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

Ren-Wu Huang, Xi-Yan Dong, Bing-Jie Yan, Xiang-Sha Du, Dong-Hui Wei, Shuang-Quan Zang\* and Thomas C. W. Mak

Abstract: Silver-chalcogenolate cluster assembled-materials (SCAMs) are a category of promising light-emitting materials, whose luminescence can be modulated via variation of their building blocks (cluster nodes and organic linkers). Here we report the transformation of a singly-emissive [Ag<sub>12</sub>(SBu<sup>t</sup>)<sub>8</sub>(CF<sub>3</sub>COO)<sub>4</sub>(bpy)<sub>4</sub>]<sub>n</sub>  $(Ag_{12}bpy, bpy = 4,4'-bipyridine)$ into a dual-emissive  $[(Ag_{12}(SBu')_6(CF_3COO)_6(bpy)_3)]_n$  (Ag\_12bpy-2) via cluster-node isomerization, whose critical importance was highlighted in dictating the photoluminescence properties of SCAMs. Moreover, the newlyobtained Ag<sub>12</sub>bpy-2 served as a novel platform to construct visual thermochromic Ag<sub>12</sub>bpy-2/NH<sub>2</sub> via *de novo* mixed-linker synthesis, together with dichromatic core-shell Ag12bpy-2@Ag12bpy-NH2-2 via solvent-assisted linker exchange. This work provides new insight into the significance of metal arrangement on physical properties of nanoclusters and also serves as an excellent paradigm in the designed assembly of functional SCAMs-based luminescent materials.

Atom-precise metal chalcogenolate nanoclusters<sup>[1-8]</sup> are a new category of materials with many unusual properties, the most important of which is luminescence.<sup>[5]</sup> Among them, low-cost Ag chalcogenolate clusters (SCCs)<sup>[1a-f, 2b-e, 4]</sup> remain largely unexplored in contrast to Au thiolate clusters, and currently their structure-luminescence correlations are poorly understood. Structural isomers and pseudoisomers are excellent species to investigate structure-property relationships, which are favorable for guiding the design and synthesis of unique functional materials. Through cluster-to-cluster transformation,<sup>[6]</sup> numerous new thiolated Au/Ag or their alloy clusters have been synthesized; nevertheless, the core size or the metal counts have often been observed to change during the process. Very recently, a few cases of atomically precise structural isomerism with the core size remaining constant were reported, such as pseudoisomers  $Au_{28}(SR)_{20}$ ,<sup>[7a]</sup> and  $Au_{24}(SR)_{20}$ <sup>[7b]</sup> with different R groups,  $Ag_{62}S_{12}(SR)_{32}/Ag_{62}S_{13}(SR)_{32}$  with different metal valence states,<sup>[8]</sup> Au<sub>44</sub>(SR)<sub>28</sub>/Au<sub>44</sub>(SR)<sub>26</sub> with different ligand and metal valence states,<sup>[9]</sup> as well as the first genuine structural isomers Au<sub>38T</sub>/Au<sub>38Q</sub>.<sup>[10]</sup> These cases offer important insights into the structure and property evolution of gold and silver clusters. To the best of our knowledge, structural isomers of SCCs with

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constant metal counts, metal oxidation states and ligand species, together with their corresponding luminescent properties, have been seldom reported.

SCAMs, the assemblies of silver-chalcogenolate cluster either self-assembled via non-covalent interactions<sup>[1c]</sup> or coordination-assembled by covalent bonds<sup>[11]</sup> are emerging solid-state luminescent materials. Wherein, the coordinationassembled SCAMs, also called silver-chalcogenolate clusterbased metal–organic frameworks, are recently developed by us, and their potential emitting functionalities are expected to be modulated by their building blocks — silver-chalcogenolate cluster nodes and organic linkers.

Dual-emissive luminescent materials are superb in sensing because of their internally referenced (ratiometric) signals.<sup>[12]</sup> SCAMs may be promising candidates in this respect, yet unexplored to date; when SCC chromophores are dominated by an emitting triplet state of cluster-centered (3CC) nature for a long-wavelength emission<sup>[1, 2, 5, 13]</sup> that is generally highly temperature-dependent, organic linkers will simultaneously emit a shorter wavelength from a high-energy n- $\pi^*$  and/or  $\pi$ - $\pi^*$ transition excited state.<sup>[14]</sup> Notably, the prerequisite can be fulfilled only when a geometric architecture satisfies an adaptable electronic structure, because the lowest unoccupied molecular orbital (LUMO) of SCAMs could involves empty  $\pi^*$ orbitals of peripheral aromatic ligands,<sup>[11b]</sup> in which a single emission derived from SCC cluster-to-ligand charge transfer was observed. Transformation or isomerism of silver cluster nodes would enable us to achieve dual-emissive SCAMs and understand the structure-property relationship.

