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EDGE ARTICLE

Ligand-switching and counteranion-induced hierarchical self-assembly of silver-NHC complexes†

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The self-assembly of the rigid, bent, chiral bis(triazol-ylidene) ligands with the linear coordinated group 11 metal centers brought about dramatic architectural variation of metallosupramolecular assemblies from the familiar dinuclear M_2L_2 to the trinuclear cylindrical foldamers M_3L_3 through a small variation of the R group of ligand. The foldamers $[(S)-2 \cdot Ag]_3(X)_3$ further underwent counteranion-triggered hierarchical self-assembly into well-grown nanofibers capable of gelating solvents.

The metal-directed self-assembly of small molecules to build up metal-organic supramolecular structures has opened up exciting opportunities to fabricate new materials.¹ While the manipulation of M–N and/or M–O coordination interactions is the most widely used construction principle for the generation of supramolecular entities, self-assembly based on coordination of carbon donors with metals has recently started to attract intensive interest.^{2–4} Given that N-heterocyclic carbenes (NHCs) show powerful coordination ability toward a wide range of metal ions to form M–C bonds,³ the use of metal-carbene bonds (M–C (NHC)) should be an ideal strategy to create metallosupramolecular architectures. Recently, Hahn *et al.* reported the first sandwich-like hexanuclear silver(I) NHC “molecular containers” with cyclic hexa-NHC ligands and the cylindrical polynuclear metallosupramolecular architectures containing three or four silver(I) ions sandwiched between two tri- or tetra-NHC ligands, which featured exclusively M–C(NHC) bonds.⁴ Son *et al.* prepared the first organometallic hollow spheres bearing $\{(NHC)_2Pd\}$ species through formation of 3D infinite networks of tetrahedral tetra-NHC building blocks. These showed excellent activities as heterogeneous catalysts in one-pot three-component Strecker reactions of ketones.⁵

Following our continuous interest in fabricating hybrid inorganic-organic nano-scale materials based on coordination of bis-azoles (nitrogen donors),⁶ we wished to explore self-assembly of bis(azole-based NHC) ligands (carbon donors) and metals.

Generally, the rigid, bent bis-NHC ligands preferably form mononuclear complexes (ML) with transition metals, and in the case of the linear coordinated group 11 metal centers (*i.e.*, Cu(I), Ag(I), Au(I)), binuclear complexes (M_2L_2).^{3,7} Inspired by our previous research on chiral bis-bicyclic triazolium salts,⁸ we logically envisioned whether a small change of the substitution pattern (R groups) could switch the twist angles of *in situ* generated bis(NHC) building blocks through hindered rotation along the C–N bond between the carbene nucleus and the central phenylene link, which determines the orientation of interaction site of carbene with metal ion. Thus, the bis(NHC) ligands may assemble with the linear coordinated metal ions to bring about dramatic architectural variation of metallosupramolecular assemblies (Fig. 1).

In this contribution, we describe an unprecedented substituent-switching and counteranion-triggered self-assembly of rigid, bent, chiral bis(triazol-ylidene) ligands (L) with linear coordinated Ag(I) or Au(I) ions (M) to make the nano-scale, cylindrical foldamer structures, which may further evolve into well-defined nanofibers capable of gelating solvents. This is a completely new phenomenon observed in the hierarchical self-assembly of NHC ligands with metals.

The silver-NHC complexes were prepared by the reaction of chiral bis-bicyclic triazolium salts, **1**·2HCl, **2**·2HCl or **3**·2HCl, with silver oxide, followed by anion-exchange in the presence of NaBF₄ or KPF₆ to afford the corresponding fluoroborate or

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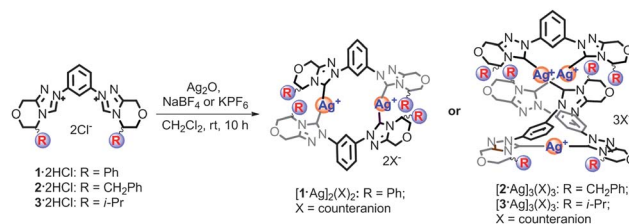


Fig. 1 Substituent-switching architectural variation of silver-NHC complexes.

