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Structure-dependent mechanochromism of two Ag(I) imidazolate chains†

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Two Ag(I)-imidazolate compounds with distinct chain-like structures, namely, [Ag(dm-bim)]$_n$ (**1**, dm-bim = 5,6-dimethylbenzimidazole) and [Ag(m-bim)]$_n$ (**2**, m-bim = 2-methylbenzimidazole), were synthesized and structurally characterized, respectively. Compound **1** with helical chains exhibited unique luminescence mechanochromism due to short Ag···Ag interactions (2.986 Å).

Nowadays, novel functional coordination polymers (CPs) have gained attention due to their potential applications in the realms of gas absorption, catalysis, luminescence and sensing.[1–4] For CPs, there are unique flexible and dynamic frameworks.[5] Some external stimuli could tune their luminescence properties. To explore some new kinds of stimuli-responsive materials, mechanochromic luminescent metal complexes have been developed to be a special subclass and may be used in the field of mechanosensors, data storage or optical recording devices.[6] To date, several metal-containing compound systems including Cu(I), Zn(II), and noble metal ions have been reported showing excellent luminescence mechanochromism.[7–9] However, CPs with mechanochromic properties are still rarely reported.[9b,10] Moreover, mechanosynthesis of CPs is full of challenges, although mechanochemical processes have a long history.[11]

Herein, we report two Ag(I) imidazolate coordination polymers with chain-like structures. Compound [Ag(dm-bim)]$_n$ (**1**, dm-bim = 5,6-dimethylbenzimidazole Fig. S1a†) shows promising mechanical-grinding-triggered-luminescence change from yellow green to pale blue, while no obvious luminescence change is observed by grinding compound [Ag(m-bim)]$_n$ (**2**, m-bim = 2-methylbenzimidazole Fig. S1b†). In addition, compound **1** can be obtained *via* solvent-assisted mechanosynthesis.

Pale yellow crystals of compound **1** and **2** were solvothermally synthesized.‡ X-ray single crystal structural determination reveals that both compounds feature chain-like structures.§ Their phase purity has been confirmed by powder X-ray diffraction (PXRD) (Fig. S2†). They are stable in air and in common solvents (DMF, methanol, H_2O, *etc.*). There is no obvious weight loss before 300 °C for each compound, indicating the absence of solvent guests in the structure (Fig. S3†).

In the structure of compound **1**, each Ag^+ ion is coordinated to two N atoms from two dm-bim ligands and the average Ag–N bond length is 2.0620 Å. Meanwhile, each dm-bim ligand connects two Ag^+ ions and the average Ag–Ag distance is 6.0267 Å. The alternating link of Ag^+ ions and dm-bim ligands constructs 2_1 helical chains. The perpendicular helical chains showed obvious Ag···Ag interactions (2.986 Å) (Fig. 1a and 2a).[12] More chains packed into a layer along the *ab* plane due to this kind of interactions (Fig. 1b). Furthermore, we could also find weak C–H···π contacts (3.935 Å) between adjacent chains (Fig. 2a).

In the structure of compound **2**, the coordination mode of the metal centers and ligands is the same as compound **1**. However, the angle of two adjacent m-bim ligands is 180° and they exhibit a zigzag chain (Fig. S3a†). The C–H···π (3.648 Å) and π–π interactions (3.947 Å) were separately found in the structure, but there are no Ag···Ag interactions (Fig. 2b, S4b and c†). In contrast, **1** and **2** had similar chain structures and different packing modes; it was mainly because of the different position of the methyl group in the two ligands, and the steric effects led to distinct structure disparity.

