

Two Solvent-Dependent Zinc(II) Supramolecular Isomers: Rare *kgd* and Lonsdaleite Network Topologies Based on a Tripodal Flexible Ligand

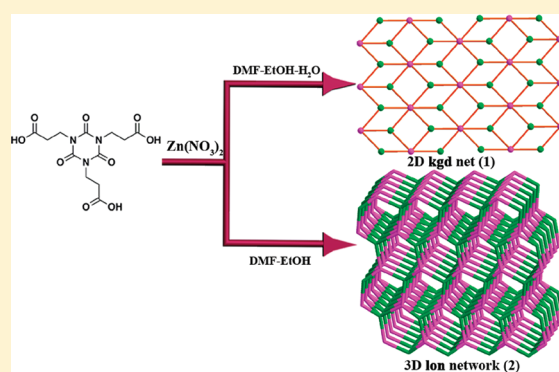
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S Supporting Information

ABSTRACT: Two Zn(II) supramolecular isomeric metal–organic frameworks (MOFs) based on well-designed tripodal tris(2-carboxyethyl)isocyanuric acid (H_3tci), formulated as $[(Me_2NH_2)Zn(tci) \cdot 0.5DMF]_n$ (**1**) and $[(Me_2NH_2)Zn(tci) \cdot 2DMF]_n$ (**2**) (Me_2NH_2 = protonated dimethylamine, DMF = *N,N*-dimethylformamide) have been solvothermally synthesized and characterized. Compounds **1** and **2** are supramolecular isomers controlled by solvent systems and exhibit a structural progression from a rare two-dimensional *kgd* sheet to a three-dimensional framework with unusual Lonsdaleite (*lon*) topology. The structural dissimilarity between them was dependent on the coordination environments of the Zn(II) ion and linking modes of the *tci* ligand influenced by solvent systems. The photoluminescence behaviors of **1** and **2** are also discussed.



Because of their intriguing structural diversity¹ and potential applications in gas storage and separation,² catalysis,³ and luminescent materials,⁴ metal–organic frameworks (MOFs) have witnessed explosive growth in the field of solid state functional materials.⁵ However, how to rationally realize the preferred structures with specific properties still remains a fundamental scientific challenge due to a number of factors that can influence the construction of MOFs, including the reactant stoichiometry, temperature, pH, solvent, reaction time and template agents.⁶ A variant of one of the foregoing factors may lead to a drastic change in the dimensionality and topology. Supramolecular isomerism, the phenomenon whereby more than one network structure is obtained from the same building blocks in an identical ratio, has become a significant branch in the field of supramolecular chemistry and crystal engineering.⁷ Rational realization of a supramolecular isomerism system, even the simplest one, is still tremendously difficult and generally depends on the subtle variation of assembly environments. Among them, the effect of solvent has been demonstrated in a number of examples by control of kinetical and/or thermodynamical conformers as well as the coordination modes.⁸ Nevertheless, control of the supramolecular isomers accompanying the change of novel topologies by solvent variable is still scarce.⁹ One elegant case being observed is that two supramolecular isomers based on the identical paddlewheel secondary building units (SBUs) show Kagomé

net and NbO topology, respectively, induced by different solvents.^{9a}

On the other hand, compared to the well-known rigid tripodal spacers such as 1,3,5-benzenetricarboxylic acid and 1,3,5-tris(4-carboxyphenyl) benzene,¹⁰ the tripodal symmetrical tris(2-carboxyethyl)isocyanuric acid (H_3tci) ligand is particularly interesting for several reasons: (i) three highly flexible arms ($-CH_2-CH_2-$); (ii) three rotation-free carboxyl groups; and (iii) the existence of two potential conformations, *cis-cis-cis* and *cis-cis-trans* with a small transformation energy barrier. Although a few instances of *tci*-based MOFs have been documented,¹¹ it has been underdeveloped to date. Recently, the Kitagawa group used this versatile ligand to construct two isomorphous MOFs which exhibit reversible single-crystal to single-crystal phase transformations to form two different stable forms with a change in dimensionality from a two-dimensional (2D) sheet to a three-dimensional (3D) framework triggered by a specific guest.¹²

