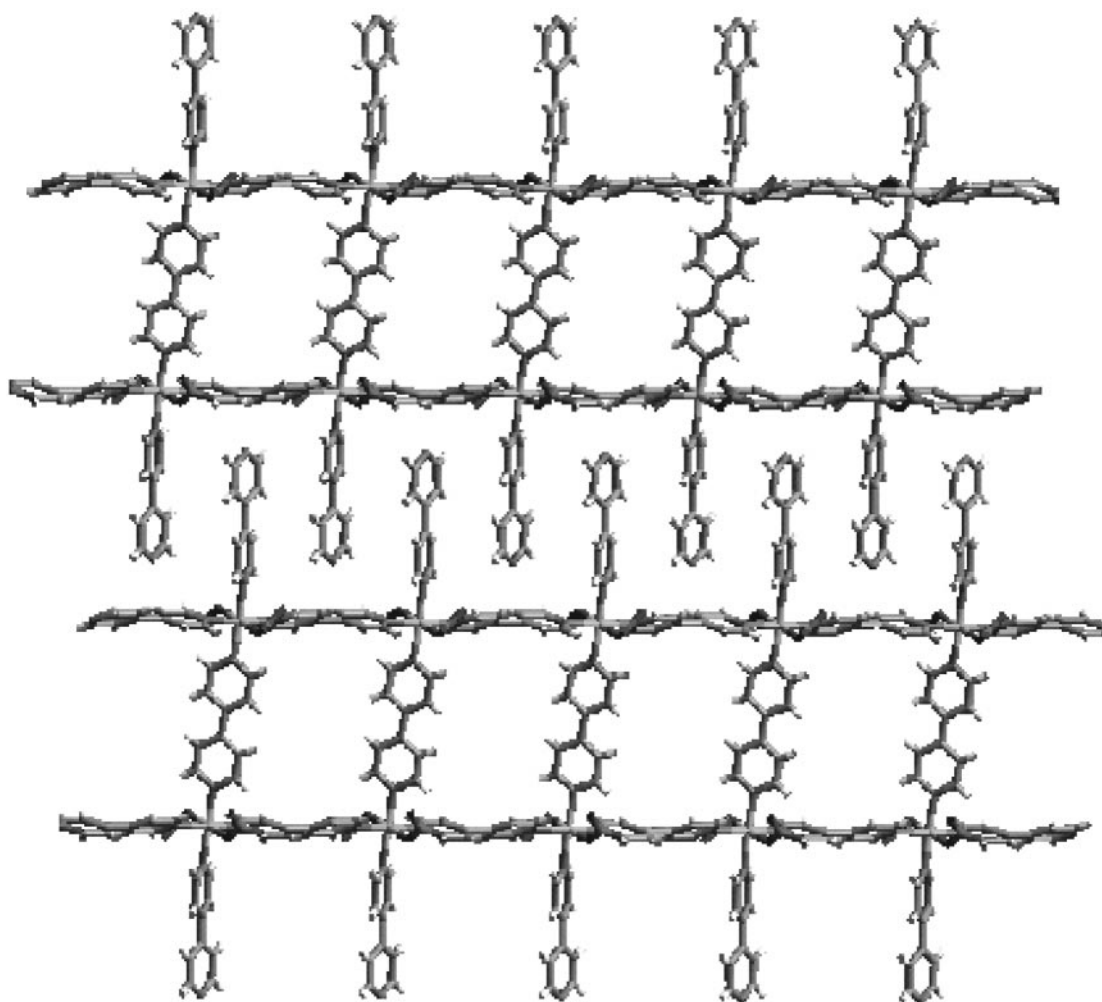
with 2D square grid networks that have (4,4) topology (9i, 9j). The structures of  $\{[\text{Ni}(4,4'\text{-bipy})_2(\text{NO}_3)_2] \cdot 2\text{Pyrene}\}_n$ , **2** (9j), and  $\{[M(4,4'\text{-bipy})_2(\text{NO}_3)_2] \cdot 3\text{C}_{10}\text{H}_8\}_n$  ( $M = \text{Co}, \text{Ni}$ ), **3** (9i), exhibit a complementary topological relationship between chemically different nets with different topologies. Specifically, **2** exhibits (4,4) pyrene nets whereas **3** contains (6,3) naphthalene nets. We have also observed that 2D nets of pyrene molecules can enclose pairs of ferrocene molecules (14). The structure of  $\mathbf{1} \cdot 2\text{C}_{14}\text{H}_{10}$  can be described in similar terms, as reported herein.