hexafluorophosphate salts. The resulting complexes $[(R)\text{-}1\cdot\text{Ag}]_2(\text{PF}_6)_2$, $[(R)\text{-}1\cdot\text{Ag}]_2(\text{BF}_4)(\text{Cl})$, $[(S)\text{-}2\cdot\text{Ag}]_3(\text{BF}_4)_3$, $[(S)\text{-}2\cdot\text{Ag}]_3(\text{PF}_6)_3$, $[(R)\text{-}2\cdot\text{Ag}]_3(\text{BF}_4)_3$, and $[(S)\text{-}3\cdot\text{Ag}]_3(\text{PF}_6)_2(\text{Cl})$ were confirmed by NMR spectroscopy, elemental analysis, ESI-TOF-Mass spectrometry, and single crystal X-ray diffraction analysis (Fig. 2 and Figs. S2, and S3, ESI†).⁹ A general view of the geometry of these complexes clearly disclosed that a small variation of the R group adjacent to the carbene center critically switches the final structure.

As shown in Fig. 2a–c, the ligand $(R)\text{-}1\cdot 2\text{HCl}$ gave rise to a C_2 -symmetrical dimeric cation framework $[(R)\text{-}1\cdot\text{Ag}]_2^{2+}$,

typically comprising nearly linear $\text{Ag}(\text{NHC})_2$ units. The plane calculations revealed that the dihedral angles between the two NHC rings connected by a 1,3-phenylene unit in $[(R)\text{-}1\cdot\text{Ag}]_2(\text{BF}_4)(\text{Cl})$ and $[(R)\text{-}1\cdot\text{Ag}]_2(\text{PF}_6)_2$ were 52.03° and 37.66° , respectively. Whereas $[(R)\text{-}1\cdot\text{Ag}]_2^{2+}$ appeared in a familiar dinuclear M_2L_2 conformation,^{3,7} both $(S)\text{-}2\cdot 2\text{HCl}$ and $(R)\text{-}2\cdot 2\text{HCl}$ created a C_3 -symmetrical, trinuclear cyclic foldamer (Ag_3L_3), which encapsulated two counteranions into the cavity (Fig. 2d–k). These novel coordination structures were built from three $[2\cdot\text{Ag}]^+$ subunits in a head-to-tail orientation, which were fairly different from the known trinuclear silver NHC complexes

