The self-assembly of a heteronuclear complex monitored with ESI-MS and fluorescence spectrophotometry†

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A strategy of separate steps was utilized to research the self-assembly of $\{[Tb_2Ag_6(H_2O)_{12}(CDO)_6]\cdot 6H_2O\}_n$ (Tb-Ag-CDO), monitored with ESI-MS and fluorescent technology.

Although a great many heteronuclear complexes with excellent function or novel topology structures have been prepared *via* one-pot syntheses,[1] it is still a puzzle 'how the self-assembly proceeds'. In the past four decades, metal complexes of tetradentate Schiff bases have been extensively used by Sinn and Harris as 'complex ligands' to synthesize heterobinuclear MM′ and heterotrinuclear MM′M complexes.[2] It was their pioneering works that provided us with a feasible way to utilize the stepwise method to analyze the one-pot process. However, it is always a great challenge presented to trace the self-assembly process. Recently, cryospray mass spectrometry (CSI-MS) was utilized to probe the self-assembly process of poly-oxometalate clusters in solution.[3] Santillan and Carrano have also studied the building blocks to construct coordination polymers *via* ESI-MS technology.[4] In order to monitor the self-assembly of 3d/4d–4f heteronuclear complexes, we set out to integrate electrospray ionization mass spectrometry (ESI-MS) along with fluorescent technology to investigate the self-assembly process. ESI-MS allows the analysis of solution-phase species in the gas phase without perturbation of their solution distribution.[5] In addition, the fluorescence can carry out real-time monitoring.[6]

The novel 3D 4d–4f complex $\{[Tb_2Ag_6(H_2O)_{12}(CDO)_6]\cdot 6H_2O\}_n$ (**Tb-Ag-CDO**) together with a 1D complex $[Ag(\mu_2\text{-}H_2O)(HCDO)]_n$ (**Ag-CDO**)‡ were initially obtained by mixing Tb³⁺, Ag⁺ and H₂CDO (chelidonic acid) in one pot, which was monitored in real time with a camera of high resolution (Fig. 1 and Fig. S1†).[7] Clear solution was obtained under reflux for 1 h. After standing at room temperature for 1 h, tiny crystals appeared as shown in Fig. 1a. Subsequently, colourless needle crystals formed in great quantities with the time process (Fig. 1b, 12 h later), and were further determined using PXRD measurements as pure **Tb-Ag-CDO** (Fig. S2†). It should be noted that crystals of a different shape (light yellow) had sprouted, and emerged plentifully as time proceeded (Fig. 1c). These crystals were collected and further confirmed as pure **Ag-CDO** by PXRD measurements (Fig. S3†). After two weeks (Fig. S1†), observation *via* microscope showed that **Tb-Ag-CDO** partly dissolved and lost their
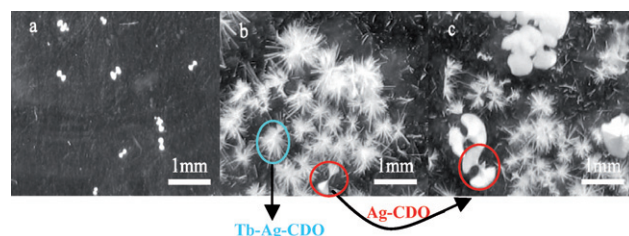
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† Electronic supplementary information (ESI) available: Crystallographic file in CIF format, photographs of the crystals, complementary drawings, luminescent spectra, and PXRD patterns. CCDC reference numbers 701572 and 701573. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b904704m
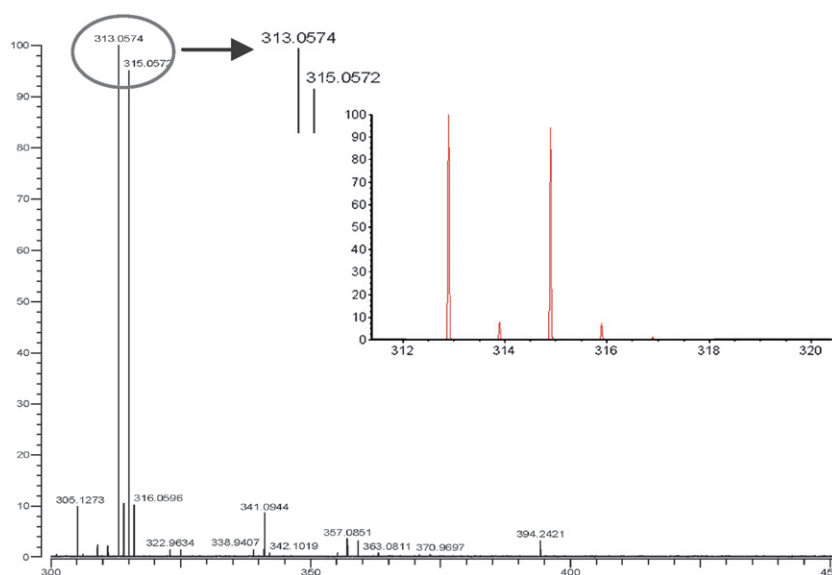