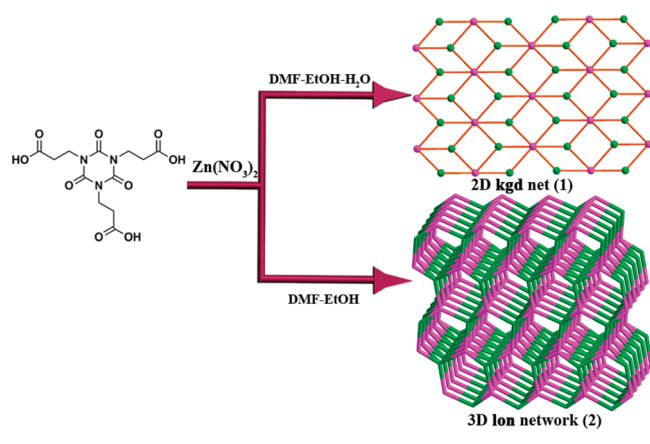
Bearing in mind all of the points mentioned above and based on our recent work on transition metal carboxylates compounds,¹³ we selected flexible C_3 -symmetric H_3tci to construct two supramolecular isomers $[(Me_2NH_2)Zn(tci) \cdot 0.5DMF]_n$ (**1**)

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Scheme 1. Synthetic Procedures of the Title Compounds 1 and 2



and $[(\text{Me}_2\text{NH}_2)\text{Zn}(\text{tci}) \cdot 2\text{DMF}]_n$ (**2**) (Me_2NH_2 = protonated dimethylamine, DMF = *N,N*-dimethylformamide) controlled by the solvent systems (Scheme 1). Both of them are anionic frameworks neutralized by a dimethyl ammonium cation generated from the hydrolysis of DMF and show a rare 2D **kgd** sheet and 3D framework with unusual Lonsdaleite (**lon**) topology, respectively.

Colorless crystals of **1** and **2** were synthesized by solvothermal reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 4,4'-biphenyldicarboxylic acid and H_3tci in a similar process (sealed tube, 90 °C) but with DMF–EtOH– H_2O (1 mL, v/v/v, 5:2:1) and DMF–EtOH (1 mL v/v 5:2) solvent systems, respectively. Phase purity of **1** and **2** is sustained by the powder X-ray diffraction patterns (Figure S1, see Supporting Information). For **1** and **2**, most peak positions of simulated and experimental patterns are in good agreement with each other. The dissimilarities in intensity may be due to the preferred orientation of the crystalline powder samples. The solid FT-IR spectra (Figure S2, Supporting Information) of **1** and **2** show characteristic absorption bands for carboxyl groups.¹⁴

The crystal structure of **1** was determined by single-crystal X-ray diffraction analysis (see Supporting Information). Complex **1** crystallizes in monoclinic space group $C2/c$ with an asymmetric unit that contains one Zn(II) ion, one tci ligand, half DMF molecule, and one dimethyl ammonium cation. All three carboxyl groups are deprotonated and make the framework neutral; one DMF molecule has been cleaved to a dimethyl ammonium cation. As shown in Figure 1a, the Zn1 is coordinated by five oxygen atoms from five carboxyl groups of five individual tci ligands, displaying a distorted square-pyramidal geometry. The distortion of the ZnO_5 square-pyramid is indicated by the calculated value of the τ_5 factor,¹⁵ which is 0.04 for Zn1 (for ideal square-pyramidal geometry, $\tau_5 = 0$). The Zn–O bond lengths range from 1.9574(16) to 2.0678(18) Å, which are comparable to the related MOFs.¹⁶ The Zn1 and its symmetry-related equivalent (Zn1^{iii}) have a separation of 2.9604(5) Å. Four carboxyl groups with *syn-syn* coordination modes bridge a pair of adjacent Zn(II) centers to form a paddlewheel SBU. The tci ligand adopts a pentadentate $\mu_5\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1$ coordination mode, of which two carboxyl groups adopt the same *syn-syn* coordination fashion, while the third carboxyl group bridges one Zn(II) ion in a monodentate *anti* fashion at the axial position.