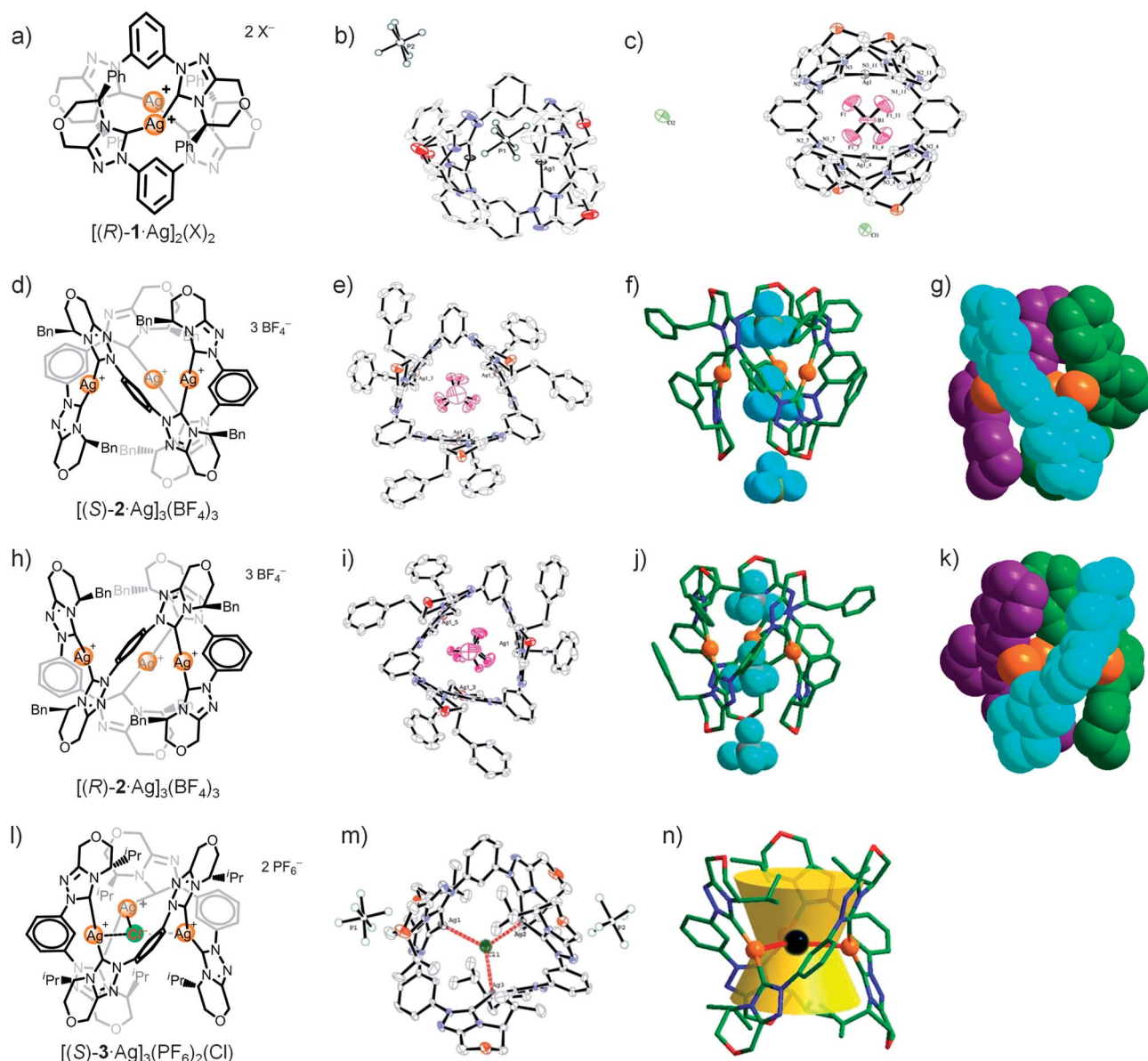


Fig. 2 a) Structural formula of $[(R)\text{-}1\cdot\text{Ag}]_2(\text{X})_2$ (X = counteranion); crystal structures of b) $[(R)\text{-}1\cdot\text{Ag}]_2(\text{PF}_6)_2$ and c) $[(R)\text{-}1\cdot\text{Ag}]_2(\text{BF}_4)(\text{Cl})$ (the site occupancy factor of chloride in the crystal unit cell is equal to 0.5); d) structural formula of $[(S)\text{-}2\cdot\text{Ag}]_3(\text{BF}_4)_3$; e) and f) crystal structures of $[(S)\text{-}2\cdot\text{Ag}]_3(\text{BF}_4)_3$; g) Spacefill Model of cation framework $[(S)\text{-}2\cdot\text{Ag}]_3^{3+}$ (the benzyl groups were omitted for clarity); h) structural formula of $[(R)\text{-}2\cdot\text{Ag}]_3(\text{BF}_4)_3$; i) and j) crystal structures of $[(R)\text{-}2\cdot\text{Ag}]_3(\text{BF}_4)_3$; k) Spacefill Model of cation framework $[(R)\text{-}2\cdot\text{Ag}]_3^{3+}$ (the benzyl groups were omitted for clarity); l) structural formula of $[(S)\text{-}3\cdot\text{Ag}]_3(\text{PF}_6)_2(\text{Cl})$; m) and n) crystal structures of $[(S)\text{-}3\cdot\text{Ag}]_3(\text{PF}_6)_2(\text{Cl})$ (two PF_6^- in n, and solvent molecules were omitted for clarity). All hydrogen atoms were omitted for clarity. Color code in b), c), e), i), and m): C (light gray), Cl (green), B and F of BF_4^- (pink), P and F of PF_6^- (indigo), N (blue), O (red), and Ag (dark gray).

