

Self-Assembly of Silver(I) Coordination Polymers from AgX (X = BF₄[−], ClO₄[−], CF₃COO[−], and SO₃CF₃[−]) and a Rigid Bent 3,6-Dicyano-9-phenylcarbazole Ligand: The Templating Effect of Anions

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One rigid bent bridging ligand with highly planar π -conjugated spacers, 3,6-dicyano-9-phenylcarbazole (dcphcz), was designed and synthesized. The coordination reactions of dcphcz with a series of Ag^I salts with different counterions has been investigated. Four coordination polymers were obtained by solution reactions and characterized by IR, elemental analysis, and single-crystal X-ray diffraction. The solid-state structures of {[Ag(dcphcz)]BF₄}_n (**1**) and {[Ag(dcphcz)]ClO₄}_n (**2**), exhibit similar 1D “zigzag” patterns. The complex {[Ag(dcphcz)]Ag₂(dcphcz)(H₂O)₂}(SO₃CF₃)₃·C₆H₆·(H₂O)₂ (**3**) includes two different one-dimensional (1D) chain units: one forms double-layer two-dimensional (2D) metal-organic frameworks (MOFs) through intermolecular Ag–O–Ag bridging interactions, the other features double-layer 2D supramolecular networks through C–H...O

hydrogen-bonding interactions. The complex [Ag₂(dcphcz)-(CF₃COO)₂]_n (**4**) features a bundle of novel nanotubular structures, which contain silver chains formed by carboxylate spacers. Furthermore, all these complexes are connected by face-to-face π ... π stacking interactions between carbazolyl planes, affording a series of three-dimensional (3D) architectures with different structural geometries. The structural diversities of these complexes demonstrated that counteranions and bridging ligands play essential roles in the construction of supramolecular frameworks. In addition, the luminescence properties of the free ligand dcphcz and complexes **1–4** were investigated.

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Introduction

The design and synthesis of metal-organic coordination polymers have attracted intensive attention not only because of their novel topologies and intriguing structural diversity,^[1] such as nanotubes^[2] and various metal-organic frameworks (MOFs),^[3] but also because of their unique chemical and physical properties and their potential applications as optoelectronic, magnetic, and porous materials.^[4] In fact, the ultimate aim of supramolecular and coordination chemistry is to control the structure of the target products and investigate the relationship between the structures and physicochemical properties. Generally, the topology of a coordination polymer generated from the self-assembly of metals and ligands can be controlled by ingenious design of the organic ligand,^[5] selection of proper metal ions and counterion,^[6] solvent system,^[7] pH value of solution,^[8] and

the molar ratio of the reagents.^[9] On top of these factors, a bridging ligand as a “*building block*” is a pivotal point in manipulating the network structures. Because of configuration, coordination activity, and relative orientation of the donor groups, the organic spacers take important roles in determining the structure and geometry of the polymers. Rigid linear ligands have already been extensively studied^[3n,10] for designing polymers; however, bent ligands still remain a challenge in self-assembly due to their unpredictable coordination geometry.

It is well recognized that the carbazole moiety not only possesses highly planar π -conjugated systems, but also can be easily functionalized at its 3-, 6-, or 9-positions and covalently linked to other functional moieties.^[11] Furthermore, the thermal stability of organic compounds can be greatly improved upon incorporation of a carbazole moiety in the core structure.^[12] Therefore, thermally stable molecules possessing dual functions, light-emitting and hole-transporting, should be achieved by using carbazole as the central core. Currently, compounds with highly π -conjugated systems are of great interest due to their various applications in chemical sensors, molecular optical and electronic devices.^[13]

Herein, we report the design and synthesis of a new organic molecule with large angular and highly planar π -con-

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jugated spacers based on carbazole, 3,6-dicyano-9-phenylcarbazole (dcphcz). In most cases, the conformation of coordination polymers from bent bidentate ligands are hardly predictable because of the variation of coordination geometry, such as *cis*, *trans*, or intermediary.^[7,14] On the other hand, these variations also provide more chances for designing novel polymeric patterns. The ligand dcphcz does not have a conformational diversity owing to the particular structure of carbazole as the central core, neglecting the rotationality of the terminal phenyl ring of dcphcz. The coordination reactions of dcphcz and the Ag^I ion with different counterions were investigated aiming at expanding dcphcz units through the “soft” Ag^I metal ion and exploring the templating effects of counterions in the self-assembly process. It has been reported^[6b,6c,10c,15] that the –CN functional group on the aromatic ring serves as a good candidate for coordination bonding in the self-assembly of Ag-supramolecular architectures. With a d¹⁰ electronic configuration, the Ag^I ion often has irregular coordination geometries and shows a strong tendency to display versatile coordinations. Thus, the Ag^I ion is much more accommodating towards ligands and is expected to form polymer structures more readily than other d¹⁰ metal ions. At the same time, the ancillary ligation by different counterions, such as NO₃[–], BF₄[–], ClO₄[–], SO₃CF₃[–], CF₃COO[–], PF₆[–], and SbF₆[–], may cause a significant structural change of the polymer.^[6,10c,14,15] With different polymeric motifs, four new Ag-containing coordination polymers, {[Ag(dcphcz)]BF₄}_n (**1**), {[Ag(dcphcz)]ClO₄}_n (**2**), {[Ag(dcphcz)][Ag₂(dcphcz)(H₂O)₂](SO₃CF₃)₃·C₆H₆·(H₂O)₂]}_n (**3**), and [Ag₂(dcphcz)(CF₃COO)₂]_n (**4**), were synthesized based on ligand 3,6-dicyano-9-phenylcarbazole and their luminescence properties were characterized in this work.

Results and Discussion

Synthesis and Characterization

3,6-Dicyano-9-phenylcarbazole (dcphcz) was synthesized in high yield by using the modified Ullmann condensation procedure depicted in Scheme 1, where 3,6-diiodo-9-phenylcarbazole reacts with CuCN in the presence of an HMPA

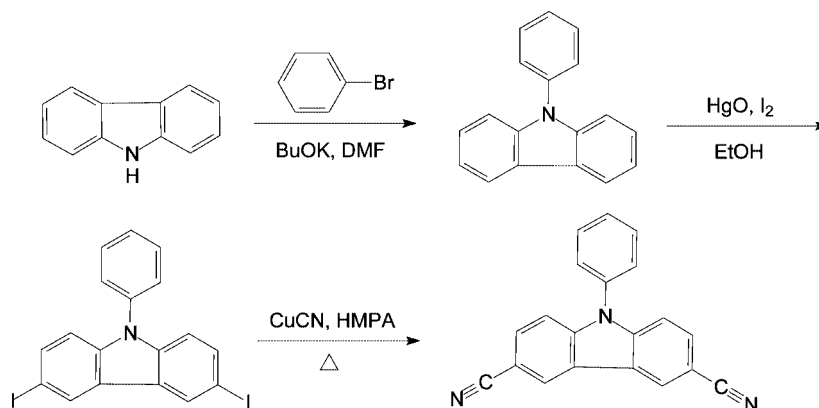
catalyst. The dcphcz is very soluble in common organic solvents, such as CH₂Cl₂, CHCl₃, THF, benzene, toluene, and CH₃CN. The slow diffusion of a CH₂Cl₂ solution of dcphcz into a benzene solution of AgX (X = BF₄[–], ClO₄[–], SO₃CF₃[–], and CF₃COO[–]) afforded a 3:2 ratio of Ag^I salt/dcphcz ligand adduct for SO₃CF₃[–] and 1:1 adducts for BF₄[–], ClO₄[–], and CF₃COO[–], which may result from the subtle templating effects of the counterions. It was observed that the products do not depend on the ligand/metal ratio; however, increasing the metal/ligand ratio resulted in somewhat higher yields and better crystal qualities. Complexes **1–4** are stable in air at room temperature only for a short time. All these complexes are insoluble in CH₂Cl₂, CHCl₃, THF, benzene, and CH₃CN, but moderately soluble in MeOH, and soluble in DMF.

