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Luminescence enhancement and tuning *via* multiple cooperative supramolecular interactions in an ion-paired multinuclear complex†

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[(3,5-(CF$_3$)$_2$Pz)(AgL)$_2$]$^+$[Ag$_5$(3,5-(CF$_3$)$_2$Pz)$_6$(CH$_3$CN)]$^-$ (L = 2-(N,N-diethylanilino-4-yl)-4,6-bis(3,5-dimethylpyrazol-1-yl)-1,3,5-triazine) shows bright and tunable emissions influenced by its supramolecular structure. Columnar stacks are assembled *via* cooperative interactions that include Ag^I···Ag^I argentophilic bonding, π···π stacking and Ag^I···π interactions.

Metal···metal, π···π, and metal···π supramolecular interactions play crucial roles in transport and storage of charge and energy, both in natural systems and synthetic materials.[1] Examples include the cofacial porphyrin dimer in the light-harvesting antennae of green plants and photosynthetic bacteria,[2] the stacked base pairs of duplex DNA and RNA in natural systems,[3] and the π stacking array of conjugated polymers in materials science.[4] Many cofacial molecular materials possess high hole and charge mobility, rendering them significant in optoelectronic devices.[5–7]

Argentophilic (Ag^I···Ag^I) bonding and Ag^I···arene (metal···π) supramolecular interactions are common motifs in silver(ı) coordination compounds that promise unique photonic, electro-conductive, sensing, and catalytic applications.[8–12] We are interested in constructing luminophores with multiple attractive interactions (*e.g.* metallophilic, π···π, and M···π contacts) in a single molecule. Such combinations are expected to impart fascinating luminescence and unipolar or ambipolar electrical conductivity based on the cooperativity and electronic communication between the aforementioned interactions. Here we report the synthesis and remarkable structural and luminescence properties of a new ion-paired cluster Ag(ı) anilino-bis(pyrazolyl)-triazine complex **1** (Scheme 1). Ambipolar ligands such as L convey remarkable photophysical properties (*e.g.*, L is a superior antenna for Eu(ııı) sensitized phosphorescence *via* unique *singlet* energy transfer).[13] This work is the first among our ongoing efforts to expand the coordination chemistry of such chromophoric ligands to transition metal centers with

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Scheme 1 Synthesis and chemical structure of **1**.

expected improvement in photophysical properties *vs.* non-fluorescent ligands such as polypyridyls.

The synthesis of **1** (Scheme 1) is based on reaction of L with the cyclic trinuclear silver(ı) complex [(3,5-(CF$_3$)$_2$Pz)Ag]$_3$.[14] We have shown that such cyclic trimers form mononuclear or dinuclear analogues upon reaction with other ligands.[15] Hereby, reaction of [(3,5-(CF$_3$)$_2$Pz)Ag]$_3$ in CH$_2$Cl$_2$ with chromophore L in CH$_3$CN affords compound **1** as orange crystals in 68% yield.§

The crystal structure of **1** shows a dinuclear cation (Fig. 1a) and pentanuclear anion (Fig. 1b).¶ The cation comprises two 4-coordinate Ag^I centers by coordination of one N atom from bridging [3,5-(CF$_3$)$_2$Pz]$^-$ (avg. Ag–N = 2.168 Å) and three N atoms from the chelating L molecule; the two planar [AgL] units adopt a cofacial arrangement of L chromophores (Fig. 1a). This arrangement is facilitated by an intramolecular argentophilic bond (3.089(9) Å) that is further supported by the nearly perpendicular bridging [3,5-(CF$_3$)$_2$Pz]$^-$ ligand to the AgL plane. The Ag···Ag distance in the cation of **1** is similar to that observed for Ag(ı)-terpyridine complexes (3.005–3.142 Å).[16]
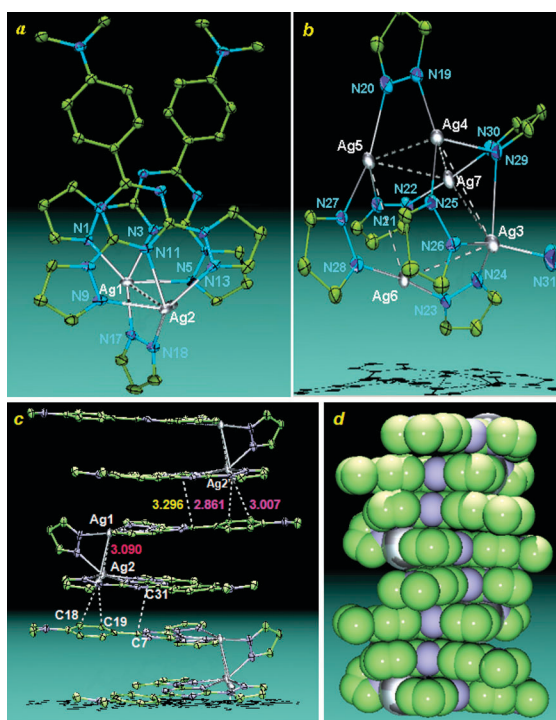
The two planar L chromophores in the cation are in parallel planes to one another but are partially staggered with a torsion angle of 53.34° about the Ag1–Ag2 axis. The cofacial dimer cations of **1** are stacked through strong Ag^I···π interactions (2.861 and 3.007 Å) and slightly-offset head-to-tail π···π stacking interactions (3.296 Å) to furnish a supramolecular

