

A New Route to Supramolecular Isomers via Molecular Templating: Nanosized Molecular Polygons of Copper(I) 2-Methylimidazoles

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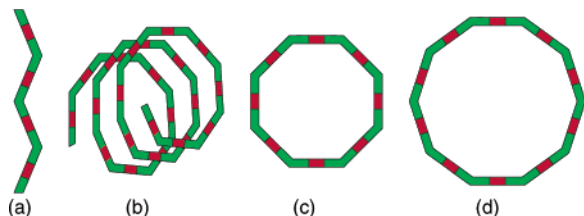
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The design and preparation of supramolecular macrocyclic architectures has attracted intense interest in the past decade. Successful strategies have been developed for the construction of metal macrocyclic structures with triangular and square shapes,¹ but molecular polygons of higher numbers of sides are thus far scarce; just a few cases (up to octagon) are known,² although a series of mesoscopic metalocycles without crystal structures has also been reported.³ In principle, different molecular polygons can be rationally constructed by proper selection of corners (with an appropriate angle) and linear components; however, it is still a challenge to control the formation of such supramolecular isomers in coordination polymers.⁴

Simple imidazolate derivatives are bent exo-bidentate ligands, and can be expected to show a linear or slightly bent im—Cu^I—im geometry in binary copper(I) imidazoles which may have different architectures or supramolecular isomers in the 1:1 metal/ligand ratio. Scheme 1 illustrates some supramolecular isomers that may be generated by utilizing an angular ligand (M—L—M ca. 135–145°) and a linear two-coordinate metal ion (such as Cu^I): polygons (octagon for 135°, nonagon for 140°, and decagon for 145°), helices, and zigzag chains. Additional supramolecular isomers include larger rings (nonplanar), and catenanes may also be possible. However, only one-dimensional (1D) metal—organic polymeric architectures rather than the discrete polygonal ones have been observed for Cu^I imidazoles.⁵

Scheme 1. Schematic Representation of Four Structural Supramolecular Isomers Possible for an Angular Ligand (135–145°) and a Linear Spacer: (a) Zigzag Chain, (b) Helix, (c) Octagon, and (d) Decagon



Following our recent report of a hydrothermal approach of tuning the reduction degree of Cu^{II} ions into Cu^I for generation of mixed-valence Cu^I/Cu^{II} imidazolate polymers,⁶ we could now synthesize a Cu(I) 2-methylimidazolate (mim) [Cu(mim)]_n (**1**),⁷ which exhibits a zigzag chainlike structure (Figure 1). In the structure of **1**,⁸ the Cu^I—L—Cu^I angles vary in the range of 145–152°, and the dihedral angles of a pair of mim ligands bound to a Cu^I atom vary in the range of 52°–86°, implying the flexibility for the formation of other possible polymeric structures via tuning of the configuration. A question that arises here is what can induce the formation of a circular structure? Geometrically, the formation of a ring structure requires the hydrophobic mim methyl groups pointing inward the ring. It can therefore be speculated that, at a certain orientation, a polygonal structure may possibly be formed by templating with

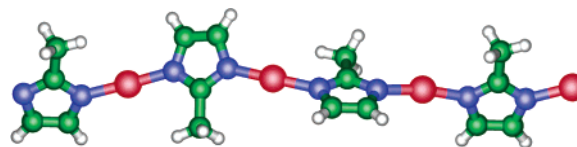


Figure 1. Perspective drawing of **1** (color code: Cu, red; C, green; H, gray; N, blue).

hydrophobic, especially circular, organic molecules such as toluene, benzene, and cyclohexane in the reaction system. This speculation did lead to the isolation of predesigned, organically cornered, uniform molecular octagons ([Cu₈(mim)₈]·toluene (**2**),⁷ as well as [Cu₈(mim)₈]·benzene and [Cu₈(mim)₈]·cyclohexane (see Supporting Information (SI)), which were generated with the corresponding solvents. Furthermore, higher molecular decagons [Cu₁₀(mim)₁₀]·(*p*-xylene)₂ (**3**)⁷ and [Cu₁₀(mim)₁₀]·(naphthalene)₂ (see SI) have also been obtained by using larger organic molecules as templates.

The chainlike **1** and the above neutral molecular polygons are isomers in a broad sense of supramolecular isomerism. In the crystal structures of **1**–**3**,^{8–10} the coordination geometries of Cu^I atoms are similar, and each Cu^I atom is ligated in a basically linear fashion by two N atoms from the μ -bridged mim groups (Cu—N 1.851(4)–1.875(4) Å, N—Cu—N 170.5(2)–176.5(3)°).

