Polyoxometalate-Based Hybrid Supramolecular Polymer via **Orthogonal Metal Coordination and Reversible Photo-Cross-Linking**

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S Supporting Information

ABSTRACT: To enrich the building blocks and functions of supramolecular polymer, functioned inorganic polyoxometalate clusters were introduced through a novel and efficient orthogonal self-assembly strategy. The design principle is based on the organic modification of polyoxometalates (POMs) with coordination groups and electrostatic interaction of POMs with surfactants capped by photo-cross-linkable groups. Because of the relatively independent nature of these two interactions, it is possible to prepare POMs-based supramolecular cross-linked network through coordination-



photo-cross-linking and vice versa, leading to the formation of main-chain-type POMs-based supramolecular polymer networks and gels. The responsiveness of these two interactions also endows the resulted supramolecular polymer with different responsiveness to light and coordination. Therefore, orthogonal self-assembly supramolecular polymerization of POMs provides a facile strategy to improve the processability of inorganic clusters, paving a new avenue toward cluster-based materials and electronic devices.

1. INTRODUCTION

Supramolecular polymers are usually constructed from different monomers via intermolecular interactions.¹⁻³ Different interactions such as hydrogen bonding,⁴ coordination,⁵ electrostatic interactions,⁶ host-guest interaction,⁷ and so on have been used in supramolecular polymerization. The flexibility and responsiveness nature of supramolecular interactions enable supramolecular polymers with applications in different areas, such as self-healing materials,8 smart catalysts,⁹ drug and gene delivery vehicle,¹⁰ and so on. Generally, there are still several problems obstructing the development of supramolecular polymer systems.¹¹ One is about the molecular structure and molecular weight. Because of the possible side reactions of intermolecular/intramolecular cyclization, linear supramolecular polymers with higher molecular weight are very difficult to prepare. The other problem is about the functionalization of supramolecular polymers. One of the possible solutions to these problems is to use functioned rigid monomers. To enrich the composition and functions of supramolecular polymers, functional building blocks such as metal complexes,¹² π -conjugated systems,¹ functioned clusters (polyhedral oligomeric silsesquioxane (POSS),¹⁴ polyoxometalates (POMs),^{15,16} boron cluster,¹⁷ etc.), and so on have been introduced into supramolecular polymers.

Polyoxometalates (POMs) are a kind of functioned inorganic cluster with multiple composition and well-defined structure. The varied compositions endow POMs with properties ranging from fundamental research such as catalysis, energy storage, photo/electrochromism, and magnetism to industrial catalysis.¹⁸⁻²¹ Therefore, POMs are potential candidates for functioned supramolecular polymers.²²⁻ Taking advantage of their negatively charged characteristic and organic modification, POMs have been introduced to supramolecular polymer systems through controlled polymerization and ionic self-assembly.²⁵⁻²⁷ By using the strategy of controlled polymerization, one can prepare only side-chain and POMs-labeled polymers. New polymerization methods, especially combination of different interactions, should be explored to prepare different topological polymers. Orthogonal self-assembly allows the integration of two and more separated interactions in one system, 28,29 which are broadly used to prepare diverse supramolecular polymers.

Herein, we designed a rigid POMs-based monomer by integrating the organic modification of POMs with terpyridine ligands and ionic graft of photo-cross-linkable coumarin groups. By use of the orthogonal interactions of coordination and photo-cross-linking, POMs-containing supramolecular polymers are prepared and well characterized. Because of the orthogonality and responsiveness of these two interactions, the prepared supramolecular polymer displays multiple responsiveness. Such a kind of strategy can be also extended to other cluster systems and be potentially applied in different areas such as chromism, smart catalyst, and so on.

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2. EXPERIMENTAL SECTION

2.1. Materials. $[N(C_4H_9)_4]_4[\alpha-Mo_8O_{26}]$, $Mn(OAc)_3\cdot 2H_2O$, and $[N(C_4H_9)_4]_4EDTA$ were prepared according to the corresponding literature.^{30–32} *N,N*-Dimethylacetamide (DMAc) and acetone were dried with CaH₂ overnight and distilled prior to use. Fe(OTf)₂ (98%) was purchased from Shanghai CIVI Chemical Technology Co., Ltd., and ethyl bromoacetate (98%) was purchased from Aladdin. Other chemicals and solvents were purchased from MACKLIN and used as received.

