# Noninterpenetrating Square-Grid Coordination Polymers With Dimensions of 25 × 25 Å$^2$ Prepared by Using *N*,*N*′-Type Ligands: The First Chiral Square-Grid Coordination Polymer[**]

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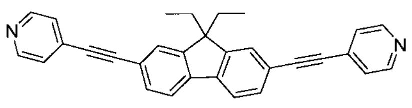
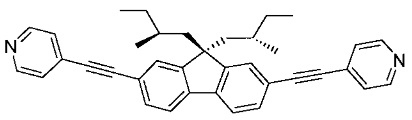
Self-assembled coordination polymers with well-defined channels or pores have attracted intense interest as microporous frameworks in which to carry out spatially confined reactions that are potentially catalyzed by functional appendages projecting to the inside of a framework structure.[1–8] Accordingly, noninterpenetrating square-grid (or rectangular-grid) polymers are an important class of networks that have predictable openings and can accommodate guest molecules that meet size-exclusion criteria.[9, 10] A challenge has been to modify such square-grid polymers through the incorporation of chiral moieties and allow their use in chiral recognition applications.

A large number of square-grid polymers are known, which were initially based on cyano ligands, and more recently have been based on *N*,*N*′-bipyridine-type ligands.[11] Many of these form interpenetrating frameworks that preclude their use as porous materials. There are, however, a fair number of noninterpenetrating square-grid coordination polymers, and Zaworotko recently classified their structures based on the stacking of the grids.[11] *N*,*N*′-bipyridine-type ligands are convenient linkers for achieving square-grid architectures with predictable grid dimensions, as demonstrated by Fujita et al. using 4,4′-bipyridine (**1**) to form $[\{[Cd(\mathbf{1})_2(H_2O)_2](NO_3)_2\}_n]$. More recently the longer 4,4′-bis(4-pyridyl)biphenyl (**2**) ligand in $[\{[Ni(\mathbf{2})_2(NO_3)_2]\cdot 4\,o\text{-xylene}\}_n]$ was reported by the same group. The latter polymer, for example, had grid dimensions of 20 × 20 Å$^2$, making it the largest at that time.[12] The stacking of the grids, in the case of noninterpenetrating frameworks, further determines the maximum accessible channel size that can be achieved in such systems. While it has been suggested, based on existing systems, that longer ligands will favor the formation of interpenetrating over noninterpenetrating grid structures,[13] it appears that the attachment of side chains that project perpendicular from the linker, can inhibit interpenetration and enable the formation of large square grids with infinite channels.[14]

An important issue in such noninterpenetrating square-grid systems is to achieve control over the size of the channels, which can be effected by using two *N*,*N*′-bipyridine ligands of different lengths[9] or by modifying the ligand to effect the shape of the grid. We decided to employ the latter strategy and modified the ligand to gain control over the physical dimensions of the grid and, more importantly, gain control over the internal chemistry of the channels. Herein, we report the synthesis[15] of two new types of very long, *N*,*N*′-bipyridine-based ligands containing side chains that project perpendicular to the linking direction: 9,9-diethyl-2,7-bis(4-pyridylethynyl)fluorene (**3**), and chiral 9,9-bis[(*S*)-2-methylbutyl]-2,7-bis(4-pyridylethynyl)fluorene (**4**), and their use in the formation of noninterpenetrating square-grid polymers containing chiral and nonchiral chemical environments in large channels. Treatment of **3** or **4** with copper nitrate in ethanol leads to exceptionally large, noninterpenetrating, square-grid polymers with grid dimensions of 25 × 25 Å$^2$.



**3**



**4**

Single crystals of $[Cu(\mathbf{3})_2(NO_3)_2]$ (**5**) were grown by carefully layering a solution of $Cu(NO_3)_2\cdot 3H_2O$ ((8.0 mg, 0.033 mmol) in ethanol (1.65 mL) onto a solution of **3** (28.0 mg, 0.066 mmol) dissolved in dichloromethane (2.0 mL). Crystals of $[Cu(\mathbf{4})_2(NO_3)_2]$ (**6**) were grown using a similar procedure: $Cu(NO_3)_2\cdot 3H_2O$ (6.0 mg, 0.025 mmol) was dissolved in ethanol (1.0 mL) and the solution was layered onto **4** (24.8 mg, 0.05 mmol) dissolved in dichloromethane (2.0 mL); crystals were obtained after two days.