The neutral, flattened octagon of **2** consists of eight Cu^I ions, eight mim anions with a toluene molecule in the cavity (Figure 2). Such molecular octagon is the structurally characterized uniform (metal-to-ligand ratio being 1:1 in our case) polygon of the highest number of sides, and only the structure of a nonuniform octagon is known hitherto.^{2h} The inner and outer diameters of the octagon are ca. 0.99 and 1.86 nm, respectively. The octagon is bisected by a crystallographic mirror plane through the top and bottom methyl groups of mim ligands in Figure 2. Most of the mim rings are basically coplanar (deviations ca. 4.3–10.4°) with the octagon plane defined by the Cu^I atoms, whereas one mim (at the bottom) is twisted by 61.6° from the plane. The octagons further stack to a thick (ca. 5.5 Å) sheet, via short intermolecular Cu···Cu contacts (2.786(1)–2.879(1) Å), which has only weak van der Waals interactions with the adjacent sheets (see SI). Both [Cu₈(mim)₈]·benzene and [Cu₈(mim)₈]·cyclohexane are isostructural to **2** (see SI), but the solvent molecules are disordered.

A pair of Cu^I atoms and a pair of mim groups (the top and bottom ones) are orientated in two possible orientations in the structure of **3**¹⁰ which results in two configurations of decagons in **3**. One is very flattened (Figure 3) in which the mim rings have deviations ca. 9.7–15.0° with the plane defined by the Cu^I atoms, whereas the other is more distorted from an ideal decagon in which the top and bottom mim rings are nearly perpendicular (ca. 72°) to the decagonal plane (see SI). This larger decagon has the inner and outer sizes of ca. 1.36 and 2.34 nm, respectively. The decagons are stacked via short Cu···Cu contacts (2.828(1)–2.89(1) Å) to a 3D network featuring 1D channels (diameter ca. 0.5 nm). Disordered

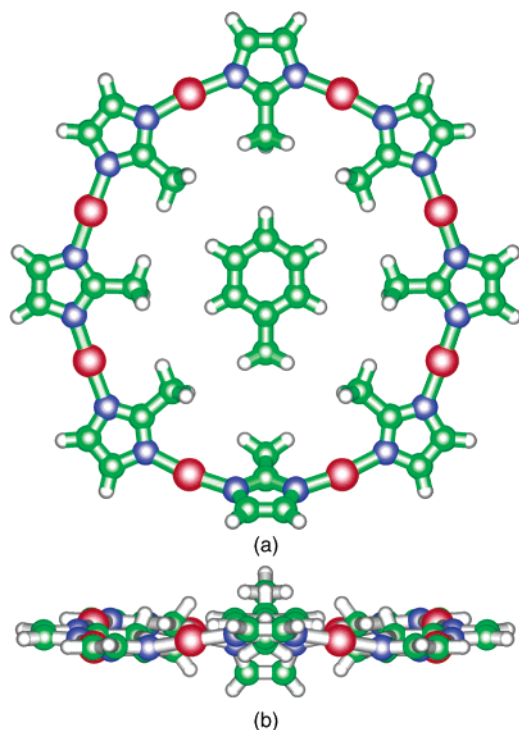


Figure 2. Perspective drawings of 2: (a) top-view, (b) side-view.

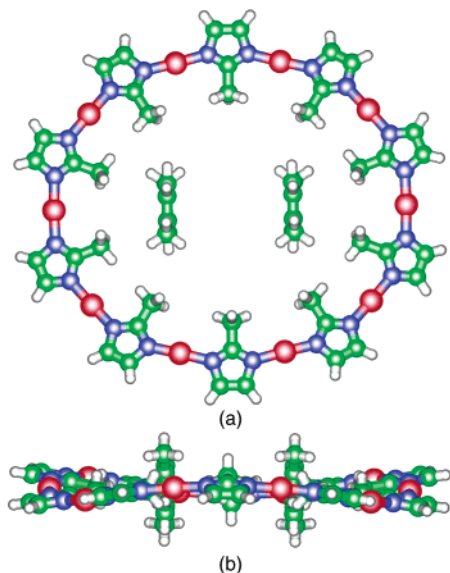


Figure 3. Perspective drawings of 3: (a) top-view, (b) side-view.

p-xylene guests are located in the cavities, and one orientation of some solvent guests is shown in Figure 3.

