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Novel Macrocycles Bearing Dithienylethene Units and Urea Functional Groups: Synthesis, Structure and Photochromic Property†

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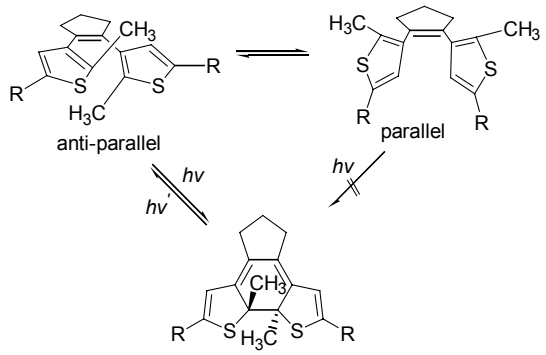
Two novel photochromic macrocycles **1** and **2** bearing dithienylethene units and urea building blocks have been synthesized, and their photochromic properties are described. Macrocycle **2** shows good photochromic properties, while the relatively smaller size of macrocycle **8b** exhibits photochemically inactive properties due to the unfavourable ring conformational constraint. Moreover, the crystal structures of the urea-protected precursor macrocyles **3a**, **3b**, and **8b** are presented.

Keywords photochromism, macrocycles, dithienylethene, urea derivatives, supramolecular chemistry

Introduction

Macrocyclic molecules bearing photochromic units are an intriguing class of compounds, which are capable of playing the role of basic building blocks for unique molecular switches and smart materials.[1] Among many known photochromic compounds, dithienylethene moiety has been proved to be the most promising switchable unit due to its excellent fatigue resistance and thermal stability.[2] On accounts of such outstanding properties, an increasing number of dithienylethene derivatives with enhanced photochromic properties by introducing some unique functional groups have been reported in recent years.[3] Moreover, dithienylethene moiety has shown broad applications in areas ranging from photo-switchable molecular machines[4] and photo-responsible supramolecular polymers[5] to biological systems.[6] Photocyclization of dithienylethene can proceed only from the antiparallel conformer of open-isomers, while the photochemical reactivity of dithienylethene can be hindered when two thienyl rings are fixed in mirror symmetry (parallel conformer) in the molecule (Scheme 1).[7] Based on this unique property, we have already reported a new photochemical approach to investigate ring-chain mechanism of supramolecular polymers by introducing a dithienylethene unit into bifunctional ureidopyrimidinone (UPy) derivatives.[8] The two UPy functional groups of the target compound can dimerize intramolecularly in dilute solution through quadruple hydrogen bonding to form a cyclic monomer with two thienyl rings fixed in a parallel conformation, which prohibits its photocyclization.

Scheme 1 Photochromic reactions of dithienylethenes



Whereas the fabrication of monomeric or polymeric dithienylethene derivatives is well documented, macrocyclic architecture of dithienylethenes is relatively less common.[1d,9] Therefore, it is an attractive challenge to realize self-assembly of macrocyclic molecules bearing dithienylethene units. In 2012, Iwasawa and coworkers[10] have reported the guest-induced self-assembly of a macrocyclic boronic ester containing photochromic diarylethene units, which showed high quantum yield of photoisomerization due to the favorable conformational constraint. Macrocyclic host molecules containing urea groups are also an interesting class of molecular building blocks, which can self-assemble into unique three-dimensional nanoscale structures due to hydrogen

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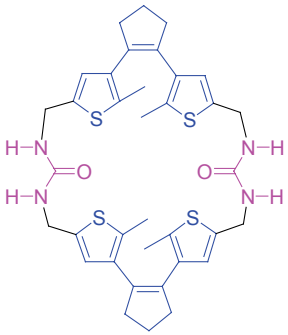
† Dedicated to Professor Hongwen Hu on the occasion of his 89th birthday.

bonds originated from urea groups.[11] In 2008, Feringa and coworkers[12] have reported dithienylethene-bisurea-based low molecular weight gelators which are able to function as photo responsive organogels that show a remarkable gel-to-liquid transition upon irradiation by incorporating urea group into dithienylethene molecules. Inspired by these, we envisioned that the strategic introduction of dithienylethene units into a urea-based macrocyclic framework would achieve both photochromic responsiveness and unique self-assembly behavior simultaneously. In the present study, two novel photochromic macrocycles **1** and **2** bearing urea groups are synthesized, and their structures and photochromic reactivities are described (Scheme 2).

