Contents lists available at ScienceDirect



journal homepage: www.elsevier.com/locate/jphotochem

# Photo-induced secondary assembly of bis(terpyridyl)dibenzo-24crown-8/Zn<sup>2+</sup> supramolecular polymer



Photochemistry

Photobiology

Chao Xu<sup>a</sup>, Yong Chen<sup>a,b</sup>, Heng-Yi Zhang<sup>a,b</sup>, Yu Liu<sup>a,b,\*</sup>

<sup>a</sup> Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry

<sup>b</sup> Collaborative Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin 300071, PR China

#### ARTICLE INFO

\_\_\_\_\_

ABSTRACT

Article history: Received 21 March 2015 Received in revised form 16 April 2015 Accepted 20 April 2015 Available online 23 April 2015

Dedicated to Professor Yoshihisa Inoue on the occasion of his 65th birthday.

Keywords: Bis(terpyridyl)dibenzo-24-crown-8 Anthryl-dibenzylammonium Photo/thermo-induced molecular assembly Supramolecular polymer constructed via a hierarchical induced assembly strategy and characterized by UV/vis NMR, viscometry and DLS. Therein, the coordination linkage of bis(terpyridyl)dibenzo-24-crown-8 **1** with Zn<sup>2+</sup> produces the **1**/Zn<sup>2+</sup> supramolecular polymer as the primary assembly. Then, the anthryl-dibenzylammonium guest **2** was grafted to the **1**/Zn<sup>2+</sup> supramolecular polymer via the non-covalent association of dibenzylammonium moieties on guests with the dibenzo-24-crown-8 rings on supramolecular polymer. Furthermore, the supramolecular polymer with anthryl grafts underwent a photo-induced secondary assembly to produce the supramolecular gel, which could be reversibly disassembled by a thermo-induced dissociation of anthracene dimers. These photo/thermo-induced hierarchical assembly/ disassembly behaviors will provide a potential way to construct degradable hierarchical supramolecular assemblies employing environment-friendly external stimuli, such as light and heat, as controlling method.

A crown ether-based supramolecular gel with a three-dimensional network structure was successfully

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Supramolecular polymers constructed by metal-directed selfassembly via host-guest association and metal-ligand interactions attract more and more attention owing to their numerous interesting properties and potential applications [1–12]. Therein, the non-covalent host-guest association gives the good selectivity and convenient responsiveness to these polymers, and the metalligand interactions endow them with various coordination geometries, strong coordination binding abilities, and some properties in electromagnetic aspects [13–20]. Among the various building blocks for the construction of this type of supramolecular polymers, crown ethers, especially dibenzo-24-crown-8 (DB24C8), and terpyridine are regarded as two of the most powerful ones. The inherent advantage of using DB24C8 and terpyridine as building blocks includes (1) DB24C8 can not only be easily functionalized through the derivatization of phenyl rings but also form the steady and responsive 1:1 inclusion complexes with dibenzylammonium (DBA) guests through a cooperative combination of  $[N^+ - H \cdots O]$ and  $[C-H\cdots O]$  hydrogen bonds and  $\pi - \pi$  stacking [21-24]. (2) The

E-mail address. yund@nankal.edu.cn (1. Liu

http://dx.doi.org/10.1016/j.jphotochem.2015.04.014 1010-6030/© 2015 Elsevier B.V. All rights reserved.

