Solvent-induced supramolecular isomers, structural diversity, and unprecedented *in situ* formation of both inorganic and organic ions in inorganic-organic mercury(II) complexes

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Synthesis of 1. A CH_3CN/H_2O solution (4:2, 6mL) of HgI_2, L1 in a ratio of 1:1 was sealed in a Teflon reactor, and heated at 160˚C for 3 days, and then cooled to room temperature at 3˚C/h. Subsequently, block crystals were obtained in 68% yield based on HgI_2, respectively. EA(%): calc. C 27.97, H 1.82, N 7.25; exp. C 27.67, H 1.67, N 7.10.

Synthesis of 2. A CH_3CN solution (6mL) of HgI_2, L1 in a ratio of 1:1 was sealed in a Teflon reactor, and heated at 160˚C for 3 days, and then cooled to room temperature at 3˚C/h. Subsequently, block crystals were obtained in 63% yield based on HgI_2, respectively. EA(%): calc. C 29.51, H 2.10, N 8.60; exp. C 29.15, H 2.25, N 8.33.

Synthesis of 3. A $CH_3CN/CHCl_3$ solution (4:2, 6mL) of HgI_2, L1 in a ratio of 1:1 was sealed in a Teflon reactor, and heated at 160˚C for 3 days, and then cooled to room temperature at 3˚C/h. Subsequently, block crystals were obtained in 8% yield based on HgI_2, respectively.

Synthesis of 4. A $CH_3CN/CHCl_3/H_2O$ solution (4:1:1, 6mL) of HgI_2, L1 in a ratio of 1:1 was sealed in a Teflon reactor, and heated at 160˚C for 3 days, and then cooled to room temperature at 3˚C/h. Subsequently, block crystals were obtained in 6% yield based on HgI_2, respectively.

X-ray Crystallography. Diffraction intensities of all compounds were collected on a Bruker Apex CCD area-detector diffractometer (Mo-Kα, λ=0.71073 Å). Absorption corrections were applied by using the multi-scan program SADABS. The structures were solved by direct methods and refined with a full-matrix least-squares technique within the SHELXTL program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. The organic hydrogen atoms were generated geometrically (C-H 0.96 Å), except for that on acylamide groups which are found and refined freely.

Measurements Details. The C, H, and N microanalyses were carried out with a Vario EL-II analyzer. Thermal analyses were carried out in air atmosphere using SETARAM LABSYS equipment with a heating rate of 5°C/min. Steady-state photoluminescence spectra were measured on a SHIMADZU RF-5301PC spectrofluorophotometer.

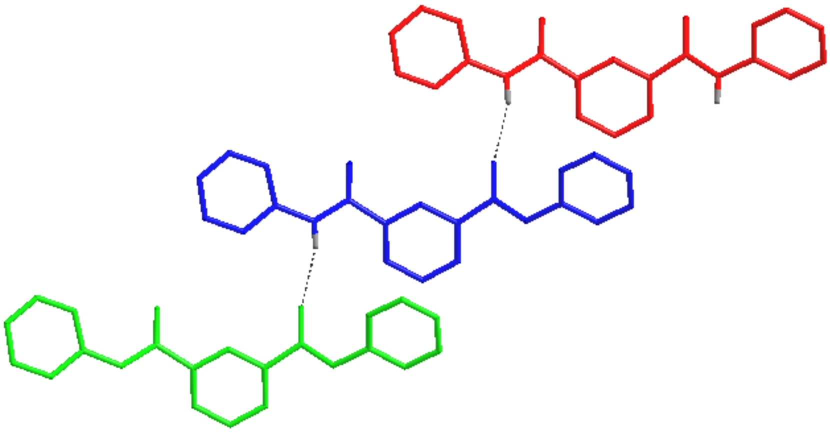

Figure S1. The hydrogen mode in the 2D undulate supramolecular net of **2**.