Fig. 1 ORTEP plots of the cation [(3,5-(CF₃)₂Pz)(AgL)₂]⁺ (a), the anion [Ag₅(3,5-(CF₃)₂Pz)₆(CH₃CN)]⁻ (b), and the cation packing columns showing the π···π and Ag···π interactions (c) in crystals of **1**. Trace (d) shows a space-filling view of the stacked columns. Hydrogen atoms, CF₃, and CH₃ groups are omitted for clarity.

structure consisting of one-dimensional columns running along the *a*-axis (Fig. 1c and d). The strong $Ag^I \cdots \pi$ inter-actions obviously stabilize the formation of supramolecular stacks by counteracting electrostatic repulsion between cations due to the attractive nature of cation···π interactions. One of the silver(I) atoms in the cation exhibits a two positional disorder with occupations of 0.67 and 0.33 for Ag2 and Ag2′, respectively (Fig. 1c). At the Ag2 position, the $Ag^I \cdots Ag^I$ attraction is strong whereas the $Ag^I \cdots \pi$ interaction is strong at the Ag2′ position. Such disorders have been suggested to minimize the stacking energy and possibly assist in charge separation and energy storage in d^{10} columnar stacks.[17]

In the pentanuclear cluster anion, five [3,5-(CF₃)₂Pz]⁻ ligands coordinate to five Ag^I atoms in a $\mu_2\text{-}\eta^1,\eta^1$ coordination mode while another [3,5-(CF₃)₂Pz]⁻ ligand serves as an asymmetric $\mu_3\text{-}\eta^1,\eta^1,\eta^1$ bridge with two N atoms coordinating to three Ag^I atoms (Ag7–N30 2.088(5) Å, Ag4–N29 2.535(5) Å, Ag3–N29 2.513(5) Å, and Ag3–N29–Ag4 89.86°). The five Ag atoms in the pentanuclear cluster can be regarded as a nearly square-pyramidal pentagon, wherein Ag7 occupies the apical site while the remaining four Ag atoms are at the equatorial plane. The shortest argentophilic distance within the anion is Ag4···Ag5 (3.222 Å). We note that such penta-nuclear complexes are quite rare among multinuclear metal clusters with diverse structures and geometries.[18,19]

The molecule L has been demonstrated to be a bright blue emitter based on its charge transfer character.[13] Compound **1** offers several strategies to fine- and coarse-tune both the emission colors and intensities based on multiple supramolecular
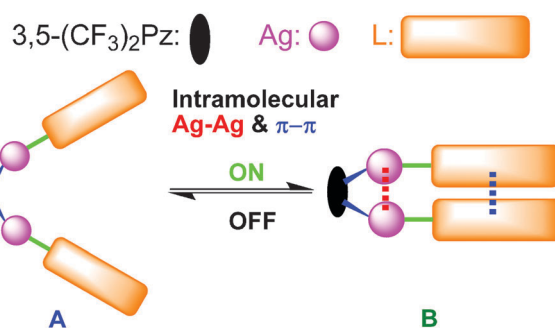
Scheme 2 Proposed conformational rearrangement of the binuclear cation. Toggling between form **A** and **B** leads to on/off switching of intramolecular interactions and affects the luminescence signal, which can be further modified upon supramolecular association (Fig. 1c and d).

