

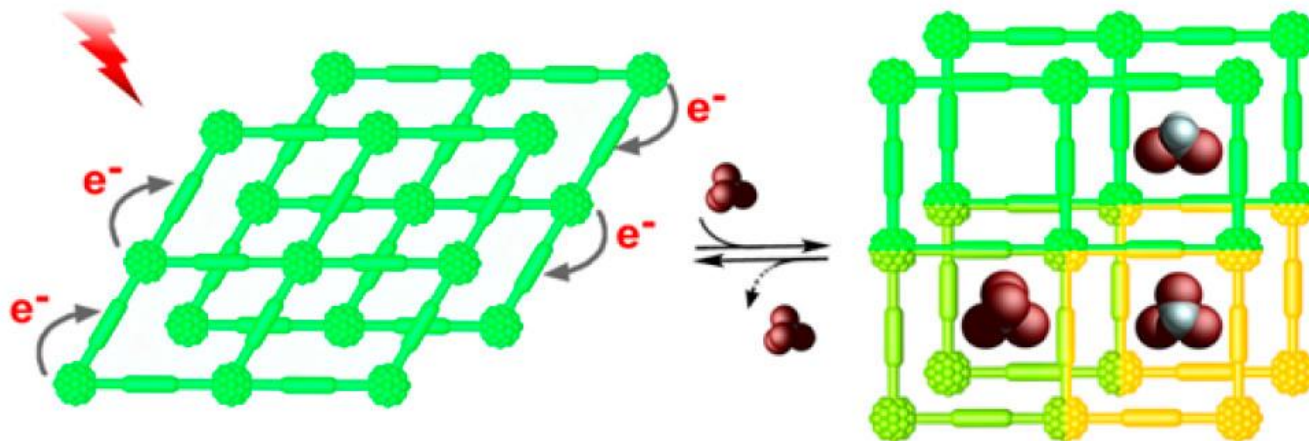
# A Flexible Fluorescent SCC-MOF for Switchable Molecule Identification and Temperature Display

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# Atomically Precise Site-specific Tailoring and Directional Assembly of Superatomic Silver Nanoclusters

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# Tandem Silver Cluster Isomerism and Mixed Linkers to Modulate the Photoluminescence of Cluster Assembled-Materials

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## Introduction:

Silver-chalcogenolate cluster-based MOFs (SCCMOFs), a new family in which the SCC nodes are extended into networks by organic linkers, have been developed to overcome the instability of SCCs and extend their luminescent application.