The structures of the ligand dcphcz and complexes **1–4** were determined by IR and elemental analysis. The IR spectrum of ligand dcphcz and complexes **1–4** show a –CN absorption band at 2219, 2251, 2251, 2220, and 2219 cm^{–1}, respectively. The rigid bidentate or tridentate ligands containing benzonitrile groups, such as 4,4'-dicyanobiphenyl,^[15n] 2,5-bis{3-[(4-cyanophenyl)ethynyl]phenyl}-1,3,4-oxadiazole,^[7] 1,3,5-tris[(4-cyanophenyl)ethynyl]benzene,^[15n] and 1,3,5-tris{4-[(4-cyanophenyl)ethynyl]phenyl}benzene,^[15k] have shown excellent bridging action to construct porous frameworks and supramolecular polymers. However, to the best of our knowledge, no supramolecular architectures based on carbazole-containing nitrile groups have been reported.

Crystal Structures

Structural Analysis of Ligand dcphcz

The structure of dcphcz was further confirmed by single-crystal X-ray diffraction, as shown in Figure 1. The central carbazolyl group is nearly planar (with a dihedral angle of 2.9° between the two benzonitrile groups). The terminal (–CN) N···N separation is 9.631 Å, which is close to that of 1,2-bis(4-pyridyl)ethyne (9.685 Å).^[16] The terminal phenyl ring is not coplanar with the carbazolyl group, as indicated by the dihedral angle of 59.5° between the terminal phenyl



Scheme 1. Preparation of the ligand dcphcz.

plane and the five-membered ring of the carbazolyl group. Evidently, the nonplanarity of the ligand is caused by the steric hindrance between C–H groups in two phenyl rings.

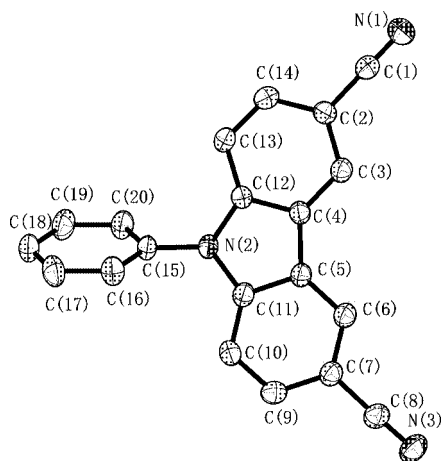


Figure 1. ORTEP diagram showing the structure of dcphez with 30% thermal ellipsoid probability and the atom-labeling scheme. Hydrogen atoms have been omitted for clarity in this and the following figures.

Figure 2 shows several intermolecular noncovalent interactions in the dcphez crystal that extends the packing in the solid-state structure. There are two kinds of C–H $\cdots$ N hydrogen-bond interactions between the –CN groups and carbazolyl groups on adjacent molecules of dcphez, which results in the formation of 1D double chains. The distances of N(1) $\cdots$ H(9) and N(3) $\cdots$ H(3) (2.620 and 2.75 Å, respectively) are significantly shorter than the sum of the van der Waals radii for nitrogen and hydrogen (ca. 1.2 Å for H, and 1.70 Å for N).^[17] The other intermolecular interac-

tion, face-to-face $\pi\cdots\pi$ stacking between terminal phenyl rings, constructs 2D networks from the 1D chain (Figure 2). At the same time, the C(3)-containing phenyl ring is involved in a moderately strong^[18] face-to-face π -stacking interaction with its symmetry-related equivalent, with an interplane distance of 3.47 Å. Thus, the dual interactions of π -stacking and H-bonding extend the 2D networks into 3D architectures.

Structural Analysis of {[Ag(dcphez)]BF₄}_n (1) and {[Ag(dcphez)]ClO₄}_n (2)

Crystallization of dcphez with AgBF₄ in a dichloromethane/benzene mixed solvent afforded **1** as an infinite 1D chain structure. As shown in Figure 3a, single-crystal analysis reveals, that there is only one Ag^I center in complex **1**. Each Ag^I ion is coordinated by two nitrogen atoms from two different dcphez ligands and two fluorine atoms from the BF₄[−] anion. The bond lengths of Ag(1)–N(1) and Ag(1)–N(3) are 2.116 and 2.119 Å, respectively. The Ag(1)–F(1) and Ag(1)–F(2) bonds (2.654 and 2.910 Å) are significantly shorter than the sum of the van der Waals radii for Ag and F (3.19 Å),^[17] which indicates the coordination between Ag^I and anion BF₄[−].

As shown in Figure 4a, the intrapolymer chain Ag $\cdots$ Ag distance is 13.378 Å. Furthermore, the 1D polymeric chain of **1** is linked into a 2D double-layer network through interpolymer C–H $\cdots$ F hydrogen-bonding interactions (Figure 5). The hydrogen-bonding system involves F(3) of the coordinated BF₄[−] counterion and H(7) and H(13) on the dcphez ligand of the neighboring chain. The F(1) $\cdots$ H(7) and F(1) $\cdots$ H(13) contacts are 2.398 and 2.563 Å, respectively. The corresponding C(7)–H(7) $\cdots$ F(1) and C(13)–H(13) $\cdots$ F(1) angles are 158.36° and 155.18°, respectively.

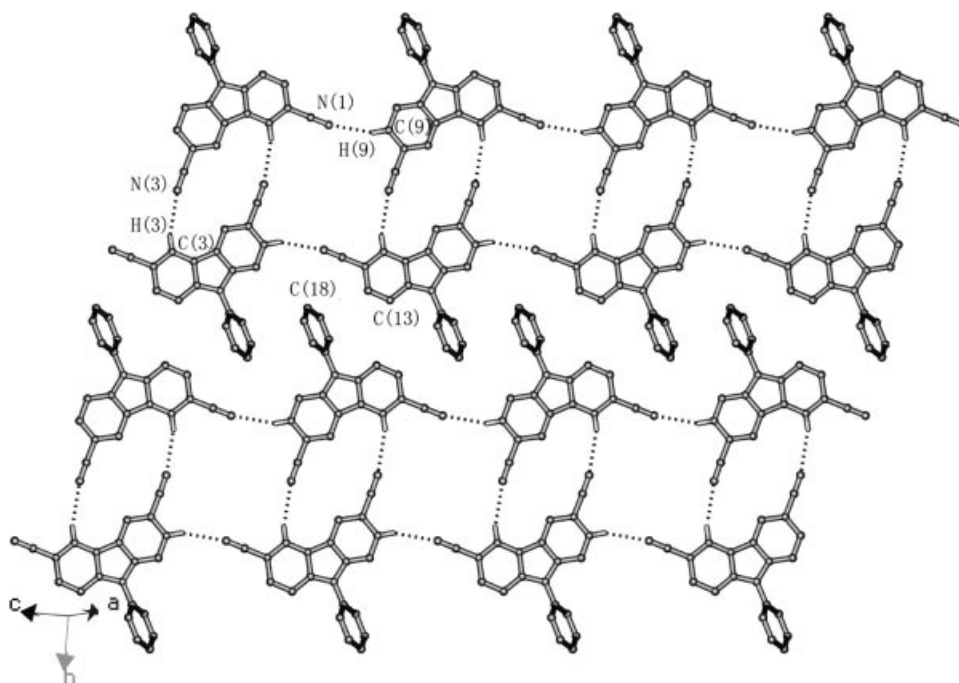


Figure 2. 2D network of dcphez, showing the π -stacking interactions between the phenyl rings and weak C–H $\cdots$ N hydrogen-bond interactions.