The photoluminescence properties of **1** and **2** in the solid state were investigated at room temperature. Upon excitation at 340 nm, two emission bands with comparable intensities are observed in **1**. The maximum wavelength at 384 nm (high energy band, HE) shows a 84 nm large blue-shift, compared

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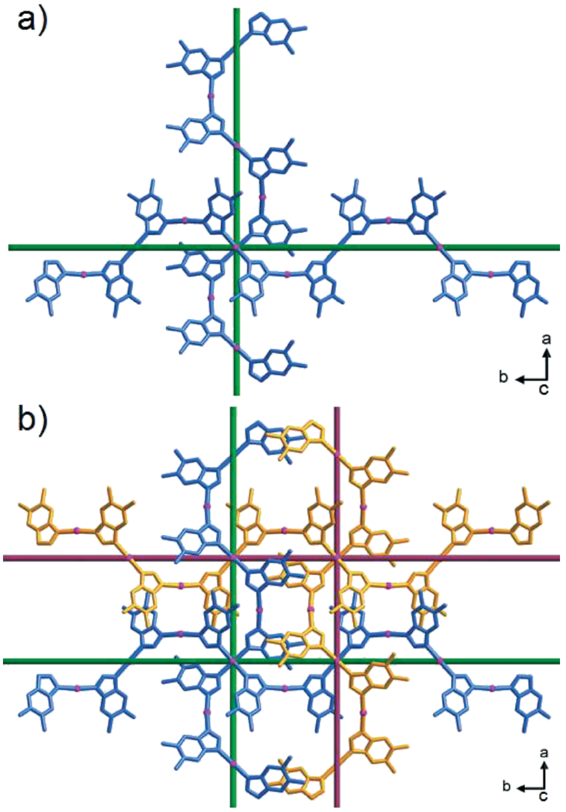

Fig. 1 (a) Two perpendicular right-handed and left-handed helical chains in **1**; (b) packed chains in **1**.

to the ligand dm-bim (468 nm) (Fig. S4a†), which may be induced by the intraligand π–π* charge transfer (ILCT).[13a,b] Another intense band at λ_{max} = 530 nm (low energy band, LE) could be similar to the cluster centered (CC) band.[13c,d] However, only one emission band can be found at λ_{max} = 590 nm in **2** under excitation at 469 nm. We tentatively assign it to the metal-to-ligand charge transfer (MLCT) excited states due to the red shift emission spectra in compound **2** in contrast to the m-bim ligand (Fig. S5b†).[13e] Such different photoluminescence properties between **1** and **2** may be caused by the strong Ag⋯Ag interactions in **1**.

Inspired by our previous studies,[10,14] the mechanochromic properties of **1** and **2** were surveyed. The dual emission spectrum displayed that the relative intensities in compound **1** changed from HE < LE to HE > LE after grinding, corresponding to the color change from pale yellow to pale blue (Fig. 3). However, only intensity change was found in the fluorogram of compound **2** before and after grinding (Fig. 4b). It turned out that compound **1** undergoes a promising mechano-induced luminescence change but compound **2** does not. Compared with most of discrete 0D complexes, the change of their emission color under grinding were attributed to the disruption of their intermolecular interactions like C–H⋯π interactions.[7,8] Moreover, it has been reported that the metallophilicity plays important roles on tuning properties of mechanochromic compounds and the packing mode of coordination polymers.[14a,15] So, the disparity may be caused by the different chain to chain packing patterns in complexes **1** and **2** and the luminescence change may be induced by the synergy of Ag⋯Ag and C–H⋯π interactions.

To get more information about the structure of the ground samples, their powder X-ray diffraction patterns were

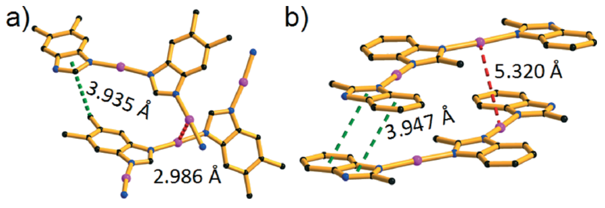

Fig. 2 (a) The coordination environment in **1**, showing Ag⋯Ag (red dashed line) and C–π interactions (green dashed line). (b) Face-to-face packing mode showing π–π interaction (green dashed line) and the Ag⋯Ag distance (red dashed line) in **2**.

