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A supramolecular photoswitch constructed by intermolecular hydrogen bond between BTEPy and TTF–COOH

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ABSTRACT

A novel supramolecular photoswitch containing bisthienylethene-pyridine (BTEPy) and carboxyl attached tetrathiafluvalene (TTF–COOH) was constructed via intermolecular hydrogen bond. FT-IR spectra, XPS characterizations, ^{1}H NMR and theoretical calculation were carried out to verify the formation of the intermolecular hydrogen bond. The supramolecular self-assemblies BTEPy · 2TTF show good photochromic properties. A molecular switch with UV/vis light as inputs and electrochemical signals as outputs was obtained.

1. Introduction

The self-assembly of functional molecules into supramolecules has attracted much interest, since it is one of the most powerful approaches towards development of new materials and devices. Among various types of photochromic compounds, bisthienylethene derivatives (BTEs) are one of the most promising materials because of their excellent fatigue resistance and thermal stability in both isomeric forms, picosecond switching times, and fairly high photocyclization quantum yields [1–4]. The open and closed isomers of BTEs differ from each other not only in their absorption but also in various physical and chemical properties, such as luminescence, refractive indices, oxidation/reduction potentials, chiral properties and magnetic interactions [5–8]. Reversible light-responsive supramolecules are most desirable since only light is used as the input stimulus without other additives needed [9,10]. Therefore, lots of supramolecular self-assembled systems employing a photochromic bisthienylethene moiety as a photoreversible switch have been reported [11–13].

Tetrathiafulvalene (TTF) [14] is a reversible and stable two-electron donor which has been intensively studied for more than two decades, mainly with the aim of developing organic superconductors. TTF and its derivatives are strong electron donors, which can be reversibly transformed into the corresponding radical cation $TTF^{\cdot +}$ and dication TTF^{2+} through either chemical or electrochemical oxidations at easily accessible potentials [15]. Because of this feature, functional molecules and supramolecules containing TTF units were used for molecular switches, logic gates, sensors, and machines [16–20].

Here, we have designed a self-assembled molecule (BTEPy · 2TTF) constructed by intermolecular hydrogen-bonding interaction between bisthienylethene-pyridine and carboxyl attached tetrathiafluvalene. Pyridine groups are widely used for interaction with carboxylic acids via intermolecular hydrogen bonds [21–29]. The self-assembled molecule BTEPy · 2TTF (Scheme 1) shows good photochromic properties which could be triggered between the colorless ring-open and colored ring-closed forms by alternating irradiation with UV and visible light. Electrochemical properties of the self-assembled molecule BTEPy · 2TTF were also discussed both experimentally and theoretically. The oxidation potential of the self-assembled complex BTEPy · 2TTF could be reversibly modulated by alternating UV and visible light irradiation. And by applying different potentials (vs Ag/AgCl), absorption spectra showed distinct absorption bands for the three states of TTF, $TTF^{\cdot +}$ and TTF^{2+}.

2. Experimental

Reagents and starting materials were used as received. Solvents were distilled and dried before use. The precursors BTEPy [30] and TTF–COOH [31] were synthesized according to published procedures, and well characterized by ^{1}H NMR and MS. The self-assembled composite was yielded by dissolving and stirring a mixture of BTEPy and TTF–COOH with molar ratio of 1:2 in THF and the solvent was removed in vacuo.

Absorption spectra were measured on a Varian Cary500 UV-Vis spectrophotometer. The optical switch experiments were carried out in a photochemical reaction apparatus with a 200 W Hg lamp. Cyclic voltammetry measurements were carried out at a platinum electrode using millimolar solutions in CH_2Cl_2 (distilled over CaH_2 prior to use) containing 0.1 M of the support electrolyte,

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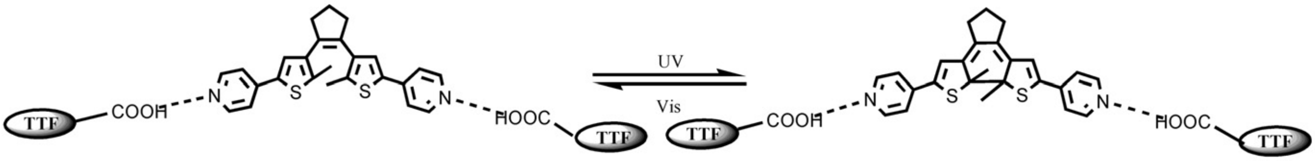

Scheme 1. Photochromic process in BTEPy · 2TTF.

tetrabutylammonium hexafluorophosphate. And it was in a three electrode cell (Pt working and counter electrodes and Ag/AgCl reference electrode) and potentiostat assembly was by VersaStarII electrochemical analyzer. Electrochemical oxidation and reduction were carried out at graphite plate as working electrode. FT-IR spectra were performed on Nicolet 380 with KBr pellets. X-ray photoelectron spectra (XPS) were measured on a Perkin Elmer PHI 5000C ESCA System. All theoretical calculations were carried out within the DFT approach in gas phase using the GAUSSIAN 03 program [32]. DFT calculations were performed using hybrid B3LYP exchange-correlation functional and the 6-31G* basis set. Throughout the calculations, the long hexylthio side chains on TTF units have been replaced by methylthio groups in order to cut the computational cost with no significant change in the electronic properties of TTF [33].