The noninterpenetrating square-grid structure of **5** is depicted in Figure 1 a.[16] The short side chains of the ligand lead to an open-grid space, in particular as the ligand orientation alternates with the fluorene group rotated by approximately 90° on opposing sides of each grid, projecting the side chains parallel and perpendicular to the plane of the grid. The grid dimension is 25 × 25 Å$^2$, making it, we believe, the largest known noninterpenetrating grid to date. While interpenetrating square-grid polymers are typically nonporous since all available space is filled by the interpenetration, even large noninterpenetrating square-grid polymers, such as the above-mentioned $[\{[Ni(\mathbf{2})_2(NO_3)_2]\cdot 4\,o\text{-xylene}\}_n]$ can have reduced porosity due to the stacking of the grids; in which case the 20 × 20 Å$^2$ openings are reduced to 10 × 20 Å$^2$. In the case of **5** the ABAB stacking of the layers (Figure 1 b; B-type grid[11]) generates reduced, yet still very large infinite channels of dimensions 16 × 16 Å$^2$. The solvent-accessible volume calculated with the PLATON program[17] is 5115.1 Å$^3$, or 54.1 % of the volume of the unit cell. Although not filled by the side chains, the channels are occupied by a sea of disordered solvent molecules and nitrate anions, which could not be defined crystallographically. A view parallel to four

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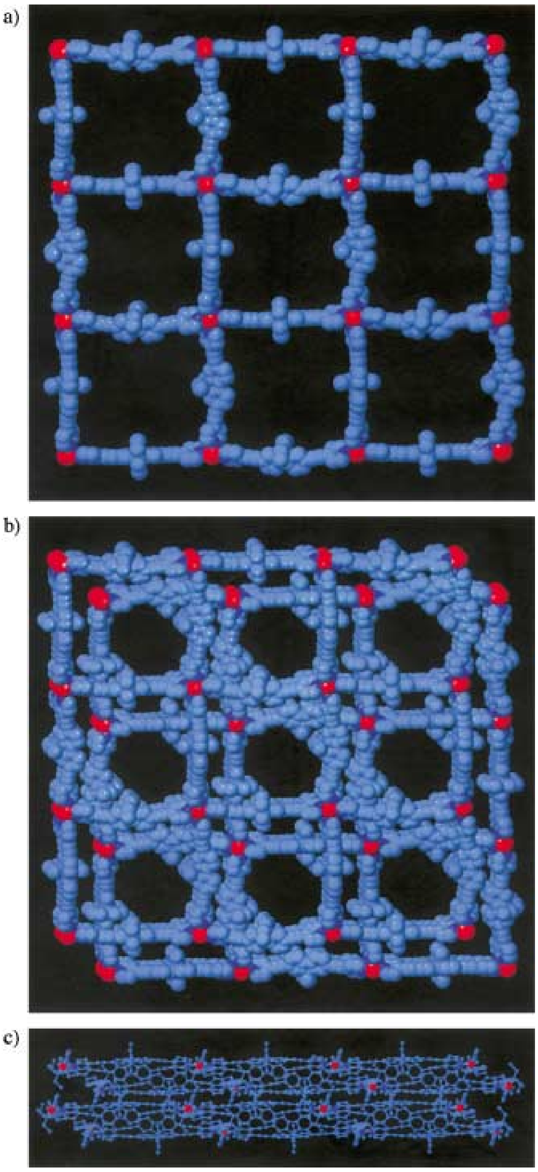

Figure 1. a) Single square-grid layer of $[Cu(\mathbf{3})_2(NO_3)_2]$ (**5**). The fluorene group is rotated by approximately 90° on opposing sides of each grid, projecting the side chains parallel and perpendicular to the plane of the grid. The ligand is shown in blue and the copper atoms in red. b) Stack of four square grid layers. The grids stack in an ABAB fashion, creating large infinite channels of dimensions $16 \times 16$ Å$^2$. c) A view parallel to four adjacent stacked grids shows that the grids are virtually planar.

adjacent stacked grids (Figure 1c) shows that the grids are virtually planar.

The major accomplishment using these fluorene-based ligands, however, is the formation of the chiral system **6** (space group $P2_1$), using the chiral ligand **4**. There are several strategies to generate chiral systems: 1) starting with the use of achiral components to make chiral structures,[18–20] 2) the use of chiral ligands in molecular squares and their aggregation into chiral clusters,[21] and 3) the use of helical chains[22] or helical frameworks;[23–25] the work described herein extends the concept of chiral molecular square complexes, assembled by using chiral ligands, to polymeric structures and, to the best of our knowledge, **6** is the first chiral noninterpenetrating square-grid coordination polymer.

The structure of the grid of **6** is shown in Figure 2a, and the ABCABC stacking of the layers in Figure 2b. In **6**, by contrast with **5**, the fluorene groups maintain the same orientation on all grid sides. This forces the R groups to project into the grid, thus taking up more space than in **5** and thereby significantly reducing the channel size. The grid dimension is still $25 \times 25$ Å$^2$; however, the ABCABC stacking significantly reduces the accessible channel dimension to about $8 \times 8$ Å, which is also reflected in a greatly diminished solvent-accessible volume of 423.2 Å$^3$ (11.8% total unit cell volume) compared to **5**. Unlike **5**, the grid plane of **6** is not planar and in Figure 2c the undulation can be clearly seen.

