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Amide- and Urea-Functionalized Dithienylethene: Synthesis, Photochromism, and Binding with Halide Anions

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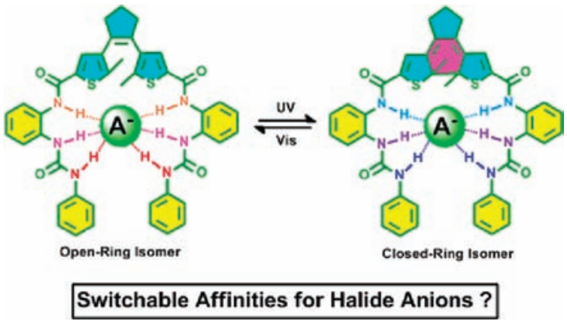
ABSTRACT



A versatile amide- and urea-functionalized dithienylethene has been successfully synthesized. Upon irradiation with UV or visible light, the compound showed excellent fatigue resistance. As a synthetic receptor, the dithienylethene displayed switchable affinities for Cl^- and Br^- anions when the UV/vis light was introduced. The switchable binding ability also had good reversibility.

In the past 40 years, anion recognition by synthetic receptors has grown to be an abundant and inspired research field, developing into a distinct branch of supramolecular chemistry due to the essential roles that anions play in a wide variety of biological, clinical, and environmental sciences.[1,2] Traditional anion receptors have stable structural configuration and binding ability; hence, modification of the structure has been the popular approach to changing the binding ability. However, the adjustment of binding ability using a simple method has proven to be a challenging project.

Dithienylethene is a classical molecular switch system that has been widely applied in molecular devices and optical memory storage media.[3] In view of the change of structural configuration that can be easily obtained by irradiation with UV/vis light, the introduction of the dithienylethene unit has been thought to be helpful to form the switchable synthetic receptor. Specifically, the varying recognition ability for guests can be controlled by UV/vis light. At present, synthetic receptors based on the dithienylethene unit have attracted some attention. For example, Tian and co-workers recently reported two dithienylethene-based fluorescence sensors, which efficiently detected mercury(II) and fluoride ions.[4] In our recent

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(1) Sessler, J. L.; Gale, P. A.; Cho, W.-S. *Anion Receptor Chemistry*; RSC Publishing: Cambridge, U.K., 2006.

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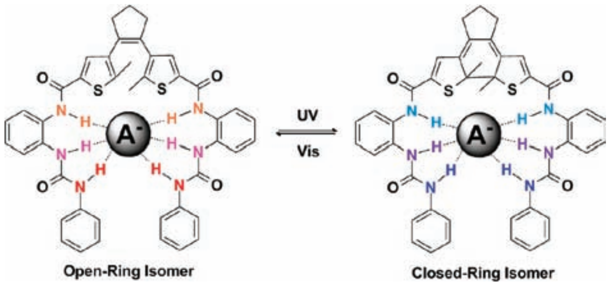
Scheme 1



research, we have also developed some work based on the use of dithienylethene as a chemosensor by the introduction of the imidazole ligand.[5] However, we still know very little about these compounds, especially in the field of switchable molecular recognition. This has provided the motivation to study this system. We have therefore synthesized an amide- and urea-functionalized dithienylethene, as shown in Scheme 1. Its photochromism and recognition properties have been well investigated. The photochromic properties indicated that the compound had high cyclization quantum yield and excellent fatigue resistance. At the same time, in its role as a synthetic receptor dithienylethene displayed switchable affinities for Cl^- and Br^- anions upon irradiation with UV/vis light.

The anion receptor **1** was synthesized with a good yield by treatment of 4,4′-(cyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-2-carbonyl chloride) with 1-(2-aminophenyl)-3-phenylurea (see Supporting Information: Scheme S1). The structure was fully confirmed by NMR spectroscopy, elemental analysis, and mass spectrometry. In the ^{1}H NMR, the hydrogen bond donors (NH) exhibited three different resonance signals, at 8.24, 9.29, and 9.99 ppm.