Scheme 2 Chemical structures of macrocycles **1** and **2**



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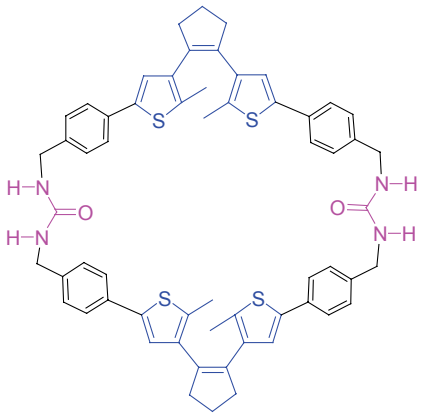

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Experimental

General methods

All reactions were performed in atmosphere unless noted. The commercially available reagents and solvents were either employed as purchased or dried according to procedures described in the literature. All yields were given as isolated yields. NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references, $CDCl_3$ was used as received. UV-Vis spectra were obtained from a Perkin-Elmer Lambda 25 and a Shimadzu UV-2401 spectrometer. L-EM and S-EM photo luminescence spectra were measured on a Lambda 55 and an Aminco Bowman Series 2 luminescence spectrometers. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan Mat TSQ 7000 instruments. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6210 TOF LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded in positive-ion mode using an Autoflex III (BrukerDaltonics, Germany) time-of-flight mass spectrometer. Compound **7** was prepared according to procedures reported previously.[12] Compound **6** was obtained from **7** according to the reported literature.[13] Compounds **11**[12] and **10**[14] are also reported previously, but the synthetic routes are different. The main spectra of the compounds, such as ^{1}H NMR, ^{13}C NMR, MS and CIF file for X-ray crystal data could be found in the Supporting Information.

Single crystal X-ray analysis

Single crystal X-ray data were measured on a Bruker SMART APEX II CCD diffractometer (Mo Kα radiation, λ = 0.71073 Å). Structure solutions and refinements were carried out using the SHELXTL-PC software package. Crystallographic data of compounds **3a**, **3b** and **8b** are presented as follows. **3a**: colorless, $C_{48}H_{62}N_6O_2S_4$, M_r = 883.30, monoclinic, space group $P2_1/c$, a = 13.2050(12) Å, b = 17.8440(16) Å, c = 11.5850(11) Å, α = 90.00°, β = 91.373(3)°, γ = 90.00°, V = 2729.0(4) Å^3, Z = 2, D_c = 1.196 g•cm^{-3}, T = 291(2) K, μ = 0.219 mm^{-1}, 4657 measured reflections, 2935 independent reflections, $F(000)$ = 1058, R_1 = 0.0872, wR_2 = 0.1108 (all data), R_1 = 0.0559, wR_2 = 0.1062 [I > 2sigma(I)], largest diff. peak and hole 0.261 and –0.191 e•Å^{-3}, goodness-of-fit on F^2 = 1.097, CCDC-830768. **3b**: colorless, $C_{24}H_{31}N_3OS_2$, M_r = 441.65, triclinic, space group $P\bar{1}$, a = 8.9298(11) Å, b = 9.0638(12) Å, c = 15.832(2) Å, α = 84.890(2)°, β = 85.452(3)°, γ = 69.210(2)°, V = 1191.6(3) Å^3, Z = 2, D_c = 1.281 g•cm^{-3}, T = 291(2) K, μ = 0.249 mm^{-1}, 4118 measured reflections, 2472 independent reflections, $F(000)$ = 492, R_1 = 0.0749, wR_2 = 0.1025 (all data), R_1 = 0.0527, wR_2 = 0.0968 [$I > 2\sigma(I)$], largest diff. peak and hole 0.443 and –0.273 e•Å^{-3}, goodness-of-fit on F^2 = 1.001, CCDC-830769. **8b**: colorless, $C_{36}H_{39}N_3OS_2$, M_r = 593.84, orthorhombic, space group $Pccn$, a = 16.2521(17) Å, b = 35.4053(16) Å, c = 11.6291(12) Å, α = 90.00°, β = 90.00°, γ = 90.00°, V = 6691.5(10) Å^3, Z = 4, D_c = 1.197 g•cm^{-3}, T = 291(2) K, μ = 0.193 mm^{-1}, 6571 measured reflections, 4781 independent reflections, $F(000)$ = 2568, R_1 = 0.0548, wR_2 = 0.0951 (all data), R_1 = 0.0405, wR_2 = 0.0921 [$I > 2\sigma(I)$], largest diff. peak and hole 0.129 and –0.132 e•Å^{-3}, goodness-of-fit on F^2 = 1.052, CCDC-830847.

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Synthesis of (4,4'-(cyclopentene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))dimethanol (5)

To a solution of **6** (0.46 g, 1.45 mmol) in ethanol (35 mL) was slowly added a solution of potassium borohydride (0.30 g, 5.6 mmol) in ethanol (7 mL) and water (7 mL). After stirring for 1 h at room temperature, the reaction mixture was extracted with ether (30 mL×2), and the combined organic layer was washed with saturated aqueous brine and dried over $MgSO_4$. Removal of the solvent gave alcohol **5** as a yellow solid (0.38 g, 82%). It was used for the following reaction without any further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.63 (s, 2H), 4.64 (s, 2H), 2.75 (t, J=7.5 Hz, 4H), 2.09−1.97 (m, 2H), 1.94 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.5, 135.5, 135.1, 134.7, 127.0, 60.1, 38.4, 23.1, 14.5.