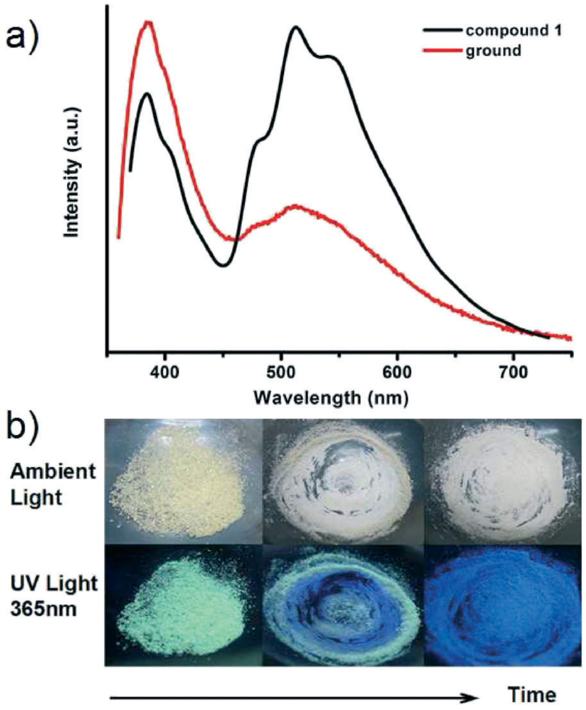

Fig. 3 (a) Solid-state emission spectra (λ_{ex} = 340 nm) for the unground (black line) sample and ground (red line) sample. (b) Photographs of samples of **1** show luminescence changes with grinding time at room temperature under ambient light and a 365 nm UV lamp, respectively.

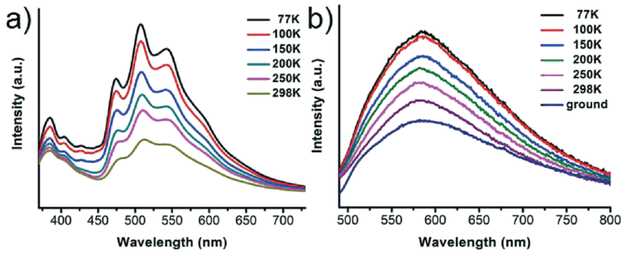

Fig. 4 (a) Photoluminescence spectra of **1** at different temperatures. (b) Solid-state emission spectra of **2** under different conditions.

recorded (Fig. S2†). Several peaks disappear and some peaks are weakening, which illustrate the change of the crystal lattice. To investigate the color-changing mechanism of **1**, its photoluminescence spectra (Fig. 4a) and lifetimes (τ) (Table S1†) were measured under different conditions. The results show that the fluorescence intensity increased with decreasing temperature. Moreover, the lifetimes (τ) increased when the temperature was decreased. In contrast to an unground sample of **1**, the lifetimes (τ) of ground samples were also augmented at 298 K. However, the quantum yield of **1** (1.75%) decreased after grinding (less than 1%) under room temperature. To be more specific, the intensity at LE increased faster than that at HE. An explanation could be that the shorter Ag⋯Ag distance leads to a stronger Ag⋯Ag contact at lower temperature. Furthermore, with the decrease of low temperature, two shoulder peaks at LE become more distinct; it may be induced by the multiple ligand-based emissive states because of complex crystal packing effects.[13c] Especially, the sample becomes more disordered after grinding and these irregular packing modes changed the synergy of interactions such as Ag⋯Ag and C–H⋯π, which should be responsible for the fluorescence intensity and lifetimes. Comparably, the temperature-dependence PL spectrum of **2** was also analysed, while only intensity change was found in the spectra (Fig. 4b).