In this work, we first transformed tetragonal  $Ag_{12}bpy$  ([( $Ag_{12}(SBu')_8(CF_3COO)_4(bpy)_4$ )]<sub>n</sub>)<sup>[11b]</sup> into a new trigonal SCAM  $Ag_{12}bpy-2$ -solvents

 $[Ag_{12}(SBu^{t})_{6}(CF_{3}COO)_{6}(bpy)_{3} \cdot (DMAc_{x} \cdot toluene_{y})]_{n}$  using solvent at room temperature (RT); the solvent-free empty framework  $[(Ag_{12}(SBu^{t})_{6}(CF_{3}COO)_{6}(bpy)_{3}]_{n}$  was designated as Ag\_{12}bpy-2, and the reverse transformation was also successfully achieved (Scheme S1) by solvents. Accordingly, reversible cluster-node isomerization occurred between a separated silver core in Ag<sub>12</sub>bpy and an empty cuboctahedral one in Ag<sub>12</sub>bpy-2. This isomerization directly resulted in considerable change in electronic structure and hence distinctly different luminescence (a single green emission of Ag<sub>12</sub>bpy vs a red-blue dual emission of Ag12bpy-2 at low temperature). DFT calculations revealed that the different electron density distribution of LUMOs determined by the geometric structure of silver cluster contributed to the different emissive behavior. Moreover, a mixed-linker approach was employed for the preparation of dualemissive thermochromic Ag<sub>12</sub>bpy-2/NH<sub>2</sub>, and solvent-assisted linker exchange (SALE) for the preparation of dichromatic coreshell Ag<sub>12</sub>bpy-2@Ag<sub>12</sub>bpy-NH<sub>2</sub>-2.

In our experiments, we tested various solvents to induce its transformation in view of the remarkable stability of  $Ag_{12}bpy$  towards common VOCs,<sup>[11b]</sup> and eventually selected

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DMAc/toluene (3:1) (Table S1 and Scheme S1). When the bright-green emissive rectangular Ag12bpy crystals were immersed in DMAc/toluene (3:1) for a sufficient duration, they dissolved and new hexagonal crystals (Ag12bpy-2·solvents) (Video S1, Figures S1-S4 and Tables S1-S2). The reverse process was achieved when Ag12bpy-2.solvents crystals were immersed in CH<sub>3</sub>CN/EtOH (1:1), in which the solvated Ag12bpy-solvents were produced again in 6 hours (Video S2 and Figures S5-S10). On the whole, the transformation from Ag12bpy-solvents to Ag12bpy-2-solvents occurred via a dissolution and recrystallization mechanism controlled by solvent, while the reverse one involves a more complicated replacement/dissection-dissolutionsolvent-promoted recrystallization mechanism. (See detailed analyses in Sections S2–S3; Figures S1–S10 and Tables S1–S2). Thus.  $Ag_{12}bpy \cdot solvents \Leftrightarrow Ag_{12}bpy \cdot 2 \cdot solvents$  was controlled by the choice of solvent, which turns out to be an important factor in the stable structure of nanoclusters and SCAMs, apart from ligand choice<sup>[4]</sup> and temperature.<sup>[10]</sup> For large-scale production of Ag12bpy-2.solvents crystals, we also successfully conducted a one-pot synthesis under identical synthesis conditions.