Synthesis of 1,2-bis(5-(chloromethyl)-2-methylthiophen-3-yl)cyclopent-1-ene (4)

To a reaction flask (100 mL), **5** (0.40 g, 1.25 mmol) and dry pyridine (1.0 mL) were dissolved in dry THF (40 mL) at 0 ℃ under argon. Thionyl chloride (0.37 mL, 5 mmol) was added, and the solution was allowed to stir for 2 h. The mixture was poured into ice-water (40 mL) and extracted with ether (30 mL×2). The combined organic phases were washed with saturated $NaHCO_3$ (30 mL), dried over anhydrous $MgSO_4$ and evaporated *in vacuo* to give **4** as a brown solid (0.38 g, 85%). Since this compound was not very stable in air, it was used for the next step right away without any further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.72 (s, 2H), 4.67 (s, 4H), 2.75 (t, J=7.5 Hz, 4H), 2.09−1.96 (m, 2H), 1.92 (s, 6H).

Synthesis of urea-protected macrocycles 3a and 3b

Triazinanone (0.19 g, 1.2 mmol) was weighed into a dried round bottom flask (100 mL) under nitrogen and dissolved in 35 mL anhydrous THF. Then NaH (0.27 g, 7.0 mmol, 60% content) was added to the solution and the reaction mixture was heated at reflux for 30 min. The reaction was cooled and a solution of readily prepared dichloride **4** (0.97 g, 1.6 mmol in 40 mL THF) was added. After the addition was completed, the reaction was heated at reflux for 48 h. Then the reaction was quenched with H_2O (30 mL) and reduced to half of its original volume under vacuum. The remaining aqueous solution was extracted with $CHCl_3$ (40 mL×3). The combined organic layers were washed with brine and then dried with anhydrous $MgSO_4$. The solution was reduced *in vacuo*. The residue was purified by column chromatography on silica gel and eluted with chloroform/ethyl acetate (V∶V=20∶1) to give white precipitate **3a** (0.071 g, 10%) and **3b** (0.085 g, 12%). **3a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.60 (s, 4H), 4.57 (s, 8H), 4.13 (s, 8H), 2.74 (t, J=7.5 Hz, 8H), 2.10−1.94 (m, 4H), 1.82 (s, 12H), 1.20 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 156.1, 136.8, 135.0, 134.7, 134.4, 127.3, 61.9, 44.2, 38.5, 28.7, 23.0, 14.2; ESI-MS *m/z* (%): 905.58 ($[M+Na]^+$, 100%). **3b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.91 (s, 2H), 5.21 (d, J=15.3 Hz, 2H), 4.23 (d, J=10.4 Hz, 2H), 4.11 (d, J=10.4 Hz, 2H), 3.33 (d, J=15.3 Hz, 2H), 2.90−2.58 (m, 4H), 2.29 (s, 6H), 2.11−1.94 (m, 2H), 1.20 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.7, 136.5, 135.8, 134.8, 132.9, 131.3, 54.3, 43.9, 37.0, 28.9, 23.5, 14.3; ESI-MS *m/z* (%): 464.17 ($[M+Na]^+$, 100).

Synthesis of bis-urea macrocycle 1

The protected macrocycle **3a** (0.045 g, 0.051 mmol) was dissolved in MeOH (10 mL) and a solution of 20% diethanol amine (5 mL, pH≈2, previously adjusted with conc. HCl) was added. The mixture was heated at 85 ℃ overnight. After cooled to room temperature, precipitate was filtered and washed with H_2O (5 mL), MeOH (5 mL), H_2O (5 mL) and MeOH (5 mL) to afford **3a** as an off white solid (0.032 g, 90%). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 6.57 (s, 4H), 6.37 (t, J=6.0 Hz, 4H), 4.19 (d, J=5.8 Hz, 8H), 2.69 (t, J=7.4 Hz, 8H), 2.02−1.85 (m, 4H), 1.77 (s, 12H); HR-ESI-MS *m/z*: 711.1934 ($[M+Na]^+$).

Synthesis of 1,2-bis(5-(4-(1,3-dioxolan-2-yl)phenyl)-2-methylthiophen-3-yl)cyclopent-1-ene (12)

The dichloride **7** (0.83 g, 2.5 mmol) was dissolved in anhydrous THF (20 mL) under a nitrogen atmosphere, and *n*-BuLi (3 mL, 2.5 mol•L^{-1} solution in hexane, 7.5 mmol) was added slowly at 0 ℃. Subsequently the reaction mixture was allowed to warm to room temperature and stirred for 1 h. Then $B(OC_4H_9)_3$ (2.0 mL, 7.5 mmol) was added, followed by stirring for the next 2 h at room temperature. Degassed aq. Na_2CO_3 (10 mL of 2 mol•L^{-1} solution), $Pd(PPh_3)_4$ (0.092 g, 0.08 mmol), ethylene glycol (20 drops) and 2-(4-bromophenyl)-1,3-dioxolane (1.15 g, 5 mmol) were added and the mixture was heated at reflux with stirring vigorously for 3 h. Then additional $Pd(PPh_3)_4$ (0.046 g, 0.04 mmol) was added and continued heating with stirring for another 3 h. The reaction mixture was cooled down to room temperature, and extracted with ether (40 mL×2). The ether extract was dried over $MgSO_4$, and the solvent was removed *in vacuo*. The residue was purified by column chromatography [neutral Al_2O_3, ethyl acetate/petroleum ether (V∶V=7∶1)] to give pure **12** as a yellow solid (0.67 g, 48%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.43 (d, J=8.4 Hz, 4H), 7.43 (d, J=8.4 Hz, 4H), 7.04 (s, 2H), 5.81 (s, 2H), 4.13−4.02 (m, 8H), 2.84 (t, J=7.5 Hz, 4H), 2.13−2.03 (m, 2H), 1.99 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.3, 136.8, 136.6, 135.4, 134.9, 134.8, 127.0, 125.3, 124.4, 103.6, 65.4, 38.5, 23.1, 14.5.

