Covalent and noncovalent interpenetrating planar networks in the crystal structure of $\{[\mathrm{Ni}(4,4'\text{-bipyridine})_2(\mathrm{NO}_3)_2\cdot 2\mathrm{pyrene}\}_n$

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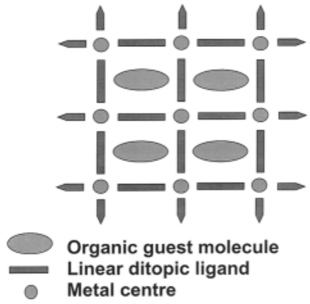
The crystal structure of $\{[\mathrm{Ni}(4,4'\text{-bipyridine})_2(\mathrm{NO}_3)_2]\cdot 2\mathrm{pyrene}\}_n$ reveals the first example of complementary, interpenetrating covalent and noncovalent 2D networks.

Crystal engineering of coordination polymer networks based upon multitopic ligands represents a growing area of coordination and supramolecular chemistry.[1,2] In this context, 2D square grid networks exemplify a particularly simple example of a predictable network. The primary reason for interest in such compounds has been their ability to afford controllable cavities that are suitable for enclathration of organic guest molecules (Scheme 1). A number of simple bifunctional spacer ligands have been examined, especially 4,4′-bipyridine (4,4′-bipy).[3–7] However, a phenomenon that mitigates against or even precludes enclathration is the filling of cavities by self-inclusion or interpenetration.[8] Interpenetrated structures have limited potential in the context of host–guest chemistry but have significant potential in terms of other bulk properties.[9] In this contribution, we report a compound that combines the above features: $\{[\mathrm{Ni}(4,4'\text{-bipy})_2(\mathrm{NO}_3)_2]\cdot 2\mathrm{pyrene}\}_n$ **1** which represents, to our knowledge, the first compound in which two very different types of 2D net interpenetrate: a square grid coordination polymer and a non-covalent planar net of pyrene molecules. A recent literature review[8] revealed that the only other example of a compound with different interpenetrating nets contains two nets of similar structure and composition.[10]



Scheme 1

A realistic motif for self-assembly of aromatic molecules is a 2D net that is sustained by edge-to-face stacking interactions. A distorted form of such a net coexists with $[\mathrm{Ni}(4,4'\text{-bipy})_2(\mathrm{NO}_3)_2]$ square grids in **1**. Blue crystals of **1** were grown by carefully layering a MeOH solution of $\mathrm{Ni}(\mathrm{NO}_3)_2\cdot 6\mathrm{H}_2\mathrm{O}$ onto a MeOH solution of 4,4′-bipy and pyrene under ambient conditions.† The coordination networks [Fig. 1(a)] possess inner cavities of *ca.* 8 × 8 Å and stack parallel to one another with an interlayer separation of *ca.* 7.9 Å (corresponding to half the *c*-axis) and bear a close resemblance to the coordination array in $[\mathrm{Cd}(4,4'\text{-bipy})_2(\mathrm{NO}_3)_2]\cdot 2\mathrm{C}_6\mathrm{H}_4\mathrm{Br}_2$.[3] An additional factor that appears to influence the packing of the grids is weak CH···O hydrogen bonding between the 4,4′-bipy ligands and nitrate anions of the adjacent grids. C···O separations are in the range of 2.877–3.149 Å. The pyridyl rings of the 4,4′-bipy ligands are not coplanar and are twisted by 32.5–48.9°.

