Supplementary Material (ESI) for Chemical Communications

Supporting Information

For Chem. Commun.

Formation of two (6, 3) networks showing structural diversity, Borromean topology and conformational chirality in the same crystal

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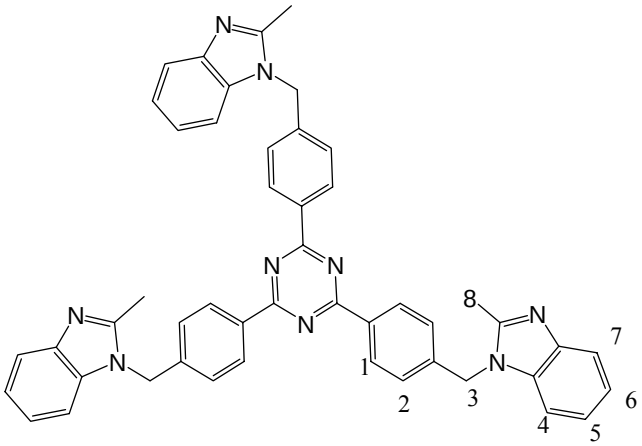
Syntheses and characterization:

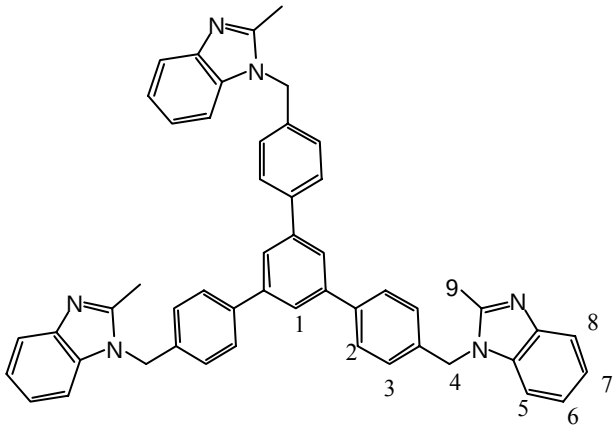
Ligand L^1. The ligand 2,4,6-tris(4-((2-methyl-benzimidazol-1-yl)methyl)phenyl)-1,3,5-trizaine ($\mathbf{L^1}$) was prepared under argon by the following method: To a solution of 2-methyl-benzimidazole (3.96g, 30 mmol) in THF (50 mL) was slowly added K_2CO_3 (4.14 g, 30 mmol) at room temperature. The mixtures was rigorously stirred for about 4 h, and then a solution of 2,4,6-tris[4-(chloromethyl)phenyl]-1,3,5-triazine (4.55 g, 10 mmol) in 50 mL of acetone was added dropwise. The resulting reaction mixture was stirred continuously overnight. The solvent was subsequently removed under reduced pressure, and the residue was washed with water (3 × 100 mL) and then with THF (2 × 20 mL). Yield: 3.41 g, 46%. ^{1}H NMR ($CDCl_3$) 8.63 (d, 6H, H1), 7.75 (m, 3H, H4), 7.26 (m, 3H, H7), 7.21-7.24 (m, 12H, H5,6,2), 5.44 (s, 6H, H3), 2.61(s, 9H, H8).



2,4,6-tris(4-((2-methyl-benzimidazol-1-yl)methyl)phenyl)-1,3,5-trizaine (L^1)

Ligand L^2. The ligand 1,3,5-tris(4-((2-methyl-benzimidazol-1-yl)methyl)phenyl)benzene ($\mathbf{L^2}$) was prepared under argon by the following method: K_2CO_3 (4.14g, 30 mmol) was slowly added to a solution of 2-methylbenzimidazole (3.96 g, 30 mmol) in THF (50 mL) at room temperature with rigorous stirring. After about 4 h, a solution of 1,3,5-tris[4-(bromomethyl)phenyl]benzene (5.85 g, 10 mmol) in 50 mL of acetone was

added dropwise, and the reaction mixture was stirred continuously overnight. After filtration, the residue was washed with THF (20 mL) and then with water (50 ml×2). Yield: 6.43 g, 87%. ^{1}H NMR (DMSO-d_6) δ 7.752 (s, 6H, H2), 7.720 (s, 3H, H1), 7.549 (m, 3H, H8), 7.475 (m, 3H, H5), 7.186 (d, 6H, H3), 7.130 (dd, 6H, H6, H7), 5.508 (s, 6H, H4), 2.541 (s ,9H, H9).