strong binding between terpyridines and metal ions (Zn<sup>2+</sup>, Fe<sup>2+</sup>, etc.) can enable the easy construction of supramolecular polymers through the intermolecular coordination of ditopic hosts bearing two terpyridine terminals with metal ions, and the resultant supramolecular polymers can be reversibly disassembled through the addition of competitive ligands or metal ions [24–27]. Following this idea, we wish to report the construction of a bis (terpyridyl)dibenzo-24-crown-8-based supramolecular polymer and its photo-induced secondary assembly behavior (Scheme 1). Herein, the bis(terpyridyl)dibenzo-24-crown-8 1 was firstly assembled to a supramolecular polymer through the Zn<sup>2+</sup>-mediated coordination linkage. Then, the anthryl-dibenzylammonium guest 2 was grafted to the supramolecular polymer via the noncovalent binding of DB24C8 rings with the dibenzylammonium moieties of guests. It is well documented that anthracene can transfer to its dimer when irradiated at wavelengths above  $\sim$ 350 nm, and the dimer dissociate when it is stimulated under the light of less than 300 nm or heating [28–31]. Benefitting from this photodimerization/dissociation property of anthracene moieties, the bis(terpyridyl)dibenzo-24-crown-8-based supramolecular polymer can undergo a photo-induced secondary assembly to form a large three-dimensional network structure. Significantly, the obtained supramolecular network shows the thermo-induced disassembly behaviors. It is our special interest to develop a



<sup>\*</sup> Corresponding author at: Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Tel.: +86 22 23503625; fax: +86 22 23503625. *E-mail address:* yuliu@nankai.edu.cn (Y. Liu).



Scheme 1. Schematic representation of the formation of supramolecular polymer and its reversible conversion with supramolecular network.

feasible strategy for producing degradable hierarchical supramolecular assemblies employing environment-friendly external stimuli, such as light and heat, as controlling method.

# 2. Experimental

## 2.1. Materials

Host **1** and dibenzo-24-crown-8 diol **3** were prepared according to the literature procedure [4,32]. 4'-Chloro-2,2',6',2"-terpyridine, benzylamine, NH<sub>4</sub>PF<sub>6</sub>, zinc triflate  $(Zn(OTf)_2)$ , 9-anthracenecarboxylic acid were purchased from Aladdin and used without further purification.

#### 2.2. Instrument

UV/vis spectra were measured in a quartz cell (light path 10 mm) on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller. The sample solution for DLS measurements was prepared by filtering solution through a 450 nm Millipore filter into a clean scintillation vial. The samples were examined on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (TurboCorr) at 636 nm at a scattering angle of 90°. NMR spectra were recorded on a Varian Mercury VX400 instrument. The photodimerization experiments were carried out using a photochemical reaction apparatus with a 500 WHg lamp.

Elemental analyses were performed on a PerkinElmer-2400C instrument.

#### 2.3. Synthesis

#### 2.3.1. Synthesis of 5

9-Anthracenecarboxylic acid (524.3 mg, 1.2 mmol) and trifluoroacetic anhydride (991.8 mg, 2.4 mmol) were mixed with 50 mL of toluene. Upon dissolution of the reactants. **4** [33] (500 mg. 1 mmol) was added dropwise with stirring. The solution was heated to 60 °C for 24 h. After cooling, the toluene was removed under reduced pressure, and the resulting yellow oil was washed by saturated sodium bicarbonate solution (50 mL), dissolved with CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and washed with water (30 mL) twice. The organic phase was dried and evaporated off. Then the residue was purified by column chromatography over silica gel (eluent: 5:1 petroleum ether/ethyl acetate) to afford the yellow solid (0.6 g, yield 60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.84 (1H, s), 8.52 (1H, s), 8.11–8.14 (2H, d, J=8.46), 8.00-8.02 (2H, d, J=8.28), 7.73-7.75 (2H, d, J=8.71), 7.51-7.55 (2H, d, J=7.79), 7.43-7.48 (2H, d, J=7.75), 6.88-6.90 (2H, d, J=8.62), 4.77-4.80 (2H, d, J=9.32), 4.03-4.06 (2H, d, J=9.20), 3.94-3.96 (2H, d, J=9.23), 3.83-3.85 (2H, d, J=8.96), 3.76(4H, s). HRMS (FTMALDI) m/z [M+Na] <sup>+</sup> calcd for C<sub>28</sub>H<sub>26</sub>O<sub>6</sub>Na<sup>+</sup> 481.1622, found 481.1625. Anal. Calcd for C<sub>28</sub>H<sub>26</sub>O<sub>6</sub>: C, 73.35; H, 5.72; O, 20.93. Found: C, 73.31; H, 5.75; O, 20.94 (Supplementary data Figs. S1 and S2).

