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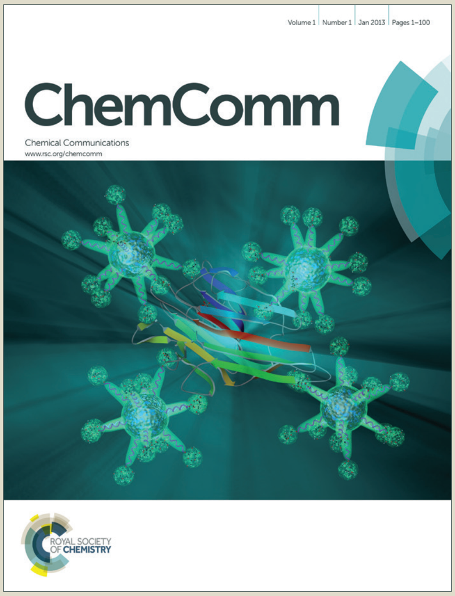

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Modulation of argentophilic interaction by bridging amine ligand: tuneable photoluminescence by excitation energy or temperature†

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A series of Ag(I) coordination oligomers with Ag-Ag distance tuned by amine auxiliary ligands were designed and synthesized. Their dual emissions could be adjusted by changing either excitation energy or temperature. The emission assignments were clarified by both experimental and DFT evidences herein.

Many complexes based on d^{10} metal ions (Au(I), Ag(I) and Cu(I)) from group 11 display intriguing photophysical properties, such as dual-emissive properties,[1] thermochromism,[2] solvatochromism,[3] concentration luminochromism,[3] mechanochromism[4,2b] and vapochromism.[5] Take the dual-emissive properties for example, the low energy (LE) emission band from metal or metallophilicity origins, often had an close relationship with metal-metal distance.[6] However, the coexistence of other non-covalent bonds (π-π stacking, hydrogen bonds, etc.) sometimes makes the maximum emission band lack the straightforward relationship with metal-metal distance.[7] Besides above properties, some complexes display thermal activated delayed fluorescence (TADF) which has a longer emission lifetime than normal fluorescence and is favoured by high temperature,[8] but may be quenched by oxygen.[9]

To the best of our knowledge, it's rare to design and synthesize the complexes with variable photoluminescence by the modulation of argentophilicity.[10] Herein we report four rational designed complexes with similar structure, exhibiting different argentophilicity and bringing about interesting difference in photophysical properties. Their UV-Vis spectra, solid state emission spectra, and emission lifetimes (τ) were studied. The analyses of geometry structures from X-ray diffraction (XRD) data, electronic structures from density functional theory (DFT) calculation and transition assignment from time-dependant density functional theory (TD-DFT) provide more insight on the photophysical properties.

The pyridine-2-yl-1H-imidazole-4,5-dicarboxylic acid (H_3pidc) was used as the main ligand to construct four coordination oligomers in which the Ag-Ag distance was tuned by introducing different amine molecules as auxiliary ligands (denoted as am) in the hope of modulation of their photoluminescent properties. In this work, ammonia (NH_3), 1,2-diaminoethane (en), and 1,3-diaminopropane (pn) were selected as auxiliary ligands, resulting in the formation of $[Ag_2(Hpidc)(NH_3)_2]$ (**1**), $[Ag_2(Hpidc)(NH_3)_2]_2\cdot 2H_2O$ (**2**), $[Ag_4(Hpidc)_2(en)_2]$ (**3**), and $[Ag_4(Hpidc)_2(pn)_2]$ (**4**). Among them, **1** and **2** as binuclear complexes behaving different intermolecular Ag-Ag contacts were firstly isolated. The problem quickly came out: how to control the intermolecular Ag-Ag distance more effectively which may play an important role on the photophysical properties of Ag(I) complexes? It should be a good idea to bridge two binuclear units through diamine ligands replacing the terminal ammonia molecules in order to fix the intermolecular Ag-Ag distance. Finally, **3** and **4** with expected structures were successfully isolated by using en and pn, respectively.

According to the XRD data at 298 K and the calculated Mayer bond orders (MBO) of **1-4**, each Ag atom has the coordination geometry of mainly linear two-coordinated geometry with somewhat distortion from normal linear geometry (See ESI for coordination environment analysis).