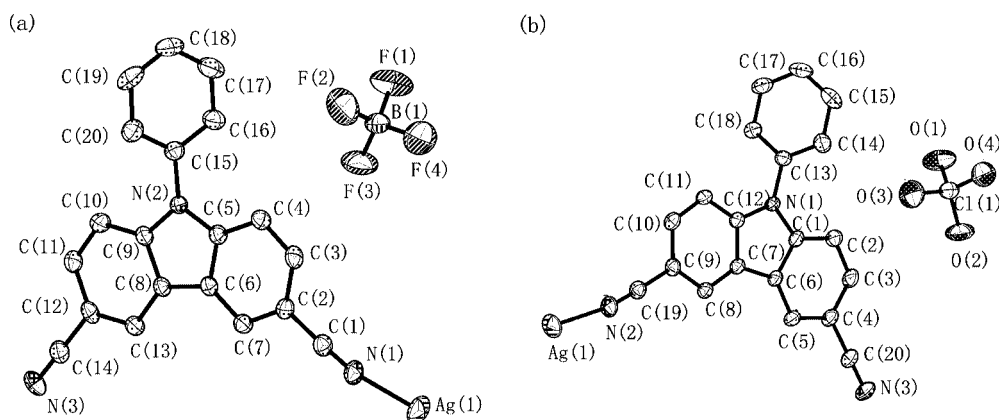


Figure 3. ORTEP diagram showing the structures of **1** (a) and **2** (b), respectively, with 30% thermal ellipsoid probability and the atom-labeling scheme.

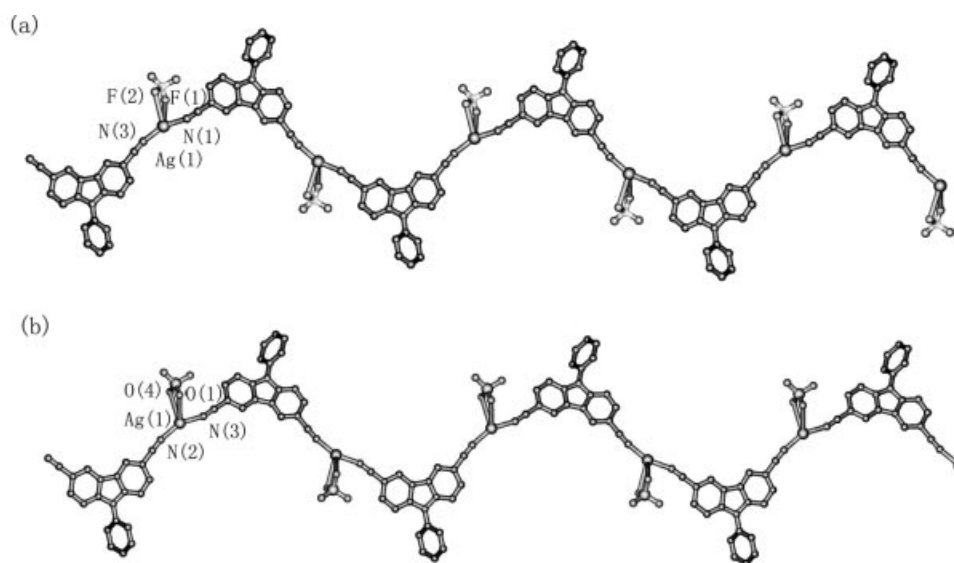


Figure 4. View of one-dimensional "zigzag" chain of **1** (a) and **2** (b).

The existence of weak C–H···X (X = F, Cl, Br, I, O, S, and N) hydrogen-bonding interactions are observed in many compounds and the structural importance is well established.^[11b,11c,15d–15j,19] These weak hydrogen bonds often contribute significantly to the alignment of the supramolecular structures in the crystalline state. In complex **1**, the BF₄[−] anion contributes to the packing of the complex by coordinating the Ag^I center in one chain and hydrogen-bonding to the F atoms in the neighboring chain. These 2D double-layer networks stack in the *ac* plane through π ··· π interactions between the lateral carbazolyl planes with an interplane distance of 3.391 Å. Of course, there is also a face-to-face π ··· π stacking in 2D double-layer networks with an interplane distance of 3.357 Å. Undoubtedly, these π -stacking interactions serve as important driving forces to cross-link the 2D double-layer networks into a 3D architecture. Some examples have shown that the organic ligands involved in the nucleation process use both coordination and π ··· π interactions to construct the framework.^[6b,20]

The other 1D zigzag chain **2** was obtained in a similar way to **1** by using AgClO₄ in place of AgBF₄. The two complexes have very similar coordination features with two dphcz chelating ligands (Figure 3b and Figure 4b), while the ClO₄[−] anion takes the place of BF₄[−] with two coordinating O atoms. The Ag–N bond lengths are close to those in complex **1**, whereas the two Ag–O bonds are somewhat longer (2.636 and 2.847 Å) than Ag–F and within the typical Ag–O bond lengths as reported previously.^[11c] The N(1)–Ag(1)–N(3) bond angle (154.02°) and the intrapolymer Ag···Ag distance (13.257 Å) are similar to those in complex **1**. Obviously, the structural similarity of **1** and **2** is generated by the similar nature of the anions (BF₄[−] and ClO₄[−]).

Recently, Ag-supramolecular complexes have been reported^[6,10c,14,15,21] based on bent organic ligands with pyridyl, cyano, aminophenyl, and acetylenylphenyl groups as the terminal coordination sites. However, these bent organic ligands exhibit potentially diverse conformations on coordi-

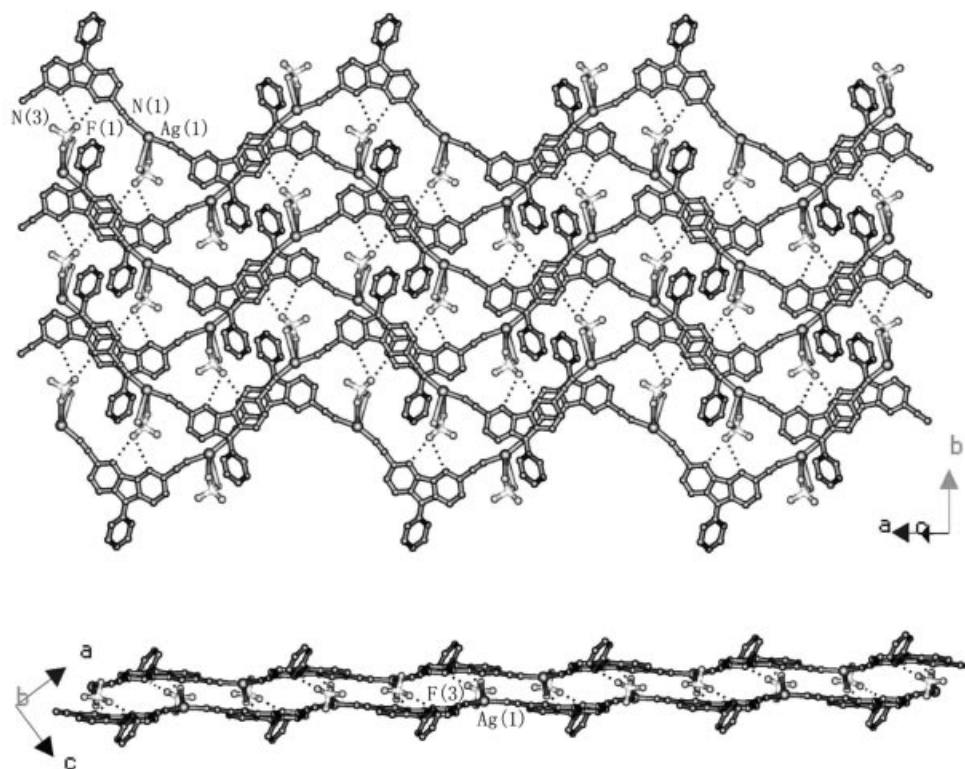


Figure 5. Top (top) and side (bottom) views of two-dimensional double-layer supramolecular networks of **1** stacked together through multiple C–H $\cdots$ F hydrogen-bonding interactions and face-to-face $\pi\cdots\pi$ stacking interactions ($d_{\pi-\pi} = 3.357$ Å).

nation; while dcphez has a conformation suitable for coordinating to metal centers retaining the bending geometry, making it easy to control and predict the structure and geometry of the resulting polymers.