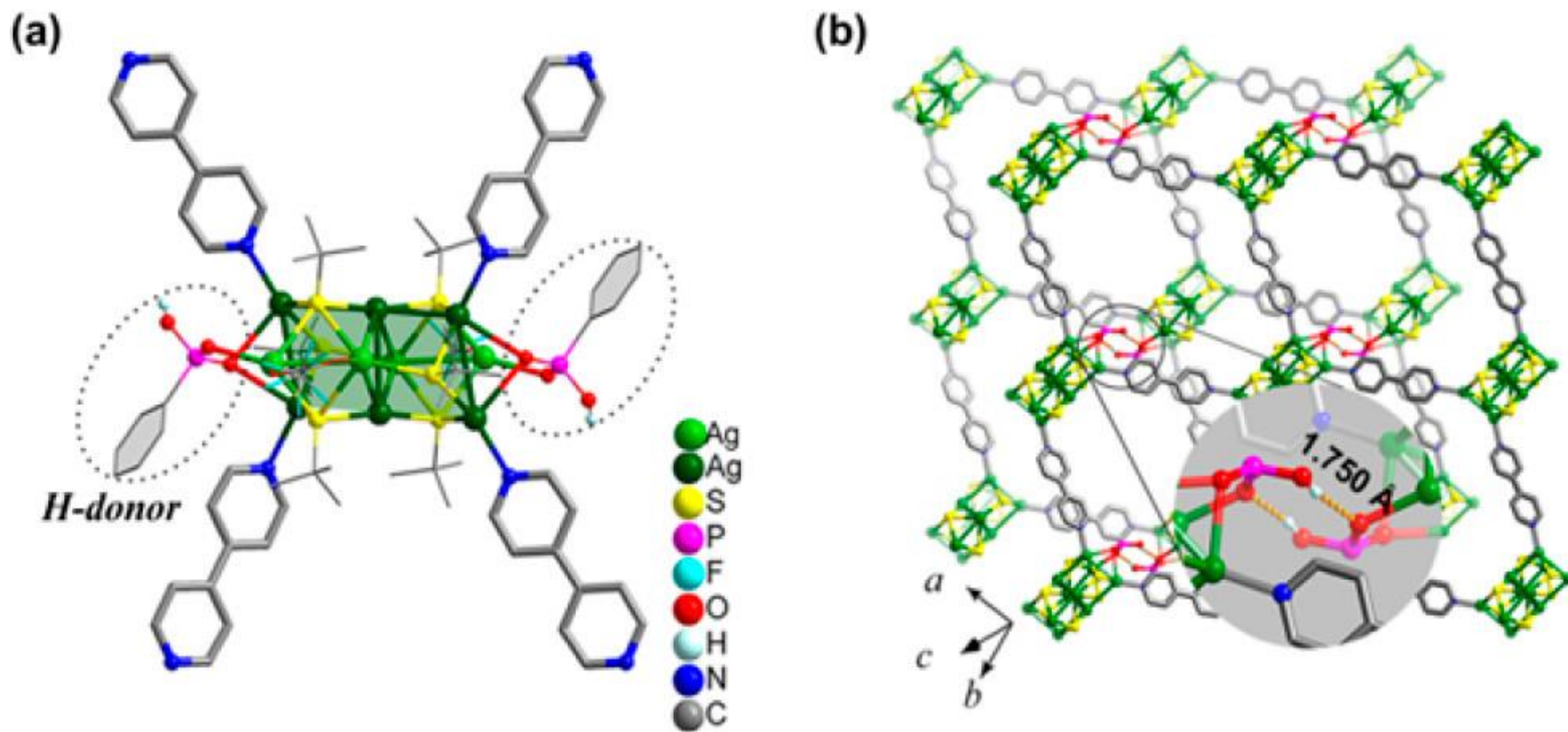
Flexible SCC-MOFs have not been explored and are expected to produce more novel or unexpected physical and chemical stimuli-responsive functionality, due to the combination of flexibility-related advantages like dynamic frameworks and induced-fit pores, the excellent inherent luminescence functionality of frameworks, and all kinds of charge transfer processes.

We report a hydrogen-bonded pillared-layered SCCMOF,  $[Ag_{10}(StBu)_6(CF_3COO)_2(PhPO_3H)_2(bpy)_2]_n$  (Ag<sub>10</sub>-bpy) (bpy = 4,4'-bipyridine), by introducing a multidentate phenylphosphonic acid (PhPO<sub>3</sub>H<sub>2</sub>) ligand as a functional hydrogen-bond donor.

The adsorption-induced dynamic gate opening process, along with obvious solvatochromism, allowed us to clearly distinguish chloromethanes (CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CCl<sub>4</sub>) by their distinctly different visible luminescence color.