SCXRD analysis revealed that **Ag**<sub>12</sub>**bpy-2·solvents** crystallizes in trigonal space group *P*-3 (Table S3); The cluster core is an empty cuboctahedron consisting of twelve Ag atoms linked through Ag(I)–Ag(I) argentophilic interaction<sup>[1e-f]</sup> (Figures 1 and S11). This cuboctahedron displays  $C_{3\nu}$  symmetry and contains eight triangular faces: two equilateral triangles with Ag2–Ag2 distances of 3.010 Å at the top and bottom surfaces, and six lateral isosceles triangles (Ag1–Ag2 2.959 Å; Ag1–Ag1# 3.818 Å), with the long side shared by a six-isosceles trapezoid capped by a  $\mu_4$ -SBu<sup>t</sup> (Figure S11). The auxiliary CF<sub>3</sub>COO<sup>-</sup> ligands are bound to Ag1 atoms in the monodentate mode. The reported cuboctahedral Ag<sub>12</sub> ( $\mu_{12}$ -Ag){Fe(CO)<sub>4</sub>}<sub>8</sub>]<sup>3-(4-/5-</sup> and [Ag<sub>12</sub>( $\mu_{12}$ -I)( $\mu_3$ -I)<sub>4</sub>{S<sub>2</sub>P-(CH<sub>2</sub>CH<sub>2</sub>Ph)<sub>2</sub>}<sub>6</sub>].<sup>[15]</sup> Empty cuboctahedral



*Figure 1.* (a, b) Perspective view of Ag<sub>12</sub>S<sub>6</sub> node with six pendent bpy linkers (ORTEP drawing with probability 50%) and stacking of 2D network structure of **Ag<sub>12</sub>bpy-2**, respectively, viewed along the crystallographic *c*-axis. Color code: Ag, green; S, yellow; C, gray; N, blue; CF<sub>3</sub>COO<sup>-</sup>, -Bu<sup>t</sup> and H atoms are omitted for clarity. (c, d) Comparison of Ag<sub>12</sub> core structures in **Ag<sub>12</sub>bpy-2** and **Ag<sub>12</sub>bpy** 

arrangements of Ag atoms are very rare. In the present case, each silver cuboctahedron is connected with six others through lumbar Ag1–N bonds by bpy linkers, leading to a highly symmetrical 2D network in the *ab* plane with the layer separation of 7.23 Å between two nearest silver atoms of adjacent lays along the *c*-axis (Figure 1b), in which weak van der Waal's interactions and hydrogen bonds (H–F and H–O) exist (Figure S12). The evacuated **Ag12bpy-2** retained its constant framework structure, which can be confirmed by the overlap between the simulated and experimental PXRD patterns (Figure S13). Its chemical formula was further verified by elemental analysis and TGA (Figure S14).

The most striking difference between Ag<sub>12</sub>bpy to Ag<sub>12</sub>bpy-2 is a symmetry variation of the Ag<sub>12</sub> core from a disconnected D<sub>2d</sub> 5–2–5 arrangement to a  $C_{3\nu}$  cuboctahedron, resulting in a shrinkage of the c-axis from a double-layer of thickness 20.02 Å to a single-layer of 11.22 Å (Table S4); the shrinkage is accompanied by shortening of the vertical dimension of the cluster core (from 8.340 Å along the -4 axis to 3.924 Å along the  $C_{3v}$  axis) (Figure 1c,d). From the  $D_{2d}$  cluster core in Ag<sub>12</sub>bpy with high dipole moment and fewer Ag–Ag bonds to the  $C_{3v}$  core in Ag12bpy-2 with nearly zero dipole moment and more argentophilic interactions (Figure 1c and Tables S4-S5), solubility and polarity of solvent possibly played a critical role (Section S2). And, the binding energy of Ag3d<sub>3/2</sub> and Ag3d<sub>5/2</sub> in Ag<sub>12</sub>bpy-2 are 0.20 eV-0.17 eV larger than that in Ag<sub>12</sub>bpy-as shown in the XPS spectra (Figure S15 and Table S6). This higher binding energy may also contribute to the formation of the resulting structure of Ag12bpy-2. The isometric silver cores naturally led to different frameworks. This work may direct more attention to the solvent's role in the synthesis of SCCs and provide some insights into the assembly of SCAMs.

With isomeric metal Ag<sub>12</sub> core in silver-chalcogenolate cluster nodes and identical linker species, **Ag<sub>12</sub>bpy-2** and **Ag<sub>12</sub>bpy** provide a pair of good models for clarifying the cluster structure-photoluminescence (PL) correlation of similar SCCs and SCAMs, without involving inherent discrepancies induced by different ligand species.