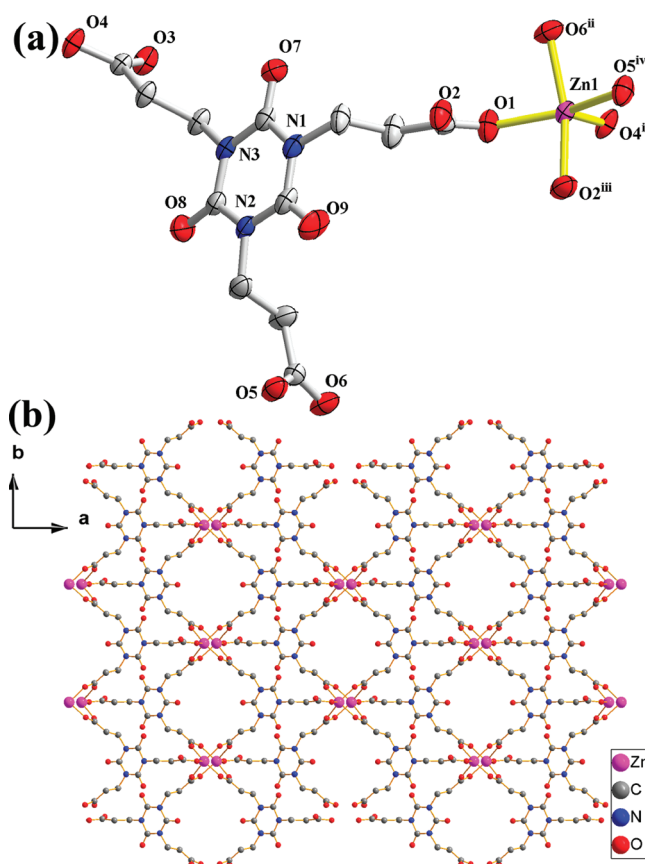


Figure 1. (a) ORTEP representation of **1** showing the local coordination environment around the Zn(II) center with 50% thermal ellipsoid probability. Hydrogen atoms have been omitted for clarity (ellipsoid codes: (i) $x + 1/2, y + 1/2, z$; (ii) $x, y + 1, z$; (iii) $-x + 1, y, -z + 1/2$; (iv) $-x + 1, y + 1, -z + 1/2$). (b) Ball-and-stick representation of the 2D sheet.

Considering the relative position of 2-carboxyethyl with respect to the C_3N_3 six-membered plane, the tci ligand in **1** shows a *cis-cis-trans* conformation, which links the paddlewheel SBUs to form a 2D sheet along the *ab* plane (Figure 1b). The solvent-accessible volume is 1574.0 Å³ per unit cell, and the pore volume ratio is calculated to be 37.1% by the PLATON program¹⁷ (symmetry code: (iii) $-x + 1, y, -z + 1/2$).

An appealing structural feature in **1** is that the 2D sheet can be seen as a rare non-interpenetrating **kgd** network by simplifying the tci ligand as a 3-connecting node and the binuclear Zn(II) paddlewheel SBU as a 6-connecting node (Figure 2a,b). Therefore, the whole 2D sheet can thus be represented as a (3,6)-connected 2-nodal net with a **kgd** topology (Figure 2c). There are twice as many 3-connecting nodes (vertex symbol of 4^3) than 6-connecting nodes (vertex symbol of $4^6.6^6.8^3$). Therefore, the short Schläfli vertex notation of the net can be represented as $\{4^3\}_2\{4^6.6^6.8^3\}$ indicated by TOPOS software.¹⁸ As we know, the three most common topologies of 2D coordination networks are regular (4,4), (6,3), and (3,6) nets,¹⁹ while the **kgd** net can be seen as offset overlap of two common (6,3) nets which were connected together by Zn(II) ions. Therefore, the tci ligands in this **kgd** net are non-coplanar and are arranged alternately up and down to form the concavo-convex **kgd** net. Although the **kgd** net can be theoretically assembled by employing a six-coordinate metal center and a trigonal tridentate ligand, it is difficult to