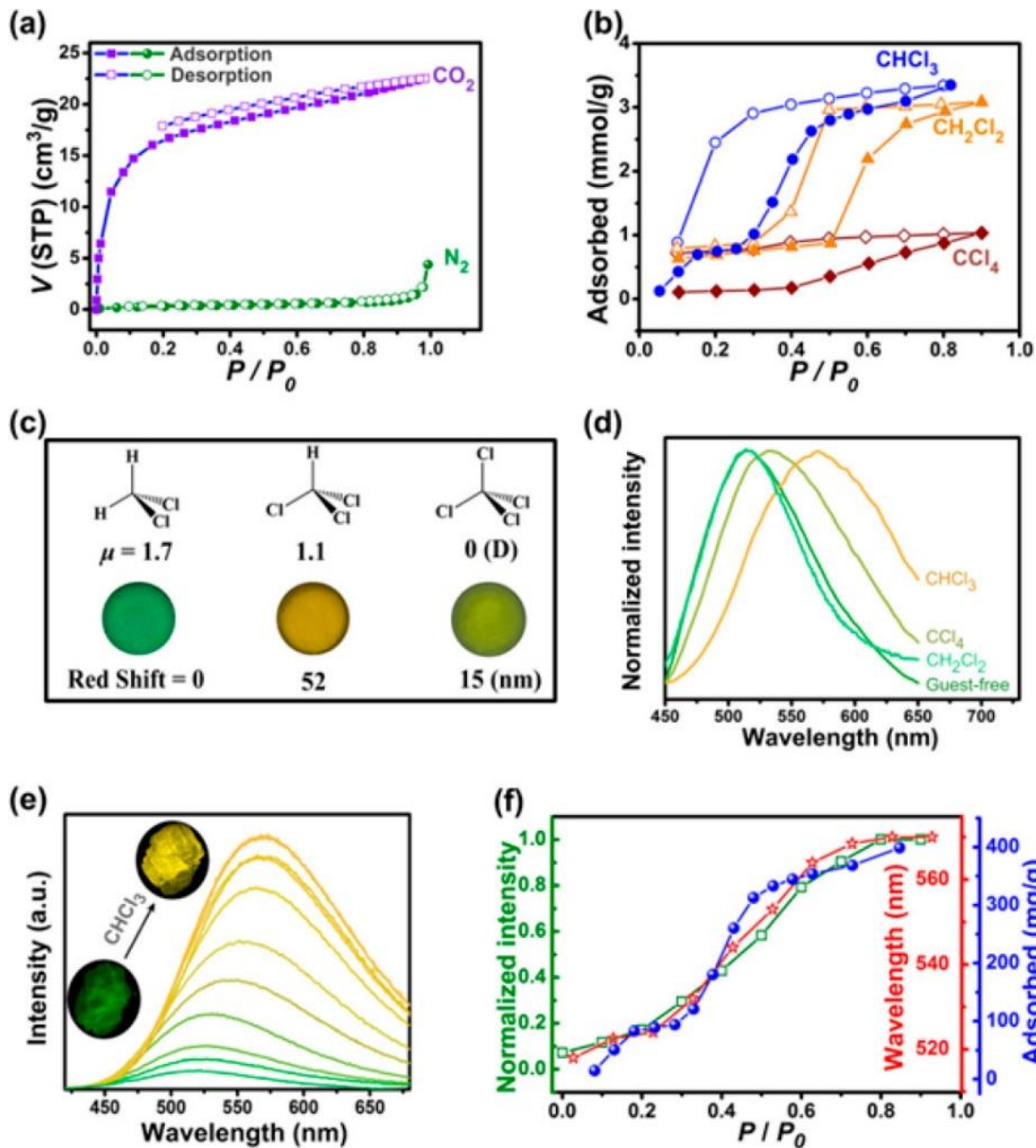
The temperature-controlled solvation dynamics in the nanocavity of the open phase that accommodated guest species considerably tuned the excited state and resulted in scarce segmented emission for specific temperature-related display among MOFs.

This dynamic structure – luminescence relationship was revealed at the molecule level via precise SCXRD combined with vapor adsorption and in situ PL, PXRD as well as density functional theory (DFT) calculations.



