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Original article

Pleated polymeric foldamers driven by donor–acceptor interaction and conjugated radical cation dimerization

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ABSTRACT

Two naphthalene (NP) and bipyridinium ($BIPY^{2+}$) alternately incorporated polymers **P1** and **P2** have been prepared through the formation of dynamic hydrazone bonds. The polymers formed NP–$BIPY^{2+}$ donor–acceptor interaction-induced pleated secondary structure. Upon reducing the $BIPY^{2+}$ units to radical cation $BIPY^{\bullet+}$, intramolecular dimerization of the $BIPY^{\bullet+}$ units induced the backbones to afford another pleated secondary structure. Adding electron-rich macrocyclic polyether bis-1,5-dinaphtho[38]crown-10 or electron-deficient cyclobis(paraquat-*p*-phenylene) cyclophane did not break the first foldamer by complexing the $BIPY^{2+}$ or NP units of the polymers, whereas the di(radical cationic) ring of the second cyclophane could break the second foldamer by forming threading complexes with the $BIPY^{\bullet+}$ units of the polymers.

1. Introduction

Foldamers are linear molecules that are driven by non-covalent forces to fold into discrete secondary structures [1,2]. Switching between the folding and extending states of foldamers represents efficient control of the conformations of long organic molecules to produce artificial secondary structures, which may exhibit interesting materials or biological functions. Currently such switching has been realized by changing the solvent composition or temperature [1d] or outside stimuli, such as pH [3,4], donor–acceptor interaction [5–7], guest complexation [8–12], metal coordination [13], light [14–19] and redox [20]. In 1964, Kosower and Cotter reported that bipyridinium (viologen) radical cations dimerized in water [21]. In the past decade, chemists have developed efficient methods for improving this inherently weak non-covalent interaction and thus utilizing it to construct advanced supramolecular architectures [22,23]. Recently, our group reported that the folding-de-folding process of tetrathiafulvalene (TTF)-bipyridinium ($BIPY^{2+}$)-alternating dynamic covalent polymers could be multiply tuned by conjugated radical cation dimerization and TTF–$BIPY^{2+}$ donor–acceptor interaction [24,25]. In this paper, we describe that two polymers, **P1** and **P2** (Fig. 1), that consist of alternately incorporated naphthalene (NP) and $BIPY^{2+}$ can form two pleated folding states which are driven by NP–$BIPY^{2+}$ donor–acceptor interaction and $BIPY^{\bullet+}$ dimerization.

2. Experimental

All solvents were dried before use according to standard procedures. All reagents were obtained from commercial suppliers and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer at 298 K, and the chemical shifts were referenced to the residual solvent peaks. Mass spectra (ESI and MALDI) were obtained on Shimadzu LCMS-2010EV or IonSpec 4.7 Tesla FTMS. Absorption spectra were measured on a Perkin-Elmer Lambda 750s UV–vis spectrometer. Luminescence spectra were measured on a Perkin-Elmer LS-55 luminescence spectrometer. Compounds **2** [26], **5a** and **5b** [24], **6** [27] and **7**·$4PF_6$ [28] were prepared according to reported methods. The synthesis route of polymers **P1** and **P2** is showed in Scheme 1.

Compound **3**: A solution of compounds **1** (0.19 g, 1.2 mmol) and **2** (1.5 g, 3.6 mmol) in toluene (10 mL) and Et_3N (2 mL) was stirred and refluxed under argon for 12 h, and then the mixture was concentrated under reduced pressure. After workup, the resulting slurry was subjected to column chromatography ($MeOH/CH_2Cl_2$ 1:20) to give compound **3** as a colorless oil (0.35 g, 45%). ^1H NMR