The existence of this chiral and porous system suggests future opportunities for chiral selectivity of host molecules

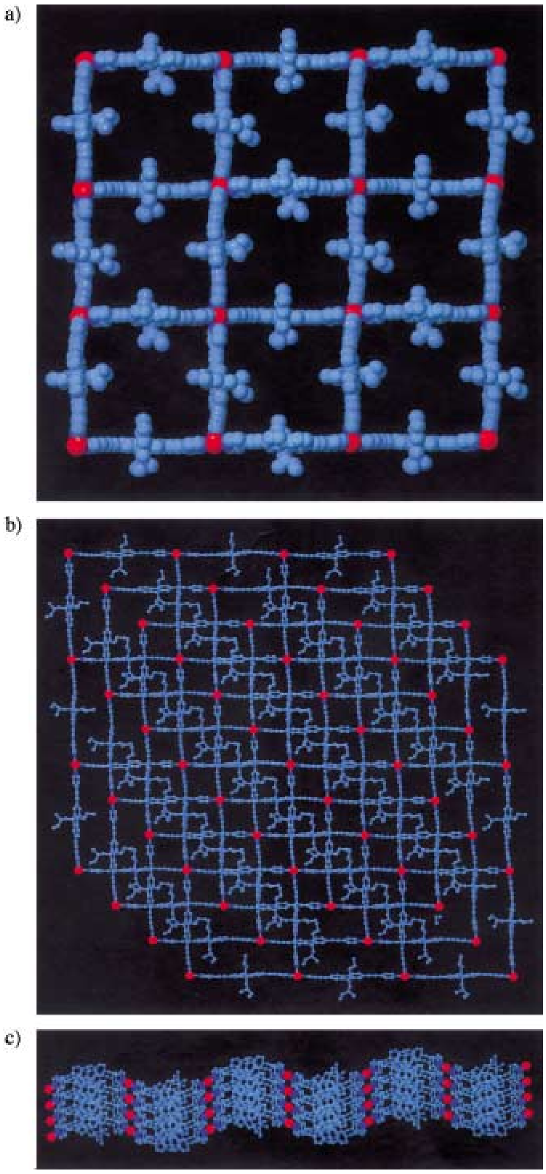

Figure 2. a) Single square-grid layer of $[Cu(\mathbf{4})_2(NO_3)_2]$ (**6**). The fluorene groups maintain the same orientation on all grid sides, forcing the side chains to project into the grid. b) Stack of four square-grid layers. The grids stack in an ABCABC fashion, creating infinite channels of dimensions $8 \times 8$ Å$^2$. c) A view parallel to four adjacent stacked grids shows that the grids are not planar but undulate.

and even, potentially, chiral-selectivity for reactions that might benefit from taking place inside spatially confined channels and its local chemical environment. The use of the new ligand **4** represents a proof-of-concept in this respect, as we have generated the new *noninterpenetrating* grid **6**, in which the organic side chains project inward. This illustrates an exciting aspect of this square-grid family, namely that it can potentially be further modified to be functional and space-specific. That is, by using different polar or nonpolar groups, the amount of space in the channel should be controllable—while the noninterpenetrating square-grid frameworks are maintained. One can readily envision their use for size-exclusion chemistry, for reactions that are promoted by reactant proximity,[3, 4] and for those catalyzed by the local chemical environment. Work towards these goals is underway and will be reported in the near future.

