Supplementary information for

Interweaving Isomerism and Isomerization of Molecular Chains

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Supplementary Index:

General methods:

Typical synthetic procedures:

Table S1. Synthetic details for the silver isopropylimidazolate.

Crystallographic details:

Table S2. Complete list of dihedral angles between adjacent im rings in 1-3.

Additional structural plots:

Figure S1. Hydrophobic interactions between sinusoidal chains in 1.

- Figure S2. Interdigitation of undulated layers in 1.
- Figure S3. Hydrophobic interactions between helical chains in 2.
- Figure S4. Packing of quintuple helices in 2.
- Figure S5. Hydrophobic interactions between helical chains in **3**.
- Figure S6. Interdigitation of chicken-wires in **3**.

Different physical properties:

Figure S7. Photograph of a bended single crystal of 2.

Figure S8. Room-temperature photoluminescence spectra of 1-3.

Thermodynamic behaviours:

Figure S9. TG curves of 1-3.

Figure S10. DSC curves of 1-3 (scanning speed 5°C/min).

Figure S11. DSC curves of **3** with different scanning speeds.

Figure S12. DSC curves of **3** (scanning speed -5° C/min).

General methods

Commercially available reagents were used as received without further purification. Thermal gravimetric (TG) analyses were performed under N_2 using a NETZSCH TG 209 system. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance diffractometer. Photoluminescence spectra were collected on an Edinburgh FLS920 spectrometer equipped with a continuous Xe900 Xenon lamp. Differential scanning calorimetry (DSC) was performed under N_2 using a Netzsch DSC 204 system.

Typical synthetic procedures

For 1: Mesitylene (1 mL) and a methanol solution of Hipim (0.1 mol/L, 2 mL) was carefully, one by one, layered on an aqueous ammonia (25%) solution of AgNO₃ (Ag⁺ 0.1 mol/L, 2 mL). After 3 weeks, single crystals were corrected, washed with methanol, and air dried (yield 30%, impurity 2 was manually separated). 2: Similar to 1 except that mesitylene was replaced by a 1:1 mixture of methanol and aqueous ammonia (2 weeks, yield 90%). 3: A methanol solution of Hipim (0.1 mol/L, 10 mL) was added dropwise into an aqeous ammonia solution of Ag₂O (Ag⁺ 0.1 mol/L, 10 mL) under stirring. White precipitate formed immediately (yield 90%).

Table S1. Synthetic details of for the silver isopropylimidazolate (Single crystals or microcrystalline powders were prepared by liquid diffusion, rapid mixing, or slow evaporation. Liquid diffusion was carried out in long glass tubes with 8 mm inner diameter. AgNO₃ or Ag₂O was dissolved in H₂O or aqueous ammonia as the silver(I) source). Slow evaporation or liquid diffusion yield pure single crystals of **2** in most cases. Single crystals of **1** can be only obtained by liquid diffusion using mesitylene as a buffering layer, but **2** always coexists. Rapid mixing generally produces pure microcrystalline **3**. These observations indicate that **2** and **3** are thermodynamic and kinetic favored isomers, respectively, and **1** is an additive induced isomer. A few single crystals of **3** were accidentally found from a diffusion tube. In single-crystal structures and TG analysis, no solvent molecule can be found in these dense crystal structures, confirming that they are genuine supramolecular isomers.

		Silver(I) salt solution						
		Ag ₂ O in NH ₃ ·H ₂ O		AgNO ₃ in NH ₃ ·H ₂ O	AgNO ₃ in H ₂ O			
		Liquid diffusion	Rapid mixing	Liquid diffusion	Slow evaporation	add NH ₃ ·H ₂ O to precipitate		
Hipim in	H ₂ O	N/A	Powder of 3	N/A	Crystals of 2	Powder of 3		
	MeOH	Crystals of 2		Crystals of 2				
	EtOH							
	Acetone			N/A				
	MeCN							
	THF		Powder of 2			Powder of 2		
	MeOH/Benzene	Small crystals of 2		Crystals of 2				
	MeOH/Toluene							
	MeOH/Mesitylene	Crystals of 1 and 2	Powder of 3	Crystals of 1 and 2				

X-ray crystallography

Diffraction intensities were collected on a Bruker Apex CCD area-detector diffractometer (Mo K α). The structures were solved with direct method and refined with a full-matrix least-squares technique with the SHELXTL program package. Anisotropic thermal parameters were applied to all non-hydrogen atoms except the disordered guest molecules. Organic hydrogen atoms were generated geometrically and refined by the riding mode. Crystal data of **1**: 123(2) K, monoclinic $P2_1/n$, a = 12.2894(8) Å, b = 16.3750(10) Å, c = 15.2554(10) Å, $\beta = 99.611(1)^\circ$, V = 3026.9(3) Å³, Z = 4, $D_c = 1.905$ g cm⁻³, final $R_1 = 0.0304$ ($I \ge 2\sigma$), $wR_2 = 0.0714$ (all data), S = 1.038; **2**: 293(2) K, triclinic P-1, a = 12.1005(8) Å, b = 18.0915(12) Å, c = 24.1686(16) Å, $\alpha = 108.532(1)$, $\beta = 96.530(1)^\circ$, $\gamma = 104.688(1)^\circ$, V = 4742.4(5) Å³, Z = 2, $D_c = 1.824$ g cm⁻³, final $R_1 = 0.0547$ ($I \ge 2\sigma$), $wR_2 = 0.1228$ (all data), S = 1.067; **3**: 293(2) K, orthorhombic $Pna2_1$, a = 20.760(3) Å, b = 36.095(6) Å, c = 13.531(2) Å, V = 4742.4(5) Å³, Z = 4, $D_c = 1.990$ g cm⁻³, final $R_1 = 0.0759$ ($I \ge 2\sigma$), $wR_2 = 0.1962$ (all data), S = 1.074 (The single-crystal quality of **3** is poor, so the *R* factors are relatively high and the residual electron density is high (near Ag atoms)). CCDC 794204-794206 contains the crystallographic data for this paper.