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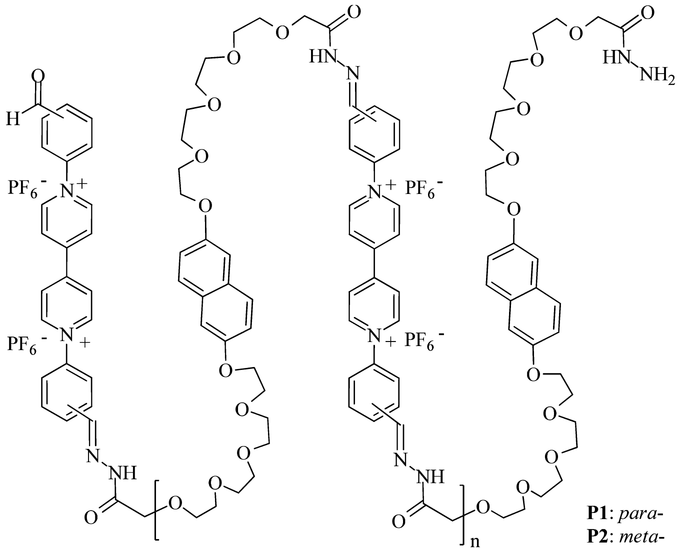


Fig. 1. The structures of polymers **P1** and **P2**.

(400 MHz, $CDCl_3$): δ 7.61 (d, 2H, J = 8.8 Hz), 7.17–7.13 (m, 2H), 7.09 (s, 2H), 4.25–4.20 (m, 4H), 4.15 (s, 4H), 3.94–3.88 (m, 4H), 3.79–3.61 (m, 30H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 154.4, 126.8, 125.1, 114.6, 105.7, 71.0, 70.9, 70.8, 70.7, 69.8, 68.6, 68.0, 51.8. MS (ESI): m/z 657.3 $[M+H]^+$. HRMS (ESI): Calcd. for $C_{32}H_{49}O_{14}$ $[M+H]^+$: 657.3122. Found: 657.3118.

Compound **4**: A solution of compound **3** (0.15 g, 0.23 mmol) and hydrazine monohydrate (1.00 mL, 98%) in methanol (10 mL) was stirred at room temperature for 2 h and then evaporated with a rotavapor. The resulting residue was triturated with CH_2Cl_2 (50 mL) and the solution washed with water (50 mL × 2) and brine (50 mL), and then dried over anhydrous $MgSO_4$. Upon removal of the solvent under reduced pressure, compound **4** was obtained as a white solid (0.15 g, 98%). ^1H NMR (400 MHz, CD_3CN): δ 8.17 (br, 2H), 7.68 (d, 2H, J = 8.9 Hz), 7.22 (s, 2H), 7.14–7.08 (m, 2H), 4.26–4.11 (m, 4H), 3.93 (s, 4H), 3.88–3.78 (m, 4H), 3.70–3.50 (m, 24H), 2.17 (br, 4H). ^{13}C NMR (100 MHz, CD_3CN): δ 170.0, 156.2, 130.7, 129.1, 119.9, 108.0, 71.8, 71.3, 71.2, 71.1, 70.7, 70.6, 70.2, 68.4. MS (ESI): m/z 657.3 $[M+H]^+$. HRMS (ESI): Calcd. for $C_{30}H_{49}N_4O_{12}$ $[M+H]^+$: 657.3347. Found: 657.3331.

Polymer **P1**: Compound **5a** (30 mg, 0.046 mmol) was dissolved in acetonitrile (5 mL). To the solution was added dropwise a solution of compound **4** (30 mg, 0.046 mmol) in acetonitrile (5 mL). The mixture was stirred at room temperature for 18 h and then the solvent was removed with a rotavapor. The resulting residue was suspended in dichloromethane and ether (1:1, 0.5 mL). The solid formed was filtrated off and washed thoroughly with ether, and dried in vacuo to give polymer **P1** as a dark brown solid (54 mg, 92%).