Fig. 1 The visible sequential crystallization of complexes **Tb-Ag-CDO** and **Ag-CDO** recorded on a camera (photographs viewed on a scale of 1 mm): (a) after 1 h; (b) after 12 h; (c) after 24 h.

regular needle shape. The final major product turned out to be light yellow crystals of **Ag-CDO**, which was further confirmed by PXRD (Fig. S4†).

In Fig 1, an interesting precipitation sequence of **Tb-Ag-CDO** and **Ag-CDO** was observed. Initially, there was a kinetic process, in which **Tb-Ag-CDO** was generated as the major product compared with **Ag-CDO** (*ca.* 4.5 : 1). As time passes, **Tb-Ag-CDO** may slowly convert into the thermodynamics product of **Ag-CDO**. This interesting crystallization process prompted us to consider whether the ligand combined with different metal ions in selection and some equilibrium existed in the reaction process. Thereupon, the self-assembly process was resolved into two-step reactions to synthesize **Ag-CDO** and **Tb-Ag-CDO** successively, which is favourable for elucidating the unknown self-assembly process.

Firstly, **Ag-CDO** was successfully prepared *via* the reaction of Ag⁺ and H₂CDO under reflux conditions in a large yield (about 90%) for 2 d. Structural determination§ reveals a 1D silver chain linked by HCDO⁻ and μ₂-H₂O molecules in **Ag-CDO**. The repeated unit in **Ag-CDO** consists of one crystallographically independent silver center, one HCDO⁻ anion, and one bridging water molecule as viewed in Fig. S5.† The Ag atom is pentacoordinated with a distorted trigonal bipyramidal coordination geometry defined by five oxygen atoms from three individual HCDO⁻ units and two bridging water molecules. Adjacent Ag atoms with strong Ag···Ag interaction (2.9905(15) Å) are bridged by two carboxylic groups to form binuclear units, which are further linked by bridging water molecular into a highly ordered 1D chain.

Ag-CDO is readily soluble in boiling water, which is favourable for the study of solution chemistry. The solution-phase species of **Ag-CDO** is studied in detail *via* ESI-MS. In Fig. 2, the main mass clusters at 313 and 315 amu correspond to [Ag(HCDO)Na]⁺ cations due to a calculated isotope pattern.[3] Thus, there is a sound reason to believe that the "stable products" of **Ag-CDO** in aqueous solution are mostly [Ag(HCDO)] building units. ¹H NMR spectra were measured simultaneously (Fig. S6†).[8]

Fig. 2 Positive-ion ESI-MS of **Ag-CDO** in water. The bottom panel shows the peak cluster associated with the [Ag(HCDO)Na]$^+$ ion, while the panel in the right corner shows the calculated isotope distribution pattern expected for the fragment proposed.

Now that **Ag-CDO** existed as [Ag(HCDO)] in aqueous solution, could these building blocks further construct **Tb-Ag-CDO** with Tb^{3+} ions? Moreover, **Ag-CDO** and **Tb-Ag-CDO** were symbiotic in the one–pot reaction, and there should be some close relationship between them. Subsequently, we successfully obtained **Tb-Ag-CDO** utilizing **Ag-CDO** and Tb^{3+} ions as the reactant. The structural analyses§ reveal that **Tb-Ag-CDO** consists of one crystallographically independent Tb(III) center, three Ag(I) centers and three CDO^{2-} anions. As shown in Fig. 3, Ag1, Ag2 and Ag3, possessing an analogous coordination environment, are four-coordinated with a distorted tetrahedral coordination geometry defined by two hydroxyl oxygen atoms and two carboxylic oxygen atoms from four HCDO$^-$ units, while Tb1 is eight-coordinated with a distorted double-capped trigonal prism geometry defined by two carboxylic oxygen atoms