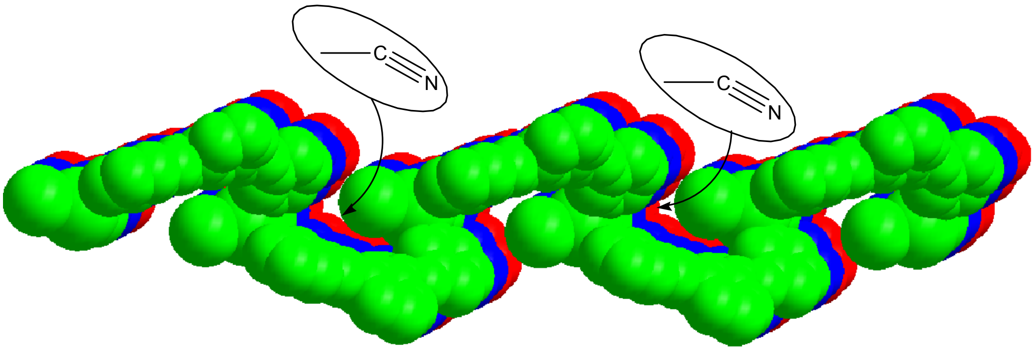

Figure S2. View of the pore structure of **2** where CH_3CN molecules are trapped.

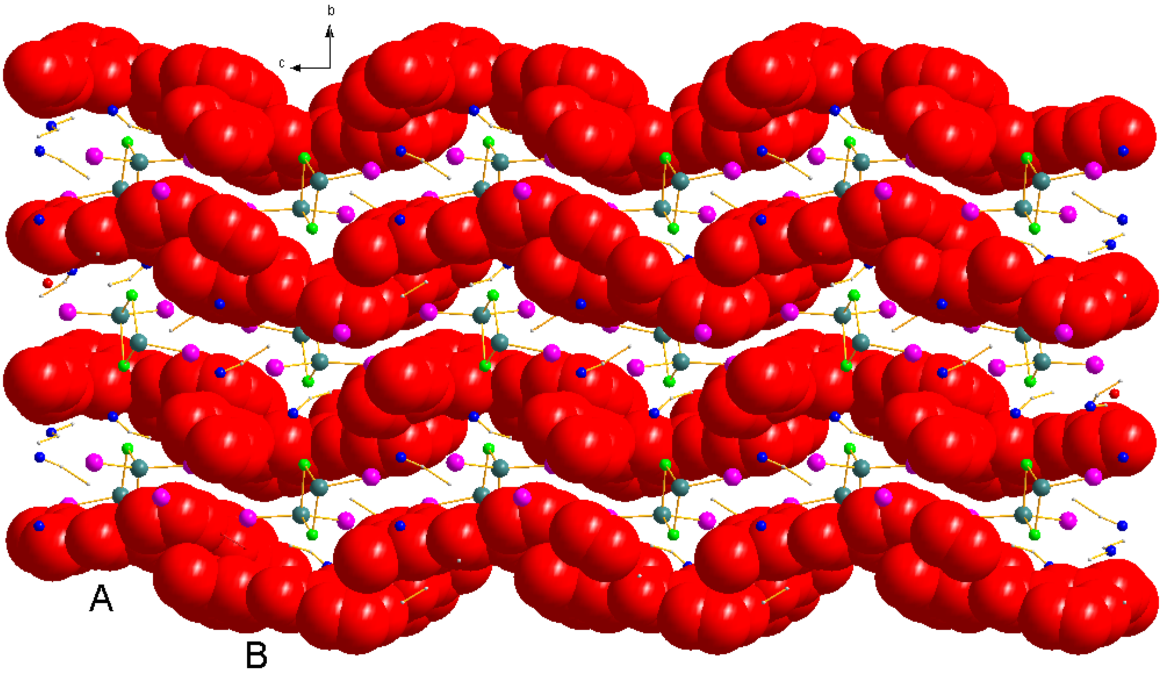

Figure S3. View of the 3D stacking mode of **3**.