1,3,5-tris(4-((2-methyl-benzimidazol-1-yl)methyl)phenyl)benzene (L ^{2})

[(AgL$^1_{2/3}$)$_3$(AgL^1)$_2$](SbF$_6$)$_5$·(CHCl$_3$)$_2$·(H$_2$O) (1). A solution of $AgSbF_6$ (17.2 mg, 0.05 mmol) in 8 mL acetone was layered onto a solution of **L** (37 mg, 0.05 mmol) in $CHCl_3$ (10 mL) in the test tube. The test tube was then sealed and left standing for *ca.* 15 days at room temperature to give colorless crystals of **1**. Yield: 71%. ^{1}H NMR (DMSO-d_6) δ 8.58 (d, 6H, H1), 8.30 (s, 0.5H, C**H**Cl$_3$) 7.62-7.59 (m, 3H, H7), 7.52-7.49 (m, 3H, H4), 7.32 (d, 6H, H2), 7.19-7.17 (m, 6H, H5,6), 5.65 (s, 6H, H3), 2.59 (s ,9H, H8). IR (KBr, cm^{-1}): 3431 (w), 3042 (w), 2932 (w), 1613 (m), 1587 (m), 1518 (s), 1458 (m), 1414 (m), 1368 (s), 1182 (m), 1015 (m), 746 (s), 660 (m).

[(AgL$^2_{2/3}$)$_3$(AgL^2)$_2$](SbF$_6$)$_5$·1.5H$_2$O (2). A solution of $AgSbF_6$ (17.2 mg, 0.05 mmol) in 12 mL acetonitrile was layered onto a solution of L (37 mg, 0.05 mmol) in $CHCl_3$ (12 mL). The solutions were left standing for *ca.* 7 days at room temperature to give colorless crystals. Yield: 61%. ^{1}H NMR (DMSO-d_6) δ 7.769 (s, 6H, H2), 7.745 (s, 3H, H1), 7.657-7.594 (m, 6H, H5, H8), 7.273-7.245 (m, 12H, H3, H6, H7), 5.605 (s, 6H, H4), 2.670 (s ,9H, H9). IR (KBr, cm^{-1}) 3439(br), 3032(w), 2936(w), 1911(w), 1780(w), 1599(m), 1516(s), 1456(s), 1412(s), 1344(s), 1290(m), 1250(w), 1215(w), 1159(w), 1013(w), 984(w), 843(w), 816(w), 745(m), 660(m).

Crystal structure determination. Reflection intensity data for complexes **1** and **2** were collected at -100 or -123°C on a Bruker Apex II CCD diffractometer, respectively, with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) using the ω-2θ scan technique. Absorption corrections were applied with the SADABS program.[1] All the structures were solved by direct methods and refined by full-matrix least-squares against F^2 of all data using the SHELXTL program package.[2] Anisotropical thermal factors were assigned to most of the nondisordered non-hydrogen atoms except those showing severe disorder as explained below. The positions of the hydrogen atoms except for water molecules were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their respective parent atoms before the final cycle of least-squares refinement. The hydrogen atoms of water molecules were not added.

Most of anionic and solvated molecules were found to exhibit severe disorder. One of SbF_6^- anion in both **1** and **2** is located at 32 special position with four F atoms show disorder imposed by symmetry. The other two

SbF_6^- anions are in sites with 2-fold symmetry, of which one is assigned with 1/6 occupancy. The central benzene ring of ligand L^2 in **2** was fix to a plane by using FLAT restraints. The $CHCl_3$ and water molecules in **1** were disordered over more than one sites and refined with fractional occupancies. Detailed refinement modeling of the disordered molecules were given in CIF files.