2.2. Characterization. ¹D (¹H, ¹³C) and ²D (¹H–¹H COSY, ¹H DOSY) spectra were recorded on a Bruker AVANCE 400 MHz spectrometer in CDCl₃ or DMSO- d_6 with tetramethylsilane (TMS) as internal reference. Diffusion-ordered spectroscopy (DOSY) experiments were taken with "ledbgp2s1d" and "ledbgp2s" pulprog. Electrospray ionization (ESI) mass spectra were acquired with a Bruker micrOTOF-Q II electrospray instrument. FT-IR spectra were performed on a Bruker Tensor 27 FT-IR spectrometer equipped with a DTGS detector (32 scans) with resolution of 4 cm⁻¹ on a KBr pellet. UV–vis spectra were collected on a Unico UV-2600A spectrophotometer scanning from 190 to 700 nm. For the UV–vis titration experiments, each sample was stirred for at least 3 min to ensure saturated coordination. For the Job's plot experiment, the total concentration of monomer **6** or 7 and Fe(OTf)₂ was controlled at 0.1

mM, while $X_{\text{Fe(II)}} \left(X_{\text{Fe(II)}} = \frac{C_{\text{Fe(II)}}}{C_{\text{Ligand}} + C_{\text{Fe(II)}}} \right)$ was varied from 0.0 to 1.0

with intervals of 0.1. Each set was stirred for at least 60 min before UV-vis measurement. For the UV irradiation-induced photo-crosslinking, three UVSP8 V1209 LED spot light sources (365 nm, 2200 mW/cm²) were applied in different directions of the cuvette with distance of 0.3 cm (Figure S8). Typically, a 10 μ M DMAc solution of 7 was used in the photo-cross-linking experiment. Organic elemental analysis (C, H, and N) was performed on a Vario EL III elemental analyzer. Scanning electron microscopy (SEM) images were acquired on a VEGA 3 LMH TESCANVEGA3LMH electron microscope and an FEI Helios G4 CX microscope. Transmission electron microscopy (TEM) images were acquired on an FEI TalosF200X electron microscope with accelerated voltage of 200 kV without staining. Supramolecular polymerization before and after UV irradiation can be monitored by rheological measurements. In this test, frequency sweep was performed by using a stress-controlled rheometer (AR-G2, TA Company) with a fixed oscillation stress of 0.5 Pa at 20 °C. The frequency range is from 0.01 to 25 Hz. The geometry is 20 mm rough-surface parallel plate with a gap of 200 μ m.

2.3. Synthesis and Preparation. Synthesis of Coumarin-Terminated Quanternized Ammonium Surfactant (2). 7-Hydroxycoumarin (1.62 g, 0.010 mol, 1 equiv), 1,12-dibromododecane (5.6 g, 0.017 mol, 1.7 equiv), and potassium carbonate (4.14 g, 0.030 mol, 3 equiv) were suspended in 50 mL of anhydrous acetone. The mixture was refluxed at 56 °C overnight. After reaction, the mixture was filtered and washed with dichloromethane. The solvent was removed by a Rotavap to give the crude product. The crude was purified on silica gel with petroleum ether and petroleum ether:dichloromethane (v/v = 2:1) as eluent to give 1 as a white solid (2.23 g, 55%). FT-IR (KBr, cm⁻¹): 1722 ($\nu_{C=O}$), 1622 ($\nu_{C=C}$), 571 (ν_{C-Br}), 496 (δ_{C-Br}). ¹H NMR (CDCl₃, 400 MHz): 7.63 (d, 1H, J = 9.6 Hz), 7.36 (d, 1H, J = 8.4 Hz), 6.83 (d, 1H, J = 8.4 Hz), 6.80 (s, 1H), 6.24 (d, 1H, J = 9.6 Hz), 4.01 (t, 2H, J = 6.8 Hz), 3.40 (t, 2H, J = 6.8 Hz), 1.91–1.23 (m, 20H). ¹³C NMR (CDCl₃, 100 MHz): 162.44, 161.36, 155.93, 143.52, 128.72, 113.03, 112.91, 112.37, 101.31, 68.67, 34.14, 32.84, 29.52, 29.44, 29.33, 28.98, 28.78, 28.18, 25.96.