Synthesis of 4,4'-(4,4'-(cyclopentene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))dibenzaldehyde (11)[12]

A solution of diarylethene **12** (1.08 g, 1.94 mmol) in wet acetone (30 mL) containing pyridinium tosylate (1.60 g, 6.40 mmol) was refluxed overnight under a nitrogen atmosphere. The mixture was cooled to room

temperature and water was added. The resultant mixture was then extracted with diethyl ether (30 mL×2). And the combined organic extracts were washed with brine (40 mL) and dried over $MgSO_4$. Removal of the solvent *in vacuo* afforded **11** as a yellow solid (0.81 g, 89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.97 (s, 2H), 7.84 (d, J=8.4 Hz, 4H), 7.62 (d, J=8.4 Hz, 4H), 7.19 (s, 2H), 2.86 (t, J=7.5 Hz, 4H), 2.18−2.06 (m, 2H), 2.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 191.5, 140.2, 138.3, 137.3, 137.2, 134.9, 134.8, 130.5, 126.2, 125.4, 38.6, 23.1, 14.7.

Synthesis of (4,4'-(4,4'-(cyclopentene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))bis(4,1-phenylene))dimethanol (10)[14]

To a solution of **11** (0.79 g, 1.69 mmol) in ethanol (45 mL) was added slowly a solution of potassium borohydride (0.40 g, 7.4 mmol) in ethanol (10 mL) and water (10 mL). After stirring for 1 h at room temperature, the reaction mixture was extracted with ether (30 mL×2) and the combined organic extracts were washed with saturated brine (40 mL) and dried over $MgSO_4$. Removal of the solvent gave diol **10** as a yellow solid (0.72 g, 90%). It was used for the following reaction without any further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.48 (d, J=8.4 Hz, 4H), 7.32 (d, J=8.4 Hz, 4H), 7.03 (s, 2H), 4.67 (s, 4H), 2.84 (t, J=7.5 Hz, 4H), 2.15−2.03 (m, 2H), 2.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.7, 139.4, 136.8, 134.8, 134.7, 134.0, 127.6, 125.5, 124.2, 65.1, 38.6, 23.1, 14.5.

Synthesis of 1,2-bis(5-(4-(bromomethyl)phenyl)-2-methylthiophen-3-yl)cyclopent-1-ene (9)

To a solution of **10** (0.28 g, 0.60 mmol) in 7 mL CH_2Cl_2 at 0 ℃, was added PBr_3 (0.11 mL, 1.2 mmol) and the mixture was stirred at 0 ℃ for 30 min and at ambient temperature for 90 min. The reaction mixture was then poured into ice and extracted with CH_2Cl_2 (20 mL×2). The organic layer was washed with brine, and dried with anhydrous Na_2SO_4. The solvent was evaporated *in vacuo*. The residue was purified by column chromatography [silica gel, ethyl acetate/ petroleum ether (V∶V=1∶6)] to give **9** as a yellow solide (0.25 g, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.48 (d, J=8.4 Hz, 4H), 7.32 (d, J=8.4 Hz, 4H), 7.03 (s, 2H), 4.67 (s, 4H), 2.84 (t, J=7.5 Hz, 4H), 2.15−2.02 (m, 2H), 2.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.0, 136.9, 136.4, 135.1, 134.8, 134.7, 129.7, 125.6, 124.5, 38.5, 33.6, 23.1, 14.6.