**Figure 1. (a) Perspective view of the coordination environment of the Ag<sub>10</sub>(StBu)<sub>6</sub> core in Ag<sub>10</sub>bpy (100 K). (b) Two-layer stack of the host framework of Ag<sub>10</sub>bpy with complementary hydrogen bonding (O–H...O, H...O distance is 1.750 Å) between interlayer –PO<sub>2</sub>OH moieties.**





**Figure 2.** (a) Sorption (filled symbols) and desorption (empty symbols) isotherms for Ag10bpy with N<sub>2</sub> (77 K) and CO<sub>2</sub> (195 K). (b) The gate-opening adsorption of CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and CCl<sub>4</sub> for Ag10bpy at room temperature. (c) The structures of chloromethanes and their luminescent responsive images (excited at 365 nm). (d) Normalized PL spectra of closed-phase Ag10bpy and Ag10bpy upon exposure to CH<sub>2</sub>Cl<sub>2</sub>, CCl<sub>4</sub>, and CHCl<sub>3</sub> excited at 365 nm. (e) PL spectra of Ag10bpy at various vapor pressures (P/P<sub>0</sub> = 0–1) of CHCl<sub>3</sub> at room temperature and luminescent images of single crystals. (f) The maximum emission peak (red) and normalized PL intensity (green) in (d) and adsorption plot (blue) as a function of CHCl<sub>3</sub> vapor pressure.