The crystal structure of **1** is formed by packing of discrete binuclear molecules ($[Ag_2(Hpidc)(NH_3)_2]$) without significant intermolecular Ag-Ag interaction (at least in the ground state) because the shortest Ag-Ag distance is *ca.* 3.57 Å, but two closest molecules of **1** will be selected as a "dimer" in the following discussions in order to facilitate comparison with other compounds. The crystal structures of **2-4** could be considered as packing of dimer of neutral binuclear unit ($[Ag_2(Hpidc)]$), wherein the dimer is mainly formed by Ag-Ag interaction and/or auxiliary ligands (Fig. 1).

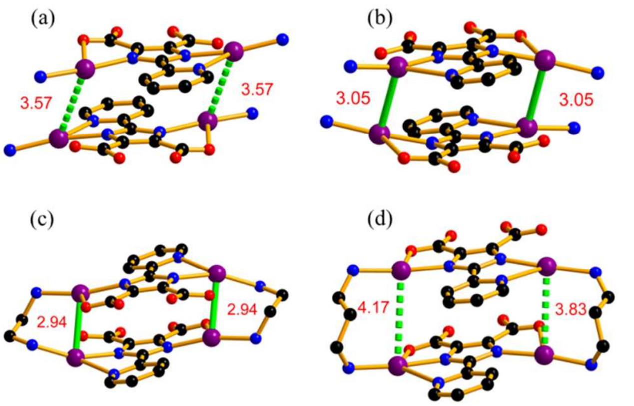

Fig. 1 The tetranuclear units in **1** (a), **2** (b), **3** (c) and **4** (d) (Ag-Ag distances are given in Å; H atoms are omitted for clarity).

In **2**, two adjacent binuclear molecules ([$Ag_2(Hpidc)(NH_3)_2$]) are held together to form a dimer through unsupported Ag-Ag interactions ($d_{\text{Ag-Ag}} \approx$ 3.05 Å), but there is no interdimer argentophilicity. Two binuclear ([Ag_2(Hpidc)]) are bridged by two diamine auxiliary ligands to give a tetranuclear molecule in **3** or **4**. There exist intra- and inter-molecular argentophilicity simultaneously in **3** ($d_{\text{intraAg-Ag}} \approx$ 2.94 Å, $d_{\text{interAg-Ag}} \approx$ 3.19 Å), but just intermolecular argentophilicity in **4** ($d_{\text{interAg-Ag}} \approx$ 3.24 Å) (Fig. 1 and Fig. S4).

As a short ditopic linker, en effectively shortens the Ag-Ag distances between two [Ag_2(Hpidc)] units in **3**, resulting in *ca.* 0.1 Å smaller of shortest Ag-Ag distances than that in **2**. The MBO of the above Ag-Ag bonds are 0.1028 for **3** and 0.1065 for **2**, respectively, suggesting slightly stronger bond strength for **3** than that for **2**. Neither **1** nor **4** has intradimer Ag-Ag interaction, but the shorter interdimer Ag-Ag distance of **4** indicates stronger Ag-Ag interaction than that for **1**. In summary, the total Ag-Ag interaction decreases in the order of **3 > 2 > 4 > 1**.

Besides coordination bond and argentophilicity, several types of non-covalent bonds (π-π, Ag-π, and/or hydrogen bond) coexist in the crystal of **1-4**, contributing to the delicate equilibrium in these crystal structures (See Table S5-S6).

The UV-Vis absorption spectra of H_3pidc and **1-4** were determined. The low energy parts for **1-4** are qualitatively simulated by TD-DFT, suggesting that our models were qualitatively correct. The low energy strong absorption bands for **1-4** are assigned as ^{1}ILCT with some contributions from ^{1}LMCT (or ^{1}LMMCT) and ^{1}LLCT. The assignment details are provided in ESI.