#### 2.3.2. Synthesis of anthryl-dibenzylammonium guest 2

A mixture of **5** (0.52 g, 1 mmol), phenylmethanamine (0.13 g, 1.2 mmol) and Et<sub>3</sub>N (0.24 g, 0.33 mL, 4 mmol) was dissolved in methanol (50 mL) and refluxed for 24 h. After cooling, NaBH<sub>4</sub> (0.61 g, 16 mmol) was added in portions at 0°C. Then the suspension was stirred for another 24 h. Then water was added to stop the reaction. After the solvent was removed under vacuum, the residue was dissolved with CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and washed with water (30 mL) twice. The organic phase was dried and evaporated off. Then the residue was purified by column chromatography over silica gel (eluent: 10:1CH<sub>2</sub>Cl<sub>2</sub>/methanol) to afford the yellow solid (0.46 g, yield 80%). To the solution of the yellow solid (0.30 g, g)0.8 mmol) in MeOH (50 mL) was added conc. HCl to adjust pH < 2, and the solvent was then evaporated off under reduced pressure. The residue was dissolved in water and a saturated solution of NH<sub>4</sub>PF<sub>6</sub> was added until no further precipitation was observed. The precipitate was filtered off, washed with water and dried to give 2 as a yellow solid (0.40 g, yield 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 8.78(1H, s), 8.13-8.21(5H, m), 7.86-7.88(2H, d, J=8.93), 7.67-7.72 (2H, d, J=9.09), 7.62–7.65(2H, d, J=8.24), 7.59–7.61(2H, d, J=8.97), 7.54-7.57(3H, t, J=6.93), 7.09-7.12(2H, d, J=8.67), 5.29(2H, s), 4.54 (2H, s), 4.22-4.25(2H, d, J=8.55), 3.83-3.85(2H, d, J=9.20), 3.66-3.68(2H, d, /=9.38), 3.60-3.63(4H, m), 3.50-3.53(2H, d, /=9.35). Anal. Calcd for C<sub>35</sub>H<sub>36</sub>F<sub>6</sub>NO<sub>5</sub>P: C, 60.43; H, 5.22; N, 2.01. Found: C, 60.60; H, 5.20; N, 1.99. ESI-MS:  $m/z [M + H]^+ = 550.30$  (Supplementary data Figs. S3 and S4).

#### 2.3.3. Synthesis of the supramolecular gel

A mixture of **1** (0.363 g, 250 mmol) and  $Zn(OTf)_2$  (0.112 g, 250 mmol) was dissolved in the solvent of  $1:1CHCl_3-CH_3CN$  (0.5 mL), and **2** (0.242 g, 250 mmol) was added into the mixture. The mixture was irradiated at the light of 365 nm at the temperature of 298.15 K for 5 h to afford the gel.

#### 3. Result and discussion

The complexation of host **1** with  $Zn(OTf)_2$  was investigated by UV/vis and NMR. As seen in Fig. 1, with the addition of varying amounts of  $Zn(OTf)_2$  to a solution of **1**, the absorption peak of **1** at



**Fig. 1.** UV/vis titration curve of **1** with increasing amount of  $Zn(OTf)_2$ . (Inset) Plot of absorbance intensity of **1** at 321 nm versus the amount of  $Zn(OTf)_2$ .