from two individual CDO units and six water molecules. It is noteworthy that the structure is solidated by Ag zigzag chains linked by plentiful Ag···Ag interactions (Fig. 3). The Ag···Ag distances of 2.8480(11) Å and 2.7936(11) Å are significantly shorter than that (2.89 Å) in metal silver, indicative of strong Ag···Ag interactions.[9] The Ag···Ag distances of 3.1657(11) Å and 3.2043(11) Å are below the sum of the van der Waals radii of two Ag atoms (3.44 Å), which indicates a weak Ag···Ag interaction. Ag atoms are linked into 1D Ag zigzag chains *via* these Ag···Ag interactions.

Tb-Ag-CDO dissolves into water slightly, and emits the characteristic green fluorescence when excited at 300 nm. Considering that hydrated Tb^{3+} ions do not show fluorescence, the second reaction process is further investigated by monitoring the change of fluorescence. Tb(NO$_3$)$_3$ was added in batches to 2.5 M aqueous solution of **Ag-CDO**, which can be regarded as the solution of [Ag(HCDO)] based on ESI-MS analysis. As shown in Fig. 4, the enhancement rate of fluorescence slowed down gradually with the addition of Tb^{3+} ions. Finally, the intensity saturated upon *ca.* 8.5/15 eq. Tb^{3+} ions (two intense emission bands at 489 and 545 nm correspond to $^5D_4 \rightarrow {}^7F_6$
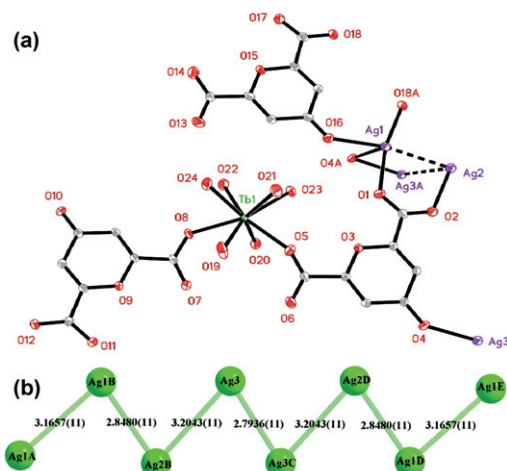

Fig. 3 (a) Coordinating environment of Tb and Ag atoms for **Tb-Ag-CDO**(A = −x, 2 − y, 2 − z). (b) The 1D Ag zigzag chain of **Tb-Ag-CDO** (A = x, y, z − 1, B = 1 − x, 2 − y, 1 − z, C = 1 − x, 1 − y, −z, D = x, y − 1, z − 1, E = 1 − x, 1 − y, 1 − z).
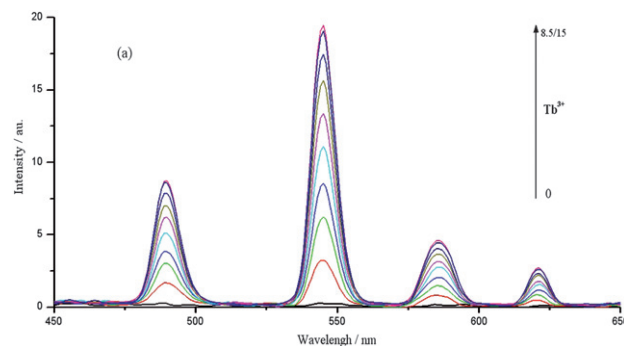

Fig. 4 Changes in the emission spectra of an aqueous solution of **Ag-CDO** (2.5 μM) upon addition of Tb^{3+} ions: 0, 1/15, 2/15, 3/15, 4/15, 5/15, 6/15, 7/15, 8/15, 8.5/15 equiv. with respect to the amount of Ag.