References

(1) Sheldrick, G. M. *SHELX 97*, *Program for Crystal Structure Solution and Refinement*, Göttingen University, **1997**.
(2) Sheldrick, G. M. *SADABS*, *Program for absorption correction with the Siemens SMART area-dector system*, Göttingen University, **1996**.

Figure S1. Partial molecular structures of (6, 3) networks in **2** showing the propeller-like *syn*,*syn*,*syn*-conformation of the ligands and coordination geometry of the Ag^+ ions: (a) left-handed arrangement of three benzimidazole arms around the central C_3 axis in each **AgL** subunit of the $(\mathbf{ML})_3$ net, and (b) left-handed arrangement of three benzimidazole arms around the central C_3 axis in each $\mathbf{AgL_{2/3}}$ subunit of the $(\mathbf{ML})_6$ net.

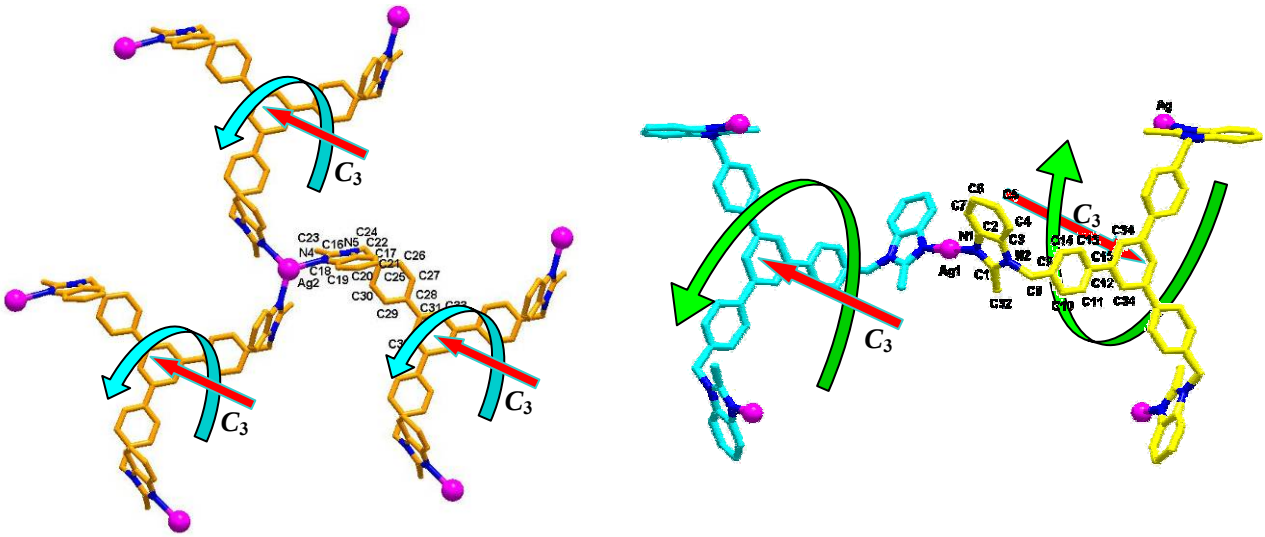
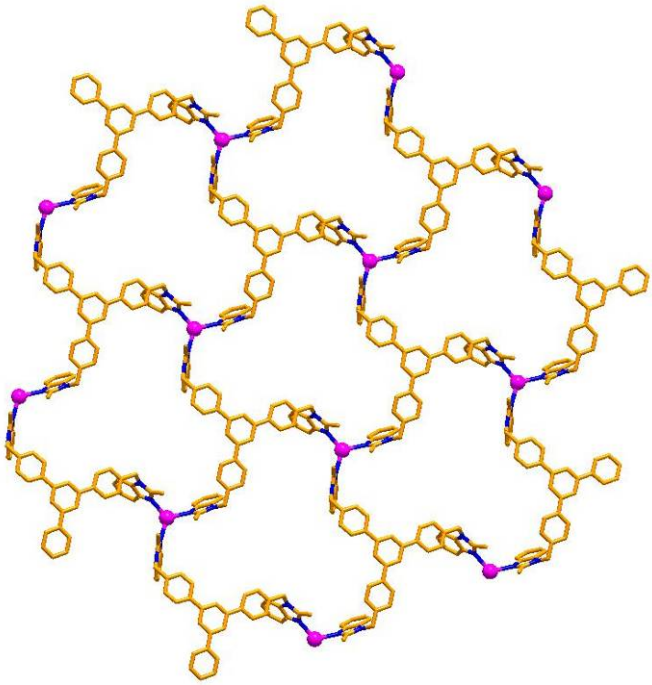
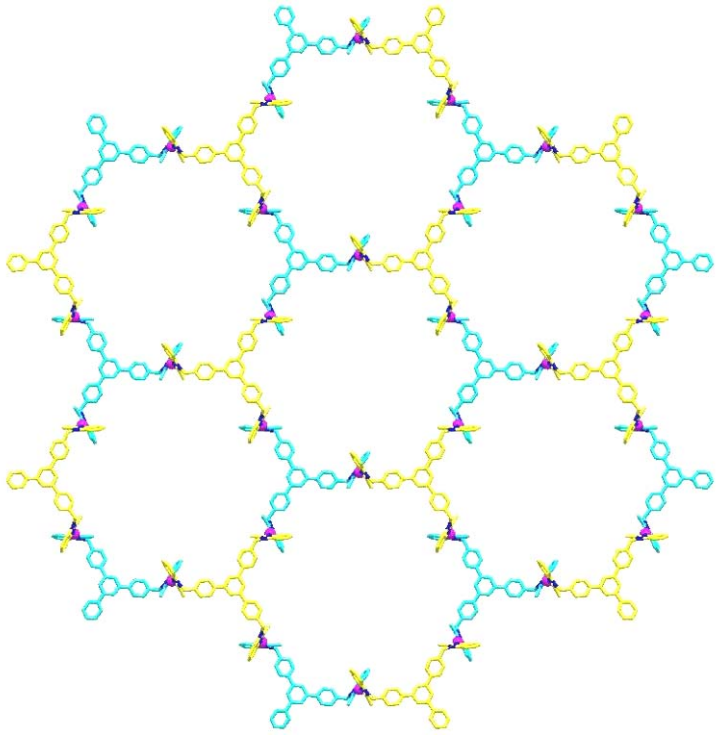