Synthesis of urea-protected macrocycles 8a and 8b

Triazinanone (0.25 g, 1.6 mmol) was weighed into an dried 250 mL round bottom flask under nitrogen and dissolved in 50 mL of anhydrous THF. Then NaH (0.26 g, 6.5 mmol, 60% content) was added to the solution and the reaction mixture was heated at reflux for 30 min. The reaction was cooled and a solution of dibromide **9** (0.97 g, 1.6 mmol in 60 mL anhydrous THF) was added. After the addition was completed, the reaction was heated at reflux for 48 h. Then the reaction was quenched with H_2O (30 mL) and reduced to half of its original volume under vacuum. The remaining aqueous solution was extracted with $CHCl_3$ (80 mL×3). The combined organic layers were washed with brine and then dried with anhydrous $MgSO_4$. The solution was reduced *in vacuo*. The residue was purified by column chromatography on silica gel and eluted with chloroform/ethyl acetate (V∶V=10∶1) to give white precipitate **8a** (0.095 g, 10%) and **8b** (0.104 g, 11%). **8a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.41 (d, J=8.4 Hz, 8H), 7.26 (d, J=8.4 Hz, 8H), 6.93 (s, 4H), 4.50 (s, 8H), 4.19 (s, 8H), 2.84 (t, J=7.5 Hz, 8H), 2.12 (s, 12H), 2.10−2.01 (m, 4H), 1.05 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 156.4, 139.3, 137.0, 136.7, 135.1, 134.6, 133.7, 128.7, 125.6, 124.4, 62.2, 54.3, 48.9, 38.0, 28.6, 23.3, 14.6; ESI-MS *m/z* (%): 1209.75 ($[M+Na]^+$, 100). **8b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.18 (d, J=8.4 Hz, 4H), 6.99 (s, 2H), 6.98 (d, J=8.4 Hz, 4H), 5.18 (d, J=15 Hz, 2H), 4.19 (s, 4H), 3.46 (d, J=15 Hz, 2H), 2.85 (t, J=7.5 Hz, 4H), 2.39 (s, 6H) 2.15−1.99 (m, 2H), 1.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 157.4, 138.3, 136.5, 136.0, 135.6, 135.0, 133.4, 128.8, 127.3, 125.2, 54.3, 49.5, 37.2, 28.9, 23.6, 14.3; ESI-MS *m/z* (%): 616.50 ($[M+Na]^+$, 100).

Synthesis of bis-urea macrocycle 2

The protected macrocycle **8a** (0.059 g, 0.049 mmol) was dissolved in MeOH (15 mL) and a solution of 20% diethanol amine (5 mL, pH was *ca.* 2, previously adjusted with conc. HCl) was added. The mixture was heated at 85 ℃ overnight. After cooled to room temperature, precipitate was filtered and washed with H_2O (5 mL), MeOH (5 mL), H_2O (5 mL) and MeOH (5 mL) to afford the bis-urea macrocycle **2** as an off white solid (0.037 g, 76%).^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.40 (d, J=8.1 Hz, 8H), 7.18 (d, J=8.1 Hz, 8H), 7.16 (s, 4H), 6.46 (t, J=6.0 Hz, 4H), 4.18 (br s, 8H), 2.81 (t, J=7.5 Hz, 8H), 2.08−1.87 (m, 4H), 1.95 (s, 12H); MALDI-TOF-MS *m/z* (%): 993.841 ($[M+H]^+$, 100).

Results and Discussion

The synthetic routes of the two macrocycles **1** and **2** are shown in Schemes 3 and 4. Compound **7** can readily undergo alithium exchange at ambient temperature, which was quenched with DMF to afford the dialdehyde **6**.[13] Reduction of **6** with KBH_4 gave diol **5**, which was treated with thionyl chloride in dry pyridine-THF to give a brown solid compound **4** in 85% yield. Since the dichloride compound **4** was not stable in air, it was used right away for the next reaction without any further purification. Compound **4** was subjected to cyclize with the triazinanone in THF/NaH to afford both the bis-urea protected macrocycle **3a** in 10% yield ("2+2" adduct) and mono-urea protected macrocycle **3b** in 12% yield ("1+1" adduct) together. The protecting group in **3a** was removed by diethanol amine in methanol to give