The solid state photoluminescence properties of **1-4** and H_3pidc have been studied. The photoluminescence of **1-4** are somewhat sensitive to different excitation energies despite of temperature (Fig. 2). High energy excitation favours high energy (HE) emission (emission peaks around 400 nm), while low energy excitation favours low energy (LE) emission (emission peaks around 550 nm). Although there are still LE emissions when excited by 250 nm light (especially for **1** and **2)**, the high energy emission bands vanish when excited by 280 nm light. The orders of emission intensities for LE peaks are **2** > **1** > **3** ≈ **4** at 295 K and **1** > **2** > **3** > **4** at 15 K. The emission colour changes from yellow to white for **1** and **2**, but from white to blue for **3** and **4** when excited by 250nm light from 15 to 295 K (Fig. S18). The emission maximum of H_3pidc is *ca.* 440 nm at room temperature when excited at 380 nm. The temperature-dependant luminescent spectra of **1-4** (Fig. S9 – Fig. S12) show that the HE peaks around 400 nm seldom red- or blue-shifted when excited by 250 nm light from 15 to 295 K, suggesting that the HE bands should probably results from intra-ligand n-π or π-π transitions in $Hpidc^{2-}$, and the Ag atoms may play some role in these transitions.

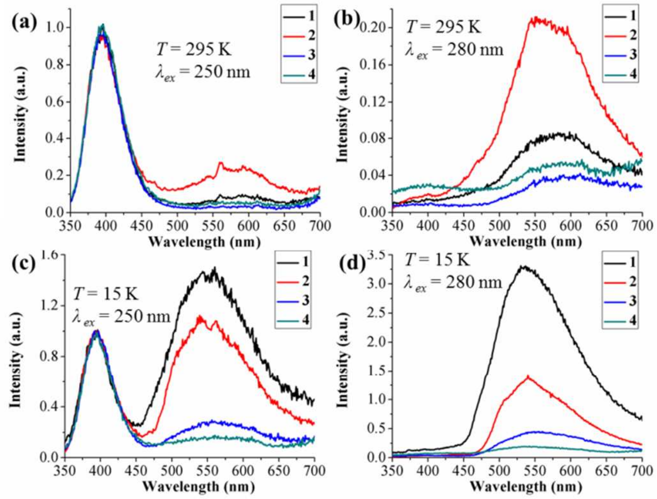

Fig. 2 The solid state photoluminescent spectra of **1-4** (a) at 295 K (λ_{ex} = 250 nm), (b) at 295 K (λ_{ex} = 280 nm), (c) at 15 K (λ_{ex} = 250 nm), and (d) at 295 K (λ_{ex} = 280 nm). All the emission intensities were normalized by the intensity of HE emission peaks upon 250 nm excitation light at 295 K for (a), (b) and at 15 K for (c), (d).

The temperature-dependant luminescent spectra also show that high temperature favours the HE bands. What's more, the emission decay determination (Table 1) displays that the lifetimes of HE peaks were *ca.* 100 μs, indicating that the HE emission should be assigned as TADF. It was found that the HE emission could be quenched when exposed to air at room temperature (Fig. S19). The LE emissions should be no doubt phosphorescences for their long wavelengths and long lifetime (longer than 1 ms).

Table 1 The analysis of Ag-Ag distances and luminescence (emission wavelength and the corresponding lifetimes (τ)). All the data were collected at room temperature.

	Bridging ligand	$d_{\text{Ag-Ag}}$[a] (intra) (Å)	$d_{\text{Ag-Ag}}$[b] (inter) (Å)	HE		LE	
				λ (nm)	τ (μs)	λ (nm)	τ (ms)
1	None	3.57	4.50	400	103.68	580	1.94
2	None	3.05	4.63	400	98.64	560	5.88
3	en	2.95	3.19	400	98.45	600	1.82
4	pn	3.84 , 4.17	3.24	400	98.87	600	2.34

[a] The intradimer Ag-Ag distance;

[b] The interdimer Ag-Ag distance.

By comparing the Ag-Ag distances and emission maximums (Table 1), it could be found that the emission maximum of LE band decrease in the order of **3** = **4** > **1** > **2**, but the argentophilicity decrease in the order of **3** > **2** > **4** > **1**. The relative strength of argentophilicity doesn't seem to have straightforward relationship with the emission maximum of LE band. The difference of argentophilicity affects the relative emission intensities rather than the emission maximum for **1-4**.

The analyses and comparisons of electronic structures shed some light on the relationship between argentophilicity and LE emissions. Although LE emissions should arise from the radioactive transitions from T_1 state according to Kasha's rule,[11] the below discussions about molecular orbitals will be mainly based on the orbitals of S_0 state for some of the calculations of T_1 state failed to converge.