The pyrene nets [Fig. 1(b)] are sustained by edge-to-face interactions and contain cavities of dimensions *ca.* 6.5 × 3.5 Å. The shortest intermolecular C–C separations (3.518 Å) are similar to those reported for related compounds such as pyrene itself[11] and 1-propynylpyrene.[12] The planes of the neighboring molecules intersect at an angle of *ca.* 60° and there are no face-to-face stacking interactions between the molecules. The pyrene nets can be regarded as distorted (4,4) nets if the node is the point in space at which the vectors of the four pyrene planes intersect. An alternate interpretation is that nodes exist at the point of the edge-to-face interactions. The pyrene net could then be regarded as a distorted brick wall form of a (6,3) net.[8] It is important to note that either a (4,4) or a (6,3) planar net is complementary from a topological sense with the (4,4) coordination polymer net and ensures that the coordination

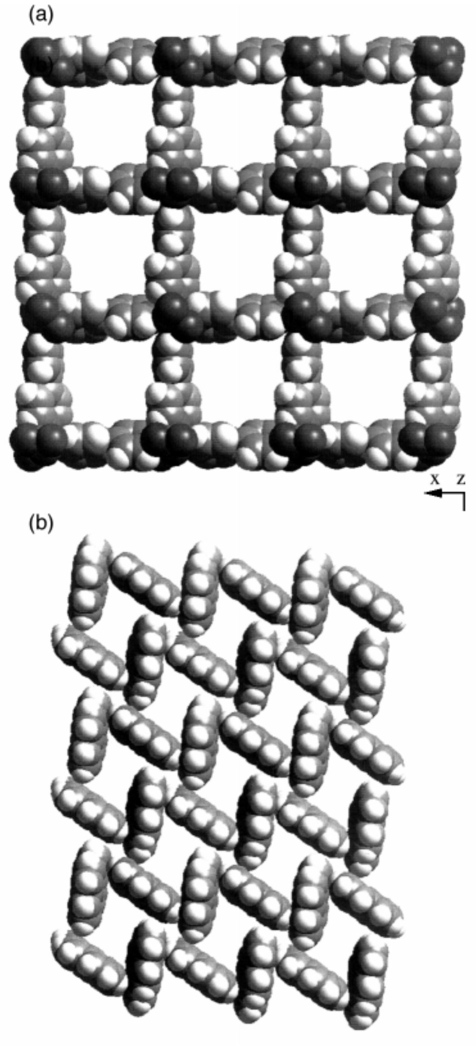


Fig. 1 (a) The square grid networks formed by $[\mathrm{Ni}(4,4'\text{-bipy})_2(\mathrm{NO}_3)_2]$ in **1**. Cavities have effective dimensions of *ca.* 8 × 8 Å. (b) An illustration of the pyrene (4,4) nets that exist in **1**. Cavities possess effective dimensions of *ca.* 6.5 × 3.5 Å.

polymer nets must pack in a staggered manner. Given that cavity size within the pyrene nets is complementary with the width and height of a single aromatic ring, it should be unsurprising that the pyrene nets thread orthogonally with the 4,4′-bipy ligands of the coordination polymer *via* face-to-face and edge-to-face interactions. The shortest carbon–carbon separation between the atoms of 4,4′-bipy ligands and pyrene molecules is *ca*. 3.40 Å and corresponds to face-to-face stacking (interplanar angle = 7.3°). The shortest C$\cdots$O separations involving pyrene 3.20 Å may be attributed to CH$\cdots$ONO$_3$ hydrogen bonds. The calculated[13] volumes of the two nets are similar: 1548.5 and 1502.0 Å^3 for the covalent and noncovalent networks, respectively. This is to be expected based upon the observation that 4,4′-bipy square grids are self-complementary as they can interpenetrate in a two-fold fashion.[5] A view of the crystal packing is presented in Fig. 2.

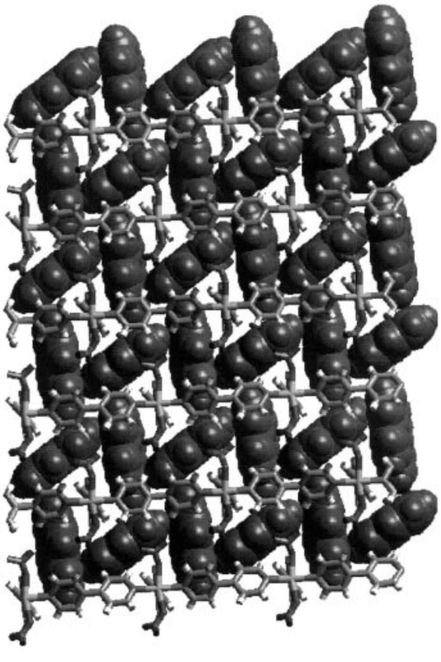


Fig. 2 A view of the crystal structure of **1** viewed down the *b*-axis. Note the stacking interactions between the pyrene molecules (space-filling mode) and square grid networks.