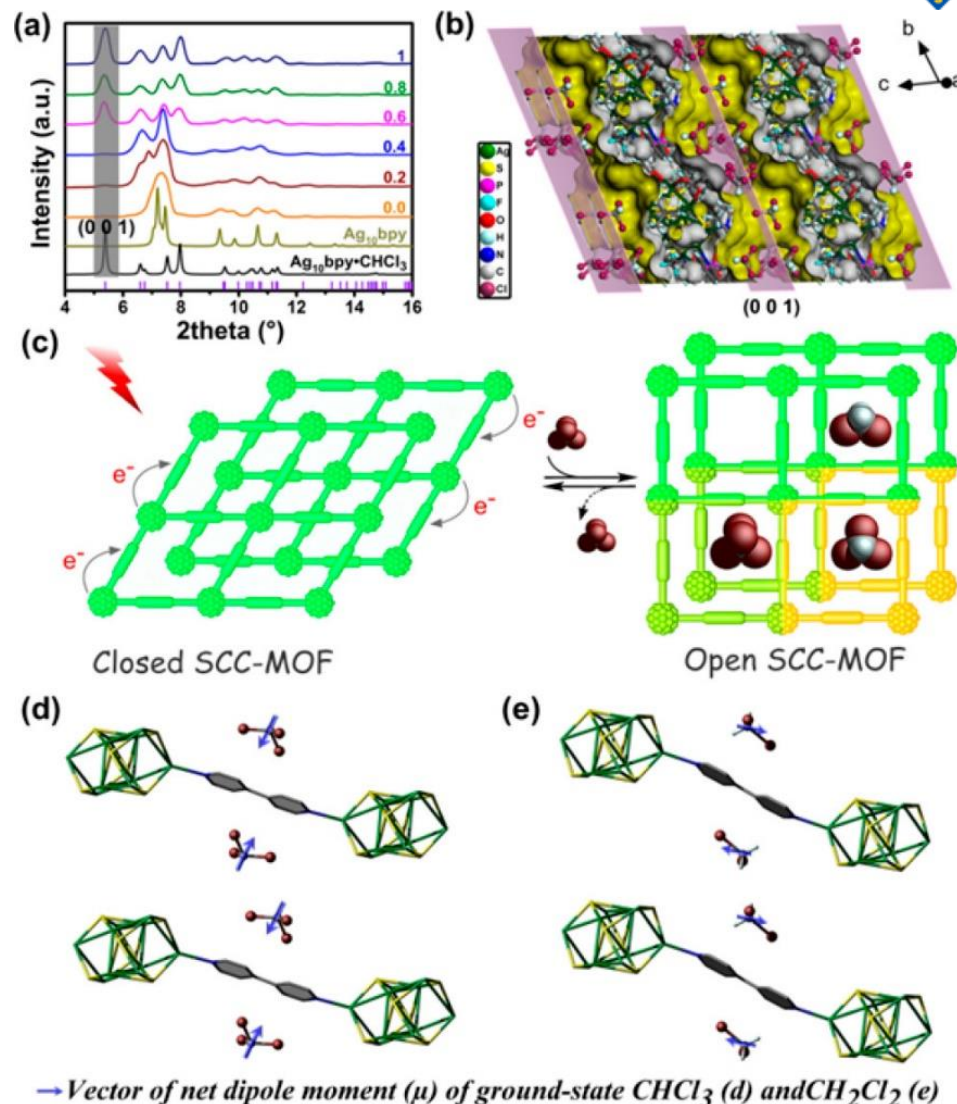


Figure 3. (a) PXRD patterns of Ag<sub>10</sub>bpy samples treated with CHCl<sub>3</sub> vapor at different partial pressures ( $P/P_0 = 0-1.0$ ), and simulated Ag<sub>10</sub>bpy-CHCl<sub>3</sub> from the single-crystal data (220 K). (b) The new peak below  $6^\circ$  in (a) corresponds to expansion of the pores, and the highlighted CHCl<sub>3</sub> (ball-and-stick mode) packs on or near the (001) plane in the Ag<sub>10</sub>bpy-CHCl<sub>3</sub> crystal structure (220 K). (c) Illustration of reversible pore open/closed structures induced by light. (d) and (e) Dipole moment vectors for ground-state CHCl<sub>3</sub> (d) and CH<sub>2</sub>Cl<sub>2</sub> (e).