262 nm gradually decreased while the absorption peaks at 312 nm and 321 nm gradually enhanced, accompanied by the appearance of a clear isosbestic point at 302 nm. In the control experiment, UV/ vis spectra of Zn(OTf)<sub>2</sub> within measurement concentration range displayed no appreciable change at 250-350 nm under comparable experimental conditions. In addition, <sup>1</sup>H NMR spectra (Fig. 2) show that, after the addition of  $Zn(OTf)_2$ , the H<sub>1</sub> and H<sub>4</sub> protons of **1** showed upfield shifts of 0.95 and 0.1 ppm, the H<sub>3</sub>, H<sub>5</sub> protons showed the downfield shifts of 0.3 and 0.15 ppm, respectively. Moreover, the H<sub>2</sub> protons splitted into two peaks, while the aromatic protons of DB24C8 ring shifted downfield. These phenomena jointly indicated that  $Zn^{2+}$  was coordinated to **1** to form metal-ligated species. The coordination stoichiometry of 1 with Zn<sup>2+</sup> was investigated by UV/Vis spectrometric titration experiments (see Fig. 1 inset), and the plot of  $A_{1/2n}$  (where A was defined as the absorption intensity of 1 at 321 nm) versus [Zn (OTf)<sub>2</sub>]/[**1**]showed an inflexion point at a molar ratio of 1, which corresponded to a 1:1 coordination stoichiometry between 1 and Zn<sup>2+</sup> [34].

The concentration-dependent <sup>1</sup>H NMR and viscometry experiments gave the evidence for the formation of supramolecular polymer. As seen in Fig. 3, all of protons on 1/Zn system showed the obvious peak broadening at a relatively high concentration. In addition, the slope of viscosity/concentration plot of 1/Zn system gave a slope of 1.08 at the low concentration range, but this value rapidly increased to 2.37 at the higher concentration range (Fig. 4)



**Fig. 2.** Partial <sup>1</sup>H NMR spectra (400 MHz, 1:1CDCl<sub>3</sub>-CD<sub>3</sub>CN, 293 K) of (a) **1** and (b) equimolar  $1/Zn(OTf)_2$  mixture ([**1**]=[ $1/Zn(OTf)_2$ ]=1.0 mM).



**Fig. 3.** Partial <sup>1</sup>H NMR spectra (400 MHz, 1:1CDCl<sub>3</sub>-CD<sub>3</sub>CN, 293 K) of (a) **1** and (b–f) equimolar **1**/Zn systems ([**1**]= 1.0 mM, [**1**/Zn]=(b) 1.00, (c) 3.00, (d) 5.00, (e) 8.00, and (f) 10.0 mM).



Fig. 4. Viscosity/concentration plot of 1/Zn system (1:1 CHCl<sub>3</sub>-CH<sub>3</sub>CN, 298 K).

[35]. These phenomena, along with the clear Tyndall effect (Fig. 5b) jointly indicated the formation of supramolecular polymers in solution, and the critical aggregation concentration (CAC) was calculated to be 9.0 mM from the inflexion point of the viscosity/ concentration plot of 1/Zn system. In addition, we further performed DLS experiments of 1/Zn system. As seen in Fig. 5a, the 1/Zn system gave an average diameter around 77 nm at the concentration of 0.5 mM. All these evidence demonstrated the formation of 1/Zn system greatly decreased to 11 nm, indicating that the 2:1 coordination of  $Zn^{2+}$  with 1 resulting from the addition of supramolecular polymers.

The association between host **1** and guest **2** was quantitatively investigated by <sup>1</sup>H NMR (Fig. 6). The aromatic  $H_d$ ,  $H_e$ ,  $H_f$  protons of **2** showed obvious upfield shifts, while the  $H_a$  and  $H_b$  protons that



Fig. 5. (a) DLS result and (b) Tyndall effect of 1/Zn system.  $([1/Zn] = [1] = [Zn(OTf)_2] = 0.5 \text{ mM})$ .