Similar to complex **1**, a double-layer architecture is formed through multiple C–H $\cdots$ O hydrogen bonding [O(2) $\cdots$ H(5) 2.594 Å, C(5)–H(5) $\cdots$ O(2) 155.75°; O(2) $\cdots$ H(8) 2.395 Å, C(8)–H(8) $\cdots$ O(2) 159.68°]. The parallel carbazole rings from adjacent chains are paired to furnish face-to-face $\pi\cdots\pi$ stacking with an interplane distance of 3.349 Å, which extends the 2D network into 3D supramolecular architectures along the *ac* plane.

Structural Analysis of $\{[Ag(dcphez)][Ag_2(dcphez)(H_2O)_2](SO_3CF_3)_3\cdot C_6H_6\cdot (H_2O)_2\}_n$ (**3**)

Bright yellow single crystals of **3** were obtained by slow diffusion of a benzene solution of $AgSO_3CF_3$ into a CH_2Cl_2 solution of dcphez. Single-crystal analysis reveals that there are three independent Ag^I centers in **3**. The ligand dcphez has a similar coordination mode in this complex relative to **1** and **2**, however, the different property of the anion alters the molecular architectures in **3**. Atoms Ag(1) and Ag(2) expand the dcphez units into two independent zigzag chains a and b, respectively, whereas atom Ag(3) is locked in the chain b through a peculiar Ag–C interaction to the phenyl ring (Figure 6). The Ag–N bond lengths in the two chains are all within the range typical for Ag–N bond lengths,^[15] though it is slightly longer in chain a [Ag(1)–N(3) 2.134 Å; Ag(1)–N(4) 2.148 Å] than in chain b [Ag(2)–N(1) 2.098 Å; Ag(2)–N(2) 2.119 Å]. The Ag(1) center in chain a also

weakly coordinates to an anionic oxygen atom [Ag(1)–O(2) 2.803 Å], and a water oxygen atom [Ag(1)–O(11) 2.738 Å], showing tetrahedral coordination geometry with an N(3)–Ag(1)–N(4) bond angle of 174.4°. While Ag(2) in the chain b center only weakly coordinates to an anionic oxygen atom [Ag(2)–O(9) 2.660 Å], showing T-shaped coordination geometry with an N(1)–Ag(2)–N(2) bond angle of 166.3°. Although these Ag–O distances are relatively long, they are all significantly shorter than the sum of the van der Waals radii for silver and oxygen (3.24 Å).^[17] The intrapolymer Ag $\cdots$ Ag distances are 12.559 and 12.308 Å for chains a and b, respectively, which are shorter than those of complexes **1** and **2**. Interestingly, a solvent benzene molecule is located in chain b through weak Ag $\cdots$ C interactions with the nearest Ag $\cdots$ C distance of 2.959 Å.

Sitting on the flank of chain a, Ag(3) has a coordination environment different to those of atoms Ag(1) and Ag(2). In addition to the coordination of two water molecules, Ag(3) has a strong interaction with a terminal phenyl ring from chain a. The Ag(3) atom sits above the phenyl rings and slightly off the center, resulting in a shortest Ag–C_{benzene} distance of Ag(3)–C(17) (2.523 Å) which is still within the normal range for Ag–C bond lengths (2.47–2.76 Å), while the remaining Ag–C distances [Ag(3) $\cdots$ C(16) 2.852 Å; Ag(3) $\cdots$ C(18) 2.889 Å] are beyond the limits commonly observed in Ag^I -aromatic complexes.^[14,15f–15j,22] Thus, it is concluded that the benzene ring coordinates to the Ag(3) ion with an η^1 -bonding mode. The η^1 -type interaction between the Ag^I ion with a phenyl ring has already been observed in many complexes,^[14,15j] although it is less

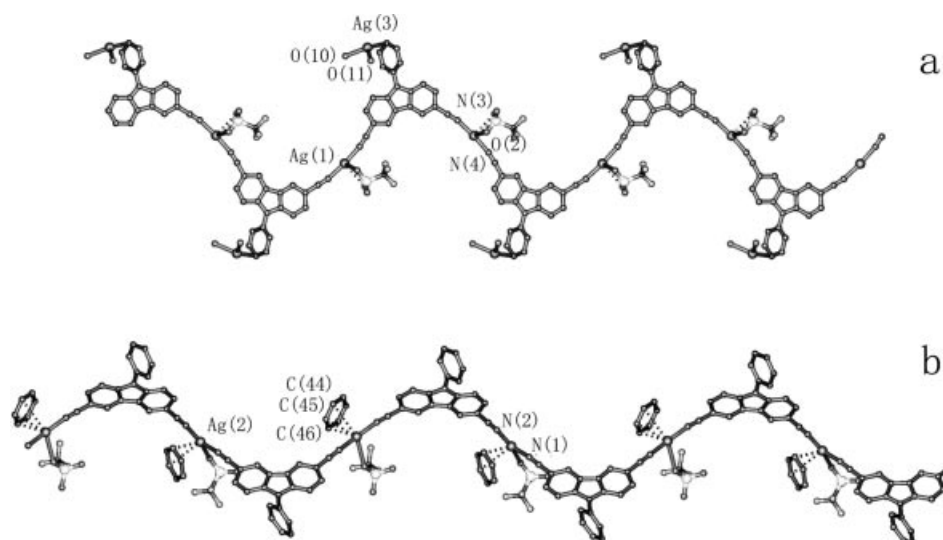


Figure 6. Views of the “zigzag” chains a (top) and b (bottom) in complex 3.

common than the η^2 -type interaction in which the metal ion interacts with one edge of the phenyl ring.

As shown in Figure 7, the packing style of **3** from chains a and b is different from **1** and **2**. Chains a extend along the crystallographic *b* axis and generate a 2D double-layer metal–organic framework containing irregular channels through Ag–(μ -O_{water})–Ag and Ag–(μ -SO₃CF₃)–Ag bridging and face-to-face π – π stacking with an interplane distance of 3.552 Å. Chains b link together into a 2D double-layer supramolecular network through interpolymer C–H...

O interactions [O(7)···H(30) 2.436 Å, C(30)–H(30)–O(7) 138.23°; O(9)···H(34) 2.656 Å, C(34)–H(34)–O(9) 125.35°] and face-to-face π – π stacking between adjacent b chains with an interplane distance of 3.485 Å (Figure 8). Consequently, chains a and b stack in an ...ABC... sequence along the *a* axis in complex **3**. The parallel carbazole rings from adjacent chains a and b are also paired to furnish π – π stacking with a centroid–centroid distance of 3.879 Å and a dihedral angle of 8.4°, which extend two 2D networks into a 3D architecture along the *ac* plane (Figure 9). In ad-

