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A novel single-side azobenzene-grafted Anderson-type polyoxometalate for recognition-induced chiral migration†

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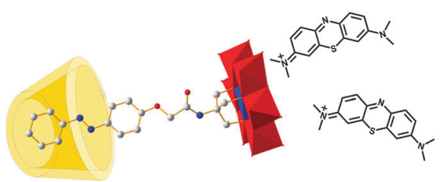
A three-component supramolecular hybrid system based on host–guest recognition and electrostatic interaction has been developed for a consecutive chiral transfer from an alpha-cyclodextrin to cationic dyes *via* the bridge of a new azobenzene-grafted Anderson-type polyoxometalate cluster.

Polyoxometalates (POMs) are a class of discrete nano-scale inorganic polyanion clusters, which possess various advantageous functions for potential applications in the fields of catalysis, medicine, photochromic materials, *etc.*[1] Recently, the covalent and non-covalent organic modifications of POMs draw much more research attention due to their synergistic properties compared to each individual component.[2] Molecular hybridization plays a significant role in the construction of self-assembled architectures in crystals, films and solutions. Interestingly, the strategy has been extended to the creation of chiral POM clusters and their self-assemblies. Typically, chiral organic units are introduced into POM's framework *via* coordination, hydrogen bonding or covalent linkage, yielding stable enantiomers of chiral hybrids.[3] Alternatively, chiral cations are also used to replace the counter ions, forming surface-enwrapped POMs (SEPs) through electrostatic interaction. This approach can be also applied to induce the chirality of heteropoly blues.[4] However, it is still a challenge to transfer the chirality of POM clusters because of their structural rigidity and quick racemization in a solution system. The induced circular dichroism (ICD) of achiral molecules, derived from chiral units through various interactions, has been widely studied.[5] Due to the fast attenuation of chirality against the distance from the chiral centre, so far, effective methods to deal with the continuous chiral transfer referring to POMs *via* multi-supramolecular interactions have rarely been reported. The first example of recognition between guest group-modified POM and cyclodextrins (CD) was reported recently; however, the inclusion chirality was not involved.[6]

To obtain stable chiral POMs in aqueous solution through a different route from reported ones, we synthesized a new single-side azobenzene-grafted Anderson-type POM. The main reason why we prepared the umbrella-shaped Anderson-type POM hybrid is that the covalently grafted azobenzene group on one side of the disc-like POM could be used as an antenna group for chiral induction and could be stably sustained in solution. On the other hand, the empty space on the free side of the POM could draw in dye counter ions that can serve as the chiral acceptor, forming a consecutive chiral transfer chain (Scheme 1). By just adjusting the multi-supramolecular interactions within the three-component system, we successfully carried out the modulation of the chiral transmission.

The single-side-modified Anderson-type hybrid bearing azobenzene group covalently, is synthesized in tetrabutyl ammonium (TBA) salt following a modified procedure previously reported in literature.[7,8] FT-IR and ^{1}H NMR (Fig. S1 and S2, ESI†) spectra and elemental analysis (Table S1, ESI†) confirm the proposed chemical structure. The single crystal of the POM is also obtained from the mixed solvent of distilled water and ethanol (1 : 4 in v/v) at pH 5, and the structure analysis identifies the cluster structure of $[C_6H_5N{=}NC_6H_4OCH_2CONHC(OCH_2)_3AlMo_6O_{18}(OH)_3]^{3-}$ (named as Azo-POM). Further details of the X-ray structural analysis are summarized in Table S2 (ESI†). Compared to the hybrid with three TBA counter ions preparing at pH 6–7, only two TBA counter



Scheme 1 Schematic drawing of chiral recognition and transfer by using hybrid POM as a bridge of α-cyclodextrin and dye molecules. Ball-and-stick and polyhedral representation of the prepared umbrella-shaped Azo-POM, where colour code: MoO_6 and AlO_6 units in red and blue polyhedrons; C, N, and O atoms in grey, blue and red sphere, respectively. H atoms are omitted for clarity.