The photochromic behavior of compound **1** induced by photoirradiation in DMSO was measured at room temperature. As shown in Figure 1, the absorption maximum of compound **1** was observed at 273 nm ($\varepsilon = 3.84 \times 10^4$ L mol^{-1} cm^{-1}) as a result of a π–π^* transition.[6] Upon irradiation with 302 nm UV light, the colorless solution turned purple and a new absorption band at 542 nm ($\varepsilon = 0.10 \times 10^4$ L mol^{-1} cm^{-1}) appeared due to the formation of the corresponding ring-closed isomer **1c**. Moreover, a well-defined isosbestic point was observed at 327 nm, which indicated that compound **1** was cleanly converted to the photocyclized product. Upon irradiation with visible light ($\lambda > 402$ nm), the colored **1c** underwent a cycloreversion reaction and returned to the initial colorless ring-opened isomer **1o**. In particular, compound **1** showed very good reversibility, and no apparent deterioration was observed after repeating the above process seven times, which indicated that the compound **1** had very excellent fatigue resistance. The cyclization and cycloreversion quantum yields of **1** were 0.43 and 0.0077, respectively.

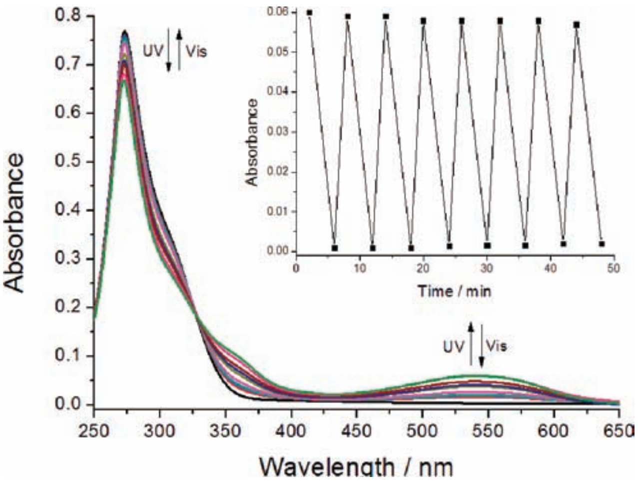


Figure 1. Absorption spectral changes of dithienylethene **1** by photoirradiation in DMSO (2.0×10^{-5} mol/L). (Inside) Fatigue resistance of dithienylethene **1** in DMSO.

Simultaneously, the photochromic process demonstrated by **1** has been characterized by means of NMR spectrometry (see Supporting Information: Figure **S2**). In the open-ring state, compound **1** showed three different NH signals at 9.99 (amide-H_a), 9.26 (urea-H_c), and 8.20 (urea-H_b) ppm. When the d^6-DMSO solution of **1** underwent UV light irradiation and achieved a photostationary state, the amide-H_a and urea-H_b showed the 0.04 and 0.03 ppm upfield shifts, respectively, as a result of the changes of structural configuration between the two isomers. However, no obvious change was observed in the urea-H_c, possibly due to the greater distance from the reactive center. Furthermore, from the integrated area of the NH signals, the photocyclization yield was calculated to be 34%.

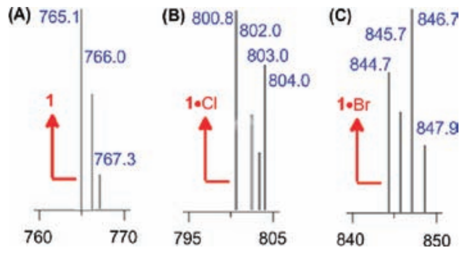


Figure 2. ESI mass spectra of **1** (A), **1**·Cl (B), and **1**·Br (C).

The amide and urea functional groups, well-known for their ability to interact with anions, were used as indicators for halide anions using ^{1}H NMR spectroscopy. For the fluoride anion, the resonance signals (H_a, H_b, and H_c) of the multiple hydrogen bond donors exhibited the same

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(5) Huang, S. Y.; Li, Z. Y.; Li, S. S.; Yin, J.; Liu, S. H. *Dyes Pigm.* **2012**, *92*, 961–966.

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downfield shifts (see Supporting Information: Figure S3). When the concentration of fluoride anions exceeded the equivalent concentration of dithienylethene, all the NH signals completely disappeared. However, a new signal at around 16.00 ppm (See Supporting Information: Figure S4) was observed when the fluoride anion reached 5.0 times the equivalent dithienylethene concentration, due to the formation of $[FHF]^-$, a result in good agreement with previous reports.[8] Similar downfield shifts of all NH resonance signals were observed in the titration experiments with chloride and bromide anions (see Supporting Information: Figures S5 and S6), which can be attributed to the formation of complexes between receptor **1** and anions. The existence of the complexes was further confirmed by ESI mass spectroscopy. In Figure 2, the peaks at 800.8 and 846.7 (*m*/*z*) proved the presence of the 1:1 complexes **1**·Cl and **1**·Br. For the iodide anion, however, no obvious chemical shifts were observed even when 10.0 equiv of iodide anion were added; the ESI mass spectroscopy still supported the formation of the 1:1 complex **1**·I (see Supporting Information).