Mechanosynthesis is very attractive due to its high efficiency, low pollution emission and appropriate use of raw materials and energy.[11] For the exploration of a simple synthesis method for the two compounds, the mechanosynthesis experiment was performed by using the method of liquid-assisted grinding (LAG, Fig. 5). Fortunately, compound **1** was successfully synthesized. We firstly mixed Ag_2SO_4 (0.1643 g) and dm-bim (0.4621 g) together. Then, 10 drops of $NH_3{\cdot}H_2O$ were added. After 30 min of grinding in a mortar at room temperature, the resulting sample was washed with *N*,*N*-dimethylformamide (DMF) and methanol 3 times, respectively. Powder X-ray diffraction (Fig. S1†), solid-state photoluminescence spectroscopy (Fig. S5a†) and the elemental analyses (calcd. (%) for $C_{36}H_{36}Ag_4N_8$: C 42.71, H 3.58, N 11.07; found: C 43.55, H 4.05, N 11.57) were further performed to prove the resulting powder has the same structure as compound **1**. However, the mechanosynthesis of compound **2** failed.

In conclusion, two Ag(I)-imidazolate coordination polymers were successfully synthesized and characterised. Moreover, compound **1** could be synthesized by a mechanosynthesis method. Compound **1** also exhibits promising mechanochromic properties, which proves its potential as a luminescence candidate material.

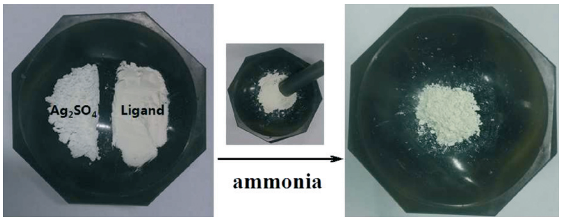

Fig. 5 Diagram of solvent-assisted mechanosynthesis of compound **1**.

Acknowledgements

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Notes and references

‡ *Synthesis of [Ag(dm-bim)]$_n$ (**1**): a mixture of Ag_2SO_4 (0.0352 g), dm-bim (0.0567 g), 1,3-dimethyl-2-imidazolidinone (DMI, 1.5 ml), H_2O (1.5 ml), acetonitrile (0.5 ml) and ammonia (0.5 ml) was sealed in a 20 ml vial and stirred for 15 min. Then the vial was heated to 80 °C for 1 day. After cooling to room temperature, colorless crystals were obtained in 66% yield. Synthesis of [Ag(m-bim)]$_n$ (**2**): a mixture of Ag_2SO_4 (0.0270 g), m-bim (0.0851 g), N,N-dimethylacetamide (DMA, 1.5 ml), H_2O (1.5 ml), acetonitrile (0.5 ml) and ammonia (0.5 ml) was sealed in a 20 ml vial and stirred for 15 min. Then the vial was heated to 80 °C for 1 day. After cooling to room temperature, colorless crystals were obtained in 70% yield.*

§ Crystal data for **1**: $C_{36}H_{36}Ag_4N_8$, M = 1012.21, monoclinic, a = 20.633(4), b = 20.797(4), c = 16.615(3) Å, β = 91.842(4)°, V = 7126(2) Å^3, T = 293 K , space group *C*2/*c*, Z = 8, 27 767 reflections measured, 8023 independent reflections (R_{int} = 0.0183). The final R_1 value was 0.0231 ($I > 2\sigma(I)$). The final w$R(F^2)$ value was 0.0781 ($I > 2\sigma(I)$). The final R_1 value was 0.0270 (all data). The final w$R(F^2)$ value was 0.0829 (all data). The goodness of fit on F^2 was 0.664. Crystal data for **2**: $C_8H_7AgN_2$, M = 239.03, orthorhombic, a = 12.2337(11), b = 9.5487(8), c = 13.0666(13) Å, V = 1526.4(2) Å^3, T = 293 K , space group *Pbca*, Z = 8, 10 798 reflections measured, 1721 independent reflections (R_{int} = 0.0213). The final R_1 value was 0.0334 ($I > 2\sigma(I)$). The final w$R(F^2)$ value was 0.0569 ($I > 2\sigma(I)$). The final R_1 value was 0.0410 (all data). The final w$R(F^2)$ value was 0.0597 (all data). The goodness of fit on F^2 was 1.194.

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