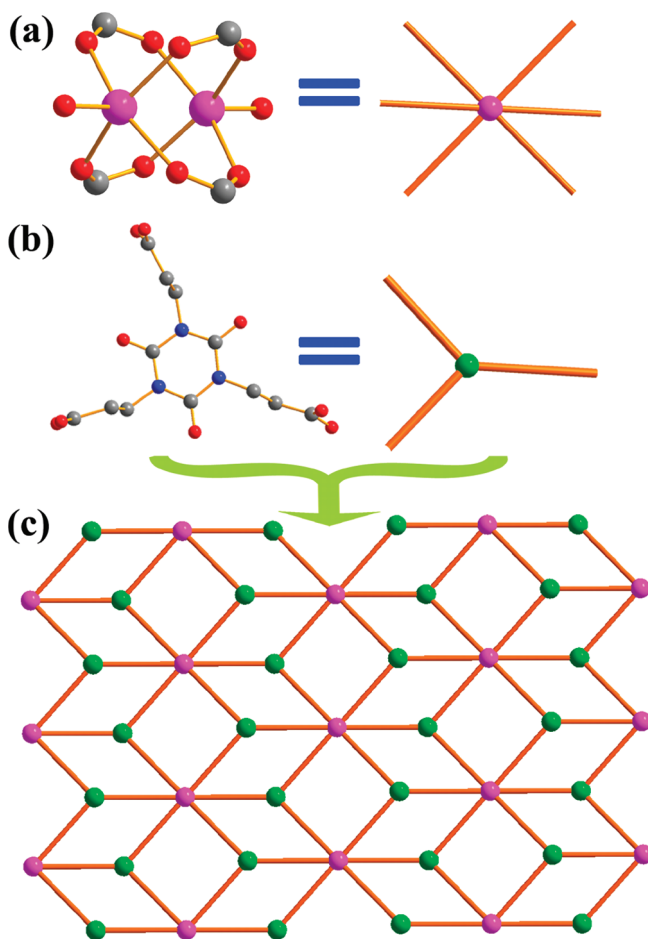


Figure 2. Ball-and-stick and schematic representations of simplified 2D sheet with **kgd** topology (c) containing 8-connected (a) and 4-connected nodes (b).

achieve in coordination networks due to the requirement of nearly planar 6-connecting node, which illustrates why there are few cases in spite of various known coordination polymers based on trigonal ligands.²⁰ Recently, one cationic **kgd** net based on a rigid trigonal N-donor ligand 2,4,6-tris[4-(1H-imidazole-1-yl)-phenyl]-1,3,5-triazine and six-coordinate Cd(II) was constructed and exhibited high thermostability as well as potential porosity.²¹

Supramolecular isomeric 3D framework of **2** was obtained under similar reaction conditions but with DMF–EtOH as solvent systems. Single-crystal X-ray analysis revealed that it crystallized in the orthorhombic crystal system with a chiral space group of *Pca*2(1) (Flack parameter: 0.006(18)) and the asymmetric unit of **2** consists of one Zn(II) ion, one tci ligand, two DMF molecules, and one dimethyl ammonium cation from the hydrolysis of DMF. **2** is also an anionic framework which is neutralized by the lattice dimethyl ammonium cations. As shown in Figure 3a, the Zn1 is coordinated by four oxygen atoms from four carboxyl groups of four individual tci ligands, displaying a slightly distorted tetrahedral geometry. The distortion of the tetrahedron can be indicated by the calculated value of the τ_4 parameter introduced by Houser²² to describe the geometry of a four-coordinated metal system, which is 0.93 for Zn1 (for perfect tetrahedral geometry, $\tau_4 = 1$). The Zn–O bond lengths fall in the range of 1.948(3)–1.989(2) Å. The bond angles around the Zn center are in the range of 99.66(13)–116.74(11)°. The tci ligand