Discrete supramolecular isomers were suggested to be thermodynamically favored compared with the chain ones. The difficulty in isolation of the desired polygons using imidazoles may be due to the fast formation of the chains, indicating that the polygons are disfavored in the kinetic point of view. On the basis of our observation, we may suggest that the use of alkyl-containing mim bridges and hydrophobic, circular template molecules should be responsible for the formation of uniform polygons. It should also be noted that no crystallographically characterized examples of two supramolecular isomers of polygons of higher numbers of sides containing the same organic and metal components have been documented thus far.³

In summary, we have successfully isolated two different polygons of higher numbers of sides constructed by simple, bent exo-bidentate organic ligands and two-coordinate Cu^I ions in the presence of different molecular templates. This work represents a new, facile route for synthesis of organically cornered polygons via templates, which may possibly be extended to different molecular polygons with appropriate metal ions and exo-bidentate ligands, upon templating with organic molecules in different sizes.

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Supporting Information Available: Synthesis details and additional plots. An X-ray crystallographic file in CIF format for the structural determination of 1–3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) A mixture of Cu(NO₃)₂·3H₂O (0.242 g, 1.0 mmol), Hmim (0.081 g, 1.0 mmol), aqueous ammonia (25%, 5 mL), and methanol (2 mL) was stirred for 15 min in air, then transferred and sealed in a 23-mL Teflon reactor, which was heated at 160 °C for 80 h. Upon cooling to room temperature at a rate of 5 °C h⁻¹, the resulting yellow needle crystals of **1** were isolated (yield ca. 30%). Elemental analysis calcd (%) for **1** (C₄H₅CuN₂): C 33.22, H 3.48, N 19.37; found: C 33.18, H 3.54, N 19.32. The pale-yellow plate crystals of **2** (yield ca. 15%) and **3** (yield ca. 35%) were produced by a similar process that uses toluene (2 mL) and *p*-xylene (2 mL) in place of methanol, respectively. Elemental analysis calcd (%) for **2** (C₃₉H₄₈Cu₈N₁₆): C 37.50, H 3.87, N 17.94; found: C 37.45, H 3.95, N 17.91; for **3** (C₅₆H₇₀Cu₁₀N₂₀): C 40.55, H 4.25, N 16.89; found: C 40.42, H 4.41, N 16.78. All of **1–3** are basically insoluble in common organic solvent; **1** and **2** are relatively stable compared to **3** that is oxidized in a few minutes upon exposure in air. Preliminary measurements of solids **1–3** showed photoluminescence at room temperature with the emission peaks at 495, 512, and 515 nm, respectively.
- (8) Crystal data for **1** (C₄H₅CuN₂) at 293 K: Monoclinic, *C2/c*, *a* = 17.0610(15) Å, *b* = 11.2990(10) Å, *c* = 8.3845(7) Å, *β* = 110.0780(10)°, *V* = 1518.1(2) Å³; *Z* = 12, *ρ* = 1.899 g cm⁻³, *μ* = 4.164 mm⁻¹, *F*(000) = 864, 2*θ*_{max} = 54.0°. Final residuals (for 98 parameters) were *R*₁ = 0.0314 for 1638 reflections with *I* ≥ 2*σ*(*I*), *R*₁ = 0.0349, *wR*₂ = 0.0829, and *S* = 1.061 for all 4340 data.
- (9) Crystal data for **2** (C₃₉H₄₈Cu₈N₁₆) at 123 K: Orthorhombic, *Cmc2₁*, *a* = 20.7600(14) Å, *b* = 10.8497(7) Å, *c* = 21.0042(14) Å, *V* = 4731.0(5) Å³; *Z* = 4, *ρ* = 1.754 g cm⁻³, *μ* = 3.571 mm⁻¹, *F*(000) = 2504, 2*θ*_{max} = 56.0°. Final residuals (for 276 parameters) were *R*₁ = 0.0431 for 5321 reflections with *I* ≥ 2*σ*(*I*), *R*₁ = 0.0531, *wR*₂ = 0.0978, and *S* = 1.035 for all 15355 data.
- (10) Crystal data for **3** (C₅₆H₇₀Cu₁₀N₂₀) at 293 K: Monoclinic, *C2/m*, *a* = 14.4446(11) Å, *b* = 27.559(2) Å, *c* = 11.9914(9) Å, *β* = 126.7750(10)°, *V* = 3823.6(5) Å³; *Z* = 2, *ρ* = 1.441 g cm⁻³, *μ* = 2.766 mm⁻¹, *F*(000) = 1672, 2*θ*_{max} = 52.0°. Final residuals (for 219 parameters) were *R*₁ = 0.0592 for 3838 reflections with *I* ≥ 2*σ*(*I*), and *R*₁ = 0.1020, *wR*₂ = 0.1869, *S* = 0.994 for all 11807 data.

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