When excited at UV light, Ag<sub>12</sub>bpy-2 emitted weak orange light at RT which turned very bright at low temperature (Figure S16), which is completely different from green luminescence of Ag<sub>12</sub>bpy (Figure 2a,b).<sup>[11b]</sup> To preclude the solvent's influence on emission of host framework (Figure S16), we first evacuated Ag<sub>12</sub>bpy-2. To our delight, Ag<sub>12</sub>bpy-2 actually displayed a dual (blue and red) emission (Figure 2c,d), which is highly sensitive to different excitation energies and temperatures, as shown in the excitation spectra and three-dimensional excitation-emission matrix (3D-EEM) luminescence spectra (Figures 2c, S17-S18). Excitation at 320 nm favors high-energy blue emission (a set of emissive peaks at approximately 463 nm), whereas the lowenergy emission at 620 nm is more preferentially excited by 280 and 365 nm light at 83 K. Remarkably, the low-energy peak (620 nm, excited at 365 nm) increased 582-fold with the decrease in temperature, and simultaneously the HE peak (463 nm, excited at 365 nm) with a vibrational structure increased 17-fold (Figure S19). The moisture in air could not enter the pore of Ag<sub>12</sub>bpy-2, and its structure remained unchanged after repetitive variabletemperature ΡL measurements (Figures S13-S14), guaranteeing the quality and availability of its measured emission properties. In contrast, for Ag<sub>12</sub>bpy, only a PL emission band at 507 nm with a lifetime of 12.35 µs at 83 K was observed, which is excitation- and temperature-independent.<sup>[11b]</sup>

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For Ag<sub>12</sub>bpy-2, compared with the emission of uncoordinated bpy ligands<sup>[16]</sup> (Figure S20), we assigned the group peaks at approximately 463 nm in Ag<sub>12</sub>bpy-2 to the  $\pi$ ,  $\pi^*$ triplet state of bpy with the observed lifetime of 10.1 ms at 83 K (Figure 2e); the low-energy PL band at 620 nm with an observed lifetime of 85.5 µs at 83 K (Figures 2f and S21) was tentatively assigned to triplet states in the dodenuclear Ag-S cluster nodes of ligand-to-metal-metal charge transfer (LMMCT; S  $\rightarrow$  Ag) character mixed with metal-centered (ds/dp) states. [1c, 2h-i, 5a-c, 8] In contrast, for Ag<sub>12</sub>bpy, a single emission band centered at 507 nm was observed in the whole temperature range (Figure 2b)<sup>[11b]</sup> for which a excitation peak at 365 nm along with a shoulder at 338 nm at 83 K implied dual possible transitions with different energy were responsible (Figure S22). We assumed that the low-energy one arose from interligand trans-metallic chargetransfer transition (ITCT, S/Ag  $\rightarrow$  bpy) usually observable in closed-shell metal coordination complexes such as those of Zn(II) and Cd(II) as well as Pt(II) etc.<sup>[17,18]</sup> containing both Nheterocyclic and thiolate ligands. The high-energy one originated from LMMCT (S  $\rightarrow$  Ag) probably mixed with metal-centered (ds/dp) transitions,<sup>[2,5]</sup> which could then relax to the ITCT excited state(s). The assumption gained further support from electronwithdrawing F substitution on bpy ligands of Ag<sub>12</sub>bpy,<sup>[18]</sup> in which two separate excitation peaks were responsible for a single phosphorescence band at 543 nm, a 36-nm redshift relative to that of the complex without F substituent (Figure S23).



*Figure 2.* The 3D-EEM PL spectra of  $Ag_{12}bpy$  (a) and  $Ag_{12}bpy-2$  (c) were measured at 83 K. The PL profiles of  $Ag_{12}bpy$  (b) excited at 365 nm and  $Ag_{12}bpy-2$  (d) excited at 280 nm. (e, f) Temperature-dependent time-resolved PL decays at 463 nm and 620 nm of  $Ag_{12}bpy-2$ , respectively (excited at 355 nm).

Obviously, the stark emissive discrepancy (Table S7) must be associated with the structure of the cluster or framework topology in view of their identical chemical components (ligands, linkers, and monovalent silver ions), which caused the distinct



*Figure* 3. The comparision between the selected molecular orbitals representations of  $Ag_{12}bpy$  and  $Ag_{12}bpy-2$ . Note LUMO to LUMO+7 in  $Ag_{12}bpy$  are degenerate<sup>[11b]</sup> (Table S9); LUMO+1 to LUMO+6 in  $Ag_{12}bpy-2$  have close energies (Figure S24 and Table S8).

difference of their electronic structures and resultant different PL emissions. Through structural analysis, the excimer/exciplex emission associated with aromatic chromophores stacking was precluded, owing to the lack of close  $\pi$ - $\pi$  interaction among interlayer bpy linkers. Therefore, the structures of Ag-S cluster in the two complexes should play the key role in determining their PL emissions.