**Fig. 6.** Partial <sup>1</sup>H NMR spectra (400 MHz, 298 K,  $CD_3CN:CD_3Cl = 1:1$ ) of (a) **2** and (b) **1+2** at the concentration of 2 mM.

are located adjacent to the ammonium site showed the downfield shifts when interacting with **1**. These indicated that the DBA moiety of **2** was incorporated with the DB24C8 ring of **1**, which is basically consistent the reported results that DB24C8 could bind DBA with a moderate binding constant of ca.  $1.2 \times 10^3 \,\text{M}^{-1}$ [36]. The <sup>1</sup>H NMR spectrum of  $1/\text{Zn}^{2+}/2$  (Fig. 7) also showed the similar chemical shifts, indicating that **2** was incorporated with 1/Zn through the host–guest interactions.

After validating the association ability of 1/Zn polymers toward anthryl-dibenzylammonium guests, we started to investigate the photo-driven secondary assembly of 1/Zn/2 system. When irradiating a solution of 1/Zn/2 system at 365 nm for ca. 5 h, the intensity of absorption peak at 349 nm that was assigned to the anthryl groups decreased 74% (Fig. 8). Moreover, the <sup>1</sup>H NMR (Fig. S5) and MS (Fig. S6) experiments demonstrated that the guest 2 totally converted to its dimers under our experimental conditions (irradiation at 365 nm for 5 h). In addition, the original diameter of 1/Zn (77 nm measured by DLS) increased nearly 10 times after the irradiation of 1/Zn/2 system (773 nm measure by DLS, Fig. 9). These

**Fig. 8.** UV/vis spectra of 1/Zn/2 before and after irradiation at 365 nm ([1/Zn/2] = 0.05 mM, the UV/vis spectra of gels were measured by dissolving the gels to a concentration of 0.05 mM).

phenomena jointly indicated that, via the photodimerization of the anthryl groups in 1/Zn/2 system, most of 1/Zn/2 can be further cross-linked to larger secondary assemblies. In the control experiment, the DLS data of  $1/Zn^{2+}/2$  at a lower concentration (0.01 mM) before and after light irradiation showed that, at a lower concentration, the average diameter of  $1/Zn^{2+}/2$  showed no obvious changes before (57 nm) and after (63 nm) light irradiation. This result indicated that the inter-chain polymerization, but not the intra-chain polymerization, played the predominant role in the formation of secondary supramolecular assembly.

The visible evidence for the formation of photo-driven secondary assembly came from an inverted vial test (Fig. 10). By irradiating an equimolar mixture of 1/Zn and 2 at 365 nm for 5 h, the aqueous solution turned into a soft gel that couldn't flow down in the inverted vial. A possible structure of gel was illustrated in Scheme 1. Herein, the anthryl-dibenzylammonium guests 2 were grafted to 1/Zn supramolecular polymers through the non-covalent binding between DB24C8 cavities in the 1/Zn supramolecular polymers.



Fig. 7. <sup>1</sup>H NMR spectra (400 MHz, 1:1CDCl<sub>3</sub>-CD<sub>3</sub>CN, 293 K) of equimolar 1/Zn(OTf)<sub>2</sub>/2 mixture ([1/Zn(OTf)<sub>2</sub>/2] = 2.0 mM).



Fig. 9. DLS result of 1/Zn/2 system ([1/Zn/2] = 0.5 mM).



Fig. 10. The sol-gel transitions triggered by light irradiation and heating ([1/Zn/ 2] = 250 mM).



**Fig. 12.** Absorption changes of 1/Zn/2 assembly at 349 nm under light irradiation (365 nm) and heating (303.15K) ([1/Zn/2] = 0.05 mM).

Subsequently, numerous 1/Zn supramolecular polymers grafted by anthryl-dibenzylammonium guests were joined together through the photodimerization of the anthryl groups to form a non-covalent 3D polymer network that was able to retain the solvent. Interestingly, upon heating the gel at 303.15 K for 30 h, the gel underwent a gel-to-sol conversion to produce a clear solution that could not revert to gel upon cooling. In the control experiments (Fig. 11), when irradiated the solutions containing the free 2 and 1/2 mixture for 5 h, these solution could not turn into the soft gel but still maintained the solution state.