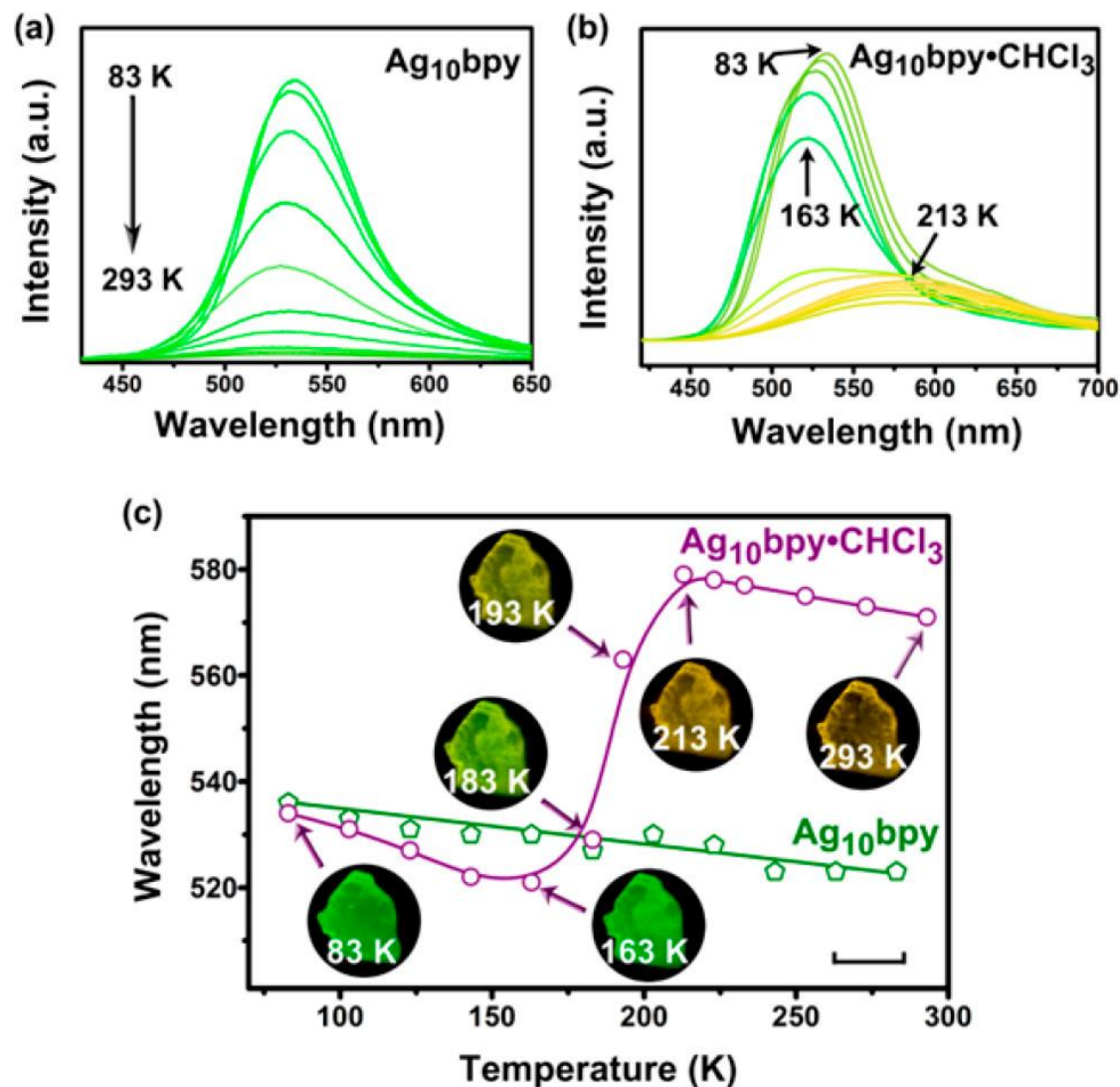
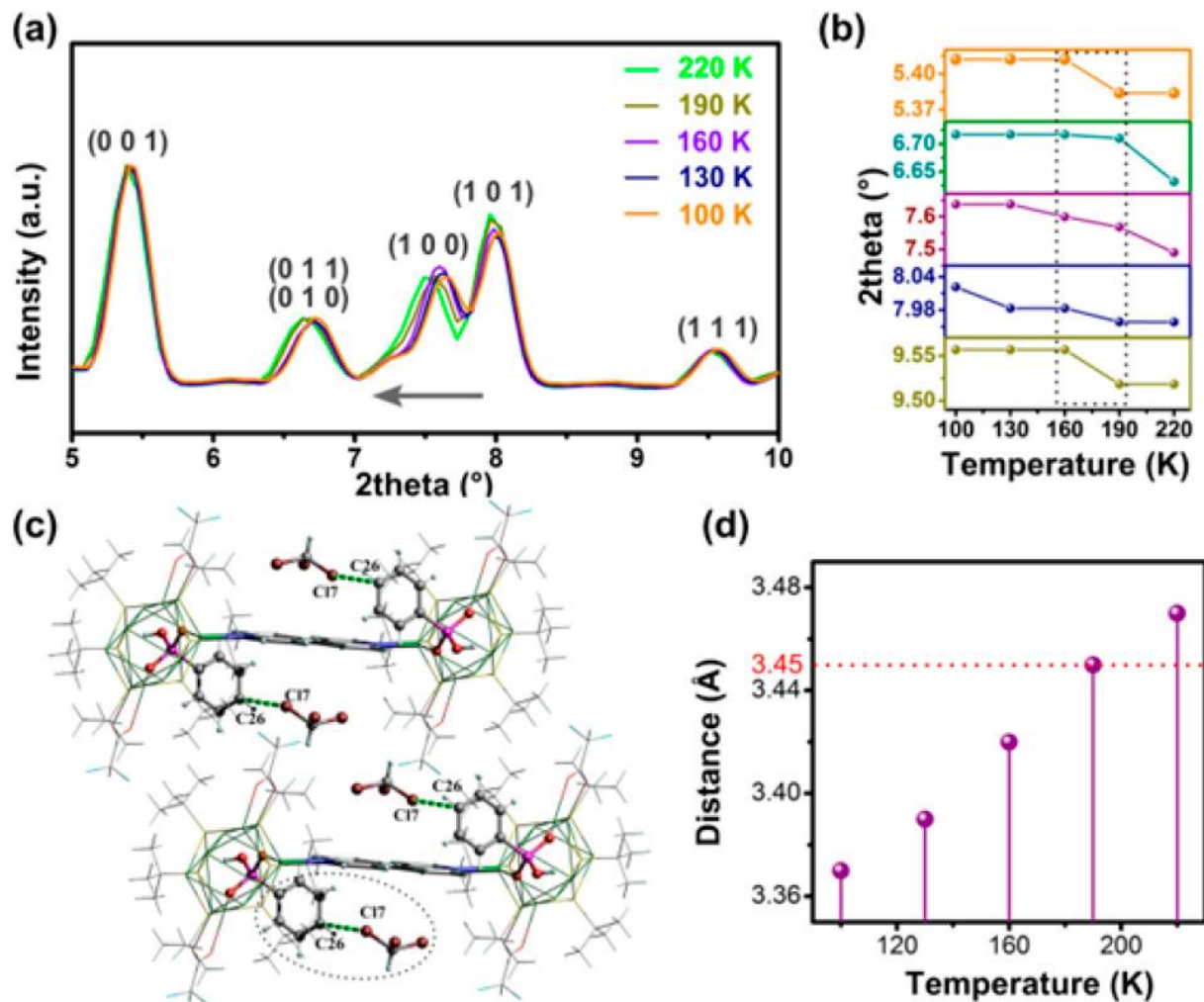


