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## Electrochemical stimulus-responsive supramolecular polymer based on sulfonatocalixarene and viologen dimers<sup>†</sup>

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## A water-soluble supramolecular polymer based on homoditopic calixarene and viologen has been constructed, and its reversible formation can be well controlled by electrochemical stimulus.

Construction of supramolecular polymers, where monomer units are brought together by noncovalent interactions instead of covalent polymerization and/or cross-linking, is emerging as a smart design principle for responsive materials capable of self-repairing and self-healing.<sup>1</sup> The directionality and strength of the supramolecular binding are important because of the fact that hydrogen bonding and metal coordination, as the more favored noncovalent interactions, have been widely employed to drive the self-assembling of supramolecular polymers.<sup>2,3</sup> The host-guest interactions are relatively less explored and are still an immature project to build supramolecular polymers, with crown ethers and cyclodextrins as relatively common host monomer units.<sup>4,5</sup> More excitingly, some of them are responsive to external stimuli, such as competitive guest molecules,<sup>4c</sup> acid-base,<sup>6</sup> and photochemistry,<sup>4d</sup> and thus have the potential to exhibit similar mending capability with an indefinitely repeatable process.

Herein, we report a novel supramolecular polymer by *p*-sulfonatocalix[4]arene-based homoditopic receptor upon iterative complexation with a homoditopic viologen connector, and its assembly process can be reversibly controlled by electrochemical stimulus. Despite some calixarene-based supramolecular polymers in previous and more recent works,<sup>7</sup> no such electrochemically-responsive system has been reported before. Electrochemical stimulus is playing an increasingly large role in controlling supramolecular assembly/disassembly because it does not contaminate the system.<sup>8</sup>

*p*-Sulfonatocalix[4]arene and viologen were selected as host–guest pairs because of their high complexation stability,<sup>9</sup> which renders them able to build truly polymeric materials. On the other hand, the complex stability constant is dramatically sensitive to the redox process of viologen, decreasing in magnitude from dication to radical cation, to neutral form, which means that assembly/disassembly of the polymer can be manipulated by electrochemical switching and redox control.

A minimum of two interacting sites is needed to form supramolecular polymers from two complementary monomers, and therefore, the ditopic *p*-sulfonatocalix[4]arene host (*bis*-SC4A) and methyl viologen guest (*bis*-MV<sup>4+</sup>) were synthesized (Scheme 1). <sup>1</sup>H NMR spectroscopy presents the obvious evidence for the host–guest complexation (Fig. S5, ESI†). Upon addition of *bis*-SC4A, the *bis*-MV<sup>4+</sup> protons H<sub>1-4</sub> undergo pronounced upfield shifts due to the ring current effect of aromatic nuclei of calixarene. The  $\Delta\delta$  values are 2.14 ppm for H<sub>1</sub>, 2.47 ppm for H<sub>2</sub>, 1.64 ppm for H<sub>3</sub> and 0.43 ppm for H<sub>4</sub>. Moreover, there are almost negligible complex-induced shifts for H<sub>5</sub> and H<sub>6</sub>. We can therefore infer that *bis*-MV<sup>4+</sup> is captured by *bis*-SC4A with the methylpyridinium portion immersed into the cavity, while the bridged ethylene group is located outside.<sup>9</sup>