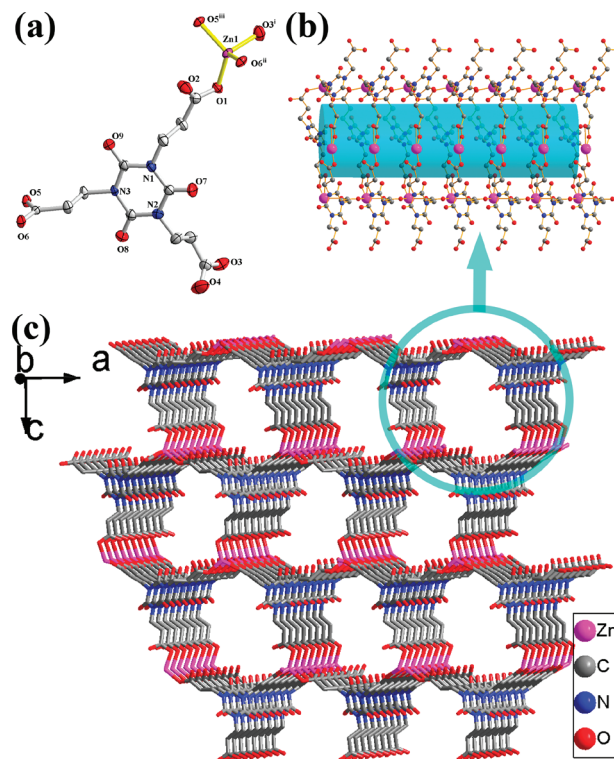


Figure 3. (a) ORTEP representation of **2** showing the local coordination environment around the Zn(II) center with 50% thermal ellipsoid probability. Hydrogen atoms have been omitted for clarity (symmetry codes: (i) $-x + 3/2, y, z + 1/2$; (ii) $-x + 1, -y + 1, z + 1/2$; (iii) $-x + 1, -y + 2, z + 1/2$). (b) Ball-and-stick representation of the 1D nanotube. (c) The 3D framework with the 1D channels.

similar to that in **1** adopts a *cis–cis–trans* conformation and shows a $\mu_4\text{-}\eta^1:\eta^1:\eta^0:\eta^1:\eta^0:\eta^1$ coordination mode. Two carboxyl groups adopt the same *syn* monodentate bridging fashion, but the third one bridges one Zn(II) ion in a bidentate *syn-anti* fashion. The tci ligand using its one $\mu_2\text{-syn-anti}$ and one $\mu_1\text{-syn}$ carboxyl group links the tetrahedral Zn(II) centers to form a one-dimensional (1D) nanotube (Figure 3b) along the *b* axis with a diameter of approximately 3.5 Å occupied by DMF molecules and dimethyl ammonium cations. The 1D nanotubes are extended along the *ac* plane by tci to form the resulting 3D porous framework (Figure 3c). PLATON calculation suggests that the resulting effective free volume, after removal of guest DMF molecules and dimethyl ammonium cations, is 47.0% of the crystal volume (1229.1 Å³ out of the 2612.7 Å³ unit cell volume).

A better insight into the structure of **2** can be achieved by the standard procedure of reducing multidimensional structures to simple node-and-linker reference nets known as the topological approach.²³ The framework of **2** has a Lonsdaleite (**lon**) topology, which has both chair and boat conformations in fused six-membered rings, if we consider both Zn(II) ion and $\mu_4\text{-tci}$ ligand as tetrahedral four-connecting nodes (Figure 4). A variety of interpenetrated and non-interpenetrated MOFs with **dia** topology have been successfully obtained by connecting the tetrahedral nodes.²⁴ Although both topologies are expected to be energetically very similar,²⁵ **dia** topology is overwhelmingly dominant for tetrahedral nodes based on the experimental results.²⁶ The well-known **lon** structures are mainly found in some inorganic compounds including ice (*I_h* form), tridymite,