In addition to the responsiveness, another important advantage of the supramolecular gel is the repetitiveness toward external stimuli. As seen from Fig. 12, the decreased intensity of anthryl absorption peak at 349 nm, which resulted from the light irradiation at 365 nm, recovered its original level when heating at 303.15 K for 30 h due to thermo-induced dissociation of anthracene dimers. Significantly, this cycle could repeat tens of times, indicating the good repetitiveness of the reversible photo-induced secondary assembly and the thermo- induced disassembly.



Fig. 11. Photodimerization experiments of (a) only 2, (b) 1/Zn/2 system, (c) 1/2 system before (top) and after (bottom) light irradiation.

#### 4. Conclusion

In summary, a supramolecular gel with a three-dimensional network structure was successfully constructed following the pathway of the primary assembly of bis(terpyridyl)dibenzo-24-crown-8 by metal coordination polymerization, grafting of anthryl-dibenzylammonium guests and photo-induced secondary assembly. This supramolecular gel can reversibly convert to the soluble 1/Zn/2 assembly under heating and recovered under light irradiation. The stimuli-responsive sol-gel transformation property, along with the ease of preparation, will make this supramolecular gel well suitable for a variety of important biomedical and industrial applications.

#### Acknowledgements

We thank 973 Program (2011CB932502) and NSFC (91227107, 21432004, and 21272125) for financial support.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2015.04.014.

#### References

- P. Wei, X. Yan, F. Huang, Supramolecular polymers constructed by orthogonal self-assembly based on host-guest and metal-ligand interactions, Chem. Soc. Rev. 44 (2015) 815–832.
- [2] T.F.A.D. Greef, M.M.J. Smulders, M. Wolffs, A.P.H.J. Schenning, R.P. Sijbesma, E.W. Meijer, Supramolecular polymerization, Chem. Rev. 109 (2009) 5687–5754.
- [3] X. Yan, F. Wang, B. Zheng, F. Huang, Stimuli-responsive supramolecular polymeric materials, Chem. Soc. Rev. 41 (2012) 6042–6065.
- [4] J. Zhan, Q. Li, Q. Hu, Q. Wu, C. Li, H. Qiu, M. Zhang, S. Yin, A stimuli-responsive orthogonal supramolecular polymer network formed by metal-ligand and host-guest interactions, Chem. Commun. 50 (2014) 722–724.
- [5] K.P. Wang, Y. Chen, Y. Liu, Polycation-induced secondary assembly of amphiphilc calixarene and its multi-stimuli responsive gelation behavior, Chem. Commun. 51 (2015) 1647–1649.
- [6] Y.L. Liu, Y. Yu, J. Gao, Z.Q. Wang, X. Zhang, Water-soluble supramolecular polymerization driven by multiple host-stabilized charge-transfer interactions, Angew. Chem. In. Ed. 49 (2010) 6576–6579.
- [7] K.D. Zhang, J. Tian, D. Hanifi, Y. Zhang, A.C.H. Sue, T.Y. Zhou, L. Zhang, X. Zhao, Y. Liu, Z.T. Li, Toward a single-layer two-dimensional honeycomb supramolecular organic framework in water, J. Am. Chem. Soc. 135 (2013) 17913–17918.
- [8] T. Xiao, X. Feng, Q. Wang, C. Lin, L. Wang, Y. Pan, Switchable supramolecular polymers from the orthogonal self-assembly of quadruple hydrogen bonding and benzo-21-crown-7 – secondary ammonium salt recognition, Chem. Commun. 49 (2013) 8329–8331.
- [9] L. Hsu, C. Weder, S.J. Rowan, Stimuli-responsive mechanically-adaptive polymer nanocomposites, J. Mater. Chem. 21 (2011) 2812–2822.
- [10] Z.M. Hudson, C.E. Boott, M.E. Robinson, P.A. Rupar, M.A. Winnik, I. Manners, Tailored hierarchical micelle architectures using living crystallization-driven self-assembly in two dimensions, Nat. Chem. 6 (2014) 893–898.
- [11] T. Ito, E. Nishiuchi, G. Fukuhara, Y. Inoue, T. Mori, Competitive photocyclization/rearrangement of 4-aryl-1,1-dicyanobutenes controlled by intramolecular charge-transfer interaction. Effect of medium polarity, temperature, pressure, excitation wavelength, and confinement, Photochem. Photobiol. Sci. 10 (2011) 1405–1414.
- [12] H. Yamaguchi, Y. Kobayashi, R. Kobayashi, Y. Takashima, A. Hashidzume, A. Harada, Photoswitchable gel assembly based on molecular recognition, Nat. Commun. 3 (2012) 603.
- [13] A. Breul, I.R. Moraes, R. Menzel, M. Pfeffer, A. Winter, M.D. Hager, S. Rau, B. Dietzek, R. Beckert, U.S. Schubert, harvesting of polymerizable 4-hydroxy-1,3-