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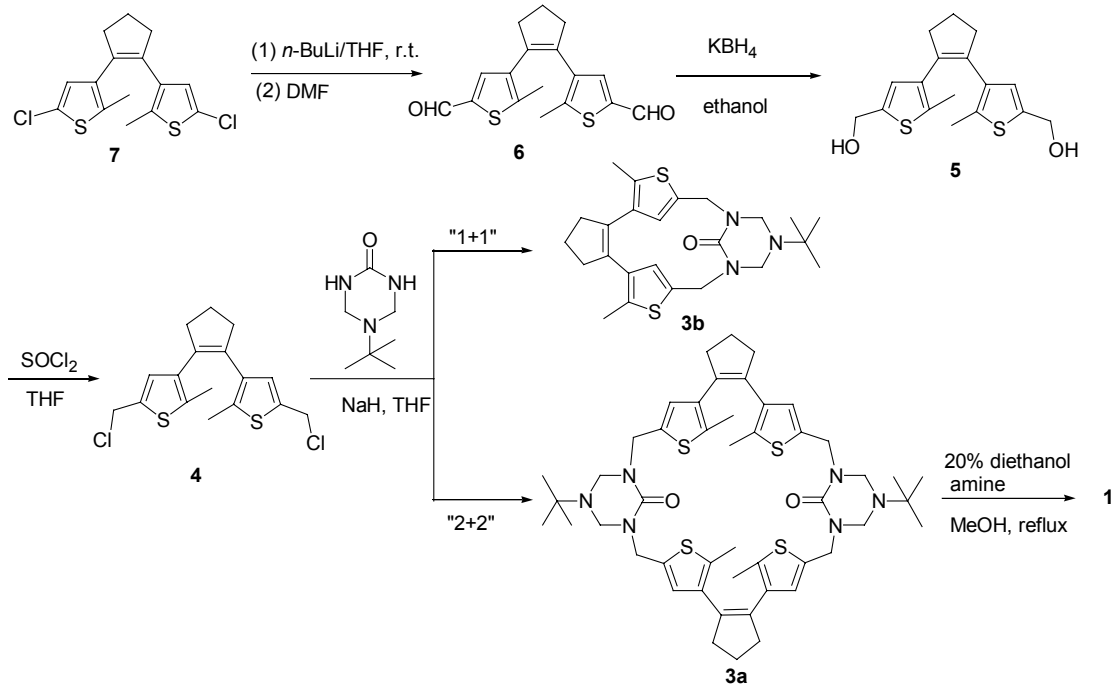
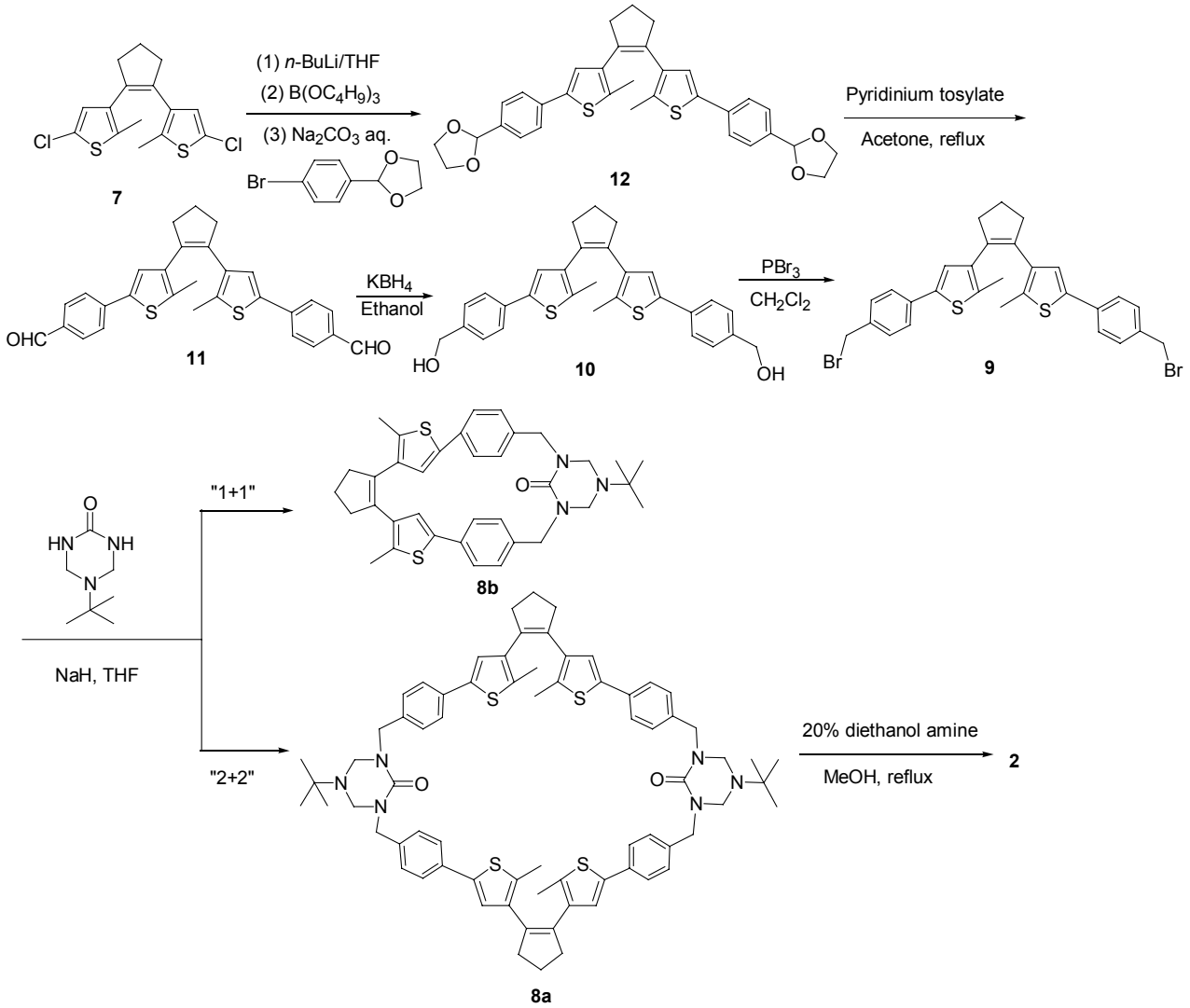
Scheme 3 Preparation of macrocycle **1**



Scheme 4 Preparation of macrocycle **2**



the target bis-urea macrocycle **1** in 90% yield.