To gain more insights into cluster structure-luminescence relationship in Ag<sub>12</sub>bpy and Ag<sub>12</sub>bpy-2, we performed DFT and TD-DFT calculations (Section S6, Figures 3, S24–26 and Tables S8–11). The DFT results showed that for Ag<sub>12</sub>bpy, the eight lowest degenerate unoccupied molecular orbitals (LUMO-LUMO+7) are all characterized by  $\pi^*$  orbitals of bpy ligands, while LUMO+8 is localized at the cluster center<sup>[11b]</sup> (Figure 3, Table S9). In contrast, for Ag<sub>12</sub>bpy-2, LUMO with sphere-like appearance is centered on cluster, while LUMO+1 to LUMO+6 with close energies are distributed on bpy ligands (Figures 3 and S24). It is suggested that an inversion between bpy-localized and cluster-localized unoccupied molecular orbitals in the two complexes (Figure 3), was engendered by the variation of cluster structures.

Absorption transition analysis from TD-DFT calculations further revealed that for **Ag**<sub>12</sub>**bpy-2**, LMMCT (S  $\rightarrow$  Ag) transitions mixed with a metal-centered (ds/dp) <sup>[1c, 2h-i, 5a-c, 8]</sup> could occur from 280 to 360 nm, and the efficient intraligand transitions of bpy mainly appear around 320 nm (Figure S25 and Table S10), which match its PL excitation spectra (Figure 2c). For **Ag**<sub>12</sub>**bpy**, the main LMMCT (S  $\rightarrow$  Ag) transitions in cluster occur around 338 nm and the main ITCT transitions<sup>[17]</sup> (S/Ag  $\rightarrow$  bpy) center around 365 nm (Figure S26 and Table S11), which are well consistent with PL excitation spectra (Figures 2a and S22).

Based on the above experimental and theoretical results, a simplified schematic state diagram showing photoluminescence of the pair of complexes is presented (Figure S27). For  $Ag_{12}bpy$ , a single phosphorescence band (centered at 507 nm) is likely due to the lowest triplet excited state(s) (T<sub>1</sub>, Figure S27a) that mainly involves optimal interligand trans-metallic charge-transfer (ITCT, S/Ag  $\rightarrow$  bpy) transitions (①), and could also be formed from cluster-centered transitions (mixing of LMMCT and ds/dp, ②) followed by possible CT and ISC. In contrast, for  $Ag_{12}bpy$ -2, dual phosphorescence with respective maxima at 463 nm and 620 nm were assigned to originate from two separate triplet excited states (T<sub>1</sub>' and T<sub>2</sub>', Figure S27b) that arose mainly from cluster-centered transitions (mixing of LMMCT and ds/dp, ①') and intraligand transitions (②'), respectively. The results showed

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that varying cluster structure is an efficient strategy to modulate the electronic structure and luminescence of SCAMs, which can be generalized to further types of metal cluster-based assembled-materials.