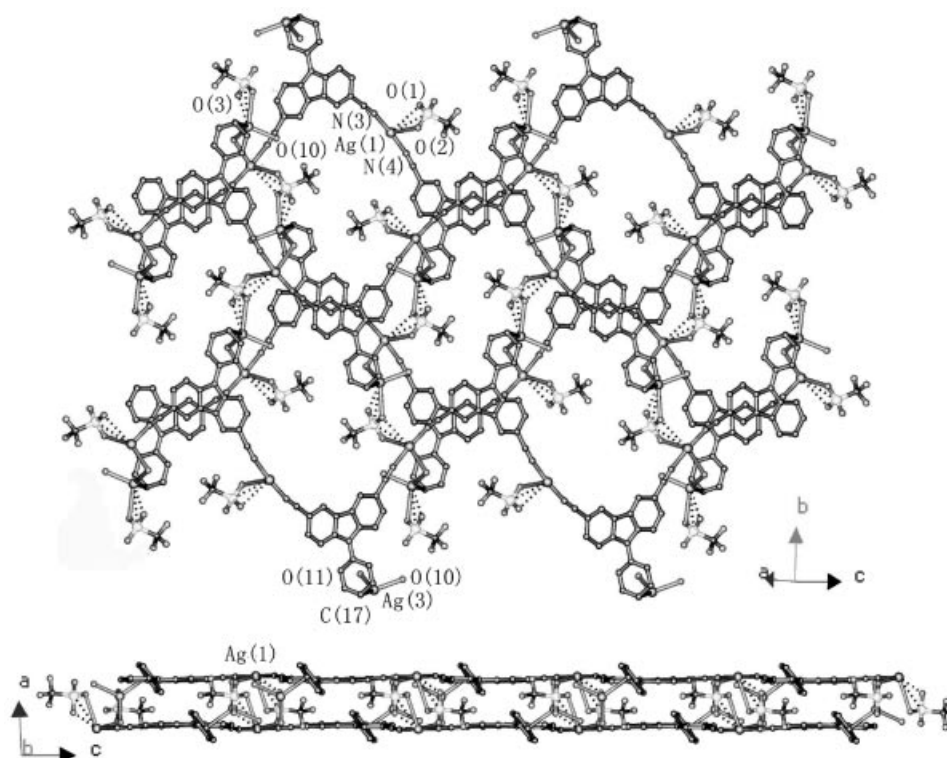


Figure 7. Top (top) and side (bottom) views of 2D double-layer metal–organic frameworks (MOFs) of chain a stacked together through μ -O and μ -SO₃CF₃ bridging and face-to-face π – π stacking interactions ($d_{\pi-\pi}$ = 3.552 Å).

dition, the chains a and b are also linked through interpolymer $O\cdots H$ hydrogen-bonding interactions. The $O(8)\cdots H(10A)$ distance of 1.945 Å and the $O(8)\cdots H(10A)-O(10)$ angle of 162.67° indicate a very strong hydrogen-bonding interaction. To the best of our knowledge, it is the first example that independent 2D + 1D polymers coexist in one crystal without mutual interpenetration. The shortest interchain $Ag(1)\cdots Ag(2)$ separation is 3.593 Å between chains a and b, which is slightly longer than the sum of the van der Waals radii of two silver atoms, 3.44 Å. It can be concluded from the architecture of the three complexes that the counterions (polar $SO_3CF_3^-$ vs. nonpolar ClO_4^- and BF_4^-) play a key role in determining the polymeric structures of complex 3.

Structural Analysis of $[Ag_2(dcpchz)(CF_3COO)_2]_n$ (4)

In order to further investigate the effect of the counterion on the long-range order of the Ag^I -dcpchz coordination

polymer, the more strongly coordinating $CF_3CO_2^-$ anion was used instead of the weakly coordinating BF_4^- , ClO_4^- , and $SO_3CF_3^-$ anions. Yellowish crystals of 4 were obtained.

Single-crystal X-ray analysis of 4 reveals a novel two-dimensional nanotube from two different crystallographic silver(I) centers. As shown in Figure 10, each $Ag(1)$ center is coordinated by two nitrogen atoms of $-CN$ groups and two oxygen atoms from two different $CO_2CF_3^-$ anions, resulting in a severely distorted tetrahedral environment, with the angles around the $Ag(1)$ center ranging from 98.1 to 150.05°. The $Ag(1)-N(1)$ and $Ag(1)-O(1)$ bond lengths are 2.371 and 2.263 Å, respectively, while the coordination sphere around each $Ag(2)$ center is composed of four oxygen atoms from four $CO_2CF_3^-$ anions with two different $Ag-O$ distances (2.235 and 2.570 Å). Thus, the final coordination geometry around the $Ag(2)$ center is irregular with bond angles ranging from 75.30 to 163.84°. The $Ag(1)$ and

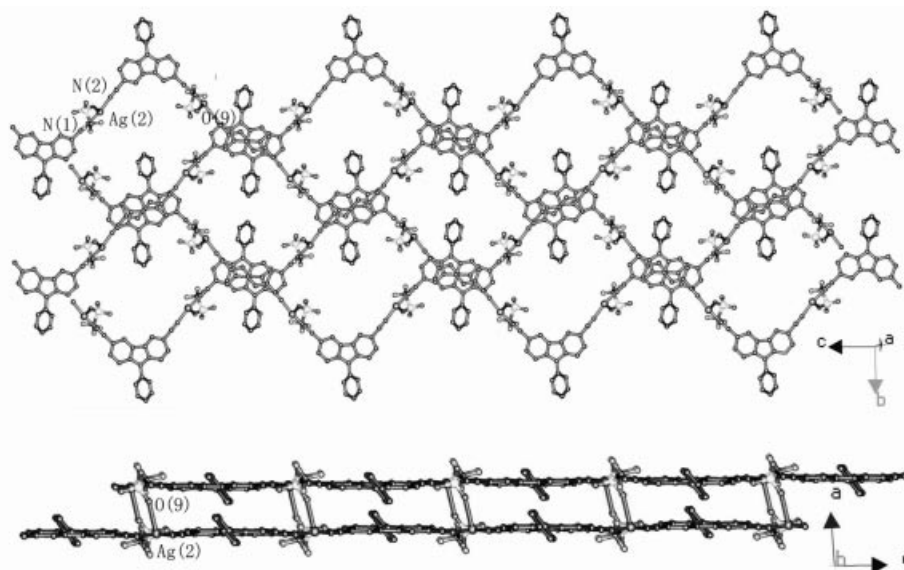


Figure 8. Top (top) and side (bottom) views of two-dimensional double-layer supramolecular networks of chain b stacked together through multiple $C-H\cdots O$ hydrogen-bonding interactions and face-to-face $\pi\cdots\pi$ stacking interactions ($d_{\pi-\pi} = 3.485$ Å).

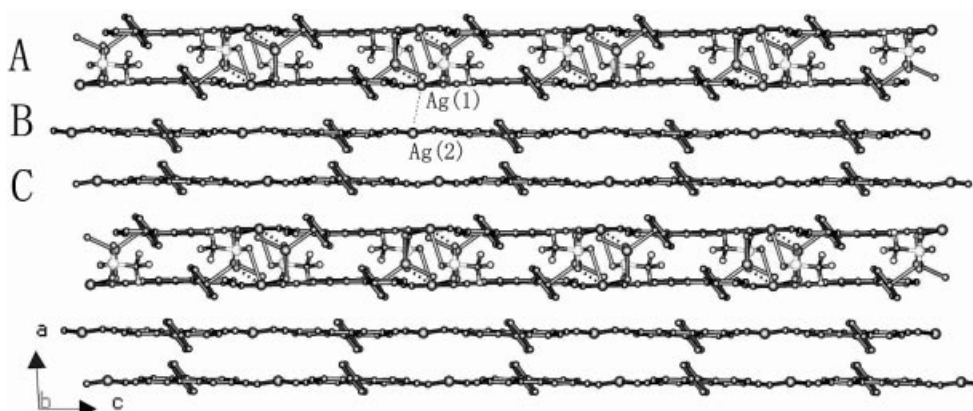


Figure 9. View of the packed structure (parallel to ac plane) in complex 3, showing ...ABC... packing sequence of chains a and b in the crystal lattice. Some of the $SO_3CF_3^-$ anions, water, and benzene molecules have been omitted for clarity in this figure.

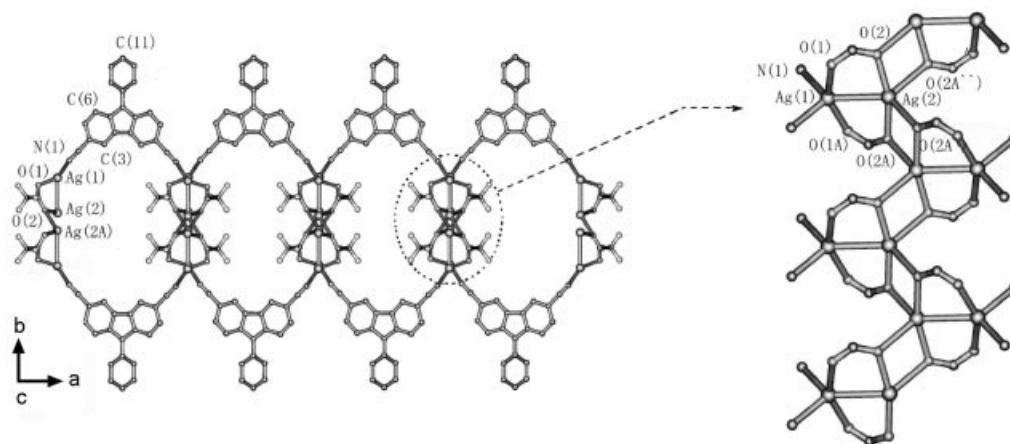


Figure 10. Perspective view of **4**, showing a one-dimensional macrocycle-containing chain.