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[15] **3**: 9,9-Diethyl-2,7-diethynylfluorene (0.26 g, 0.96 mmol), 4-bromopyridine hydrochloride (0.47 g, 2.40 mmol), [Pd(PPh$_3$)$_2$Cl$_2$] (0.05 g, 0.07 mmol), CuI (0.14 g, 0.072 mmol), and PPh$_3$ (0.50 g, 0.01 mmol) were dissolved in triethylamine (20 mL) in a dry Schlenk flask thoroughly flushed with nitrogen, and heated to 70 °C for 24 h. After aqueous workup and column chromatography (CH$_2$Cl$_2$/MeOH), **3** (0.39 g, 96 %) was isolated as a yellow powder: m.p. 191–194; $^1$H NMR (CDCl$_3$): $\delta = 8.60$ (dd, 4H, $J = 1.7, 4.7$ Hz), 7.70 (d, 2H, $J = 7.7$ Hz), 7.54 (d, 2H, $J = 8.0$ Hz), 7.52 (s, 2H), 7.39 (dd, 4H, $J = 1.7, 4.4$ Hz) 2.06 (q, $J = 7.1$ Hz, 4H), 0.32 (t, $J = 7.1$ Hz); $^{13}$C NMR: $\delta =$ 150.3, 149.6, 141.5, 132.0, 131.9, 131.4, 131.1, 128.4, 128.3, 126.2, 125.3, 120.9, 120.1, 94.8, 87.1, 56.3, 32.5, 8.3. **4**: 9,9-Bis[(*S*)-2-methylbutyl]-2,7-di(trimethylsilylethynyl)fluorene (2.00 g, 5.23 mmol) and 4-bromopyridine hydrochloride (3.05 g, 15.68 mmol) were dissolved in triethylamine (10 mL) in a dry Schlenk flask thoroughly flushed with nitrogen. KOH/EtOH solution (10 % solution; 10 mL) was then added followed by the addition of [Pd(PPh$_3$)$_2$Cl$_2$] (0.08 g, 0.11 mmol), CuI (0.03 g, 0.16 mmol), and PPh$_3$ (0.08 g, 0.30 mmol). The flask was once again flushed with nitrogen then heated to 70 °C for 14 h. After aqueous workup and column chromatography (CH$_2$Cl$_2$/MeOH), the product **4** (1.05 g, 39 %) was isolated as a pale yellow powder: m.p. 173–175; $^1$H NMR (CDCl$_3$): $\delta = 8.60$ (d, 4H, $J = 5.0$ Hz), 7.70 (d, 2H, $J = 8.4$ Hz), 7.58–7.51 (m, 4H), 7.41 (d, $J = 5.7$ Hz), 2.14–2.07 (m, 2H), 1.93–1.86 (m, 2H), 0.94–0.75 (m, 4H), 0.58 (dd, 8H, $J = 14.8, 7.3$ Hz), 0.26 (dd, 6H, $J = 15.6, 6.8$ Hz); $^{13}$C NMR (CHCl$_3$): $\delta = 151.7$, 151.4, 151.0, 149.6, 141.4, 141.3, 131.7, 131.2, 127.4, 127.2, 127.0, 120.5, 120.2, 95.1, 87.0, 54.9, 54.8, 47.9, 47.8, 31.1, 30.9, 30.7, 30.6, 20.9, 20.8, 10.9, 10.8.

[16] Crystal data **5**: Cu(C$_{30}$H$_{24}$N$_2$)$_2$(NO$_3$)$_2$(solvent)$_x$; $M_r = 992.61$, rectangular green bar, dimensions $0.40 \times 0.20 \times 0.18$ mm$^3$, monoclinic, $P2_1/c$, $a = 33.373(3)$, $b = 33.578(3)$, $c = 8.5066(9)$ Å, $\beta = 97.029(3)^\circ$, $V = 9461.0(2)$ Å$^3$, $Z = 4$. Intensity data covering a hemisphere of reciprocal space measured ($\omega$ scan mode) to $2\theta_{max} = 50.1^\circ$ with a Bruker SMART APEX CCD diffractometer (Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å), at 293(2) K. A total of 55524 reflections collected; 16730 independent, 6324 with $I > 2\sigma(I)$. Lorentzian polarization and absorption corrections applied (SADABS, $\mu = 0.260$ mm$^{-1}$, $T_{max}/T_{min} = 0.980/0.856$). Structure solved with direct methods; refined against $F^2$ using all data (SHELXTL version 5.1): $R1 = 0.0541$, $wR2 = 0.1338$ ($I > 2\sigma(I)$). The sea of diffusely scattering solvent accounted for with the SQUEEZE program (solvent-accessible void volume = 5115 Å$^3$, or 1407 e$^-$/cell).[17] The final $\rho_{calcd}$, $F(000)$, and $M_r$ reflect known contents only. Crystal data **6**: Cu(C$_{37}$H$_{36}$N$_2$)$_2$(NO$_3$)$_2$(CH$_2$Cl$_2$)·2(C$_2$H$_5$OH), $M_r = 1381.98$, green plate, dimensions $0.22 \times 0.12 \times 0.03$ mm$^3$, monoclinic, $P2_1$, $a = 10.432(3)$, $b = 31.631(9)$, $c = 10.910(3)$ Å, $\beta = 96.126(6)^\circ$, $V = 3579.6(2)$ Å$^3$, $Z = 2$. Intensity data covering a hemisphere of reciprocal space measured ($\omega$ scan mode) to $2\theta_{max} = 45.4^\circ$ with a Bruker SMART APEX CCD diffractometer (Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) at 173(2) K. A total of 16560 reflections collected; 9462 independent, 2408 with $I > 2\sigma(I)$. Lorentzian polarization correction applied; no absorption correction ($\mu = 0.44$ mm$^{-1}$). Structure solved with direct methods; refined against $F^2$ using all data (SHELXTL version 5.1): $R1 = 0.0700$, $wR2 = 0.1184$ ($I > 2\sigma(I)$).

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