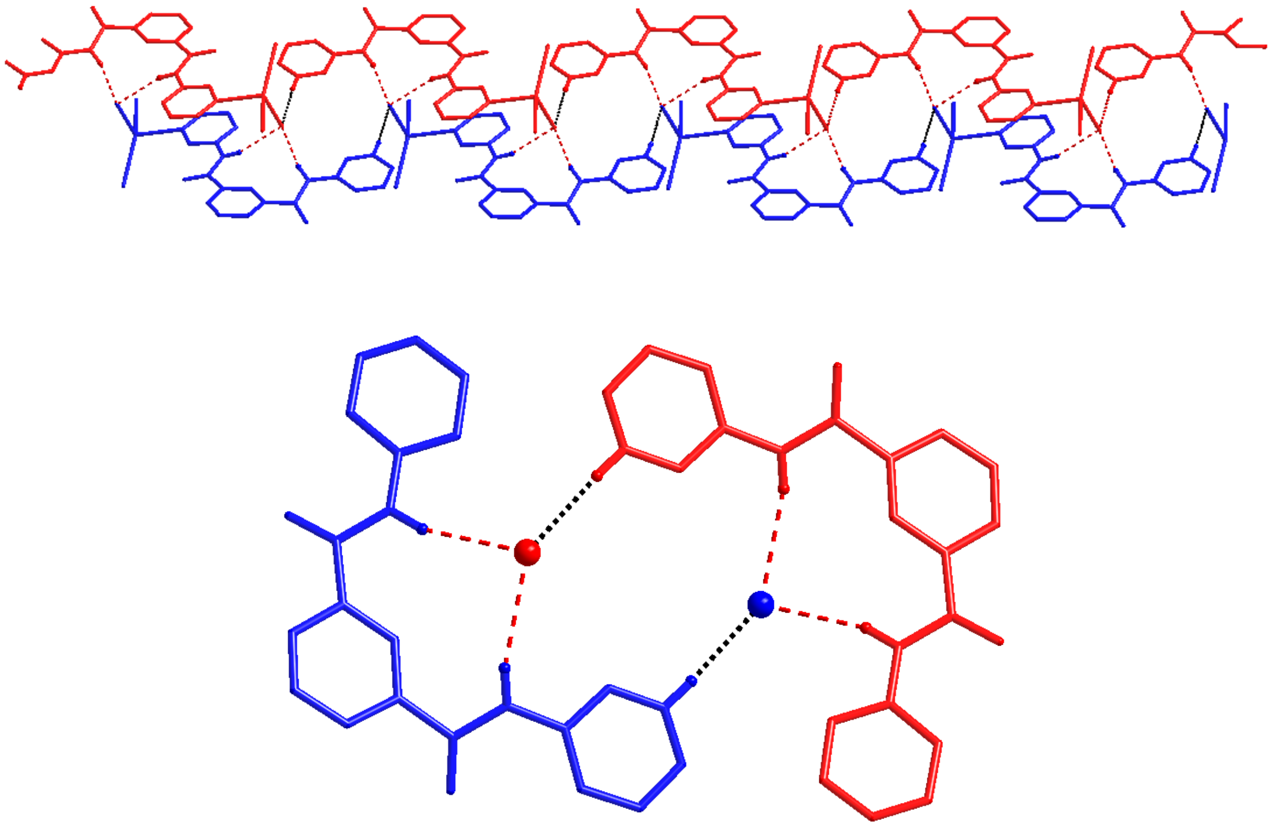

Figure S4. View of the hydrogen bonded structure between two helical chains and the three-fold hydrogen bonds for Cl^- ion. Note that the red or blue ball represents Cl^- ion.

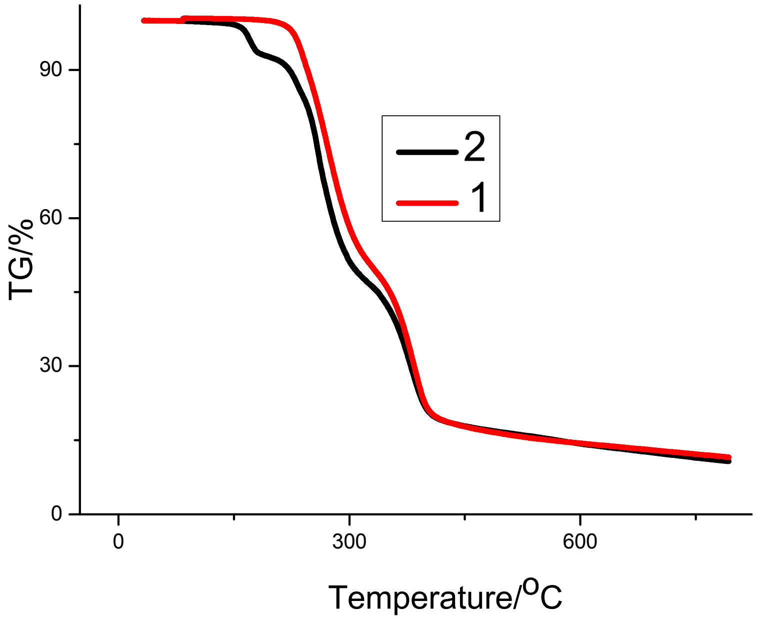

Figure S5. The TG plots of **1** and **2**.