## EXPERIMENTAL

### Preparation of $\mathbf{1} \cdot 2\text{C}_{14}\text{H}_{10}$

In a typical reaction, 0.290 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1.0 mmol) was dissolved in 10 ml of methanol and layered over 0.468 g of 4,4'-bipy (3.0 mmol) and 1.250 g of phenanthrene (7.0 mmol) in 10 ml of methanol and 10 ml of 1,4-dioxane. The resulting mixture produced pink prismatic crystals of the complex  $\mathbf{1} \cdot 2\text{C}_{14}\text{H}_{10}$  on standing for 1–2 days. The yield was 0.650 g (70%).  $\mathbf{1} \cdot 2\text{C}_{14}\text{H}_{10}$  appears to be stable in air for several hours, but the crystals eventually became opaque.

The presence of the hydrocarbon molecules has been confirmed by IR spectroscopy: 791.8 1222.5, 1291.2, 1438.7,



**FIG. 1.** Illustration of the molecular railroad architecture exhibited by **1** and how lateral interdigitation affords a planar open framework network. Important bond distances and angles are as follows: Co–O, 2.100(4) and 2.117(4) Å; Co–N, 2.135(4), 2.151(4), 2.159(4), and 2.190(4) Å; O–Co–O, 179.18(17)°; N–Co–N, 88.89(16), 90.00(16), 92.41(16), 176.98(19), and 178.37(18)°; O–Co–N, 84.35(18)–97.50(17)°.

1532.3, 1604.2, 3067.8  $\text{cm}^{-1}$  and 794.2, 1223.3, 1293.8, 1437.6, 1535.2, 1606.4, 3077.6  $\text{cm}^{-1}$  for **1** and **2**, respectively. TGA analysis reveals 55.25% weight loss from 190°C to 260°C. These data are in agreement with the loss of two phenanthrene molecules and one molecule of 4,4'-bipy. Further decomposition of the complex was registered above 280°C.

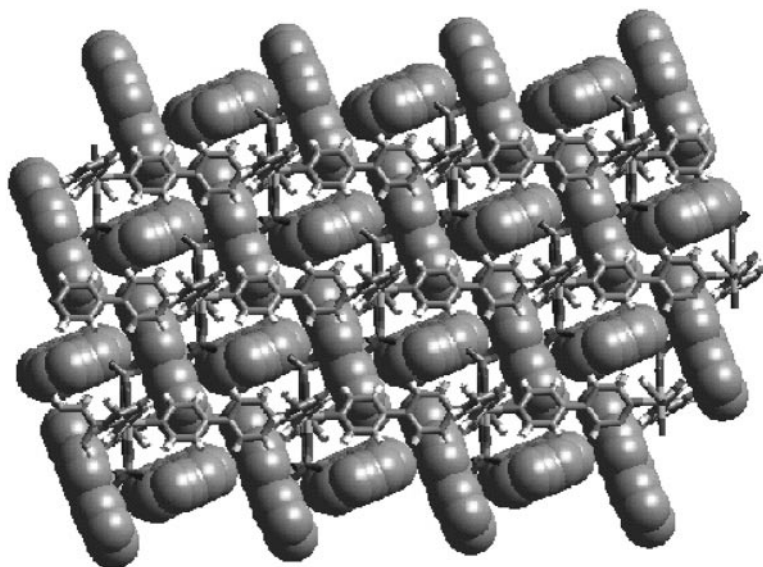
#### *X-Ray Crystallography*

Intensity data were recorded at 173 K on a Bruker SMART CCD diffractometer. The structure was solved by direct methods. Nonhydrogen atoms were refined anisotropically whereas hydrogen atoms were placed in calculated positions and given isotropic  $U$  values based on the atom to which they are bonded. There are three independent

phenanthrene molecules, two of which appear to be disordered around a crystallographic center of inversion. Atoms C9 and C10 of the third independent phenanthrene molecule appear to be disordered over two positions. The net result, a “pyrene-like” disordering model, has been observed in another example of a phenanthrene clathrate (15). Hydrogen atoms of the disordered atoms were not included in the refinement. All calculations were effected using the SHELXTL suite (16). Table 1 lists details of cell parameters, data acquisition, and structure refinement.