Figure S2. Two kinds of (6,3) networks in **2** .



$(ML)_3$ type (6, 3) network



$(ML)_6$ type (6, 3) network

Figure S3. Layered packing: (a) in *a* direction in **1** without counter anions and solvents; (b) in *a* direction in **1** with counter anions and solvents; (c) in *a* direction in **2** with counter anions and solvents; and (d) in *c* direction in **2** with counter anions and solvents.

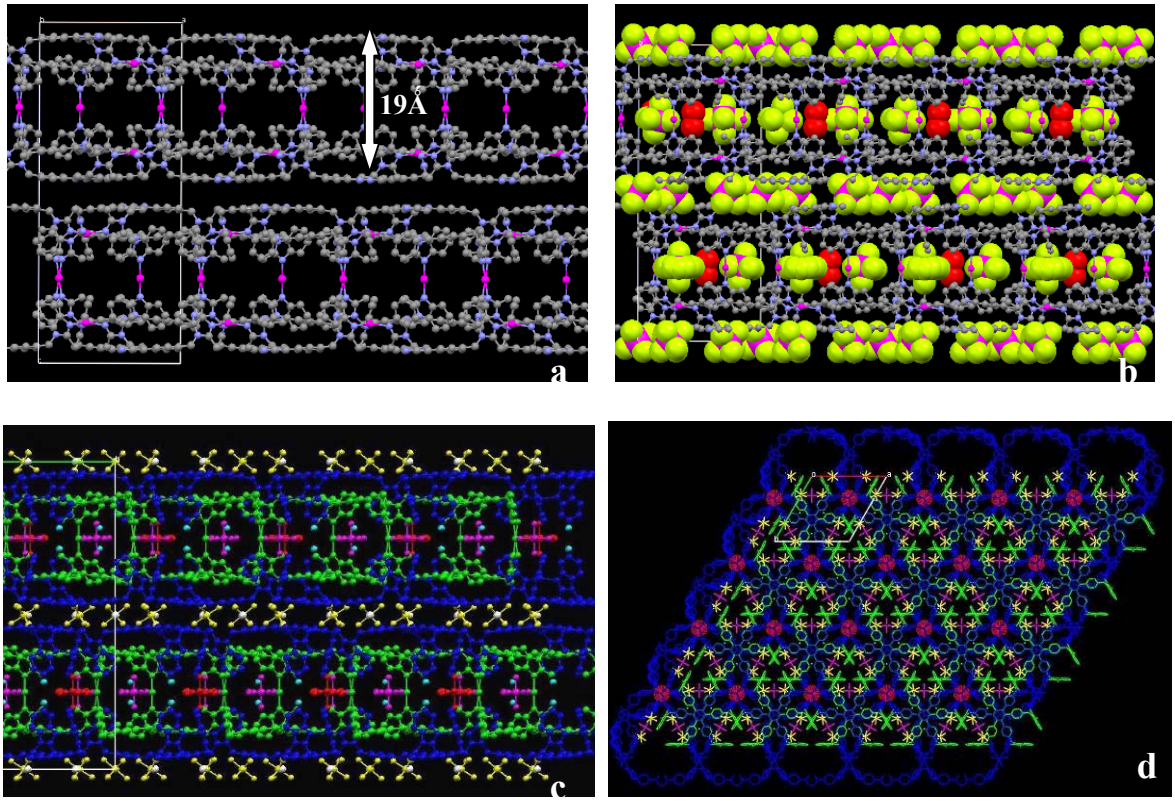


Figure S4. Comparison of the powder X-ray patterns for **1** (top) and **2** (bottom): a) experimental, b) simulation based on the single-crystal refinement results by program Mercury 1.4.1.