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ions are found (Fig. S3, ESI†). Considering the weak acidic environment, it is reasonable to think that one TBA counter ion was replaced by a protonated water during crystallization. An elemental analysis of the crystalline product clearly confirms the change of TBA counter ions in crystals (Table S1, ESI†). To increase the solubility of the synthesized cluster in water, sodium ions are then used to replace the TBA counter ions following the previous procedure,[9] and $Na_3(Azo\text{-}AlMo_6O_{18})$ (abbreviated as Na–Azo-POM) is obtained. ^1H NMR (Fig. S4, ESI†) spectrum and an elemental analysis (Table S1, ESI†) are also carried out to identify the replacement of the counter ions.

Because the CD recognition-induced chirality is closely related to the matching space with the guest component, as well as its binding, we evaluated the interaction of synthesized POM with CDs bearing different sizes of cavity. The sample solutions were obtained by simply dropping CDs in water into an aqueous solution containing equal molar amounts of Na–Azo-POM to a final concentration of 2.1×10^{-4} mmol ml^{-1} at room temperature. After a while of curing, the recognition and chiral transfer from CDs to azobenzene group of Azo-POM were examined through circular dichroism spectrum (CDS). As shown in Fig. 1, γ-CD exhibits insensitivity on chiral induction signal for guest Azo-POM, while β- and α-CDs show obvious induction activity due to both positive and negative Cotton effects. The activity appears at around 345 and 443 nm, apparently sourcing from azobenzene group in POMs. It is known that CDs bear the internal chirality in inner cavity, and this result indicates that there exists a chiral transfer from CDs to Azo-POM. Thus, the achiral POM can be induced to yield chirality that can be stably maintained in aqueous solutions (Fig. S5 and S6, ESI†). To utilize the stronger recognition capability under the same environment and to keep the specificity, we selected α-CD as the recognition host and chiral inducer of the synthesized hybrid POM in the following study. The 2D ROESY NMR spectrum indicates that H–H correlations take place between protons in the inner cavity of α-CD and phenyl groups of *trans*-state Azo-POM, unequivocally demonstrating the existence of a strong inclusion interaction (Fig. S7, ESI†). In contrast, there is no such interaction occurring for the *cis*-state Azo-POM. In comparison to α-CD alone, the peaks corresponding to protons located in the cavity of α-CD in mixture solutions were found to have larger chemical shifts up-field in corresponding 1D selective ROESY NMR spectrum (Fig. S8, ESI†), confirming the tight inclusion.

Due to the hydration-induced electrostatic dissociation, alkaline metal ion counter ions are not closely associated with the polyanion clusters in aqueous solutions. But when organic cations bearing hydrophobic terminal are added into the cluster solution, their electrostatic connection with Azo-POM can greatly increase. This happens because the charge neutralization leads to the formation of a stabilized ionic pair accompanied by the enhanced hydrophobicity. Methylene blue (MB) is an organic cationic dye, which has strong long-wavelength absorption and could be considered as an appropriate candidate for the ionic combination with Azo-POM. The stability of MB after mixing with POM was checked by UV-Vis spectrum (Fig. S9, ESI†), and no obvious degradation was found in the present experimental conditions. By adding a suitable amount of MB into the α-CD included Azo-POM aqueous solution (MB : Azo-POM in 3 : 5 mole ratio) with stirring at room temperature and curing for 12 h, we obtained a three-component solution. After an extra standing, the electrostatic interaction between MB and Azo-POM is characterized by ^1H NMR spectra in mixture solution of D_2O and DMSO-d_6 (1 : 1 in v/v) (Fig. 2). In comparison with MB alone, the proton peaks corresponding to MB.