To strengthen the blue emission in Ag<sub>12</sub>bpy-2 and obtain visual temperature sensing by color in a wider range, we introduced the blue-emissive bpy-NH2<sup>[19]</sup> with unchanged length and unaltered connectivity (Figures 4a, S28-S29) to form a mixed-linker single crystal Ag12bpy-2/NH2·solvents (m:n) (m:n = bpy:bpy-NH<sub>2</sub> is the reaction stoichiometric ratio) via de novo synthesis (Figures S30-S42). The evacuated frameworks of Ag<sub>12</sub>bpy-2/NH<sub>2</sub> (m:n) are isoreticular with Ag<sub>12</sub>bpy-2, confirmed by their consistent unit-cell parameters (Table S12) and welloverlapped PXRD patterns (Figure 4b). The -NH<sub>2</sub> groups are partially and homogeneously distributed in Ag12bpy-2/NH<sub>2</sub>·solvents (m:n = 1:8, 1:4, 1:1), resulting in a very low occupancy of the amino N atoms. We appropriately analysed the series of crystal data of these mix-linker SCAMs containing the higher content of bpy-NH<sub>2</sub> (Section S7), according to their electron density maps by comparison with that of neat Ag12bpy-NH2-2-solvents only having bpy-NH2 linkers (Figure S30). They all demonstrate their iso-structuralism with Ag12bpy-2·solvents (Figures S31-S34), and the bpy:bpy-NH<sub>2</sub> ratio of determined by crystallographic analysis is consistent with their <sup>1</sup>H NMR results (Table S13). The actual contents of bpy-NH<sub>2</sub> in Ag<sub>12</sub>bpy-2/NH<sub>2</sub>·solvents (m:n) series were determined by <sup>1</sup>H NMR spectra of the digested single crystals (Figures S35-S36 and Table S14). The elemental analysis cannot differentiate the different bpy-NH<sub>2</sub> content especially in Ag<sub>12</sub>bpy-2/NH<sub>2</sub> (m:n  $\geq$ 4:1), in which the differences of composition percent (%) of C, H, N elements are less than 0.04%. The results also demonstrate the advantages of SCAMs, that is by incorporating two linkers in the same framework in different relative compositions, one of which is even trace sometimes, we can continuously tune the emission of the isostructural SCAMs (see below). The bulk of Ag<sub>12</sub>bpy-2/NH<sub>2</sub> (m:n) crystals where no macroscopic domains was dominated by linker bpy or bpy-NH<sub>2</sub> was also verified by <sup>1</sup>H NMR spectra and by emission measurements, respectively, using different batches of samples (Figures 4c-f, S35-S42).

As expected, the introduction of bpy-NH<sub>2</sub> greatly increased the blue luminescence component, whose temperaturedependence was much less than that of the silver cluster-based red components (Figures S37-S39). The ratio of two emission peaks intensity (l<sub>2</sub>, 620 nm)/(l<sub>1</sub>, 447 nm) was largely temperature- and concentration-dependent. At an optimized concentration (m:n = 20:1), the emissive intensity increased approximately 460- and 17-fold for I<sub>2</sub> and I<sub>1</sub>, respectively, when excited at 365 nm from 83 K to 293 K, (Figure S39). Accordingly, continuous emissive color variation from purple pink to blue was observed in the CIE chromaticity diagram (Figure 4d). To assess the self-calibrated performance, we correlated the temperature (T) to the emission intensity ratio  $l_2:(l_1 + l_2)$ , and linear correlation<sup>[2a,5b,12]</sup> was found in the range 83-233 K (sensitivity 0.347 %  $K^{-1}$ ), which is a relativley wide temperature range and a moderate sensitivity<sup>[12]</sup> (Figure 4e).

In view of the highly symmetric trigonal crystal system, we selected a few mixed-linker  $Ag_{12}bpy-2/NH_2$ -solvents (20:1) macrocrystals and sliced them along the [001] direction, which exposed the interior rectangular {010}/{100} surfaces. The nearly identical emissive colors of the interior {010}/{100} surfaces compared to the exterior hexagonal {001} surfaces further demonstrated the characteristic of a hybrid  $Ag_{12}bpy$ -

 $2/NH_2 {\cdot} solvents$  with the linkers (bpy and bpy-NH\_2) being well mixed (Figure 4f).



*Figure 4.* (a) Schematic of the preparation of the mixed-linker  $Ag_{12}bpy-2/NH_2$  via *de novo* synthesis. (b) PXRD profiles of  $Ag_{12}bpy-2/NH_2$  (m:n = bpy:bpy-NH<sub>2</sub>) (the m:n values refer to stoichiometric ratio of the starting reactants; (c) Temperature-dependent emissive spectra of the evacuated  $Ag_{12}bpy-2/NH_2$  (20:1). (d) CIE coordinates in the range 83–293 K. (e) The working curve and equation of the evacuated  $Ag_{12}bpy-2/NH_2$  (20:1) (excited at 365 nm). (f) Thermochromic images of the exterior {001} surfaces (*A*) and the exposed interior {010}/{100} planes (*B*) of  $Ag_{12}bpy-2/NH_2$ ·solvents (20:1) single crystals under UV-light irradiation.