Figure 4. (a, b) 100 K photoluminescence spectra of Ag<sub>10</sub>bpy and Ag<sub>10</sub>bpy·CHCl<sub>3</sub> (83–293 K) under 365 nm excitation. (c) Emission peak maxima of the PL spectra of Ag<sub>10</sub>bpy·CHCl<sub>3</sub> (purple line) and Ag<sub>10</sub>bpy (green line) as a function of temperature. Insets: photoluminescence images of Ag<sub>10</sub>bpy and Ag<sub>10</sub>bpy·CHCl<sub>3</sub> at different temperatures





**Figure 5.** (a) Comparison of the PXRD patterns of Ag10bpy·CHCl<sub>3</sub> at different temperatures. (b) Abrupt increase of d-values of the crystal planes through CHCl<sub>3</sub> molecules occurs at 160 K. (c) Cl...π interactions (Cl7...C26) between nearest CHCl<sub>3</sub> molecules around the chromophore (bpy) moieties and benzene rings of the PhPO<sub>3</sub>H groups. (d) Dependence of the temperature from 100 to 220 K on the Cl7...C26 distance (Å) in the single-crystal structures of Ag10bpy·CHCl<sub>3</sub>; the red dotted line represents the sum of the van der Waals radii of interacting atoms Cl7 and C26.

# Conclusion:

We have successfully synthesized a novel flexible SCC-MOF that exhibits a remarkable framework breathing phenomenon upon adsorption of VOCs, being accompanied by distinct responsive fluorescence.

Thus, chloromethanes ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ) were unprecedentedly clearly distinguished by their distinctly different visible luminescence colors using this flexible SCC-MOF sensor.

More importantly, solvation dynamics of the included solvent molecules is demonstrated to regulate scarcely temperature-dependent segmented emission among MOFs and lead to striking chromic variation in a narrow temperature range.

This work significantly advances the development of flexible late transition metal (Ag, Au, Cu, Pd)-cluster-based metal-organic frameworks for light emitting materials, chemosensors, and temperature display, and it also offers a new perspective of investigating complicated guest-framework interaction at the molecular level via luminescent SCC-MOFs.



Thank you!