Compound 1 (1.90 g, 4.64 mmol, 1 equiv) and *N*,*N*-dimethyldodecylamine (2.28 g, 10.68 mmol, 2.3 equiv) were dissolved in 50 mL of ethanol and refluxed at 80 °C overnight. The reaction mixture was concentrated to ca. 5 mL and then precipitated in 100 mL of diethyl ether to give target surfactant **2** as a white powder (2.89 g, 99%). FT-IR (KBr, cm⁻¹): 1728 ($\nu_{C=0}$), 1614 ($\nu_{C=C}$), 1350 (ν_{C-N}). ¹H NMR (CDCl₃, 400 MHz): 7.63 (d, 1H, *J* = 9.6 Hz), 7.36 (d, 1H, *J* = 8.4 Hz), 6.82 (d, 1H, *J* = 8.8 Hz), 6.79 (s, 1H), 6.23 (d, 1H, *J* = 9.6 Hz), 4.01 (t, 2H, *J* = 6.4 Hz), 3.50 (q, 4H, *J* = 8 Hz), 3.39 (s, 6H), 1.86–1.18 (m, 40H), 0.87 (t, 3H, J = 7.2 Hz). ¹³C NMR (CDCl₃, 100 MHz): 162.44, 161.39, 155.86, 143.67, 128.81, 112.97, 112.77, 112.35, 101.32, 68.65, 63.92, 51.40, 31.88, 29.58, 29.38, 29.23, 28.90, 26.27, 25.89, 22.81, 22.67, 14.13.

Synthesis of Terpyridine Symmetrically Organic-Modified Polyoxometalate TBA₃[TPY-MnMo₆] (Monomer **6**). Potassium hydroxide (15.60 g, 0.28 mol, 4.67 equiv), 4-hydroxybenzaldehyde (7.33 g, 0.06 mol, 1 equiv), and 2-acetylpyridine (13.44 mL, 0.12 mol, 2 equiv) were dissolved in ethanol (100 mL), and then ammonium hydroxide (150 mL) was added and heated at 50 °C for 24 h. Adjusting the pH to 7 by dropwise addition of acetic acid, we collected the formed precipitate and washed with ethanol (20 mL) three times. The grass green powder was recrystallized twice in a mixture of chloroform and methanol (CHCl₃:CH₃OH (v/v) = 1:2), yielding 8.48 g of 3 as a white crystal; yield 43%. FT-IR (KBr, cm⁻¹): 1610 $(\nu_{C=C})$, 1583 $(\nu_{C=C})$, 1522 $(\nu_{C=N})$, 1394 (ν_{C-C}) , 793 (γ_{C-H}) . ¹H NMR (DMSO- d_{61} 400 MHz): 9.85 (s, 1H), 8.75 (d, 2H, J = 4.8Hz), 8.65 (s, 2H), 8.65 (d, 2H, J = 7.6 Hz), 8.02 (dd, 2H, J = 7.6, 1.2 Hz), 7.79 (d, 2H, J = 8.8 Hz), 7.51 (dd, 2H, J = 7.2, 4.8 Hz), 6,97 (d, 2H, J = 8.4 Hz). Anal. Calcd for $C_{21}H_{15}N_3O$ (325.36 g/mol): N, 12.91; C, 77.52; H, 4.65. Found: N, 13.24; C, 77.98; H, 4.34. 13C NMR (DMSO-d₆, 100 MHz): 159.43, 155.95, 155.59, 149.76, 137.86, 128.68, 128.37, 124.89, 121.34, 117.50, 116.68.

Compound 3 (3.00 g, 9.22 mmol, 1 equiv) and finely grinded potassium carbonate (3.82 g, 27.66 mmol, 3 equiv) were dispersed in 15 mL of anhydrous DMAc and stirred for 10 min at room temperature, and then ethyl bromoacetate was added dropwise. The mixture was heated at 60 °C for 24 h. The reaction mixture was filtered and precipitate in 70 mL of water. After drying at 60 °C in a vacuum oven, 4 was obtained as a white solid (3.53 g, 93%).³³ FT-IR (KBr, cm⁻¹): 1751 ($\nu_{C=O}$), 1585 ($\nu_{C=C}$), 1516 ($\nu_{C=N}$), 789 (γ_{C-H}). ¹H NMR (DMSO- d_6 , 400 MHz): 8.76 (d, 2H, *J* = 4.8 Hz), 8.67 (s, 2H), 8.66 (d, 2H, *J* = 8.8 Hz), 8.03 (dd, 2H, *J* = 7.6, 1.2 Hz), 7.88 (d, 2H, *J* = 8.4 Hz), 7.52 (dd, 2H, *J* = 7.2 Hz), 1.24 (t, 2H, *J* = 7.2 Hz). ¹³C NMR (DMSO- d_6 , 100 MHz): 169.07, 161.17, 159.25, 156.06, 155.49, 149.81, 149.37, 137.92, 130.80, 128.72, 128.17, 124.97, 121.39, 117.87, 117.61, 115.85, 65.19, 61.23, 14.55.