Interestingly, although both nets appear to be inherently centrosymmetric at first glance, the title compound crystallizes in the non-centrosymmetric space group *Pn* and is therefore polar. Pyrene molecules that lie opposite each other across the grid cavities in the *ac*-plane are clearly not related by inversion and are therefore crystallographically nonequivalent (Fig. 3). Indeed, they are not coplanar. Each set of four pyrene molecules in the *ac*-plane that surround the grid cavities adopts a bowl-like conformation and the bowls ‘stack’ in a parallel fashion along the *b*-axis. Additionally, the orientation of alternating pyrene molecules along the *b*-axis is slightly different, which leads to a doubling of the *b*-axis and the observed superstructure. An alternative possibility was also considered during structure refinement: random disposition of pyrene molecules in the crystal and crystallographic disorder. This artificial increase of the lattice symmetry did not afford a satisfactory refinement. Thus, the bulk polarity in **1** is a consequence of the symmetry of the supramolecular assembly of pyrene molecules.

In summary, the interpretation of the structure of **1** as interpenetrating covalent and noncovalent nets is to our knowledge unique and important in the context of understanding the structure and stoichiometry of compounds that are based upon interpenetrated covalent and noncovalent nets. **1** also illustrates how polarity in crystals can be generated from subtle packing of achiral components, as illustrated by the chiral nets of pyrenes. We are presently seeking other examples of compounds that contain complementary but chemically different nets.

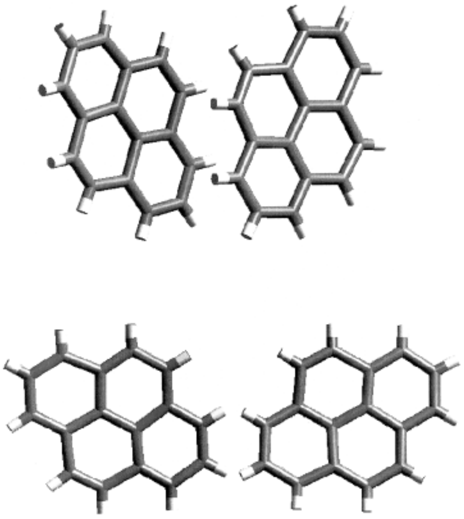


Fig. 3 An illustration of how the relative orientations of the pyrene molecules preclude a centre of inversion in **1**.

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Notes and references

† *Crystal data* for **1**: C$_{52}$H$_{36}$N$_6$NiO$_6$, monoclinic, space group *Pn*, a = 11.3602(6), b = 22.771(1), c = 15.8580(9) Å, β = 93.956(1)°, V = 4092.4(4) Å^3, Z = 4, D_c = 1.460 g cm^{-3}, λ = 0.7107 Å, F(000) = 1864. 14 277 reflections out of 15 136 unique reflections measured at 200 K on a Siemens SMART/CCD diffractometer using the θ scan mode ($4 < 2\theta < 56°$) afforded on convergence final *R*-factors of $R1$ = 0.041 and $wR2$ = 0.103 (1172 parameters refined, the highest electron density peak and hole were 0.75−0.66 e Å^{-3}). H atoms were placed in calculated positions. All other atoms were anisotropically refined. The absolute structure could not be determined unambiguously as refinement of the absolute structure Flack parameter afforded a value of 0.48(2), although refinement in the other enantiomorph afforded $R1$ = 0.043. The crystallographic calculations were conducted using the SHELXS-86 and SHELXL-93 programs.[14,15]

CCDC 182/1281. See: http://www.rsc.org/suppdata/cc/1999/1327/ for crystallographic files in .cif format.

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