Based on the tetranuclear unit ($[Ag_2(Hpidc)(NH_3)_2]_2$) of **1** to **4** as well as two adjacent tetranuclear molecules of **3** or **4** taken from crystal structures at 298 K, the composition of Ag (denoted as Ag%) in the lowest unoccupied molecular orbitals (LUMOs) decreases in the order of **1** > **2** > **3** > **4** by Hirshfeld composition analyses. Based on the calculation models of **1** and **2** taken from their crystal structures at 100 K, respectively, Ag% in the LUMOs of **1** (35.04%) is still larger than that of **2** (29.84%). It is possible that Ag% in the LUMOs is always **1** > **2** > **3** > **4** at all the temperatures involved in our luminescent determinations. It's a pity that the calculations of T_1 states based on the crystal structure of **1** at 298 K and of **2** at 100 K failed to converge, the singly occupied molecular orbitals (SOMOs) of T_1 state of all the other above models shows the same trends of Ag% compared to that of Ag% in LUMOs for S_0 state. The large contribution of heavy metal atoms often favours the phosphorescence and makes the emission become more metal-centred[7a]. As a result, the order of intensities of LE emission is **1** > **2** > **3** > **4** at low temperature (for example, at 15 K). However, it is well-known that the phosphorescence is sensitive to vibrational relaxation, which often leads to the phosphorescence quench at high temperature (for example, at room temperature) or liquid solution. The lack of strong Ag-Ag interaction in **1** bring about the more discrete packing, which may lead to the stronger vibrational relaxation than **2**, especially at 295 K. This may be the main reason that the LE emission of **1** is weaker than **2** at room temperature. It should be noted that none of the Ag% in HOMOs, LUMOs or SOMOs is larger than 40%, suggesting that the ligands (mostly $Hpidc^{2-}$, sometimes NH_3 for **1** and **2**) play more important roles in these orbitals and indicating that the LE emissions are not very metal-centred. This may be the main reason that the different Ag-Ag interactions don't cause significant differences in the LE emission energies for **1-4**. However, the effects of intermolecular interactions still could not be precluded.

After grinding the crystalline sample of **1**, it was surprising to observe that the HE emission becomes less sensitive to temperature and the LE band become less sensitive to different excitation energies compared to the sample before grinding (Fig. S17). However, It shows that no new diffraction peak appears but the diffraction peak becomes weaker and wider from the powder X-ray diffraction (PXRD) pattern before and after grinding for **1** (Fig. S6).

In conclusion, four emissive Ag(I) coordination oligomers were obtained and their photophysical properties were studied from both theoretical and experimental aspects. All these complexes display that HE excitation favours HE emission (thermal activated delayed fluorescence) and LE excitation favours LE emission (phosphorescence). The argentophilicity affects the relative intensities rather than emission energies of phosphorescences which may result from the lager contributions of ligands than that of metals in the frontier molecular orbitals and the coexistence of non-covalent interactions other than argentophilicity.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, crystal data (CCDC number 98828-98833 for **1-4**, respectively), coordination environment analysis in detail, additional physical measurements and analysis (PXRD, UV-Vis absorption, emission spectra), computational details and discussions. X-ray crystallographic files in CIF format for **1-4**. For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x.

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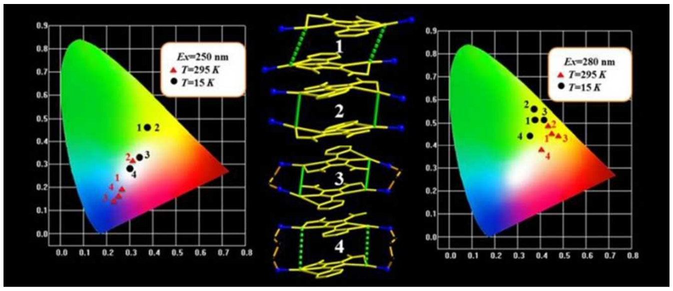
Graphic Abstract



From binuclear to tetranuclear silver(I) oligomers through short bridging amine ligand replacing terminal one: different argentophilicity leads to dual emission modulated by excitation energy and temperature, giving different emission colours.