like Ag_3L_2 .^{3,4c,d,10} In $[\text{2} \cdot \text{Ag}]_3^{3+}$, the dihedral angles between the two NHC rings tied by a 1,3-phenylene moiety were *ca.* 83°, and larger than those observed in $[(R)\text{-1} \cdot \text{Ag}]_2^{2+}$. In addition, $[(S)\text{-2} \cdot \text{Ag}]_3(\text{BF}_4)_3$ underwent transmetalation with $[\text{Au} \cdot \text{Cl}(\text{SMe}_2)]$ to form $[(S)\text{-2} \cdot \text{Au}]_3(\text{BF}_4)_3$ with retention of the nuclearity and geometry of the supramolecular structure (Fig. 3).⁹

The isostructural $[(S)\text{-2} \cdot \text{Ag}]_3(\text{BF}_4)_3$ and $[(R)\text{-2} \cdot \text{Ag}]_3(\text{BF}_4)_3$ showed two chiral cylindrical structures with opposite orientations of the NHC–Ag–NHC units in the crystal structures (comparing Fig. 2d–g with 2h–k), and the mirroring Cotton effect in the circular dichroism (CD) spectra (Fig. S7†).¹¹ The question then arises, what will a racemic mixture of $\text{2} \cdot \text{2HCl}$ assemble into? Interestingly, the ^1H NMR spectrum indicated that the reaction of this racemic mixture with silver oxide gave one set of signals in a simple pattern, which were in good accordance with those observed in $[(S)\text{-2} \cdot \text{Ag}]_3(\text{BF}_4)_3$ and $[(R)\text{-2} \cdot \text{Ag}]_3(\text{BF}_4)_3$ (Fig. 4). The resulting mixture was CD silent. However, bulk samples of crystals generated by careful crystallization of the mixture were CD active. The randomly picked bulk samples showed the sign and intensity of CD similar to those observed in either $[(S)\text{-2} \cdot \text{Ag}]_3(\text{BF}_4)_3$ or $[(R)\text{-2} \cdot \text{Ag}]_3(\text{BF}_4)_3$ at the same concentrations (Fig. S7†). Furthermore, the X-ray analysis revealed that the structure of bulk samples was either $[(R)\text{-2} \cdot \text{Ag}]_3(\text{BF}_4)_3$ or $[(S)\text{-2} \cdot \text{Ag}]_3(\text{BF}_4)_3$. On the basis of the above observations, it can be concluded that the coordination-driven self-assembly of a racemic mixture of $\text{2} \cdot \text{2HCl}$ was able to undergo a self-recognition and selection process according to the absolute configuration both in the formation of chiral cylindrical foldamers and the crystal growth process, giving the enantiomerically pure form in each bulk sample.

The reaction of $(S)\text{-3} \cdot \text{2HCl}$ with Ag_2O gave $[(S)\text{-3} \cdot \text{Ag}]_3(\text{PF}_6)_2(\text{Cl})$ rather than $[(S)\text{-3} \cdot \text{Ag}]_3(\text{PF}_6)_3$ even in the presence of a large excess amount of KPF_6 . In contrast to the C_3 -symmetrical structures created by $(S)\text{-2} \cdot \text{2HCl}$, $(S)\text{-3} \cdot \text{2HCl}$ gave rise to “back to back twin bowls” of C_1 -symmetrical trinuclear architecture (Fig. 2l–m, and Fig. S3, ESI†). The Cl^- anion located itself in the centroid of the encapsulator, and strongly drew the three surrounding silver ions, which led to a great deviation of the NHC–Ag–NHC angle away from the linear coordination geometry (the C–Ag–C angles were 142.8(2)°, 152.2(2)° and 159.7(2)°),^{3,12} and further drove the dihedral angles between the two NHC rings (55.46°, 56.29° and 63.81°) away from those observed in $[\text{2} \cdot \text{Ag}]_3^{3+}$ ($\sim 83^\circ$).

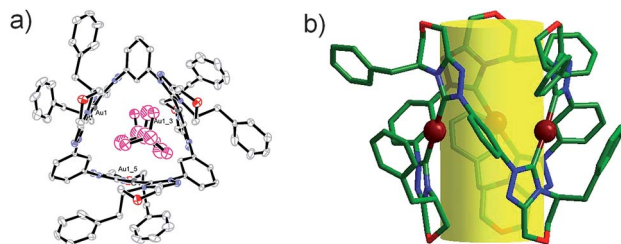


Fig. 3 X-ray crystal structures of $[(S)\text{-2} \cdot \text{Au}]_3(\text{BF}_4)_3$. All hydrogen atoms were omitted and the counteranions in b) were omitted for clarity. Color code in a): C (light gray), N (blue), B and F of BF_4^- (pink), Au (dark gray), and O (red).