Compound **7** was converted into the bis(boronic) esters via *n*-BuLi/$B(OBu)_3$, which was directly used for the Suzuki coupling with the ethylene glycol protected bromobenzaldehydes to give the corresponding diacetal derivative **12** in 48% yield. Deprotection of **12** with PPTS in acetone under reflux afforded the formyl-substituted diarylethene **11** in 89% yield. The diol compound **10** was then obtained by reduction of **11** with KBH_4 in ethanol at room temperature in 90% yield. Bromination of the diol **10** with PBr_3 in CH_2Cl_2 yielded dibromide **9** in 71% yield. The dibromide **9** was cyclized with the triazinanone in THF/NaH to afford both the bis-urea protected macrocycle **8a** in 10% yield ("2+2" adduct) and mono-urea protected macrocycle **8b** in 11% yield ("1+1" adduct) together. The protecting group in **8a** was removed with the use of diethanol amine in methanol to yield the target bis-urea macrocycle **2** in 76% yield.

The urea-protected macrocycles **3a**, **3b**, **8a** and **8b** were characterized by ^{1}H NMR,^{13}C NMR and MS techniques. Furthermore, single crystals suitable for X-ray diffraction were obtained by slow evaporation from hexane/dichloromethane solution of **8b** or from hexane solution of **3a** and **3b**. The X-ray diffraction study gave unambiguous assignment of the urea-protected macrocyclic structures of **3a**, **3b** and **8b**. The crystal structures of **3a**, **3b** and **8b** (including part of atomic labeling) are given in Figure 1. In contrast to the good solubility of **3a** and **8a** in $CHCl_3$, both macrocycles **1** and **2** are insoluble in $CHCl_3$ and only show low solubility in DMSO. Thus it is hard to perform ^{13}C NMR spectra for macrocycles **1** and **2**. However, macrocycles **1** and **2** were clearly characterized by ^{1}H NMR and HR-ESI-MS or MALDI-TOF-MS (For spectra, please see Supporting Information). We have also tried to cultivate crystals for bis-urea macrocycles **1** and **2** to get insight into the three dimensional self-assembly behavior induced by urea groups. However, no single crystal of **1** or **2** suitable for X-ray diffraction was obtained due to their poor solubilities. In the^{1}H NMR spectrum of macrocycle **1**, the methyl-H, and thienyl-H resonance were observed at δ 1.77 and 6.57 in DMSO-d_6, respectively. Similar signals were observed at δ 1.95 and 7.16 in DMSO-d_6 for macrocycle **2**. The mass spectra provided further evidence for the formation of the bis-urea macrocycles. The spectra of macrocycles **1** and **2** showed the *m/z* ratio at 711.1934 for $[\mathbf{1}+Na]^+$ and 993.841 for $[\mathbf{2}+H]^+$, respectively, which were in good consistency with the theoretic results.

The photochromic reaction of dithienylethene moeity is based on the reversible ring-closing and ring-opening reactions as shown in Scheme 1. Upon irradiation with UV light, the open-ring isomer is converted into the closed-ring isomer, which could be converted back into open-ring isomer by irradiating with visible light. The photo isomerization behavior of the macrocyclic urea derivative **2** was monitored by UV-vis

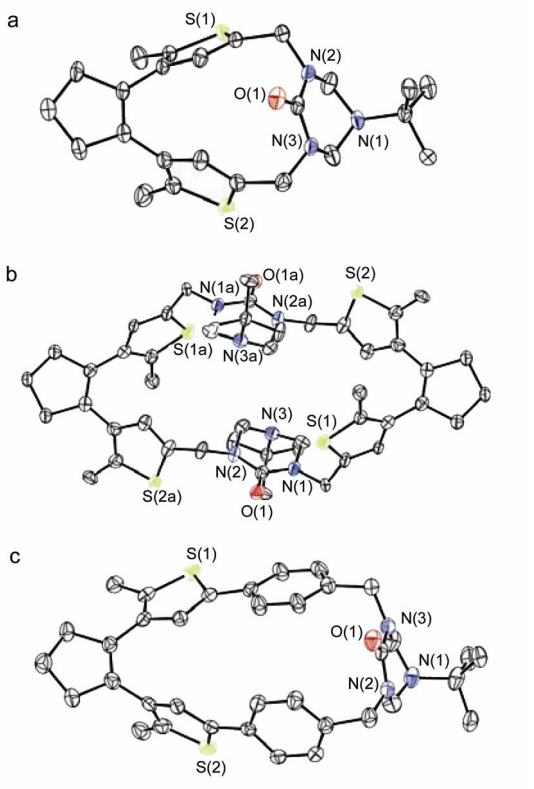


Figure 1 ORTEP view of the compounds (a) **3b**, (b) **3a**, and (c) **8b** with 30% thermal ellipsoids and labeling scheme. Hydrogen atoms and solvent atoms are omitted for clarity.