Compound 4 (1.50 g, 3.64 mmol, 1 equiv), finely grinded potassium carbonate (1.00 g, 7.28 mmol, 2 equiv), and tris(hydroxymethyl)methylaminomethane (Tris) (0.44 g, 3.64 mmol, 1 equiv) were suspended in 15 mL of anhydrous DMAc and heated at 50 °C for 48 h. After reaction, the mixture was concentrated and precipitated in 60 mL of water. The white precipitate was collected and dried at 60 °C in a vacuum oven to give **5** (1.37 g, 77%). FT-IR (KBr, cm⁻¹): 1651 ($\nu_{C=O}$), 1585 ($\nu_{C=C}$), 1518 ($\nu_{C=N}$), 791 (γ_{C-H}). ¹H NMR (DMSO- d_6 , 400 MHz): 8.76 (d, 2H, J = 4.8 Hz), 8.68 (s, 2H), 8.66 (d, 2H, J = 8.4 Hz), 8.03 (t, 2H, J = 7.6 Hz), 7.91 (d, 2H, J = 8.4 Hz), 7.53 (dd, 2H, J = 7.2 Hz), 7.28 (s, 1H), 7.18 (d, 2H, J = 8.4 Hz), 4.81 (t, 3H, J = 5.6 Hz), 4.59 (s, 2H), 3.62 (d, 6H, J = 5.6 Hz). ¹³C NMR (DMSO- d_6 , 100 MHz): 168.21, 159.07, 156.01, 155.47, 149.76, 149.24, 137.86, 130.84, 128.72, 124.93, 121.36, 117.80, 116.07, 67.57, 62.43, 60.44.

Compound **5** (0.500 g, 1.028 mmol, 3.5 equiv), $[N(C_4H_9)_4]_4[\alpha Mo_8O_{26}]$ (0.633 g, 0.294 mmol, 1 equiv), and $Mn(CH_3COO)_3 \cdot 2H_2O$ (0.118 g, 0.440 mmol, 1.5 equiv) were dissolved in 15 mL of anhydrous DMAc. The mixture was heated at 80 °C for 24 h. The reaction mixture was filtered while hot to remove a black solid, and the orange filtrate was exposed to diethyl ether vapor. After 24 h, monomer **6** was obtained as an orange cubic crystal (0.769 g, 84%).³⁴ FT-IR (KBr, cm⁻¹): 1695 ($\nu_{C=O}$), 941, 922, 905 ($\nu_{Mo=O}$), 667 ($\nu_{Mo=O-M_0}$). ¹H NMR (DMSO- d_{64} 400 MHz): 64.16 (b, 12H), 8.78 (d, 4H, J = 3.6 Hz), 8.70 (s, 4H), 8.67 (d, 4H, J = 8 Hz), 8.03 (t, 4H, J = 7.6 Hz), 7.91 (d, 4H, J = 4.4 Hz), 7.52 (dd, 4H, J = 6.8, 4.8 Hz), 7.17 (s, 4H), 4.92 (s, 4H), 3.15 (t, 24H, J = 7.6 Hz), 1.55 (quint, 24H), 1.30 (sext, 24H, J = 7.2 Hz), 0.92 (t, 36H, J = 7.2 Hz).