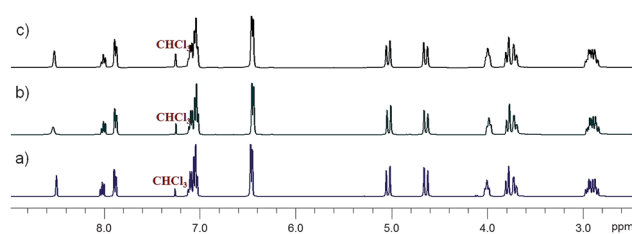


Fig. 4 ^1H NMR spectra (400 MHz, CDCl_3): a) $[(S)\text{-2} \cdot \text{Ag}]_3(\text{BF}_4)_3$; b) $[(R)\text{-2} \cdot \text{Ag}]_3(\text{BF}_4)_3$; and c) a mixture formed by the reaction of a racemic mixture of $\text{2} \cdot \text{2HCl}$ with silver oxide in the presence of NaBF_4 .

Although much work has been devoted to synthesis, characterization and catalysis of metal–NHC complexes, there are very few reports of self-assembly in solution. In particular, only two examples, palladium CNC pincer bis(imidazolydene) complexes, have been known as low molecular-mass organogelators to date.^{13,14} Our preliminary investigations demonstrated that an addition of 10 equivalents of tetrabutylammonium chloride (TBACl) could drive a clear solution of $[(S)\text{-2} \cdot \text{Ag}]_3(\text{BF}_4)_3$ or $[(R)\text{-2} \cdot \text{Ag}]_3(\text{BF}_4)_3$ in $\text{CH}_3\text{Cl}/\text{EtOAc}$ (1/10, v/v) to form an opaque gel after aging at room temperature for 24 h, indicating that the counteranions performed a crucial role in the hierarchical assembly of $[\text{2} \cdot \text{Ag}]_3(\text{X})_3$ (X = counteranion) (for ^1H NMR spectral changes, see Fig. S8†).^{15,16} The exciting phenomenon inspired us to further examine the aggregation behavior of $[(S)\text{-2} \cdot \text{Ag}]_3(\text{X})_3$ with different counteranions. Subsequently, we found that $[(S)\text{-2} \cdot \text{Ag}]_3(\text{X})_3$ (X = Cl and/or AgCl_2 , CH_3CO_2 , CF_3CO_2) could also give semitransparent gels in a series of solvents (Table S2†), whereas $[(S)\text{-2} \cdot \text{Ag}]_3(\text{X})_3$ with weakly-coordinating anions such as BF_4^- and PF_6^- preferred to yield a white suspension.¹⁷

A TEM micrograph clearly illustrated that $[(S)\text{-2} \cdot \text{Ag}]_3(\text{BF}_4)_3$ aggregated into disparate particles in DMF/PrOH (2/98, v/v) (Fig. 5a). In sharp contrast, the self-assembled texture of the isopropanol gel of $[(S)\text{-2} \cdot \text{Ag}]_3(\text{X})_3$ (X = Cl and/or AgCl_2) showed a random network of entangled fibers with an average diameter of *ca.* 15 nm (Fig. 5b). In the case of isopropanol, the critical gel concentration was 0.5 wt%, and $[(S)\text{-2} \cdot \text{Ag}]_3(\text{X})_3$ (X = Cl and/or AgCl_2) may be considered as a “supergelator” accordingly. The TEM images obtained from acetone gels of $[(S)\text{-2} \cdot \text{Ag}]_3(\text{CH}_3\text{CO}_2)_3$ and $[(S)\text{-2} \cdot \text{Ag}]_3(\text{CF}_3\text{CO}_2)_3$ displayed the presence of well-grown nanorods with average diameters of *ca.* 18 nm and 12 nm, respectively (Fig. 5c–d). To gain deeper insight into the stacking structures, the gel of $[(S)\text{-2} \cdot \text{Ag}]_3(\text{CH}_3\text{CO}_2)_3$, stained or unstained, was investigated by STEM. Both images clearly show that the individual nanorods consisted of spherical nanoparticles with bright contrast projection with a diameter in the range of 2–3 nm, which was in concordance with the size of the cation framework estimated by the crystal structure of $[(S)\text{-2} \cdot \text{Ag}]_3^{3+}$ (Fig. 5e–f).