spectroscopy. Upon irradiating a mixed CH_2Cl_2/DMSO (V : V=1 : 1) solution of **2** with UV light of 313 nm, a new band appeared at 529 nm, corresponding to closed-ring isomers (Figure 2). During this procedure, the colorless solution turned pale purple immediately (<10 s) and gradually changed to a deep red-purple (1 min). Upon exposure of the red-purple solution to the visible light (>400 nm) for 5 min, the colored solution was completely bleached, which indicated that the close-ring form reverted to the open-ring form (Figure 3). That is to say, the bis-urea macrocycle **2** could show good photochromic properties, which is consistent to our original assumption. Moreover, we have also examined the photochemical reactivity of **8a**, the precursor of **2**. Upon irradiating with UV light, **8a** quickly changed into the closed form within 13 s and reverted to the open-ring form within 65 s upon exposure to visible light (>400 nm), indicating that **8a** possesses good photochromic property. Although both **8a** and **2** are capable of undergoing photochemical reaction, **8a** showed more sensitive to light irradiating and could accomplish the photochemical reaction within very short time, which might be due to the good solubility of **8a** and the tendency to adopt antiparallel conformation of the two thienyl rings. However, no new absorption band was observed upon irradiation with UV light in the CH_2Cl_2 solution of macrocycle **8b**, which indicated that the two dithienylethene units in the open-ring form were

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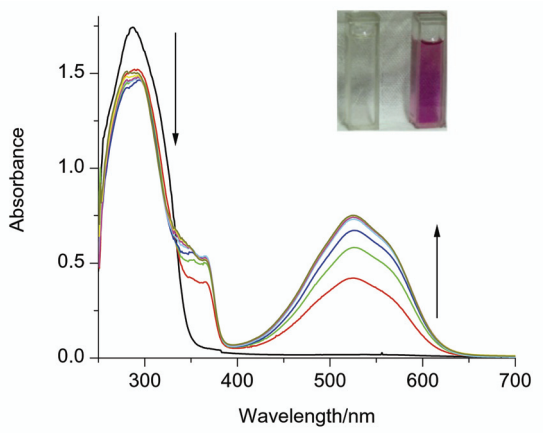

Figure 2 UV/Vis absorption spectral changes of **2** (2.5×10^{-5} mol/L) in DMSO/CH_2Cl_2 (V : V=1 : 1) upon 313 nm light irradiation at 0, 10, 20, 30, 40, 50, 60, 70 s. The inset shows the color change of solution before (left) and after (right) UV irradiation.

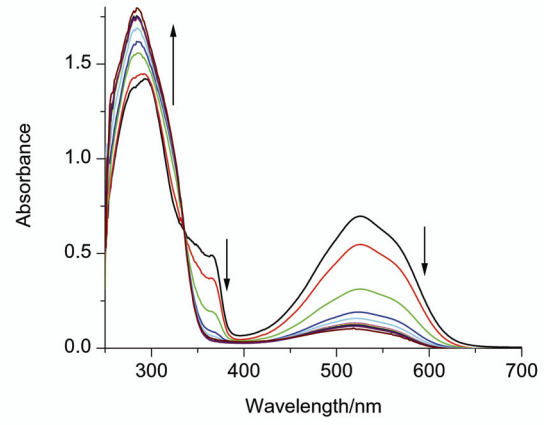

Figure 3 UV/Vis absorption spectral changes of the ring-closed isomer **2** (2.5×10^{-5} mol/L) in DMSO/CH_2Cl_2 (V : V=1 : 1) upon the visible light irradiation at 0, 20, 40, 60, 80, 100 s and 2, 3, 5, 10, 30 min.

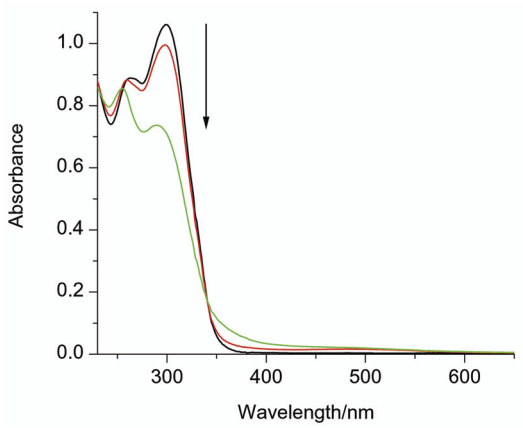

Figure 4 UV/Vis absorption spectral changes of **8b** (4×10^{-5} mol/L) in CH_2Cl_2 upon 313 nm light irradiation at 0, 1, and 5 min.

adopted with parallel conformation due to the fact that ring constraint and photo-reaction was forbidden. Moreover, **8b** showed some extent of decomposition if elongating the exposure time upon UV light. Since both the absorption band of the open form and the closed form of macrocycle **1** were exhibited in UV region, it is inconvenient for us to investigate the photoisomerization behavior of **1** by using UV-vis spectroscopy (Figure S26).[15]

Conclusions

In summary, we have successfully prepared two novel macrocycles **1** and **2** bearing dithienylethene units and urea groups. In particular, macrocycle **2** shows good photochromic properties, while the relatively smaller size of macrocycle **8b** exhibits photochemically inactive properties due to the unfavourable ring conformational constraint. Further research efforts will focus on growing single crystals of **1** and **2** and studying their self-assembly behavior directed by their urea groups. Furthermore, we will also explore the possibilities of functionalization of such macrocycles. This work is now underway in our laboratory.

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