Preparation of Orthogonal Self-Assembly Monomer 7. A solution of monomer 6 (0.356 g in 15 mL of MeCN) was added dropwise to the solution of excess amount of surfactant 2 (0.844 g, 1.350 mmol, 10 equiv) in a mixture of $CHCl_3$ and MeCN (1:3 (v/v),



60 mL). A light orange precipitate formed immediately. The mixture was stirred for 4 h, filtered, and dried under vacuum to give monomer 7 as a light orange powder (0.19 g, 40%).^{35,36} FT-IR (KBr, cm⁻¹): 1730 ($\nu_{C=O}$), 1614 ($\nu_{C=C}$), 943, 918, 901 ($\nu_{Mo=O}$), 671 ($\nu_{Mo-O-Mo}$).¹H NMR (DMSO- d_{64} 400 MHz): 64.18 (b, 12H), 8.77 (d, 4H, *J* = 3.6 Hz), 8.70 (s, 4H), 8.66 (d, 4H, *J* = 7.6 Hz), 8.02 (t, 4H, *J* = 7.2 Hz), 7.98 (d, 3H, *J* = 9.6 Hz), 7.91 (s, 4H), 7.61 (d, 3H, *J* = 8.4 Hz), 7.51 (t, 4H, *J* = 6.4 Hz), 7.16 (s, 4H), 6.94 (s, 3H), 6.92 (d, 3H, *J* = 8.8 Hz), 6.27 (d, 3H, *J* = 9.2 Hz), 4.92 (s, 4H), 4.04 (t, 6H, *J* = 6.0 Hz), 3.18 (t, 12H), 2.96 (s, 18H), 1.77-1.10 (m, 120H), 0.83 (t, 9H, *J* = 6.0 Hz). Anal. Calcd for C₁₅₉H₂₂₆N₁₁MnMo₆O₃₇·6H₂O (3514.13 g/mol): N, 4.25; C, 52.72; H, 6.62. Found: N, 3.84; C, 53.14; H, 6.51. ESI-MS (negative mode, *m*/*z*): 628.2, 1437.0, 2370.2.

3. RESULTS AND DISCUSSION

3.1. Monomer Design and Synthesis. Free radical polymerization^{37,38} and ring-opening metathesis polymer-ization (ROMP)²⁷ have been used to prepare POMscontaining polymers. However, POMs were found to be potential radical quenchers,³⁹ which gave the resulted polymer with D as large as 1.8 even in the strategy of controlled radical polymerization such as conventional atom transfer radical polymerization (ATRP).³⁹ To avoid the possible radical quenching as well as the use of the precious Grubbs catalyst, a combined strategy of orthogonal coordination and photocross-linking was proposed. Therefore, we designed a polyoxometalate-based supramolecular monomer bearing coordination terpyridine (TPY) symmetrically modified on the equatorial position and photo-cross-linkable coumarin groups electrostatically attracted on the axial positions, as shown in Scheme 1. There are several characteristics of this monomer: (i) the introduction of rigid POMs cluster can avoid the cyclization in conventional organic supramolecular polymer and enable supramolecular polymer with higher molecular weight; (ii) the functioned POMs can also enrich the functionalization of supramolecular polymer.

The monomer structure and the corresponding synthetic approach are shown in Figure 1. Generally, the easily organically modified Anderson-type cluster [MnMo₆O₁₈]³⁻ was used, which was synthesized from the esterification reaction between tris(hydroxymethyl)-modified TPY (5), TBA₄[Mo₈O₂₆], and Mn(OAc)₃.^{34,40} Then, coumarin-terminated quaternized ammonium (2) was electrostatically linked to the as synthesized TPY-MnMo₆ (monomer 6) to prepare the target monomer 7 with the following characteristics: (i) Rigidity. Based on the single-crystal structure of the Andersontype [MnMo₆O₁₈]³⁻ cluster and TPY, the diameter of the disklike POMs $(0.86 \text{ nm})^{35}$ is close to the width of TPY (ca. 0.94 nm),^{34,41} which makes this cluster a rigid rod. The two TPY groups symmetrically attached to the Anderson cluster through covalent bond behave like a ditopic ligand,⁴² which can stoichiometrically form 1:2 coordination complexes with divalent metal ions, such as Fe²⁺, Zn²⁺, and so on. (ii) Flexibility. The three coumarin-terminated surfactants were electrostatically interacted with the negatively charged Anderson cluster, allowing their free movement around the POM cluster and endowing the monomer and resulted supramolecular polymer with good flexibility and solubility.³⁵ (iii) Orthogonality and reversibility. The coordination between TPY and metal ions is independent of the photo-cross-linking property of coumarin groups. Meanwhile, the reversibility of coordination and photo-cross-linking also guaranteed the resulted supramolecular polymer a fully reversible and stimulus-responsive system.