To further shed light on the plausible formation mechanism of gels, NMR spectroscopic studies of assemblies of $[(S)\text{-2} \cdot \text{Ag}]_3(\text{X})_3$ with different counteranions were carried out in CDCl_3 . The ^1H NMR spectra of $[(S)\text{-2} \cdot \text{Ag}]_3(\text{X})_3$ with relatively strong coordinating anions (*i.e.*, X = Cl and/or AgCl_2 , CH_3CO_2 , and CF_3CO_2) revealed distinct differences in chemical shift regions from those observed in $[(S)\text{-2} \cdot \text{Ag}]_3(\text{BF}_4)_3$ with a weakly coordinating anion

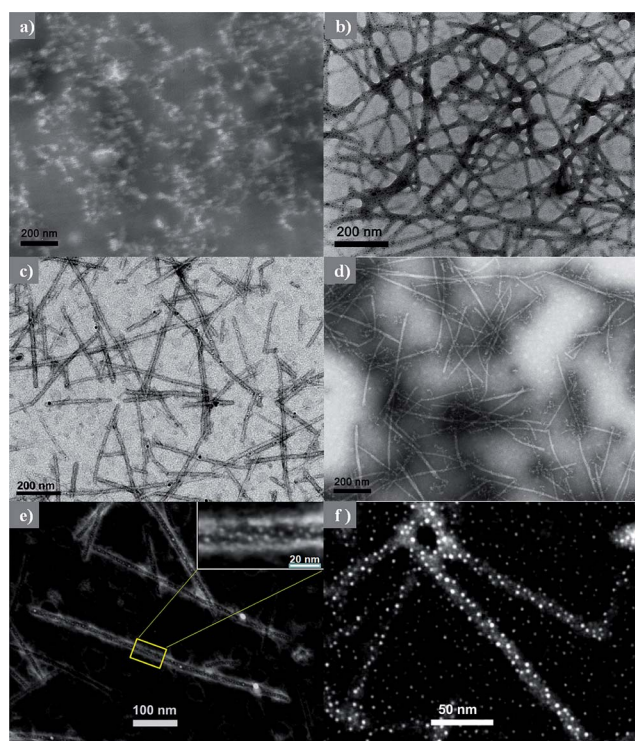


Fig. 5 a) TEM image of $[(S)\text{-}2\cdot\text{Ag}]_3(\text{BF}_4)_3$ (2 wt%) obtained in DMF/PrOH (2/98, v/v), stained with 1% aqueous phosphotungstic acid. b) TEM image of gel of $[(S)\text{-}2\cdot\text{Ag}]_3(\text{X})_3$ ($\text{X} = \text{Cl}$ and/or AgCl_2) (0.5 wt%) in PrOH, stained with 1% aqueous BaCl_2 . c) TEM image of gel of $[(S)\text{-}2\cdot\text{Ag}]_3(\text{CH}_3\text{CO}_2)_3$ (1 wt%) in acetone, stained with 1% aqueous uranyl acetate. d) TEM image of gel of $[(S)\text{-}2\cdot\text{Ag}]_3(\text{CF}_3\text{CO}_2)_3$ (2 wt%) in acetone, stained with 1% aqueous phosphotungstic acid. e) and f) STEM images of gel of $[(S)\text{-}2\cdot\text{Ag}]_3(\text{CH}_3\text{CO}_2)_3$ (1 wt%) in acetone, stained with 1% aqueous uranyl acetate, and unstained, respectively. The inset shows a zoomed-in image marked in e).