thiazole monomers by energy transfer toward photoactive Os(II) metal complexes in linear polymers, Polym. Chem. 5 (2015) 2715–2724.

- [14] S. Moghaddam, C. Yang, M. Rekharsky, Y.H. Ko, K. Kim, Y. Inoue, M.K. Gilson, New ultrahigh affinity host–guest complexes of cucurbit uril with bicyclo octane and adamantane guests: thermodynamic analysis and evaluation of M2 affinity calculations, J. Am. Chem. Soc. 133 (2011) 3570–3581.
- [15] Z.S. Kean, S. Akbulatov, Y.C. Tian, R.A. Widenhoefer, R. Boulatov, S.L. Craig, Photomechanical actuation of ligand geometry in enantioselective catalysis, Angew. Chem. Int. Edit. 53 (2014) 14508–14511.
- [16] F.S. Han, M. Higuchi, D.G. Kurth, Metallo-supramolecular polymers based on functionalized bis-terpyridines as novel electrochromic materials, Adv. Mater. 19 (2007) 3928–3931.
- [17] B. Zheng, F. Wang, S. Dong, F. Huang, Supramolecular polymers constructed by crown ether-based molecular recognition, Chem. Soc. Rev. 41 (2012) 1621–1636.
- [18] J. Zhao, Y.M. Zhang, H.L. Sun, X.Y. Chang, Y. Liu, Multistimuli-responsive supramolecular assembly of cucurbituril/cyclodextrin pairs with azobenzenecontaining bispyridinium guest, Chem. Eur. J. 20 (2014) 15108–15115.
- [19] Y. Liu, Z. Huang, X. Tan, Z. Wang, X. Zhang, Cucurbit[8]uril-based supramolecular polymers: promoting supramolecular polymerization by metal-coordination, Chem. Commun. 49 (2013) 5766–5768.
- [20] L. He, J. Liang, Y. Cong, X. Chen, W. Bu, Concentration and acid-base controllable fluorescence of a metallosupramolecular polymer, Chem. Commun. 50 (2014) 10841–10844.
- [21] S. Dong, Y. Luo, X. Yan, B. Zheng, X. Ding, Y. Yu, Z. Ma, Q. Zhao, F. Huang, A dualresponsive supramolecular polymer gel formed by crown ether based molecular recognition, Angew. Chem. Int. Ed. 50 (2011) 1905–1909.
- [22] P.R. Ashton, E.J.T. Chrystal, P.T. Glink, S. Menzer, C. Schiavo, N. Spencer, J.F. Stoddart, P.A. Tasker, A.J.P. White, D.J. Williams, Pseudorotaxanes formed between secondary dialkylammonium salts and crown ethers, Eur. J. Chem. 2 (1996) 709–728.
- [23] Z.J. Zhang, H.Y. Zhang, H. Wang, Y. Liu, A Twin-Axial Hetero[7]rotaxane, Angew. Chem. Int. Edit. 50 (2011) 10834–10838.
- [24] H.B. Cheng, H.Y. Zhang, Y. Liu, Dual-stimulus luminescent lanthanide molecular switch based on an unsymmetrical diarylperfluorocyclopentene, J. Am. Chem. Soc. 135 (2013) 10190–10193.