Ag(2) atoms are bridged by two carboxyl groups with an Ag–Ag distance of 2.992 Å, which is slightly longer than for metallic silver (ranging from 2.803 to 2.987 Å) and shorter than for other reported ligand-unsupported Ag–Ag distances (ranging from 3.011 to 3.655 Å).^[14,23] To form the nanotube, each carboxyl group of CF_3CO_2^- connects to three Ag atoms through its two oxygen atoms: one oxygen atom bridges two Ag atoms, while another oxygen atom attaches to the third Ag atom. Therefore, CF_3CO_2^- acts as a μ_2 -bridge and links two Ag(2) units, resulting in linear distorted ladder-like Ag chains. The ligand dphcz is therefore bridged by Ag(1) atoms, producing a condensed nanotubular structure with dimensions of about 12×13 Å. The adjacent nanotubes are in line through multiple Ag–O_{carbonyl} bonding (Figure 11). Of course, the whole structure can also be regarded as parallel Ag chains linked by dphcz spacers.

Analogously, adjacent 2D architectures containing 1D open channels along the *c* axis direction stack in the *ab* plane through noncovalent face-to-face $\pi \cdots \pi$ interactions

between the carbazoyl planes of dphcz ligands with an interplane distance of 3.355 Å for **4**. However, the open channels are fully filled with the terminal phenyl group of dphcz from adjacent 2D units. These noncovalent interactions serve again as important driving forces for cross-linking the 2D structure into a 3D architecture.

The different polymeric motifs from the four complexes indicate that the counteranions and bridging ligands are two crucial factors in designing the structure and geometry of the self-assemblies. The properties of the bridging ligands, such as π -conjugated spacers and relative orientation of the donor groups, take important roles in controlling the structural topologies of their metal–organic supramolecular architectures. In this system, the coordination conformation of dphcz is special because of the conformational irrotationality around the central five-membered ring of the carbazoyl group. Thus, the architecture of the complexes depends greatly on the counterions. Furthermore, $\pi \cdots \pi$ stacking between carbazole rings is the basis of the 3D architectures in the complexes **1–4**.

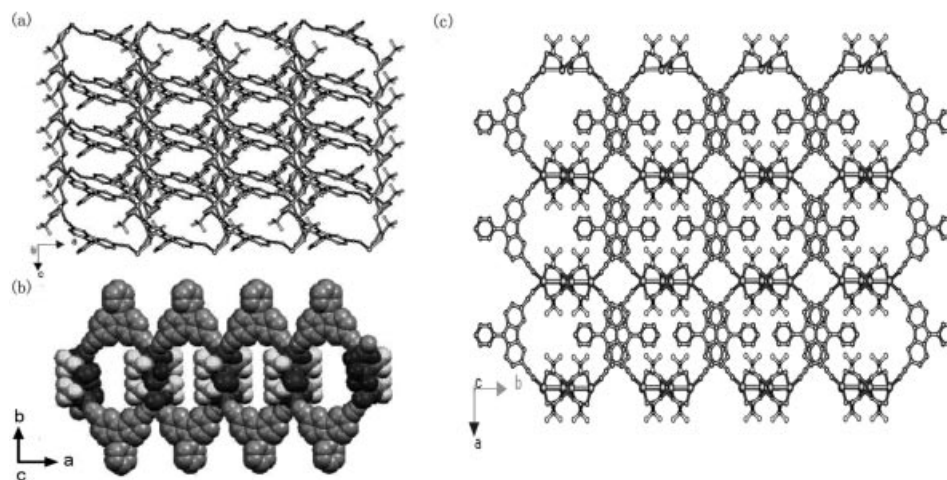


Figure 11. (a) View of two-dimensional nanotubal structure in **4** along the *ac* plane. (b) Space-filling representation of the 2D nanotubal polymer along the *c* axis. (c) View of supramolecular networks of **4** stacked together through face-to-face $\pi \cdots \pi$ stacking interactions ($d_{\pi-\pi} = 3.355$ Å).

Thermogravimetric Analysis

Thermogravimetric analysis of compound **3** was performed by heating the complex from 20 to 600 °C under N₂. The TGA curve for complex **3** showed that the first major weight loss of the lattice benzene occurred between 40 and 100 °C by 5.10% weight (calcd. 7.38%), which indicates that benzene molecules could easily escape from the crystal lattice of **3**. As shown in Figure S14, further thermogravimetric data shows the second major weight loss of the four water molecules between 110 and 145 °C by 4.11% weight (calcd. 4.78%).

Luminescent Properties

For potential applications as luminescent materials,^[24] fluorescence properties have been investigated in metal–organic coordination polymers. Because of their ability to affect the emission wavelength of organic materials, syntheses of inorganic–organic coordination polymers have employed the ingenious design of conjugated organic ligands and judicious choice of proper metal centers in order to obtain new types of luminescent materials,^[25] especially for d¹⁰ metal systems^[13c,13d,26] and highly conjugated ligand-containing complexes.^[11,13c,27] We have explored the luminescent properties of 3,6-bis(2,2'-dipyridylamino)-9-phenylcarbazole and its Ag^I coordination polymer.^[11c] The results indicated that the emission color of organic spacers ddpapcz was remarkably affected by Ag coordination compounds. Herein, the luminescent properties of 3,6-dicyano-9-phenylcarbazole and its metal complexes **1–4** were investigated.

The UV/Vis spectra of ligand dcpchz and complexes **1–4** display two intense absorption bands from $\pi \rightarrow \pi^*$ electronic transitions (from 230 to 290 nm), which originate from the carbazolyl groups (Figure S15). No difference in emission colors has been observed between free ligand and complexes in methanol, which has a broad fluorescent emission band (from 340 to 420 m), with $\lambda_{\text{max}} = 367$ nm (Figure S16). This probably implies that the polymeric complexes disaggregate in methanol solution. The dissociation of Ag-supramolecules in solvent has been reported in many other samples.^[11c,14]

Despite the similarity of emission bands in solution, the emission bands of five compounds in the solid state are significantly different (Figure S17). A very strong emission of the free ligand dcpchz with a wavelength from 375 to 575 nm ($\lambda_{\text{max}} = 404$ nm) upon excitation at 330 nm is observed, which has a redshift relative to the solution state. This can be explained by the extensive $\pi \cdots \pi$ stacking in the solid state, which is between the carbazolyl planes of one dcpchz and the neighboring molecules with an interplane distance of 3.47 Å. This $\pi \cdots \pi$ stacking lowers the excited energy of dcpchz in the solid state and causes the redshift of emission energy relative to the solution, in which the carbazolyl stacking could not exist.

Blue/green luminescence is observed with the coordination to the silver center. In the solid state, complexes **1–3**

show broad emission bands at 499 (**1**), 515 (**2**), and 492 nm (**3**), respectively, upon 330 nm excitation, whereas **4** has also a very broad emission band (bandwidth at half-height = 110 nm) with $\lambda_{\text{max}} = 425$ nm, which is in the blue region and yields visible blue luminescence. Thus, complex **4** may have potential applications as a luminescent material in organic light-emitting devices. Generally, the intraligand fluorescence emission wavelength is determined by the energy gap between π and π^* molecular orbitals of the free ligand, which is related to the extent of π conjugation in the system.^[28] Since the emission peak positions of complex **4** almost corresponded to that of the ligand dcpchz, they should be due to neither ligand-to-metal nor metal-to-ligand charge transfer and can be ascribed to the intraligand $\pi \rightarrow \pi^*$ charge transfer of dcpchz. All these complexes exhibited relatively weak emissions, which may be a result of the heavy-atom effect of silver.^[29]

It is clear that significantly different emission in **1–4** is due to the variation of anions and coordination environments, because photoluminescence behaviors closely associate with the local environments around metal ions.^[20a,30] In **1** and **2**, the anions BF₄[−] and ClO₄[−] are similar in nature and also display similar weak coordination to Ag^I. Complex **3** has two 1D chain units, which are similar to those in **1** and **2**, and the anion CF₃SO₃[−] also weakly coordinates to Ag^I although it has properties different from those of BF₄[−] and ClO₄[−]. In contrast, each Ag^I ion in complex **4** is strongly coordinated by O atoms of CF₃CO₂[−] and provides a coordination geometry different from those of **1–3**.