ITC experiments supply the quantitative information for the host-guest complexation and its thermodynamic origin. As shown in Fig. 1, the association constant of bis-SC4A with *bis*-MV<sup>4+</sup> was obtained as  $4.27 \times 10^5$  M<sup>-1</sup> with a good "N" value of 0.998 in the curve fitting. The experimental "N" value agrees well with the expected value of 1. Resembling the 1:1 complexation case of SC4A with  $MV^{2+}$  ( $\Delta H^{\circ}$  =  $-31.98 \text{ kJ mol}^{-1}$ ;  $T\Delta S^{\circ} = -3.62 \text{ kJ mol}^{-1}$ ),<sup>9</sup> the assembly process of supramolecular polymer is also driven by a favorable enthalpy change ( $\Delta H^{\circ} = -39.47 \text{ kJ mol}^{-1}$ ), accompanied with negative entropy change ( $T\Delta S^{\circ} = -7.36 \text{ kJ mol}^{-1}$ ) (Assuming that all the binding sites for the interacting species are identical,  $\Delta H^{\circ}$  and  $T\Delta S^{\circ}$  represent the values per host site, where the experimental  $\Delta H^{\circ}$  value was divided by the number of sites of host).<sup>4b</sup> It is noticed that the entropy value of *bis*-SC4A with *bis*- $MV^{4+}$  is twice as unfavorable as that of SC4A with  $MV^{2+}$ , indicating that the *n*:*n* supramolecular polymer is obviously more entropy-disfavored than the simple 1:1 complex.

The morphology of the supramolecular polymer was investigated by AFM measurement, as shown in Fig. 2. As expected, linear objects with a length in the micron range were observed. The 1D nanostructure shows the height of 1.2 nm,



Scheme 1 Schematic representation of self-assembling polymer formation by the iterative host–guest complexation between bis-SC4A and bis-MV<sup>4+</sup>.

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**Fig. 1** Microcalorimetric titration of *bis*-SC4A with *bis*-MV<sup>4+</sup> in aqueous solution (pH 7.2) at 298.15 K. (a) Raw ITC data for sequential 25 injections (10  $\mu$ L per injection) of *bis*-MV<sup>4+</sup> solution (5.00 mM) injecting into *bis*-SC4A solution (0.25 mM). (b) Apparent reaction heat obtained from the integration of calorimetric traces.

which is identical to the upper-rim size of SC4A. DLS result shows that only one relatively broad peak was observed from 60 to 200 nm (Fig. 3), indicating the formation of a variety of highly polymerized supramolecular assemblies with an average diameter of 141 nm. GPC measurement gives the weightaverage molecular weight, where two  $M_w$  (Da) values  $(2.0 \times 10^5 \text{ and } 3.6 \times 10^5)$  were obtained, meaning that there are on average 105–190 asymmetrical host and guest units in the assembly.

The electrochemical property of the supramolecular polymer was further studied by CV. As shown in Fig. 4(a), free *bis*-MV<sup>4+</sup> undergoes two consecutive two-electron reduction processes to its neutral form *bis*-MV<sup>0</sup>. Both reduction peaks of complexed *bis*-MV<sup>4+</sup> exhibit negative shift (38 mV for the first reduction process and 121 mV for the second one), which indicates that the complexation of bis-SC4A makes reduction of *bis*-MV<sup>4+</sup> more difficult, and also that the complex stability of bis-SC4A with bis-MV<sup>4+</sup> decreases gradually upon reduction. The large  $\Delta E_{\rm p}$  of the second redox is indicative of kinetic complications characterized by an electrochemical-chemical mechanism. Upon complexation with bis-SC4A, the second reduction peak undergoes a major negative shift, while the corresponding re-oxidation peak just undergoes a minor shift, meaning the second redox process of complexed bis-MV<sup>4+</sup> is irreversible. This phenomenon suggests that the re-oxidation process may adopt a different pathway from the original reduction process (Fig. S9, ESI<sup>†</sup>). Moreover, the first



Fig. 2 AFM image of the linear polymer from *bis*-SC4A and bis-MV<sup>4+</sup>.

Fig. 3 Distribution of the hydrodynamic diameter of 1.0 mM bis-SC4A aqueous solution with 1 equiv. bis-MV<sup>4+</sup> at 298 K.

re-oxidation peak splits dramatically into two peaks, located at -513 and -448 mV respectively, upon complexation.