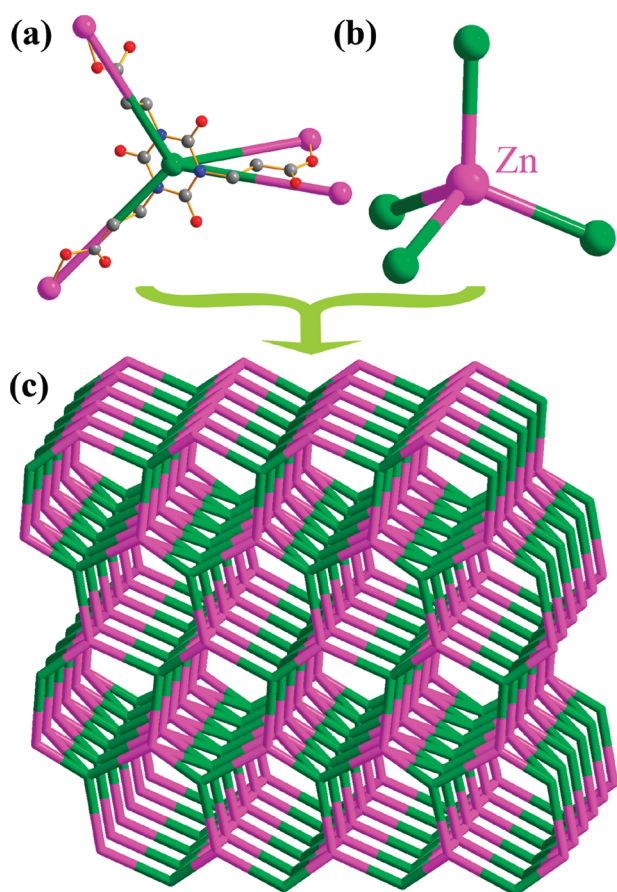


Figure 4. Ball-and-stick and schematic representations of simplified 3D sheet with **lon** topology (c) containing 4-connected tci (a) and 4-connected Zn(II) nodes (b).

and wurtzite.²⁷ The organic compound with **lon** topology was found in a hydrogen-bonded structure of 4-aminophenol and 4'-aminobiphenyl-4-ol reported by Ermer and co-workers.²⁸ Nevertheless, MOFs having **lon** topology are very rare,²⁹ which may be due to the fact that the **dia** network represents the simplest, highest symmetry structure (it is the only regular tetrahedral structure), while it is necessary to construct the **lon** structure by deconstructing the **dia** structure into more elaborate building blocks of chair and boat rings rather than of single tetrahedra. These points also have been widely discussed in detail in three reviews.³⁰

Two different MOFs **1** and **2** were synthesized on the basis of the selection of reaction solvent systems, while the other synthetic parameters were intentionally held constant. The dimensionality and topology of the networks produced in this work are determined by the coordination environments of Zn(II) and linking modes of tci ligand, which are clearly dictated by the solvent molecules. The reaction in DMF–EtOH–H₂O (1 mL, v/v/v, 5:2:1) solvent results in the formation of **1**, while **2** forms in DMF–EtOH (1 mL v/v 5:2) solvent. The experiments reveal that the water molecules are critical to form supramolecular isomers **1** and **2**. In order to explore the role of water on the assembled system of Zn(II)/tic/4,4'-biphenyldicarboxylic acid, we carried out a series of related experiments by changing the volumetric ratio of DMF–EtOH–H₂O (1 mL) from 5:2:0 to 5:2:10. However, formations of the complexes **1** and **2** show

Scheme 2. Coordination Modes of tci in **1** (left) and **2** (right)

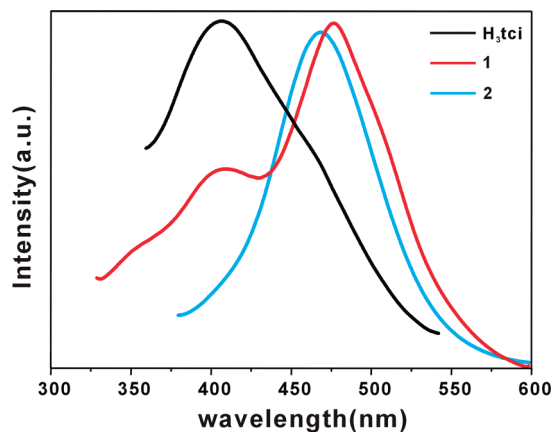
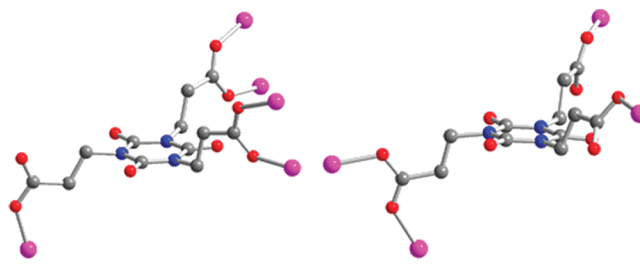