The successful preparation of target monomer 7 was confirmed by ¹H NMR, FT-IR, ESI-MS, and organic elemental analysis. As shown in Figure 2B, both the complete disappearance of signals from tetrabutylammoniums (TBAs) and the preservation of signals from TPYs as well as the integration of corresponding ¹H NMR peaks confirmed that three coumarin-terminated surfactants were attached to the

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Figure 1. Synthetic approach for monomer 7.

POMs cluster. The detailed ¹H NMR assignment is shown in Figure 2B, which was in good agreement with the corresponding ¹H-¹H COSY (Figure S2). ¹H NMR integrations from TPYs and the coumarin surfactants also indicated the completely exchange of TBAs by coumarinterminated surfactants. The POMs cluster kept intact during the cation exchange process as indicated by the characteristic broad peak around 64 ppm in ¹H NMR, attributing to the three $-CH_2$ - groups attached to the $[MnMo_6O_{18}]^{3-}$ cluster (Figure 2B, inset) as well as the characteristic triplet peaks around 1000 cm⁻¹ and the singlet at 671 cm⁻¹ in the FT-IR spectrum (Figure 2C). The ESI-MS signals at m/z of 2370.2 and 1064.5 (as shown in Figure 2D and Figure S3) matched well with the molecular structure of monomer 7, which is also in good agreement with the corresponding organic elemental analysis result. As shown in Figure S4, the UV-vis spectrum of monomer 7 displayed both absorption from coumarinterminated surfactant at 322 nm and absorption from the terpyridine group in monomer 6 at 285 nm. The relatively separated absorption peaks allowed monitoring the orthogonal self-assembly process by UV-vis spectra.

3.2. Coordination Induced Supramolecular Polymerization and Its Reversibility. The as-prepared TPY symmetrically modified monomers 6 and 7 can be treated as ditopic ligands, which can form 1-D coordination polymers with different metal ions, such as Zn^{2+} , Fe^{2+} , and Ru^{2+} . Fe^{2+} was used due to the following merits: (i) its coordination with terpyridine can be visualized as a purple color arising from the characteristic metal-to-ligand charge transfer (MLCT) absorption at 578 nm;⁴³ (ii) its relatively higher binding constant with TPYs.⁴⁴ As expected, UV-vis titration of monomers 6 and 7 with $Fe(OTf)_2$ displayed gradually increasing of the absorption at 578 nm, accompanied by the color change from colorless to purple for both monomers 6 and 7 (as shown insets in Figure 3A,B). It should mentioned that the addition of cationic Fe(II) to the solution of negatively charged POMs do not lead to any precipitation, which may imply no specific Coulomb interaction between these two charged species. To further identify the stoichiometric ratio between Fe(II) and the ditopic monomer 6 or 7, Job's plot experiments were carried out. As shown in Figure 3C,D, both monomers 6 and 7 displayed a coordination stoichiometric ratio of 1.0 with Fe(II),^{45,46} which confirmed that Fe(II) quantitatively coordinates with terpyridine groups, without any other charge-charge interaction or coordination interactions with other groups. ¹H NMR titration experiments were used to track the coordination process. As shown in Figure 3E, with the gradual addition of 1.5 equiv of Fe(II) to monomer 7, signals for the protons from terpyridine groups became broad and gradually moved to upfield,⁴⁷ especially for protons H_{16} , H_{17} , and H_{18} (Figure 3F), which were due to the shielding effect of the metal complex. After addition of 1.5 equiv of



Figure 2. (A) Chemical structure of monomer 7 and corresponding labeling of protons. (B) ¹H NMR spectra of coumarin-terminated surfactant 2, monomer 6, and monomer 7 in DMSO- d_{6j} the inset is enlarged from 61 to 67 ppm for monomers 6 and 7. (C) FT-IR spectra of coumarin-terminated surfactant 2, monomer, 6 and monomer 7. (D) ESI-MS spectrum of monomer 6 and the corresponding peak assignments.

Fe(II), the ¹H NMR spectrum became constant. It should be noted that protons from coumarin groups do not change during the addition of Fe(II). The ¹H NMR results further demonstrated that the only interaction between monomer **6** or monomer 7 and Fe(II) is the coordination between terpyridine and Fe(II); no interaction between polyoxometalate cluster or coumarin groups and Fe(II) was observed.