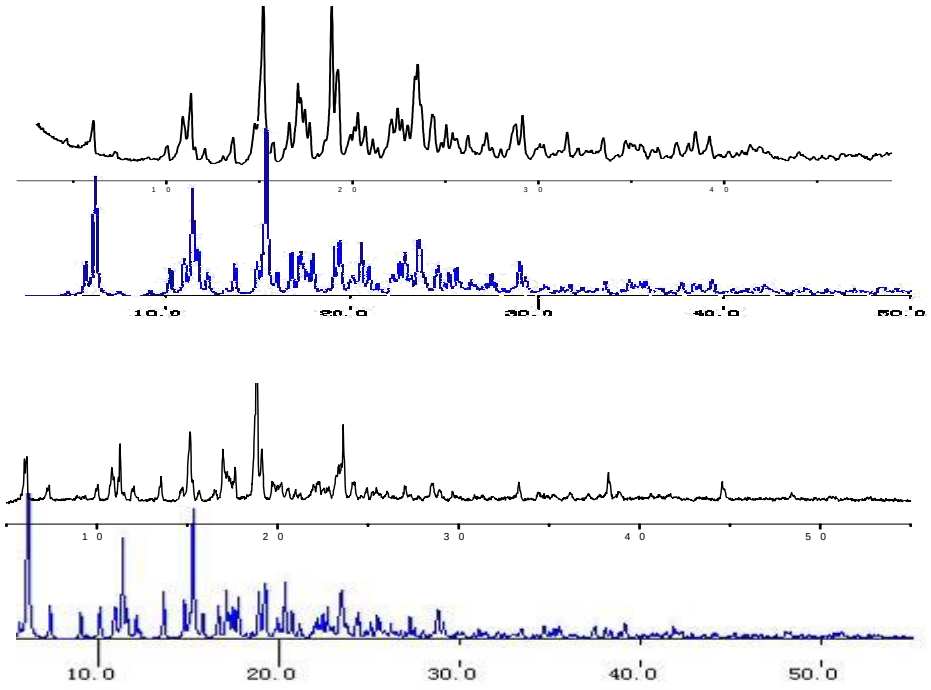


Figure S5. TGA curves of complexes **1**

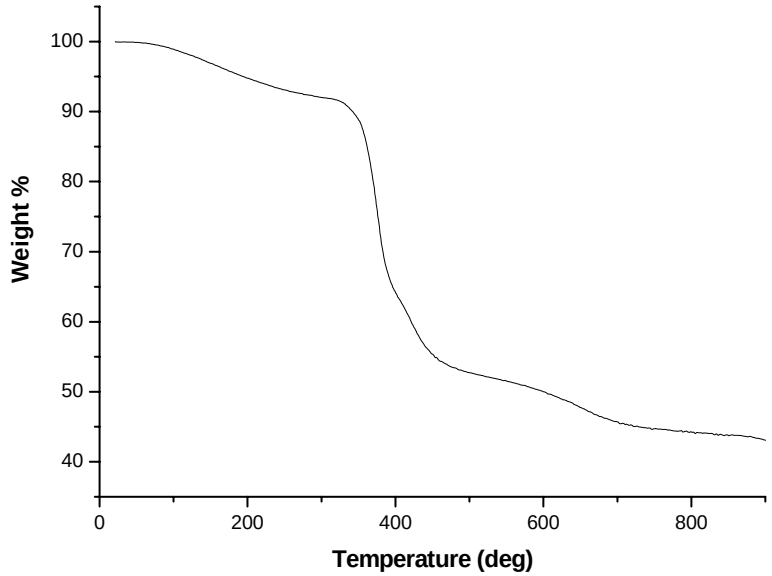


Figure S6. XRD patterns of the simulation of complexes **1** (a), as-prepared sample (b), and heating to 100 (c), 200 (d), 264 (e), 290 (f), and 345°C (g).

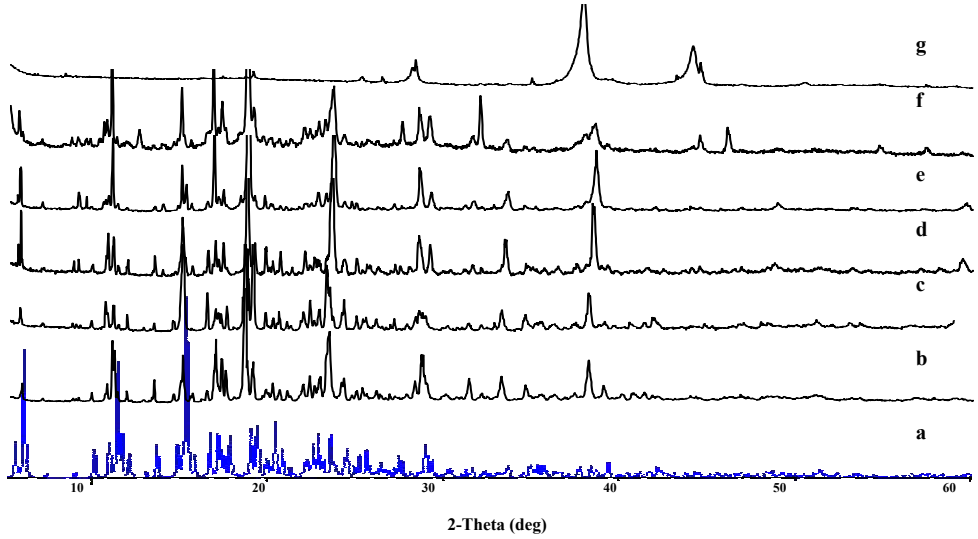


Figure S7. Solid-state emission spectra of the ligand $\mathbf{L}^1$ and complex **1.**