#### RESULTS AND DISCUSSION

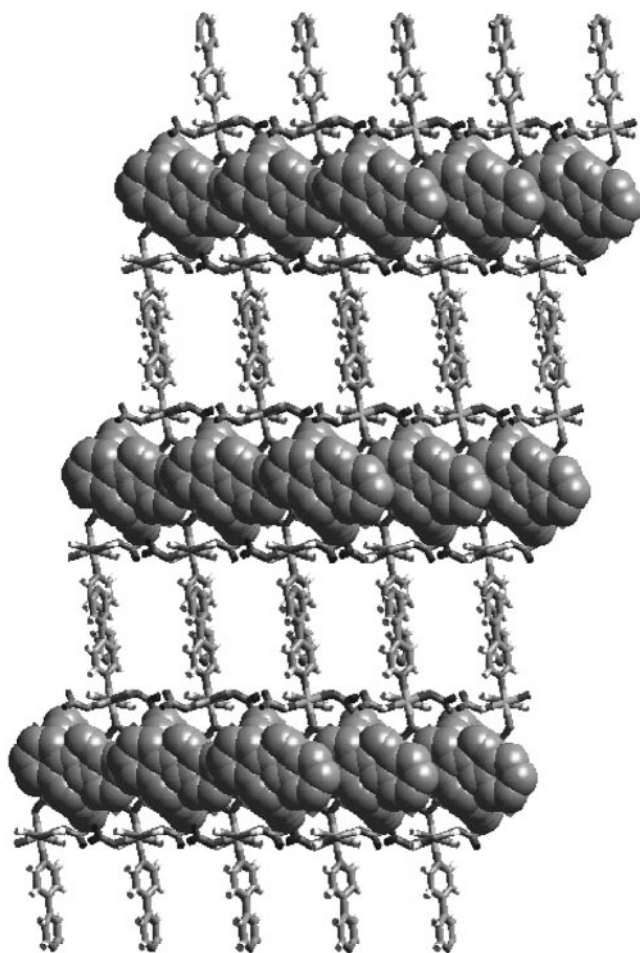
The bond distances and angles within the molecular railroad formed by **1** are within expected ranges. The manner in which the molecular railroads pack is perhaps the most



**FIG. 2.** Square (4,4) planar network of phenanthrene molecules in **1**. This figure and subsequent figures are generated using the Cerius program package (19).

salient feature of the structure. As revealed by Fig. 1, adjacent molecular railroads interdigitate because of stacking interactions between the uncoordinated 4,4'-bipyridine ligands. Interestingly, this means that the uncoordinated pyridyl moiety does not act as a hydrogen bond acceptor even though  $1 \cdot 2C_{14}H_{10}$  was crystallized from MeOH, a solvent that is capable of hydrogen bonding. The interdigitation occurs in such a manner that adjacent molecular railroads effectively form a supramolecular 2D grid that has cavities with effective cross sections of ca.  $9 \times 9 \text{ \AA}$ . These cavities are critical in the context of explaining the crystal packing.

When one examines the crystal packing of the phenanthrene molecules it becomes clear that the three crystallographically independent phenanthrene molecules can be classified as belonging to two distinct types in terms of their role in the crystal packing of  $1 \cdot 2C_{14}H_{10}$ . One type forms a 2D array of phenanthrene molecules (Fig. 2) and may be described as a square or (4,4) network in which the edges of each square are the faces of phenanthrene molecules and the corners are defined by the intersection point of four hydrocarbon moieties. Each phenanthrene molecule is therefore in close contact with four neighbors. This description of the phenanthrene array is based upon the assumption that the node of the net is a center of gravity of four neighboring molecules. The closest C–C contacts between the hydrocarbon molecules are found at 3.39–3.50 Å, corresponding with edge-to-face interactions (17). These interactions are within expected ranges and are comparable with those seen in pure phenanthrene, in which phenanthrene molecules stack with interplanar angles of  $56^\circ$  (18). The (4,4) network architecture sustains rectangular cavities that are filled by molecular railroads. The shortest interatomic separations between the