- [25] G.R. Whittell, I. Manners, Metallopolymers: new multifunctional materials, Adv. Mater. 19 (2007) 3439–3468.
- [26] Z.J. Ding, Y.M. Zhang, X. Teng, Y. Liu, Controlled photophysical behaviors between dibenzo-24-crown-8 bearing terpyridine moiety and fullerenecontaining ammonium salt, J. Org. Chem. 76 (2011) 1910–1913.
- [27] R. Vaiyapuri, B.W. Greenland, S.J. Rowan, H.M. Colquhoun, J.M. Elliott, W. Hayes, A thermoresponsive supramolecular polymer network containing pyrene-functionalized gold nanoparticles and a chain-folding polydiimide, Macromolecules 45 (2012) 5567–5574.
- [28] J. Yao, Z. Yan, J. Ji, W. Wu, C. Yang, M. Nishijima, G. Fukuhara, T. Mori, Y. Inoue, ammonia-driven chirality inversion and enhancement in enantiodifferentiating photocyclodimerization of 2-anthracenecarboxylate mediated by diguanidino-γ-cyclodextrin, J. Am. Chem. Soc. 136 (2014) 6916–6919.
- [29] C. Yang, Y. Inoue, Supramolecular photochirogenesis, Chem. Soc. Rev. 43 (2014) 4123–4143.
- [30] Y. Kawanami, H. Umehara, J. Mizoguchi, M. Nishijima, G. Fukuhara, C. Yang, T. Mori, Y. Inoue, Cross-versus homo-photocyclodimerization of anthracene and 2-anthracenecarboxylic acid mediated by a chiral hydrogen-bonding template. Factors controlling the cross-/homo-selectivity and enantioselectivity, J. Org. Chem. 78 (2013) 3073–3085.
- [31] J. Xu, Y. Chen, L. Wu, C. Tung, Q. Yang, Dynamic covalent bond based on reversible photo [4+4] cycloaddition of anthracene for construction of double-dynamic polymers, Org. Lett. 15 (2013) 6148–6151.
  [32] H.W. Gibson, H. Wang, C. Slebodnick, J. Merola, W.S. Kasse, A.L. Rheingold,
- [32] H.W. Gibson, H. Wang, C. Slebodnick, J. Merola, W.S. Kasse, A.L. Rheingold, Isomeric 2,6-pyridino-cryptands based on dibenzo-24-crown-8, J. Org. Chem. 72 (2007) 3381–3393.
- [33] M. Han, H.-Y. Zhang, L.-X. Yang, Z.-J. Ding, R.-J. Zhuang, Y. Liu, Eur. J. Org. Chem. (2011) 7271–7277.
- [34] R. Dobrawa, M. Lysetska, P. Ballester, M. Grüne, F. Würthner, Fluorescent supramolecular polymers: metal directed self-assembly of perylene bisimide building blocks, Macromolecules 38 (2005) 1315–1325.
- [35] B. Gruber, E. Kataev, J. Aschenbrenner, S. Stadlbauer, B. König, Vesicles and micelles from amphiphilic zinc(II)–cyclen complexes as highly potent promoters of hydrolytic DNA cleavage, J. Am. Chem. Soc. 133 (2011) 20704–20707
- [36] H.K. Frensdorff, Stability constants of cyclic polyether complexes with univalent cations, J. Am. Chem. Soc. 93 (1971) 600–606.