The binding behaviors of **1** in the photostationary state were further explored for halide anions. Figure 3 shows the changes of chemical shifts when compound **1**, in the photostationary state, was allowed to bind with bromide anions. As shown, the H_a, H_b, and H_c in the open-ring isomer **1o** displayed the same downfield shifts as in the original state. At the same time, similar chemical shifts for $H_{a'}$, $H_{b'}$, and $H_{c'}$ were also obtained for the closed-ring isomer **1c**. Interestingly, H_a in **1o** showed larger shifts than $H_{a'}$ in **1c** while H_b and H_c represent contrasting behavior to $H_{b'}$ and $H_{c'}$. This interesting phenomenon was also found when we studied the binding with chloride anions in the photostationary state. Finally, iodide anions did not produce any obvious changes, not only for the open-ring state but also the closed-ring state (see Supporting Information: Figures S9 and S10).

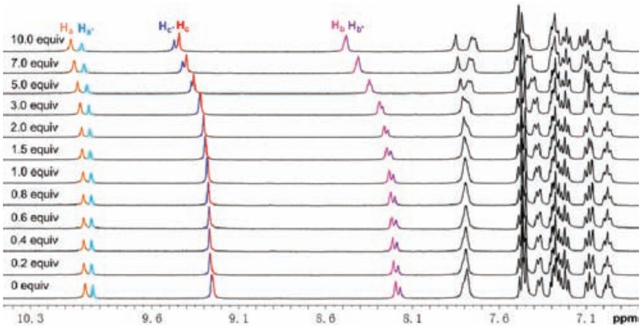

Figure 3. Partial ^1H NMR spectra (400 MHz in DMSO at 298 K) of **1** upon addition of 0−10 equiv of Bu_4NBr after irradiation with UV (302 nm) light.

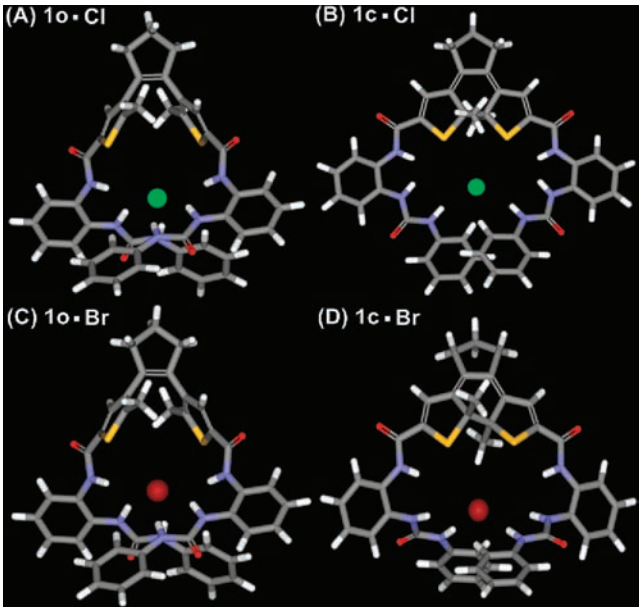

Figure 4. Top views of the energy-minimized structures for complexes **1o**·Cl (A), **1c**·Cl (B), **1o**·Br (C), and **1c**·Br (D).

The association constants (*K*) of the receptor with halide anions represent a very important parameter for evaluating the binding affinity. For **1o** and **1c**, analysis by the nonlinear least-squares method[7] was consistent with a 1:1 host/guest binding stoichiometry, which was in good agreement with the ESI mass spectroscopy. In addition, the values of *K* were determined by fitting the changes in NMR chemical shifts. The binding constants with **1o** and **1c** were calculated to be 68.4 and 57.9 M^{-1} for the chloride anion and 13.6 and 13.1 M^{-1} for the bromide anion, respectively. From the association constants of **1o** and **1c** for chloride and bromide anions, we can draw the conclusion that the open-ring isomer **1o** had greater affinities than the closed-ring isomer **1c**, a result attributed to the change of structural configuration. This result told us that the binding ability of the receptor was switchable by the very simple method of photoirradiation.