The formation of 1-D supramolecular coordination polymer can be proved by the increasing of the hydrodynamic radius and decreasing of the diffusion coefficient. As shown in Figure S5, for monomer 6 with concentration of 2 mM, the diffusion coefficient (D) attributed to the POMs cluster decreased from 8.59×10^{-11} to 3.97×10^{-11} m²/s after the addition of 1.2 equiv of Fe(II),⁴⁸ while signals for the TBAs counterions and solvents (DMSO, H₂O) do not change during the supramolecular polymerization process. All these data indicated that the supramolecular polymerization happened between the polyoxometalate clusters driven by coordination. As supramolecular polymerization is a concentration-dependent process,^{12,49} a critical concentration of polymerization is estimated by the DOSY experiment. As shown in Figure S6, different concentrations of monomer 6 from 0.5 to 10 mM were used to prepare the supramolecular polymer. For a lower concentration of 0.5 mM, although the color changed to purple after addition

of Fe(II), almost no obvious supramolecular polymerization was observed, since the *D* do not change too much (Figure S5); in the case of 2.0 mM, the *D* decreased obviously indicating the formation of supramolecular polymer; upon further increase of the concentration to 10 mM, the formed supramolecular polymer became a gel-like state, indicating the molecular weight of the resulted supramolecular polymer is high enough (Figure 4C). However, no *D* was obtained as it is not suitable for the DOSY experiment. Therefore, we can estimate that the critical polymerization concentration of monomer **6** is around 2.0 mM.^{41,50}

The formation of the 1-D coordination supramolecular polymer can also be confirmed by microscopy. As shown in Figure 4A, by drop-casting 1 mg/mL DMF solution of monomer 7 on a silica wafer, spherical aggregates constructed from nanofibers with ca. 40 nm width were observed. Addition of 1.0 equiv of Fe(II) to solution of monomer 7 resulted in the formation of fibers with lengths as long as 20 μ m and widths of 150 nm, which further proved the formation of the 1-D coordination polymer (Figure 4B). In the case of 5 mM monomer 7, a supramolecular organogel was formed after addition of 1.2 equiv of Fe(II). The SEM image (Figure 4C) revealed that the gel network was composed of longer fibers with length of several hundred micrometers.



Figure 3. UV–vis titration spectra for monomer 6 (A) and monomer 7 (B) with Fe(II) and the corresponding Job's plot for monomer 6 (C) and monomer 7 (D); insets are the corresponding images. (E) ¹H NMR spectra of monomer 7 with different equivalent of Fe(II) in DMSO- d_6 . (F) ¹H NMR spectra for monomer 7 before (bottom) and after (top) the formation of 1-D coordination polymer with Fe(II).



Figure 4. SEM images of monomer 7 in DMF (1.0 mg/mL) (A), 1-D coordination polymer formed by monomer 7 (2 mM) and 1.0 equiv of Fe(II) (B), and supramolecular organogel formed by monomer 7 (5 mM) and 1.2 equiv of Fe(II); the sample was freeze-dried before SEM (C). Insets are the corresponding optical images.



Figure 5. Optical images (A) and corresponding Tyndall scattering (B) of the supramolecular polymer solution during the addition of different amount of TBA₄(EDTA). (C) UV-vis spectra of the depolymerization process by adding different ratio of TBA₄(EDTA); the inset is the relationship between absorbance at 578 nm and the equivalent of TBA₄(EDTA).



Figure 6. UV-vis spectra of (A) photoinduced dimerization of monomer 7; inset is the time-dependent kinetic process. (B) Photoinduced depolymerization; inset is the corresponding kinetic plot.

One of the advantages of such a coordination system is the reversibility. By adding competitive ligand $\text{TBA}_4(\text{EDTA})^{32}$ to the formed 1-D supramolecular polymer, the characteristic purple color turned to colorless (Figure 5A), which implied the dissociation of the coordination interaction between terpyridine and Fe(II). By gradual addition of $\text{TBA}_4(\text{EDTA})$, UV– vis absorption at 294, 326, and 578 nm showed an opposite trend toward the coordination process (Figure 5C), especially the completely decrease of absorbance at 578 nm. Meanwhile, the Tyndall scattering decreased dramatically after the addition of TBA₄(EDTA) (Figure 5B) also indicated the depolymerization of the 1-D polymer. Such a coordination–dissociation process can be repeated at least for four cycles (as shown in Figure S7).