interactions ($M^I \cdots M^I$ metallophilic, π···π, and metal···π) in a single molecule. Thus, although the free ligand L is only weakly luminescent in polar solvents, **1** shows brilliant visible emissions in such solutions or the solid state. The photophysical data below are strongly governed by the supramolecular interactions of the different structural moieties in **1**, as illustrated in Scheme 2. The conformation of **1** could be rather flexible, akin to what we found in other Ag(I) azolate frameworks.[20] Thus, equilibrium between conformations **A** and **B** (Scheme 2), as well as association of the latter can take place—depending on factors such as solvent, concentration or temperature. In dilute solutions, for example, the monomer conformation **A** proved dominant, wherein the intramolecular $Ag^I \cdots Ag^I$ and π···π interactions are off. In concentrated solutions, the intra-molecular dimer **B** is dominant as the intramolecular $Ag^I \cdots Ag^I$ and π···π interactions are turned on. Obviously the π-dimer further aggregates as observed in the solid state (see Fig. 1c) and could be present in highly concentrated solutions at low temperatures. As shown in Fig. 2, the fluid-solution emission spectrum of **1** consists of two broad emission bands centered at 460 nm ($\tau = 1.0$ ns) and 560 nm ($\tau = 2.5$ ns), assignable to fluorescence of forms **A** and **B**, respectively. The higher-energy band is similar in profile to the fluorescence of the coordinated ligand L.[13] The intensity ratio of the two emission bands is strongly concentration dependent such that the higher-energy band is dominant in dilute solutions while the lower-energy band is dominant at higher concentrations (Fig. 2). These spectral observations, therefore, substantiate the model in Scheme 2 such that concentration-dependent transformation between conformations **A** and **B** take place in solution.

The extended stacking of chromophores in the solid state usually leads to fluorescence quenching, although Ag–Ag interaction based on significant photoluminescence changes in different aggregate states is known.[11b] However, due to the heavy atom effect of silver, which induces spin–orbit coupling, it is anticipated that intersystem crossing could be particularly efficient at low temperatures in the solid state so as to sensitize the phosphorescence from the aggregate of the coordinated chromophore L. Indeed, complex **1** exhibits multiple bright emission colors found to be phosphorescence (Fig. 2, bottom). Two bright emission bands, green and orange-red, are exhibited by the crystal, and can be isolated or mixed, at low temperatures. Among the two unstructured major emissions, the lower-energy
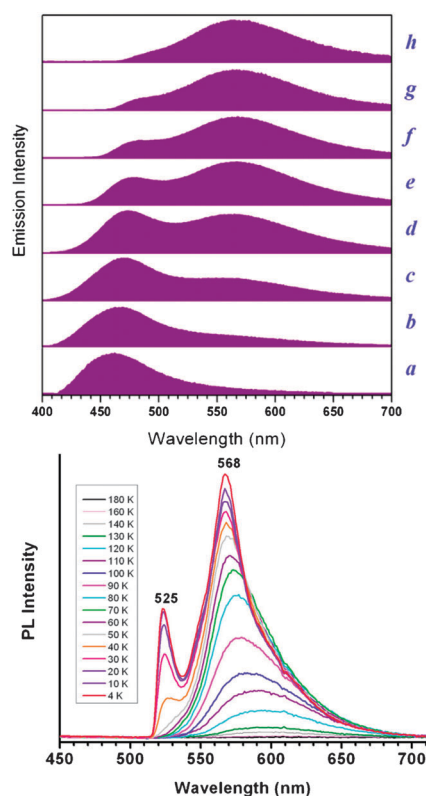
Fig. 2 Top: emission spectra of **1** in MeCN: a: 2.5×10^{-7}, b: 1.2×10^{-6}, c: 3.6×10^{-6}, d: 1.4×10^{-5}, e: 7.2×10^{-5}, f: 2.8×10^{-4}, g: 8.6×10^{-4}, and h: 2.6×10^{-3} mol L^{-1}. Bottom: crystal emission ($\lambda_{exc} = 330$ nm) *vs.* temperature.