Subsequently, we optimized the energy-minimized structures of these complexes by theoretical calculation. As can be observed from Figure 4, the open-ring complexes **1o**·Cl and **1o**·Br revealed similar structural configurations while the closed-ring complexes **1c**·Cl and **1c**·Br had an analogous binding model. According to Figure 4A, the two reactive carbons of **1o**·Cl are present in the antiparallel conformation and the dithienylethene unit showed C_2 symmetry. After the photochromic reaction, the cyclopentene ring and thiophene rings were in a plane, and the dithienylethene unit of **1c**·Cl had an axially symmetrical structure. Therefore, compared with **1o**·Cl, the **1c**·Cl had a larger cavity, which was the reason why the open-ring

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(7) Hirose, K. *J. Inclu. Phenom. Macro. Chem.* **2001**, *39*, 193–209.

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isomer possessed higher affinity for the chloride anion than the closed-ring isomer. In addition, the distances from the chlorine atom to the hydrogen atoms of the hydrogen bond donors further prove this suggestion. In Figure 4(A), the distances between the chlorine atom and hydrogen atoms were 2.70–2.71 (Cl···H$_a$), 2.41–2.42 (Cl···H$_b$), and 2.32–2.33 Å (Cl···H$_c$). In contrast, **1c**·Cl had distances from the chlorine atom to the hydrogen atoms of 4.24 (Cl···H$_{a'}$), 3.70 (Cl···H$_{b'}$), and 2.45 Å (Cl···H$_{c'}$), as shown in Figure 4B.

Similar results were also achieved from the energy-minimized structures of complexes **1o**·Br and **1c**·Br. In Figure 4C, the distances between the bromine and hydrogen atoms were 2.73–2.75 (Br···H$_a$), 2.54–2.58 (Br···H$_b$), and 2.40–2.43 Å (Br···H$_c$). In the closed-ring complexes **1c**·Br, the distances were 3.89–4.09 (Br···H$_{a'}$), 2.87–3.00 (Br···H$_{b'}$), and 2.35–2.38 Å (Br···H$_{c'}$). The data indicated that the open-ring isomer possessed higher affinity for bromine anions than the closed-ring isomer, just as for chloride.

As has been mentioned, compound **1** showed excellent reversibility between the open-ring isomer and closed-ring isomer. Now the question arises as to whether this excellent reversibility can be achieved in its recognition ability for halide anions. Therefore, we next studied the switchable affinity for chloride and bromide anions using NMR spectrometry. Upon irradiation with visible light (> 402 nm), the NH signals of the closed-ring isomer gradually weakened and disappeared after irradiation for 50 min (see Supporting Information: Figures S15 and S16). Such changes corresponded to the changes of recognition ability and increasing affinity for chloride and bromide anions. Moreover, further irradiation with UV light reduces the affinity. Satisfyingly, the switchable process could be repeated ten times without any decay, as can be seen from Figure 5. This indicated that the amide- and urea-functionalized dithienylethene synthetic receptor showed repeatable switching of its recognition ability for halide anions using photocontrol.

In summary, an amide- and urea-functionalized dithienylethene was synthesized. Its photochromic properties indicated that the compound had good reversibility, excellent fatigue resistance, and high cyclization quantum yield. This was followed by an investigation of the recognition properties of the open- and closed-ring isomers as anion receptors for halide anions. Using photoirradiation with UV/vis light, we have shown that the compound has switchable affinity for chloride and bromide anions and that the switchable recognition function could be repeated ten times without any decay. The results indicated that the adjustment of the binding ability can be easily achieved by this type of simple photoirradiation. Therefore, our studies have supplied an alternative model for the design of novel supramolecular hosts with a switchable recognition function.

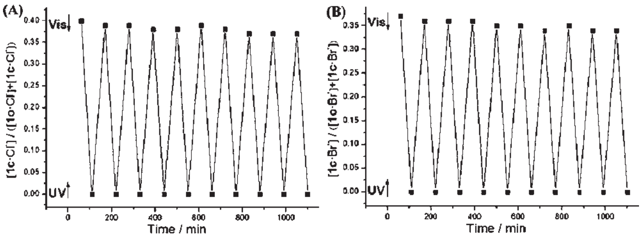

Figure 5. Fatigue resistance of switchable affinity for chloride anion (A) and bromide anion (B).

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Supporting Information Available. Details on the synthesis, characterization, anion binding and NMR, MS spectra are available in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.