In the α-CD included Na–Azo-POM complex system shift to the low field, implying the formation of an electrostatic connection with Azo-POM cluster. This assignment is supported by the emergence of deposition when the amount of MB is further increased in the triple-component solution. We also use an equivalent charge ratio of MB to replace the sodium ions of Azo-POM in water. Through the same procedure reported in literature, we intended to obtain a complex (MB–Azo-POM) bearing three MB counter ions, as confirmed by elemental analysis (Table S1, ESI†). The wholly electrostatic complex MB–Azo-POM became almost insoluble in water and its NMR spectrum in organic solvent displayed a similar moving tendency of chemical shifts as those of MB when mixing with Azo-POM in water (Fig. S10, ESI†), further confirming the electrostatic interaction between them. Therefore, we could figure out the electrostatic interactions when blending MB with Azo-POM regardless of the addition of α-CD. Apparently, the electrostatic combination is favourable for the chiral transfer between the organic–inorganic ionic pairs.

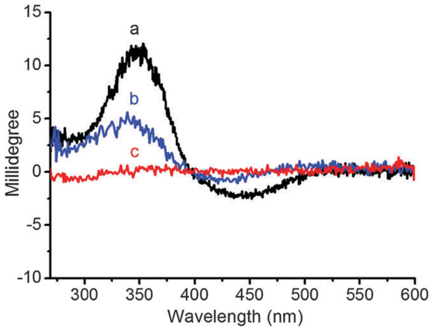

Fig. 1 CDS of Na–Azo-POM mixed with equivalent mole of (a) α-CD, (b) β-CD and (c) γ-CD in aqueous solution.

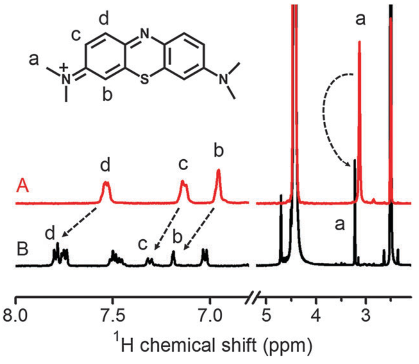

Fig. 2 ^1H NMR spectra of (A) MB and (B) MB mixing with Na–Azo-POM (MB : Azo-POM at molar ratio of 3 : 5) in D_2O/DMSO-d_6 (1 : 1 in v/v) solution.

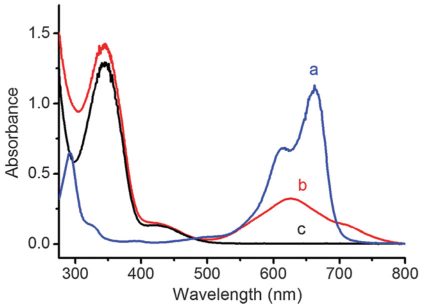

Fig. 3 UV-Vis spectra of (a) MB (3.0×10^{-5} mmol ml^{-1}), (b) MB mixing with Na–Azo-POM and α-CD, and (c) Na–Azo-POM mixed with α-CD in aqueous solution (MB : α-CD : Na–Azo-POM at molar ratio of 3 : 5 : 5).

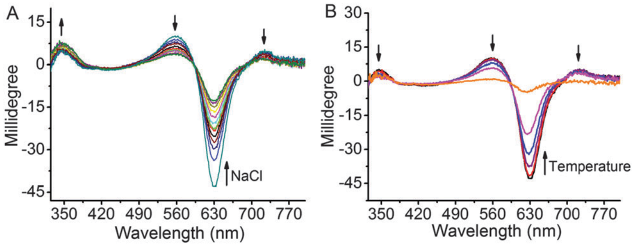

Fig. 4 (A) CDS of MB and α-CD included Na–Azo-POM (3 : 5 : 5 in molar ratio) in aqueous solution by gradually increasing the concentration of NaCl to 0, 0.043, 0.086, 0.128, 0.171, 0.214, 0.257, 0.342, 0.428, 0.599, 0.770, 1.112, and 1.454 mmol ml^{-1}. (B) CDS of MB, Na–Azo-POM mixed with α-CD in aqueous solution by gradually increasing the temperature (20, 30, 40, 50, 60, and 80 °C).