Conclusions

Four Ag^I-dcpchz coordination polymers with one-, two-, and three-dimensional supramolecular structures have been successfully prepared by the reaction of dcpchz and Ag^I salts with different counterions in solution. The roles of the counteranions in determining the molecular structures of the coordination polymers have been exhibited. The nature of the anions is the underlying reason behind the differences in the structures of this series of Ag^I complexes. In complexes **1** and **2**, the weakly coordinated BF₄[−] and ClO₄[−] anions not only act as the counteranions to balance the charge but have a spatial templating effect in building up the coordination frameworks. For **3** and **4**, the bulkier CF₃SO₃[−] and CF₃CO₂[−] anions possess stronger coordination ability than BF₄[−] and ClO₄[−] and serve as linkages to bridge the 1D chains to 2D MOFs with Ag–O contacts. Moreover, the coordinated CF₃SO₃[−] and CF₃CO₂[−] ions also possess weak interactions with ligand units, probably act as templates for the formation of the network, and consequently maintain the structural stability. In addition, for the Ag^I-dcpchz system in this work, the conformation of dcpchz does not depend on the counterion and solvent system used in the formation of the complexes.

The self-assembly of the bent organic ligands with highly planar π -conjugated spacers provides a new approach for building metal–organic frameworks consisting of a 1D open

channel. We are also intrigued by the question whether the variation of the terminal group of dicyanocarbazole will lead to MOF assemblies with open channels by introducing small groups to the 9-position of the carbazole on coordination. Further work is currently ongoing in this laboratory.

Experimental Section

Materials and Methods: All starting chemicals were of reagent-grade quality, obtained from commercial sources and used without further purification. Bromobenzene was freshly distilled. Benzene was freshly distilled from sodium/benzophenone; dichloromethane was dried and distilled from P_2O_5 under nitrogen; dmf was dried and distilled from $MgSO_4$. 1H NMR spectra were recorded with a Bruker 300 Ultrashield spectrometer operating at 300 MHz. The FT-IR spectra were recorded in the region 400–4000 cm^{-1} with a Bruker EQUINOX 55 VECTOR22 spectrophotometer and the samples were prepared using KBr pellets. Elemental analyses were carried out with an Elementar Vario EL-III analyzer. Fluorescence measurements were carried out with a JOBIN YVON Analytical Instrument FLUOROLOG-3-TAU at room temperature. Thermogravimetric analyses (TGA) were performed with a TGA-50H thermoanalyzer under N_2 (in the temperature range 20–600 °C) at a heating rate of 10 °C/min. 9-Phenylcarbazole and 3,6-diiodo-9-phenylcarbazole were synthesized according to procedures reported earlier.^[11c,31]

Caution! One of the crystallization procedures involves $AgClO_4$, which is a strong oxidizer.

Synthesis of 3,6-Dicyano-9-phenylcarbazole (dcphcz): A mixture of 3,6-diiodo-9-phenylcarbazole (0.99 g, 0.002 mol) and $CuCN$ powder (0.448 g, 0.005 mol) in HMPA (10 mL) was stirred under the protection of dry nitrogen at 160 °C for 6 h. The reaction mixture was cooled to ambient temperature, poured into aqueous $NaHCO_3$ (10%) and extracted with dichloromethane. The aqueous phase was discarded, the organic layer was washed with distilled water to neutral pH, dried with $MgSO_4$ and concentrated in vacuo. The residue was filtered to give the desired compound as a primrose solid. Yield: 0.55 g, 93%. IR (KBr): $\tilde{\nu}$ = 2219 (vs), 1631 (m), 1595 (s), 1502 (s), 1480 (s), 1455 (m) 1369 (m), 1292 (s), 1243 (s), 1185 (m) cm^{-1} . 1H NMR (300 MHz, $CDCl_3$): δ = 8.48 (d, 2 H), 7.75–7.71 (d, 4 H), 7.68–7.60 (d, 1 H), 7.49–7.52 (d, 2 H), 7.42–7.44 (d, 2 H) ppm.

Synthesis of $\{[Ag(dcphcz)]BF_4\}_n$ (1): Upon a solution of dcphcz (0.0586 g, 0.2 mmol) in 5 mL of dichloromethane was successively layered a solution of $AgBF_4$ (0.0390 g, 0.2 mmol) in benzene (4 mL). The vial was covered with aluminum foil and the solvents were allowed to diffuse slowly. Bright yellow crystals suitable for X-ray structure analysis were obtained several days later. Yield: 0.0517 g, 53%. IR (KBr): $\tilde{\nu}$ = 2251 (vs), 1631 (m), 1591 (s), 1492 (s), 1362 (m), 1294 (s), 1244 (s), 1187 (m), 1063 (vs), 821 (m) cm^{-1} . $C_{20}H_{11}AgBN_3F_4$ (488.00): calcd. C 49.23, H 2.273, N 8.611; found C 49.31, H 2.274, N 8.620.

Synthesis of $\{[Ag(dcphcz)]ClO_4\}_n$ (2): Upon a solution of dcphcz (0.0586 g, 0.2 mmol) in 5 mL of dichloromethane was successively layered a solution of $AgClO_4$ (0.0414 g, 0.2 mmol) in benzene (5 mL). The vial was covered with aluminum foil and the solvents were allowed to diffuse slowly. Bright yellow crystals suitable for X-ray structure analysis were obtained several days later. Yield: 0.0651 g, 65%. IR (KBr): $\tilde{\nu}$ = 2251 (vs), 1628 (m), 1592 (s), 1501 (s), 1479 (s), 1367 (m), 1295 (s), 1245 (vs), 1188 (m), 1092 (vs) cm^{-1} .

$C_{20}H_{11}AgClN_3O_4$ (500.6): calcd. C 47.98, H 2.215, N 8.393; found C 48.09, H 2.209, N 8.401.

Synthesis of $\{[Ag(dcphcz)][Ag_2(dcphcz)(H_2O)_2](SO_3CF_3)_3 \cdot C_6H_6 \cdot (H_2O)_2\}_n$ (3): Upon a solution of dcphcz (0.0586 g, 0.2 mmol) in 5 mL of dichloromethane was successively layered a solution of $AgSO_3CF_3$ (0.0514 g, 0.2 mmol) in benzene (5 mL). The vial was covered with aluminum foil and the solvents were allowed to diffuse slowly. Bright yellow single crystals suitable for X-ray structure analysis were obtained several days later. Yield: 0.0573 g, 57%. IR (KBr): $\tilde{\nu}$ = 2220 (vs), 1632 (m), 1596 (s), 1503 (s), 1481 (s), 1456 (m) 1369 (m), 1245 (vs), 1176 (vs), 1034 (vs) cm^{-1} . $C_{49}H_{36}Ag_3F_9N_6O_{13}S_3$ (1507.6): calcd. C 39.04, H 2.407, N 5.574; found C 39.01, H 2.402, N 5.583.