**FIG. 3.** Channels formed by interpenetration of the planar networks of molecular railroads (stick mode) and phenanthrene molecules (space-filling mode)

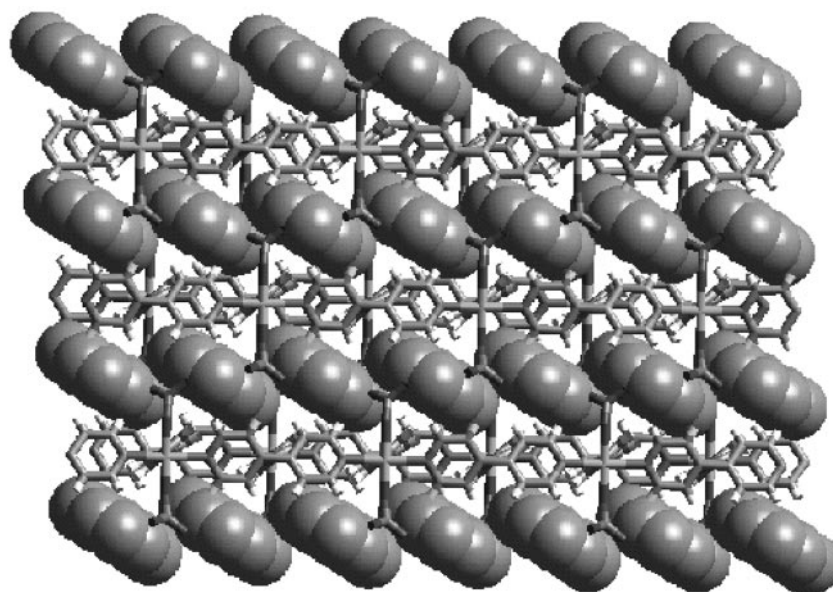


FIG. 4. Achiral chains of phenanthrene molecules that fill the channels that are formed by the interpenetrated noncovalent networks.

bipy and hydrocarbon moieties are 3.39–3.59 Å and they correspond to both face-to-face and edge-to-face interactions. The (4,4) nets thread orthogonally with respect to the planar nets of molecular railroads and therefore generate a 3D architecture that contains channels (Fig. 3). These channels contain chains of phenanthrene molecules that are assembled by face-to-face stacking (Fig. 4). The presence of three sets of independent phenanthrene molecules in the unit cell is therefore explained.

A literature search revealed only one previous example of a single-crystal structure in which phenanthrene exists as a guest molecule. In this compound, tetraphenylporphyrin·phenanthrene, the phenanthrene molecules are isolated in cavities and do not come in close contact with neighboring phenanthrene molecules. It is interesting to note that both of the commonly observed modes of aromatic stacking occur in the title compound and that what appears to be the first example of face-to-face stacking between phenanthrene molecules is observed. These phenanthrene molecules are significantly shifted and the shortest interatomic distance between them is 3.09 Å, occurring between a C–H group of one molecule and a carbon atom of the molecule below.

The structure of  $1 \cdot 2C_{14}H_{10}$  can be compared with those of compounds **2** and **3**, which also contain interpenetrating covalent and noncovalent nets. In **2**, pyrene molecules located between the layers of square grids engage in edge-to-face stacking and form a network that can be described as either a distorted brick wall form of a (6,3) net or a square (4,4) net. The pyrene nets also thread orthogonally to the coordination polymer square grids. The structures of **3** are similar in that noncovalent planar (6,3) nets of naphthalene molecules thread orthogonally with coordination polymer square grids.

We may conclude from this study and others that assembly of planar aromatic molecules into 2D noncovalent grids may be directed, and that coordination polymer networks are suitable templates for this purpose. This approach toward design of interpenetrated molecular arrays offers new and interesting possibilities for the generation of 3D molecular architectures from complementary topologic 2D networks. Further studies, attempting to generalize this observation, are in progress.

#### ACKNOWLEDGMENTS

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