Figure 5. The photoluminescence of **1**, **2**, and free ligand in the solid state.

specificities to the volumetric ratios of 5:2:1 and 5:2:0, respectively, at least for the current experimental results. No crystalline solid will be formed if the other volumetric ratios of DMF–EtOH–H₂O were used in this system. Although no different solvent molecules participated in the **1** and **2**, a different solvent system regulates the formation of different environments for the self-assembly process and influences the coordination environment of Zn(II) and linking modes of tci ligand (Scheme 2). In **1** and **2**, Zn(II) ions adopt a six-coordinated octahedral and four-coordinated tetrahedral geometries, respectively, giving binuclear Zn(II) paddlewheel SUB and mononuclear Zn(II) tetrahedral SUB, which produce six- and four-connected nodes for them. For trigonal tci ligand, despite its conformation (*cis–cis–trans*) is identical, it shows $\mu_5\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^0\text{:}\eta^1$ and $\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^0\text{:}\eta^1\text{:}\eta^0\text{:}\eta^1$ coordination modes, which act as three- and four-connected nodes for **1** and **2**, respectively. As a consequence, 2D (3,6)-connected 2-nodal net with a **kgd** topology for **1** and 3D 4-connected uninodal net with a **lon** topology for **2** were produced.

In fact, the supramolecular isomerism induced by the solvents is fortuitously observed since the water molecule does not participate in the final crystalline products. Although more theoretical and experimental efforts are required to demonstrate the role of water in controlling the different supramolecular isomers, some general rules may be assumed at this stage. Generally, the volumetric ratio of water in a mixed solvent system may influence the solvation process and coordination kinetics in solution.

The solid-state luminescent emission spectra of **1**, **2**, and H₃tci were studied at room temperature. As shown in Figure 5,

the emission of H₃tci shows a peak at 412 nm upon 300 nm excitation, which is ascribed to the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ electronic transitions. Compared with the luminescence of ligand, the emissions of **1** ($\lambda_{em} = 405$ and 474 nm, $\lambda_{ex} = 300$ nm) and **2** ($\lambda_{em} = 470$ nm, $\lambda_{ex} = 300$ nm) are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) in nature since the Zn(II) ion is difficult to oxidize or reduce due to its d¹⁰ configuration.³¹ Thus, they may be assigned to intraligand ($\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$) emission. Further, it can be observed that the emission spectra for **1** and **2** exhibit red-shifts with respect to the free H₃tci ligand, which may be ascribed to the deprotonation of the H₃tci ligand and the coordination effects of the tci ligand to the Zn(II) ions.³² And that, the difference of the emission peaks intensity for **1** and **2**, mainly derives from the differences of the coordination mode of the tci ligand, the coordination environments of the metal ions, and the rigidity of solid-state crystal packing.

In summary, we synthesized and characterized two supramolecular isomers based on Zn(II) and a tripodal flexible ligand for the first time. The choice of solvent systems exerts a profound influence on the coordination environments of Zn(II) and linking modes of the tci ligand in each framework, resulting in supramolecular isomers with rare topologies of **kgd** and **lon** nets. Moreover, the photoluminescence behaviors of **1** and **2** were also discussed.

■ ASSOCIATED CONTENT

S **Supporting Information.** The preparation of complexes **1** and **2**, Tables S1–S3, IR and powder XRD patterns. X-ray crystallographic files in cif format for the complexes **1** and **2**. CCDC 837937 (**1**) and 837938 (**2**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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