We then used the SALE approach<sup>[20]</sup> to prepare core-shell **Ag<sub>12</sub>bpy-2@Ag<sub>12</sub>bpy-NH<sub>2</sub>-2·solvents** via an *in situ* singlecrystal-to-single-crystal transformation. The isoreticular structures of the **Ag<sub>12</sub>bpy-2@Ag<sub>12</sub>bpy-NH<sub>2</sub>-2·solvents** family were prepared by time-dependent and concentration-dependent SALE processes (Table S15, Figures S43–S44). The stepwise replacement of the bpy linker with bpy-NH<sub>2</sub> was monitored by <sup>1</sup>H NMR spectra (Figures S45–S48, Tables S16–S17), luminescence spectra (Figure S49), and fluorescent confocal images (Figures 5 and S50). Additionally, no obvious indication of dissolution recrystallization phenomena were detected during the SALE process.

Cutting these Ag<sub>12</sub>bpy-2@Ag<sub>12</sub>bpy-NH<sub>2</sub>-2·solvents single crystals along the [001] direction would help us qualitatively visualize the extent of change. Figure 5a,b show the change in luminescence images of core-shell Ag<sub>12</sub>bpy-2@Ag<sub>12</sub>bpy-NH<sub>2</sub>-

**2-solvents** after two or three days at 83 K. The light blue color of the original exterior {001} surface resulted from combination of the intensely blue bpy-NH<sub>2</sub> and moderately red SCCs, whereas the cut and exposed interior {010}/{100} surfaces exhibited the red core dominated by the moderate emission of SCCs and a thin light-blue shell identical to the color from the exterior {001} surfaces. The blue shell layer growing and the red core section diminishing with exchange time could be easily visualized by the naked eye. The phenomenon lasted until the changing process was finished. Subsequently, we conducted RT confocal microscopy<sup>[21]</sup> of macrocrystals over three days at multiple focal planes moving progressively deeper into the bulk of the crystal along the *c*-axis (Figures 5c,d, S50), which provided images of the intense luminescent shell **Ag<sub>12</sub>bpy-NH<sub>2</sub>-2-solvents** with its

bpy-NH<sub>2</sub> linker and the very weak emissive core (Ag<sub>12</sub>bpy-

2-solvents). Thus, the core-shell structures of Ag12bpy-

2@Ag12bpy-NH2-2-solvents could be ambiguously identified.



*Figure 5.* Top panel (83 K): (a) Luminescence microscopy images of the light blue hexagonal (001) plane and (b) the exposed rectangular {010}/{100} planes cut along the c-axis, demonstrating that the red core scales down and blueish-white shell scales up with exchange time. Bottom panel: (c) Fluorescent confocal image (293 K) of Ag<sub>12</sub>bpy-2@Ag<sub>12</sub>bpy-NH<sub>2</sub>-2-solvents at focal planes 21.7 µm along the *c*-axis (for more focal planes see Figure S48) and (d) Schematic cross-section from (c) clearly showing the core-shell structure.

In summary, we have demonstrated a reversible solventinduced structural transformation between two Ag12bpy and Ag<sub>12</sub>bpy-2, accompanied by isomerization of Ag cluster node; moreover, silver core compression from argentophilic interactions in Ag12bpy-2 caused the energy level of the unoccupied molecular orbitals of the silver cluster centers to be lower than that of the bpy centers, engendering two emissive centers located on the silver clusters and linkers, respectively. Temperature-dependent red and blue dual-emission behavior was observed in Ag12bpy-2, while a single green one in Ag12bpy. Mixed-linker approaches were used to improve luminescent functionality: de novo synthesis generated Ag<sub>12</sub>bpy-2/NH<sub>2</sub> for thermochromism, and SALE produced coreshell single crystals of Ag<sub>12</sub>bpy-2@Ag<sub>12</sub>bpy-NH<sub>2</sub>-2.solvents. The present results provide precise and insightful silver cluster structure-luminescence correlations, as well as significant progress on the development of SCAMs functional materials.

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**Keywords:** cluster compounds • cluster assembled-materials • silver • structural transformation • luminescence

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#### COMMUNICATION

Tandem varying Ag cluster structure and tuning mixed linkers stepwise are used to achieve dual-emitting homogeneous and core-shell silverchalcogenolate cluster assembledmaterials. The arrangements of silver in cluster are demonstrated playing fundamentally important role in luminescence.



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Tandem Silver Cluster Isomerism andMixed Linkers to Modulate thePhotoluminescence of ClusterAssembled-Materials