To focus on the first redox couple, we performed the host-guest CV experiments in the range of 0.0 to -1.0 V with different scan rates (see Fig. 4(b)). To our surprise, the re-oxidation peak at -448 mV disappeared when the scan rate was still 0.1 V s<sup>-1</sup>. On increasing the scan rate from 0.1 to 2 V s<sup>-1</sup>, the undistorted CV curves indicated that electrons transferred directly to and from the inclusion complex in the first redox process. This means that *bis*-MV<sup>4+</sup> is retained in the calixarene cavity during the first redox process, which is in line with a modest deviation from reversible redox reaction ( $\Delta E_p = 78$  mV at scan rate of 0.1 V s<sup>-1</sup>). Therefore, we speculated that the re-oxidation peak at -448 mV belongs to the oxidation of free *bis*-MV<sup>2+</sup> radical accumulated in the second redox process.

A reasonable mechanism is illustrated in Scheme 2 based on these CV results. On the cathode (blue region), the complexed



Fig. 4 (a) CV curves of bis-MV<sup>4+</sup> (1.0 mM in pH 7.2 phosphate buffer solution) in the absence (red) and presence (blue) of 1 equiv. of bis-SC4A. Scan rate is 0.1 V s<sup>-1</sup>. (b) CV curves of bis-MV<sup>4+</sup> from 0.0 to -1.0 V in the presence of bis-SC4A as a function of scan rate (0.1–2.0 V s<sup>-1</sup>).



Scheme 2 Illustration for the redox process of bis-MV<sup>4+</sup> in the presence of bis-SC4A.



Scheme 3 Illustration for the assembly/disassembly of the supramolecular polymer based on *bis*-SC4A and *bis*- $MV^{4+}$  with electrochemical stimulus.

*bis*- $MV^{4+}$  turns to free *bis*- $MV^0$  via two reduction and one disassociation processes (A  $\rightarrow$  B  $\rightarrow$  C  $\rightarrow$  D). Since *bis*-SC4A allows neutral bis-MV<sup>0</sup> into its cavity, the C/D disassociating process occurs quite rapidly compared to the time scale of cyclic voltammetry. The direct electron-transfer process in the restricted scan range proved that disassociation from B to E is unfavorable. On the anode (*red region*), free bis-MV<sup>0</sup> is first oxidized to free bis-MV<sup>2+</sup> (D/E process) without association with bis-SC4A. Two alternative pathways can take place concurrently from E to A: one is the direct oxidation process of free *bis*- $MV^{2+}$  followed by a complexation process  $(E \rightarrow F \rightarrow A)$ ; the other is the oxidation process of complexed bis-MV<sup>2+</sup> after a complexation process (E  $\rightarrow$  B  $\rightarrow$  A). Consequently, two anodic peaks were observed for the first re-oxidation process. The peak at -513 mV is assigned to the B/A oxidation process and the peak at -448 mV is assigned to the E/F oxidation process. Consequently, an extensive disassembly of the supramolecular polymer occurs when *bis*- $MV^{4+}$  is fully reduced. Otherwise the E/F oxidation peak would not be observed.

CV measurements at different scan rates (see Fig. S6, ESI<sup>†</sup>) in the range of 0.0 to −1.4 V were conducted as well to further verify the mechanism. For the first redox process, the ratio of two re-oxidation peaks ( $I_{-448 \text{ mV}}/I_{-513 \text{ mV}}$ ) increases gradually along with the increase in scan rate. It does make sense that higher scan rate means there is less time for the E → B complexation process, but that conditions are more favorable for the direct E → F oxidation process.

In summary, we designed and constructed a reversible supramolecular polymer based on homoditopic calixarene and viologen using an electrochemical stimulus. In the oxidized form, the two components assemble to linear polymers with lengths of micron magnitudes, whereas in the reduced form, the polymer disassembles back to monomer units (Scheme 3). Such a reversible, noncovalent system is potentially applicable to design sophisticated polymeric materials with excellent responsive properties.

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