(Fig. S9†; for a detailed description, see ESI, Section IX†), suggesting significant differences in cation-anion interactions and noncovalent interactions of neighboring cation frameworks. Subsequently, we further investigated the orientation of counteranions in the conglomerate by the ^{19}F and ^1H NMR spectrum. The ^{19}F NMR spectrum of $[(S)\text{-}2\cdot\text{Ag}]_3(\text{BF}_4)_3$ (Fig. 6a), incapable of gelating solvents, clearly showed two fluorine atom environments at a 2 : 1 ratio consistent with the solid-stacking state (Fig. 2e–f), whereas the ^1H NMR spectrum of $[(S)\text{-}2\cdot\text{Ag}]_3(\text{CH}_3\text{CO}_2)_3$ and the ^{19}F NMR spectrum of $[(S)\text{-}2\cdot\text{Ag}]_3(\text{CF}_3\text{CO}_2)_3$ strikingly demonstrated a uniform

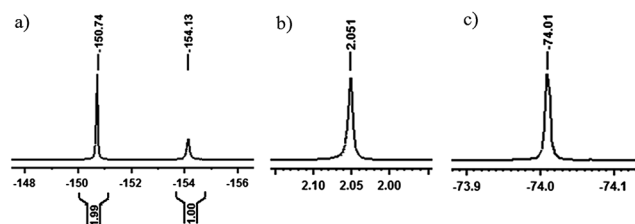


Fig. 6 The NMR spectra of the counteranions of $[(S)\text{-}2\cdot\text{Ag}]_3(\text{X})_3$ in CDCl_3 : a) $\text{X} = \text{BF}_4$ (^{19}F NMR); b) $\text{X} = \text{CH}_3\text{CO}_2$ (^1H NMR); c) $\text{X} = \text{CF}_3\text{CO}_2$ (^{19}F NMR).

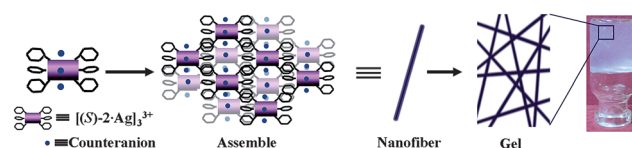


Fig. 7 A schematic representation of the self-assembly of gels.

chemical environment (Fig. 6b–c). Although the specific interactions are not completely clear at this stage, these results implied that the coordinating counteranions such as CH_3CO_2^- and CF_3CO_2^- were all homogeneously oriented outside the cavity, which might serve as the bridge to hold together the discrete cation frameworks to develop into an ordered structure through coulombic forces. These distinct aggregation behaviors (disparate particles and nanofibers) might be explained by the coordination ability of the counteranions and the number of counteranions distributed outside the cation framework (Fig. 7).

In conclusion, we have elucidated for the first time the ligand-switching and counteranion-dependent hierarchical self-assembly of chiral bis(triazol-ylidene) with the linear coordinated Ag^+ ion to construct the trinuclear, chiral cylindrical foldamer structures, which may further assemble into well-developed nanofibers capable of gelating solvents. The silver-NHC “metallo-supramolecular container” $[(S)\text{-}2\cdot\text{Ag}]_3(\text{BF}_4)_3$ can encapsulate two counteranions into the cavity, and may be transmetalated with $\text{Au}(\text{I})$ with retention of the geometry of the supramolecular structure. We foresee that these findings will open a new avenue for the design of architectural variation of metallosupramolecular assemblies and functional soft materials of metal-NHCs complexes.

Acknowledgements

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- 9 CCDC 836083 ([*(R)*-1·Ag]₂(PF₆)₂), CCDC 836084 ([*(R)*-1·Ag]₂(BF₄)(Cl)), CCDC 836085 ([*(R)*-2·Ag]₃(BF₄)₃), CCDC 836086 ([*(S)*-2·Ag]₃(BF₄)₃), CCDC 836087 ([*(S)*-2·Ag]₃(PF₆)₃), CCDC 836088 ([*(S)*-2·Au]₃(BF₄)₃), and CCDC 836089 ([*(S)*-3·Ag]₃(PF₆)₂(Cl)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif. The counteranions and solvents molecules in crystal structures of [*(S)*-2·Ag]₃(PF₆)₃ could not be precisely located in the difference maps due to their high thermal disorder. Thus, the counteranions and solvent molecules were omitted by Squeeze program, and the Squeeze results were appended to the CIF file.
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