3.3. Photoinduced Polymerization and Orthogonal Self-Assembly. Besides TPY as coordination site, the terminal coumarin groups can also undergo photoinduced dimerization to give cross-linked supramolecular polymer.^{51,52} As shown in Figure 6A, after the solution of monomer 7 was irradiated with 365 nm UV light, the UV–vis absorbance at 287 and 314 nm gradually decreased with increasing irradiation time, indicating the dimerization of coumarin

groups. The photoinduced dimerization process achieved a photostationary state within 400 min with a dimerization degree of 90%.⁵² During the photoinduced dimerization, polymerization of monomer 7 can be expected, as indicated by the increasing of Tyndall scattering (Figure S9).⁵³ Meanwhile, the photoinduced dimerization can also be depolymerized by irradiating with 254 nm UV light. As shown in Figure 6B, the depolymerization can be achieved within 30 min. Such a photoinduced dimerization and depolymerization process is reversible for at least four cycles, as shown in Figure S10. It should be noted that during the UV irradiation process no absorbance around 700 nm was observed, indicating that the POMs cluster kept their characteristic structure and composition.³³

Because of the nature of orthogonal self-assembly, the coordination and photoinduced dimerization could be operated separately and can achieve corresponding reversibility under a suitable stimulus, which can tune the reversible formation and depolymerization of supramolecular polymers. For example, in the sequence of coordination—photo-cross-linking, monomer 7 was first coordinated with Fe(II) to give a homogeneous 1-D coordination polymer solution (Figure 7A);



Figure 7. UV-vis spectra of (A) coordination and (B) photoinduced dimerization after coordination. (C) FT-IR spectra of monomer 7, after coordination with Fe(II), and further photoinduced dimerization, from top to bottom, respectively. (D) UV-vis spectra of the dedimerization process. (E, F) SEM images of the orthogonal supramolecular polymer prepared in the sequence of coordination-photo-cross-linking.

further irradiation with 365 nm UV light led to the crosslinking of the terminal coumarin groups, which resulted the formation of orthogonal supramolecular networks (Figure 7B). The coordination and photodimerization can be confirmed by corresponding FT-IR spectra, especially the characteristic coordination peaks at 1162-1266 cm⁻¹ and corresponding photodimerization signals around 1724 and 1701 cm⁻¹ (Figure 7C).⁵⁴ The peak at 1730 cm⁻¹ shifted to 1724 cm⁻¹ with a relative decrease of intensity, and the peak at 1714 cm⁻¹ shifted to 1701 cm⁻¹ with relative increase of intensity, which is in good agreement with the feature of coumarin dimerization.⁵⁵ Such kinds of supramolecular networks can be disassembled by either 254 nm photoirradiation-induced dedimerization or addition of TBA4(EDTA)-induced decoordination, as indicating by corresponding UV-vis spectra (Figure 7D). Interestingly, the mechanical property of the monomer was improved during the orthogonal supramolecular polymerization process. As shown in Figure S20, the storage

modulus (G') is much larger than the loss modulus (G'') for the coordination polymer, and both of them are independent of the frequency, showing the formation of supramolecular gel. After photo-cross-linking of the coumarin groups, both G' and G'' increased, which may indicate the formation of the crosslinked network.

The nature of the orthogonal self-assembly ensures that such supramolecular network can be also prepared in an alternate sequence of coordination—photo-cross-linking. SEM images revealed that the 1-D fiber-like structures were glued together after photo-cross-linking (Figure 7E,F).

4. CONCLUSIONS

In summary, herein we demonstrate the successful application of orthogonal self-assembly in the preparation of polyoxometalate-based hybrid supramolecular network through coordination and photodimerization. Such a strategy can be extended to other types of organically modified polyoxometalates and clusters, which may be useful in the preparation of supramolecular materials, such as photochromism devices, smart catalysts, and so on. For example, taking advantage of the metal coordination as well as the reversible multielectron redox process in POMs, the introduction of different metal ions can enrich the colors of POMs-based chromism device as well as new catalysis centers. Meanwhile, the orthogonal interaction also endows the supramolecular polymer with suitable processability, which provides a new avenue toward clustersbased electronic devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.9b01825.

2D NMR spectra, ESI-MS, UV-vis spectrum, and other materials (PDF)

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Notes

The authors declare no competing financial interest.

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