As shown in Fig. 3, when MB cations are added into the α-CD included Azo-POM solution, the absorptions at *ca.* 627 and 713 nm with a broad band decreased markedly at 560 nm, to the visible region. The bands moving to the long wavelength in comparison to isolate MB point out the electrostatic interaction-induced MB aggregation around POMs.[10] In contrast, the band at 345 nm that is ascribed to the absorption of Azo group does not show any change in its state without MB, indicating a constant inclusion state.

To confirm the chiral induction and migration, CDS of the three-component system were carried out (Fig. S11, ESI†). For the MB mixed with Na–Azo-POM, no chiral signal was found. When MB was mixed with α-CD, the chiral signal of MB molecule could still not be seen due to the bigger size of MB. The 2D ROESY NMR spectrum also confirms that no inclusion of α-CD to MB occurring through β-CD works well (Fig. S12, ESI†). In contrast, when the three components are mixed together, on one hand, a positive Cotton signal at around 345 nm and a negative signal at about 440 nm can be well ascribed to the host–guest recognition-induced chirality of the π–π* transition band of *trans*-azobenzene groups. On the other hand, the positive Cotton signals at 558 and 720 nm and much stronger negative Cotton signal at 629 nm appear and can be unequivocally attributed to the induced chirality of MB. These results concerning Cotton activity clearly prove the chiral migration from α-CD to MB bridged by Azo-POM.

Apparently, both electrostatic interactions and host–guest recognition play crucial roles in the chiral migration and can be used for modulating the chirality of Azo-POM and the MB dye molecule. With the addition of sodium chloride in the three-component system, the intensity of Cotton signals of MB obviously decreases until the concentration of the salt reaches *ca.* 1.45 mmol ml^{-1} (Fig. 4A). It is well known that the existence of electrolytes can increase the ionic strength of the solution system, which weakens the electrostatic interaction of ionic pairs.[11] As a result, the interaction between Azo-POM and MB fades gradually so that the average distance between the cationic dye and the anionic cluster becomes greater. Nevertheless, the ionic pair could not be completely decomposed by simply adding electrolytes. When the concentration of NaCl was gradually increased, the chemical shifts of MB in Na–Azo-POM-mixed solution moved close to those of isolated MB solution, indicating the weakening of the electrostatic interaction (Fig. S13, ESI†). In addition, based on the comparison of the absorption spectra (Fig. S14, ESI†), the fact that the bands of MB that are assigned to the aggregation state shift to the long wavelength demonstrates the increase in the amount of dissociated MB with the addition of salt. This change also implies that the chiral transfer from Azo-POM is blocked by weakening electrostatic interactions. As seen from the same CDS measurement in Fig. 4A, the intensity of the chiral signal of Azo group at 345 nm increases with the addition of salt, indicating that the host–guest recognition is enhanced by the ionic strength change. In contrary, when heating the three component system, accompanying by the decrease of chiral signals of MB, we also see the decrease of chiral intensity of Azo group at 345 nm (Fig. 4B). Normally, the host–guest recognition can be broken down under higher temperature. This change implies that the host–guest interaction is gradually dissociated, and consequently, the intensity of chiral signals of MB decreases greatly at the same time. Variable-temperature ^{1}H NMR spectra indicate constant electrostatic interaction between MB and Azo-POM cluster while increasing temperature (Fig. S15, ESI†). Therefore, it is reasonable to think that the chiral transfer is stopped by the decomposition between the α-CD and Azo-POM during the heating process.

A new single-side azobenzene-modified Anderson-type POM was synthesized. The novel umbrella-like hybrid cluster displays interesting property when building a three component supramolecular system with α-CD and MB dye cations *via* both host–guest recognition and electrostatic interactions. The chirality of α-CD is amplified into Azo-POM and MB cations. Furthermore, the chiral migration is modulated through simply tuning the concentration of electrolyte and heating. The present results open a new approach to drive POMs as inorganic bridging ligands for chiral transfer and amplifications to cationic molecules.

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