Synthesis of $[Ag_2(dcphcz)(CF_3COO)_2]_n$ (4): Upon a solution of dcphcz (0.0586 g, 0.2 mmol) in 4 mL of dichloromethane was successively layered a solution of CF_3COOAg (0.0442 g, 0.2 mmol) in benzene (5 mL). The vial was covered with aluminum foil and the solvents were allowed to diffuse slowly. Bright yellow single crystals suitable for X-ray structure analysis were obtained several days later. Yield: 0.0471 g, 64%. IR (KBr): $\tilde{\nu}$ = 2219 (vs), 1682 (vs), 1595 (m), 1501 (m), 1480 (m), 1292 (m), 1209 (vs), 1132 (vs) cm^{-1} .

Table 1. Selected interatomic distances [Å] and angles [°] for complexes 1–4.

Complex 1			
Ag(1)–N(1)	2.116(3)	Ag(1)–N(3)	2.119(3)
Ag(1)–F(1)	2.654	N(3)–Ag(1)–F(1)	82.77
N(1)–Ag(1)–N(3)	156.89(15)	F(1)–Ag(1)–N(1)	119.75
Complex 2			
Ag(1)–N(2)	2.112(3)	Ag(1)–N(3)	2.122(3)
Ag(1)–O(1)	2.636	Ag(1)–O(4)	2.847
N(2)–Ag(1)–N(3)	154.02(11)	O(1)–Ag(1)–N(3)	84.46
N(3)–Ag(1)–O(4)	86.06	O(1)–Ag(1)–O(4)	49.10
N(2)–Ag(1)–O(4)	115.07	N(2)–Ag(1)–O(1)	120.51
Complex 3			
Ag(1)–N(3)	2.134(5)	Ag(1)–N(4)	2.148(5)
Ag(2)–N(1)	2.098(5)	Ag(2)–N(2)	2.119(5)
Ag(3)–O(11)	2.327(6)	Ag(3)–O(10)	2.344(6)
Ag(3)–C(17)	2.523(7)	Ag(1)–O(2)	2.803
Ag(1)–O(1)	3.031	Ag(1)–O(11)	2.738
Ag(3)–O(1)	2.704	Ag(2)–O(9)	2.660
N(3)–Ag(1)–N(4)	174.4(2)	N(1)–Ag(2)–N(2)	166.3(2)
O(11)–Ag(3)–C(17)	123.5(2)	O(11)–Ag(3)–O(10)	100.56(19)
O(10)–Ag(3)–C(17)	119.9(2)	O(9)–Ag(2)–N(2)	87.04
O(9)–Ag(2)–N(1)	98.67	O(2)–Ag(1)–N(4)	86.86
O(11)–Ag(1)–O(2)	100.47	O(2)–Ag(1)–N(3)	94.99
O(11)–Ag(1)–N(4)	84.00	O(11)–Ag(1)–N(3)	90.51
Ag(1)–O(11)–Ag(3)	118.66	O(10)–Ag(3)–C(17)	119.91
O(1)–Ag(3)–C(17)	80.44	O(11)–Ag(3)–O(1)	125.53
O(10)–Ag(3)–O(1)	106.88		
Complex 4			
Ag(1)–O(1)	2.263(3)	Ag(1)–N(1)	2.371(4)
Ag(1)–Ag(2)	2.9924(7)	Ag(2)–O(2)	2.235(3)
Ag(2A)–O(2)	2.570(3)		
O(1)–Ag(1)–O(1A)	150.05(16)	O(1A)–Ag(1)–N(1A)	94.84(15)
O(1)–Ag(1)–N(1)	104.74(13)	N(1)–Ag(1)–N(1A)	98.1(2)
O(1)–Ag(1)–Ag(2)	75.02(8)	N(1)–Ag(1)–Ag(2)	130.97(11)
O(2)–Ag(2)–O(2A)	163.84(17)	O(2)–Ag(2)–O(2A')	115.94(15)
O(2A)–Ag(2)–O(2A')	75.30(12)	O(2A')–Ag(2)–Ag(1)	130.76(8)
O(2A')–Ag(2)–O(2A'')	98.48(17)	O(2)–Ag(2)–Ag(1)	81.92(9)
Ag(2)–O(2A)–Ag(2A)	104.70		

Table 2. Crystallographic data and structure refinement summary for the ligand dcphcz and complexes 1–4.

	dcphcz	1	2	3	4
CCDC	286976	608217	286975	286973	286974
Empirical formula	C ₂₀ H ₁₁ N ₃	C ₂₀ H ₁₁ AgBF ₄ N ₃	C ₂₀ H ₁₁ AgClN ₃ O ₄	C ₄₉ H ₃₆ Ag ₃ F ₉ N ₆ O ₁₃ S ₃	C ₂₄ H ₁₁ Ag ₂ F ₆ N ₃ O ₄
Formula mass	293.32	488.00	500.64	1507.63	735.1
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Crystal size [mm]	0.35 × 0.33 × 0.30	0.41 × 0.30 × 0.28	0.27 × 0.08 × 0.07	0.28 × 0.20 × 0.15	0.32 × 0.30 × 0.15
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2/ <i>c</i>
<i>a</i> [Å]	8.802(5)	10.6840(11)	10.600(17)	14.343(7)	11.2145(8)
<i>b</i> [Å]	9.011(5)	11.0728(12)	11.076(18)	15.873(7)	15.2776(11)
<i>c</i> [Å]	10.104(6)	15.3809(18)	15.23(2)	24.558(11)	7.1139(5)
α [°]	74.672(11)	90.00	90.00	90.00	90.00
β [°]	81.129(13)	90.134(3)	90.26(3)	93.095(8)	94.5540(10)
γ [°]	74.356(11)	90.00	90.00	90.00	90.00
<i>V</i> [Å ³]	741.2(8)	1819.6(3)	1788(5)	5583(4)	1214.98(15)
<i>D</i> _{calcd.} [Mg m ^{−3}]	1.314	1.781	1.860	1.794	2.009
<i>Z</i>	2	4	4	4	4
<i>F</i> (000)	304	960	992	2984	712
μ [mm ^{−1}]	0.080	1.158	1.312	1.251	1.696
Reflections collected	3714	13720	18998	26453	7439
Reflections unique	2535	3209	4071	9825	2776
<i>R</i> (int)	0.0297	0.0295	0.0329	0.0402	0.0197
Data/restraints/parameters	2535/0/208	3209/0/262	4071/0/262	9825/0/748	2776/0/179
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0620 <i>wR</i> ₂ = 0.1106	<i>R</i> ₁ = 0.0472 <i>wR</i> ₂ = 0.1169	<i>R</i> ₁ = 0.0457 <i>wR</i> ₂ = 0.1213	<i>R</i> ₁ = 0.0633 <i>wR</i> ₁ = 0.1492	<i>R</i> ₁ = 0.0390 <i>wR</i> ₁ = 0.1067
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1057 <i>wR</i> ₂ = 0.1251	<i>R</i> ₁ = 0.0578 <i>wR</i> ₂ = 0.1233	<i>R</i> ₁ = 0.0560 <i>wR</i> ₂ = 0.1283	<i>R</i> ₁ = 0.0958 <i>wR</i> ₁ = 0.1710	<i>R</i> ₁ = 0.0467 <i>wR</i> ₁ = 0.1219
GOF on <i>F</i> ²	1.005	1.050	1.035	1.035	1.021

C₂₄H₁₁Ag₂F₆N₃O₄ (735.1): calcd. C 39.21, H 1.509, N 5.716; found C 39.22, H 1.509, N 5.721.

X-ray Crystallography: X-ray diffraction data were collected with a Bruker-AXS SMART CCD area detector diffractometer at 293 K using ω -rotation scans with a scan width of 0.3° and Mo-*K* α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined with the full-matrix least-squares technique using SHELXTL.^[32] Anisotropic thermal parameters were applied to all non-hydrogen atoms. All of the hydrogen atoms in these structures are located from the differential electron density map and constrained to the ideal positions in the refinement procedure. The crystallographic calculations were conducted using the SHELXL-97 program. Crystal data and experimental details for the crystals of the ligand dcphcz and complexes 1–4 are summarized in Tables 1 and 2. CCDC-286976, -608217, -286975, -286973, and -286974 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): TGA, UV/Vis absorption spectra, emission spectra in MeOH solution and solid state.

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