band with a maximum at $\sim$600 nm dominates at higher temperatures, whereas the higher-energy emission with $\sim$525 nm maximum dominates at lower temperatures. These two over-lapping emissions can be distinguished by their respective lifetimes at lower temperatures, nearly seconds for the green emission ($\sim$0.4 s at 77 K) and milliseconds for the orange emission ($\sim$96 ms at 77 K). Visually, irradiation of solid **1** with a hand-held UV lamp at near liquid nitrogen tempera-tures results in bright orange emission that turns into green when the UV illumination is turned off, consistent with the aforementioned lifetime magnitudes. The green phosphorescence band is present in the Gd(III) complex of L, rendering an assignment to triplet emission from coordinated L.[13] The orange phosphorescence is more broad and brighter than the green band, suggesting triplet emission from aggregated stacks of the coordinated L ligand *via* Ag$\cdots$Ag, $\pi\cdots\pi$, and Ag$\cdots\pi$ interactions. Consistent with this assignment is the observation that the intensities and lifetimes of the two triplet emission bands decrease concomitantly upon heating. Finally, the overall spectral data suggest that the light harvesting and emission processes in **1** are primarily localized on the AgL cations, whereas the pentanuclear anions simply act as counterions from a photophysics standpoint. This is evidenced by the fact that the fluorous metal–organic framework FMOF-1,[20] which comprises a similar $[Ag^{I}(\mu\text{-}NN)]_n$ high-nuclearity cluster to the anionic cluster in **1**, is not luminescent even at 77 K.

In summary, we have demonstrated remarkable structural and photophysical properties for a novel silver(I) supramolecular compound consisting of a binuclear luminophoric cation ion-paired by a pentanuclear cluster. Cooperative supra-molecular interactions in the cationic stacks combined with Ag heavy-atom effects imparted fascinating luminescence across the UV/Vis region.

Notes and references

§ **1**: a solution of a mixture of L (41.6 mg, 0.1 mmol) in MeCN (5 mL) and $[(3,5\text{-}(CF_3)_2Pz)Ag]_3$ (186.4 mg, 0.2 mmol) in CH_2Cl_2 (20 mL) was stirred at 60 °C for 0.5 h. The resulting yellow precipitate was collected by filtration and washed with Et_2O and cold CH_2Cl_2. Orange single crystals of **1** were obtained by vapour diffusion of CH_2Cl_2 into MeCN solution. Mp 263–265 °C (Dec.); elemental analysis: calcd (%) for $C_{83}H_{66}Ag_7F_{42}N_{31}$: C 32.68, H 2.18, N 14.23; found (%): C 32.88, H 2.09, N 14.31. ^{1}H NMR (CDCl$_3$, RT): δ 1.20 (*t*, 12H, $J = 4$ Hz, NCH$_2$CH$_3$), 1.91 (s, 12H, CH$_3$), 2.01 (s, 3H, CH$_3$CN), 2.67 (s, 12H, CH$_3$), 3.41 (*q*, $J = 4$ Hz, 8H, NCH$_2$CH$_3$), 5.93 (s, 2H, 3,5-(CH$_3$)$_2$Pz-H), 6.00 (s, 1H, 3,5-(CF$_3$)$_2$Pz-H of cation), 6.54 (*d*, $J = 4$ Hz, 4H, Ph-H), 6.78 (s, 6H, 3,5-(CF$_3$)$_2$Pz-H of anion), 7.98 (*d*, $J = 4$ Hz, 4H, Ph-H).
¶ Crystal data for **1**: $C_{83}H_{66}F_{42}N_{31}Ag_7$, FW = 3050.76, monoclinic, $P2_1/a$, $a = 13.2664(5)$ Å, $b = 38.8979(15)$ Å, $c = 20.6041(8)$ Å, $\beta = 102.919(1)°$, $V = 10363.3(1)$ Å^3, $Z = 4$, $T = 100$ K, $D_c = 1.924$ g cm^{-3}; $R_1 = 0.0424$, w$R_2 = 0.0916$, GOF = 1.179. CCDC 640177.

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