Scheme 1 A feasible reaction pathway.

and $^5D_4 \rightarrow {}^7F_5$, two weaker emission bands at 586 and 622 nm originate from $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$, respectively.[10]

It is the stepwise strategy that turns studying the self-assembly into reality. Integrating all experimental facts, a feasible pathway to yield **Tb-Ag-CDO** is proposed in detail in Scheme 1. H_2CDO can initially combine with Ag^+ ions to generate stable precursor [Ag(HCDO)] in aqueous solution. When $Tb(NO_3)_3$ is added to the aqueous solution of **Ag-CDO**, Tb^{3+} ions may preferentially bind to [Ag(HCDO)] to generate the target product (**Tb-Ag-CDO**). With the emergence of **Tb-Ag-CDO**, the fluorescence enhanced significantly. Simultaneously, as the concentration of [Ag(HCDO)] decreased, the enhancement rate of fluorescence slowed down gradually. However, the fluorescence intensity can not reach its maximum upon 1 : 3 stoichiometry for Tb^{3+} ions and [Ag(HCDO)] to yield complete $\{[Tb_2Ag_6(H_2O)_{12}(CDO)_6]\cdot 6H_2O\}_n$, but saturates with excess Tb^{3+} ions of about 8.5/15 eq. The reason for this may be attributed to the equilibrium among **Ag-CDO**, [Ag(HCDO)] and **Tb-Ag-CDO**, which can be further confirmed by their previous sequential crystallization (Fig. S1†).

Apart from the experimental facts, the concluded reaction pathway (Scheme 2) can also be validated by the structural self-assemble. Silver ions initially combine with CDO anions to form [Ag(HCDO)] monometallic PBUs (primary building units). These PBUs can be further linked by water molecules to produce a highly ordered 1D chain (**Ag-CDO**). With the existence of Tb^{3+} ions, these PBUs can assemble with Tb^{3+} to yield initially a 2D layer structure. Further, the 2D layers are linked into a novel 3D structure via a weak
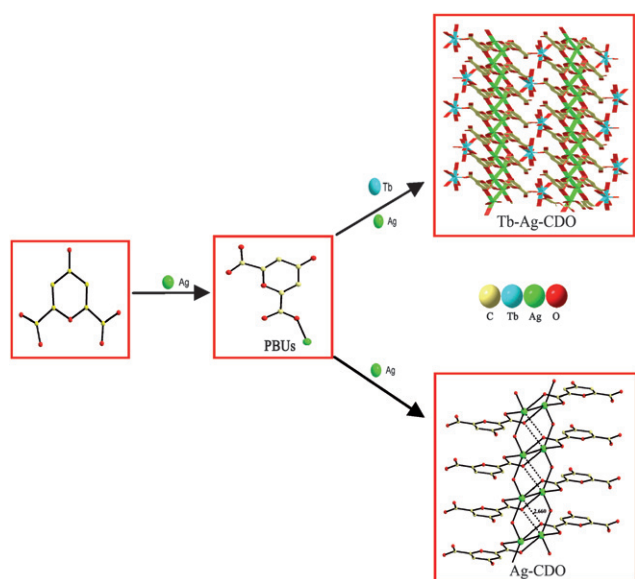
coordinating interaction of Ag⋯O (2.79 Å) together with the plentiful Ag⋯Ag interactions [3.1657(11) Å and 3.2043(11) Å]. The PBUs of [Ag(HCDO)] play a dominating role in the self-assembly process of **Tb-Ag-CDO**. That is, our concluded reaction pathway is further corroborated.

In addition, the terbium complex $\{[Tb_2(H_2O)_6(CDO)_3]\cdot 6H_2O\}_n$ (**Tb-CDO**) with a 2D layer structure (Fig S8†) could also be synthesized by mixing Tb^{3+} ions and H_2CDO under reflux conditions. However, its production cycle was always too long (2 months). Moreover, **Tb-CDO** precipitates in a low yield (ca. 15%) and is hard to dissolve in water and common organic solvent. Therefore, the process from **Tb-CDO** to yield **Tb-Ag-CDO** is difficult to achieve.

In summary, an interesting sequential crystallization process of $[Ag(\mu_2\text{-}H_2O)(HCDO)]_n$ (**Ag-CDO**) and $\{[Tb_2Ag_6(H_2O)_{12}(CDO)_6]\cdot 6H_2O\}_n$ (**Tb-Ag-CDO**) in one pot was initially observed via rapid photography technology. Subsequently, utilizing the stepwise strategy, we have preformed a thorough study on the self-assembly process of **Tb-Ag-CDO**. We first integrated the fluorescence spectra with ESI-MS to monitor the self-assembly process of the heteronuclear complex. This could provide a useful strategy for chemists to research the generation mechanism of heteronuclear complexes.

Notes and references

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Scheme 2 Constructing **Ag-CDO** and **Tb-Ag-CDO** from H_2CDO with Tb^{3+} and Ag^+ ions in the self-assembly process.

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