As expected, Ag⁺ ions and ipim⁻ ligands adopt linear and exobidentate coordination geometries, respectively (Ag-N 2.065(3)-2.077(3) Å, N-Ag-N 174.8(1)-178.2(1)° for **1**, Ag-N 2.065(5)-2.100(6) Å, N-Ag-N 172.3(2)-178.6(2)° for **2**, Ag-N 2.042(16)-2.143(17) Å, N-Ag-N 170.0(7)-178.6(6)° for **3**).

Table S2. Complete list of dihedral angles (DAs) between adjacent im rings (linked to the same Ag atom) in **1-3**.

-	1	2		3	
Ag atom	DA	joint	Ag atom	Ag atom	DA
Ag1	165.8(1)	Ag1	136.5(4)	Ag1	158.6(9)
Ag2	5.6(1)	Ag2	3.8(3)	Ag2	23.4(8)
Ag3	39.5(1)	Ag3	52.7(3)	Ag3	21.7(9)
Ag4	7.6(1)	Ag4	28.4(3)	Ag4	172.0(8)
		Ag5	139.2(3)	Ag5	18.1(8)
		Ag6	7.0(3)	Ag6	2.4(9)
		Ag7	38.1(4)	Ag7	15.7(7)
		Ag8	17.2(3)	Ag8	176.1(7)
		Ag9	134.3(3)	Ag9	18.7(7)
		Ag10	22.5(3)	Ag10	21.8(7)
		Ag11	54.6(3)	Ag11	155.9(8)
		Ag12	10.7(3)	Ag12	13.8(8)
				Ag13	3.3(9)
				Ag14	18.8(9)

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Figure S1. Hydrophobic interactions between sinusoidal chains in **1** (isopropyl groups are highlighted by gray).



Figure S2. Interdigitation of undulated layers in **1**.



Figure S3. Hydrophobic interactions between helical chains in **2** viewed along (left) and perpendicular (right) to the screw axis (isopropyl groups are highlighted by gray).



Figure S4. Packing of quintuple helices in 2 (red and green represent left- and right-handed helices).

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Figure S5. Hydrophobic interactions between helical chains in **3** viewed along the b (up) and -b (down) directions (isopropyl groups are highlighted by gray).



Figure S6. Interdigitation of chicken-wires in **3**. (red and yellow for left-handed helices, blue and green for right-handed helices)

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The three supramolecular isomers show different physical properties:

Similar to its macroscopic analogues, isomer 2 exhibits enhanced mechanical strength toward bending.^{31, 32} Single crystals of 2 can be bent to a significant extent without losing transparency, but those of 1 and 3 easily crash. On the other hand, except 2, 1 and 3 show photoluminescence at room temperature with emission maxima at 483 and 471 nm and excitation maxima at 398 and 315 nm, respectively.



Figure S7. Photograph of a bended single crystal of 2.



Figure S8. Room-temperature photoluminescence spectra of 1-3.

Thermodynamic behaviours: The crystal-to-crysal transformation from **3** to **2** is novel compared to other related examples in three aspects: 1) entanglement rearranged; 2) no guest release or uptake; 3) not solution/liquid mediated.

- Entanglement rearranged. Although many crystal-to-crystal or single-crystal-to-single-crystal structural transformations have been reported, examples are mainly based on framework contraction, expansion, distortion, individual coordination bond cleavage/formation, or even change topology, etc. Crystal-to-crystal entanglement rearrangement, requiring extensive, cooperative bond cleave/formation, has been only reported scarcely. To the best of our knowledge, Rosseinsky *et al* have reported that the amorphous phase obtained by desolvation of a 2-fold interpenetrated srs net can be converted to a 4-fold one upon exposure to ethanol vapor [ref 12a]. We have reported that a cationic silver triazolate framework with dia-f topology can reversibly transform between 5- and 6-fold interpenetration in a single-crystal-to-single-crystal manner upon dehydration and rehydration [ref 12b].
- 2. No guest release or absorption during transformation. During framework destruction and reconstruction, guest molecules can serve as temporary ligands to avoid the formation of highly unstable metal centers with low coordination numbers. However, the energetic effects of guest adsorption/desorption is mixed with that from the framework transformation, which can be hardly deconvoluted for mechanism study. The above mentioned two examples both invovle guest release/adsorption during transformation.
- Obviously, conversion from 3 to 2 is not solution/liquid mediated. Complete destruction of the molecular chains into isolated metal ions and ligands followed by reassembly is not likely occurred in the absence of solvent, since CPs decompose before melting, which is also supported by the fact that 1 does not transform to 2 upon heating.



Figure S9. TG curves of **1-3**. TG cruves show that **1-3** decompose at essentially identical temperatures of above ca. 220°C, indicating that different superstructures do not influence the decomposition temperature, or the isomers have transformed to the same superstructure before decomposition.



Figure S10. DSC profiles of 1-3 (scanning speed 5°C/min).



Figure S10. DSC curves of 3 with different scanning speeds.



Figure S11. DSC curve of **3** after heated to 200° C (scanning speed -5° C/min), which shows that the conversion from **3** to **2** is irreversible.