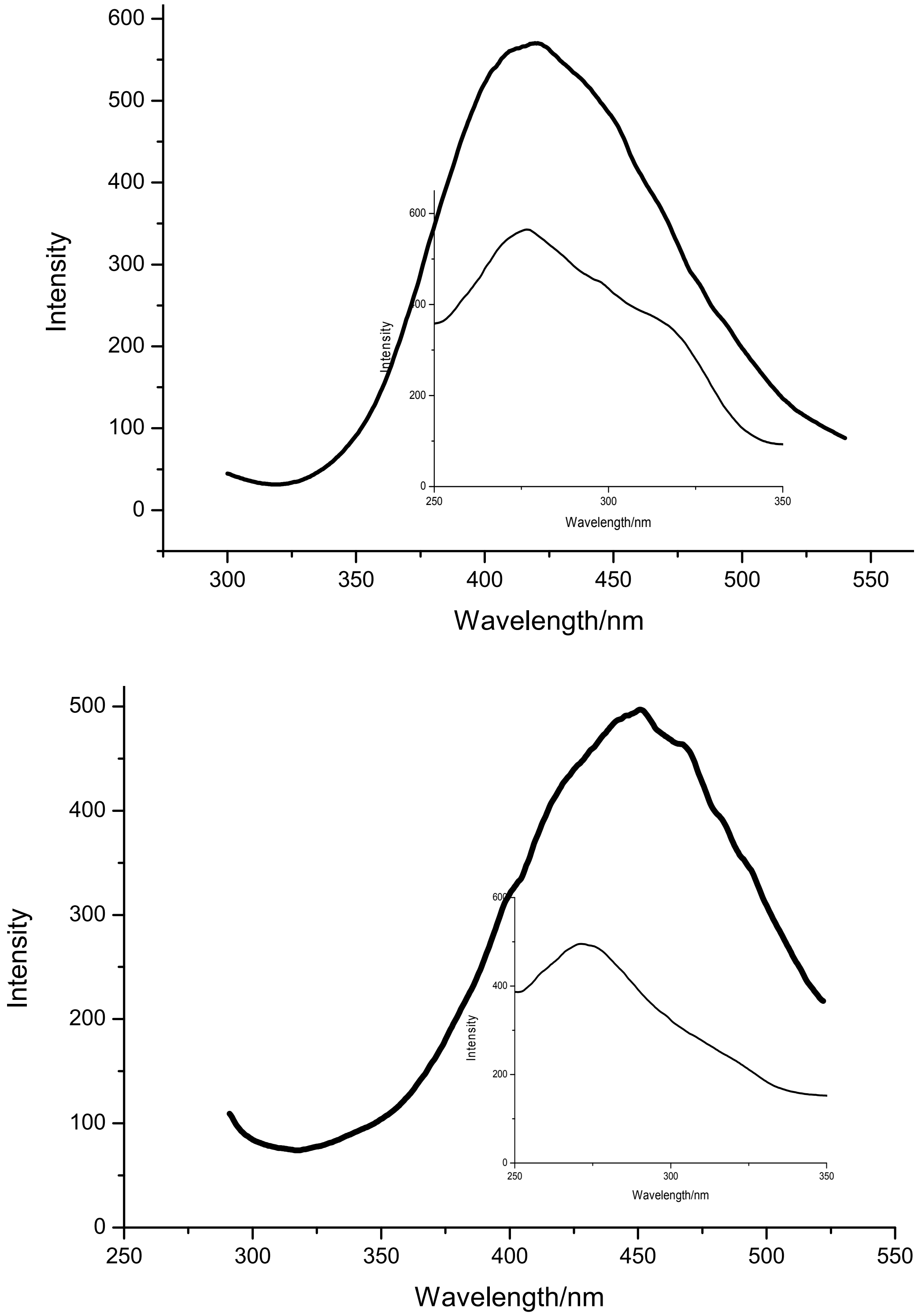

Figure S6. The luminescence spectrum of **1 (**above) and **2 (**below). The inset graph is the excitation spectrum.