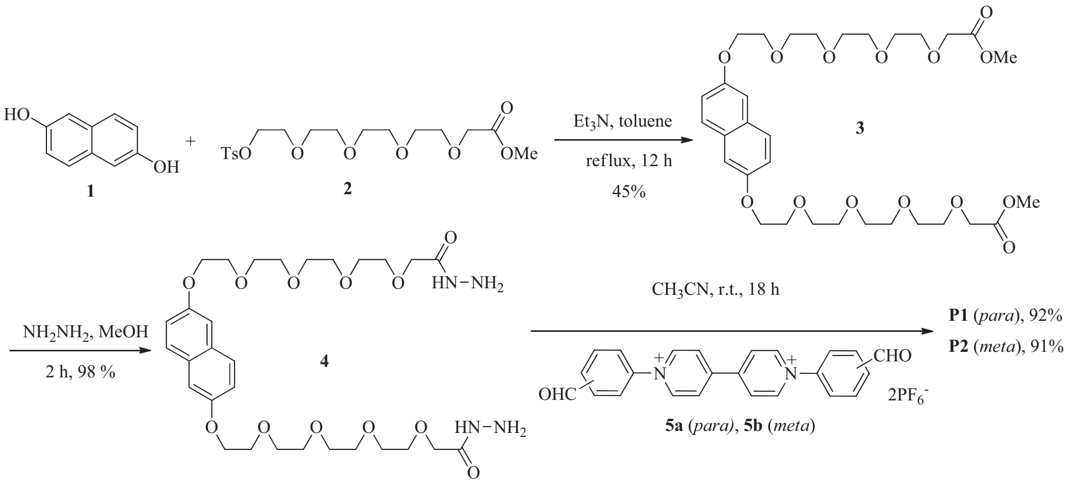
Polymer **P2**: Polymers **P2** were prepared as a dark brown solid from the reaction of **5b** and **4** in 91% yield according to the procedure described for polymer **P1**.

3. Results and discussion

Polymers **P1** and **P2** were prepared from the condensation reactions of **4** with **5a** or **5b** through the formation of hydrazone bonds in acetonitrile (Scheme 1) [24,25]. After the reactions reached equilibrium, the signal of the hydrogen atom of the aldehyde groups disappeared completely in the ^1H NMR spectra in acetonitrile-d_3. Considering the sensitivity of the ^1H NMR spectroscopy, we assumed that this observation reflected that at least 95% of the dialdehyde and the dihydrazine precursors were consumed to produce the dynamic covalent polymers and thus estimated the degree of polymerization of the two polymers to be ≥ 10. Gel permeation chromatography (GPC) experiments in acetonitrile and *N*,*N*-dimethylformamide were also performed for the two polymers, which did not afford useful results for the determination of the degree of polymerization. Both polymers were soluble in acetonitrile and thus their conformations were investigated in this solvent.

UV–vis spectra were first recorded for **P1** and **P2** in acetonitrile. Both polymers exhibited a broad absorption band centered around 515 and 520 nm, respectively (Fig. 2a), which supported the formation of the charge-transfer (CT) complexation between the electron-donating NP units and the electron-deficient $BIPY^{2+}$ units. The molar absorption coefficient (ε) of **P1** and **P2** were calculated to be *ca.* 335 and 240 L/(mol cm), respectively. The absorption was linearly correlated to the concentration within the range of 0.11–1.5 mmol/L, which indicated that the absorption band was caused by intramolecular donor–acceptor interaction. Thus, the backbone of both polymers should produce a pleated folded conformation (Folding A), as shown in Fig. 3.

Adding 5.0 equiv. of electron-rich macrocyclic polyether bis-1,5-dinaphtho[38]crown-10 (**6**) (Fig. 4), which was relative to the concentration of the $BIPY^{2+}$ units of the polymers, to the solution of **P1** or **P2** in acetonitrile did not cause observable change in the CT absorption band of both polymers. This result indicated that the



Scheme 1. Synthesis of polymers **P1** and **P2**.