3. Results and discussion

To verify the interaction mode between pyridine and carboxylic acid during the self-assembly, FT-IR spectra, XPS and ^{1}H NMR spectra were measured (The measurements were performed on the ring-open form of the BTEPy and BTEPy · 2TTF) and theoretical calculation was carried out. Room temperature FT-IR spectra of BTEPy, TTF–COOH, self-assembled BTEPy · 2TTF and mixture of BTEPy and TTF powder (BTEPy (open form):TTF = 1:2) were showed in Fig. 1a. Carboxylic acid dimers (H-bonded carbonyl) could be created in TTF–COOH solution. The band at 1686 cm^{-1} in TTF–COOH was ascribed to the stretching vibration of carboxylic acid dimers (H-bonded carbonyl) [21,25,29]. This band diminished and a new band centered at 1695 cm^{-1} was observed in the self-assembled BTEPy · 2TTF, which was attributed to the complex formation between the pyridine unit of BTEPy and the carboxylic acid units of TTF–COOH [23,25,28,29]. Upon formation of the composite, the characteristic modes of the pyridine group at 1596, 1498 and 1462 cm^{-1} shifted to 1603, 1501 and 1466 cm^{-1}, respectively. The vibrations of the pyridine group at 1539 and 1411 cm^{-1} diminished completely in the complex. The most striking feature was the presence of a broad band at 1922 cm^{-1} in BTEPy · 2TTF, indicative of strong hydrogen bonds between the carboxylic acid and pyridine moieties [21,24,25]. No apparent new absorption band around 1620 cm^{-1}, corresponding to a characteristic band of protonated pyridine, was observed in assembly, suggesting that the complex is formed through hydrogen bond interaction rather than ionic interaction [23]. Obviously, the intermolecular hydrogen bond interaction did act as a driving force for the formation of self-assembled composite, where the carboxylic acid served as the donor and pyridine group with a lone electron pair as the acceptor. From FT-IR spectra of mixture of BTEPy and TTF powder (BTEPy (open form): TTF = 1:2) in Fig. 1a, it could be get that just having a powder mixture of the two precursors might not have the same effect in creating intermolecular hydrogen bond.

Since the binding energy of *N* 1 s is very sensitive to the environmental perturbation, XPS characterization was used to verify the hydrogen bond formation [10]. The realistic error margin on the *N* 1 s binding energy value was about 0.1 eV in the XPS measurements. The *N* 1s binding energy value of the pyridine group in BTEPy was 400.4 eV (Fig. 1b). A higher binding energy feature (400.8 eV) was observed for the self-assembled complex BTEPy · 2TTF, larger by 0.4 eV than that in BTEPy. In principle, the formation of hydrogen bond or protonated nitrogen leads to an upshift of the binding energy of *N* 1 s due to the decrease in electron density in nitrogen atoms [22,24,26]. The binding energy change of 0.4 eV in the present BTEPy · 2TTF complex relative to BTEPy may be ascribed a hydrogen bond interaction [27]. And it should not be ionic interaction, because the change was supposed to be more than 2.0 eV for the ionic interaction in a protonated entity [22,24,26,27]. The binding energy of mixture of BTEPy and TTF powder (BTEPy (open form): TTF = 1:2) did not have obvious upshift compared with that in BTEPy. These results were consistent with the IR spectral data.

^{1}H NMR is a useful tool to study supramolecular interactions. In Fig. 1c, BTEPy (open form) in DMSO-d_6 shows an array of resonances corresponding to the aromatic protons in the molecule. The signal of carboxylic acid of TTF–COOH was observed at about $\delta = 12.700$ in dried DMSO-d_6. The formation of hydrogen bonds could affect the protons at the α-position of pyridine (*H*1). As shown in Fig. 1c, the *H*1 protons exhibited double peaks at 8.476. With the addition of 2 equiv of TTF–COOH, the peaks moved to 8.532 and there was a downfield shift for this pair of peaks. The hydrogen bond formation also influenced the protons at the β-position (*H*2) of pyridine, the change of chemical shift $\Delta\delta$ was 0.042 when the ratio of BTEPy (open form): TTF–COOH = 1:2. A single peak at $\delta = 7.554$ was for thienyl protons (*H*3), which also exhibited a small downfield shift after the addition of TTF–COOH. These changes arose from the fact that the weak acid TTF–COOH, acting as a proton donor, could reduce the electron density on the aryl ring of BTEPy. When TTF–COOH was increased to 3 equiv, ^{1}H NMR spectrum had no obvious changes, compared with that of 2 equiv of TTF–COOH.

The B3LYP/6-31G* optimized geometries of ring-open and ring-closed isomers for BTEPy · 2TTF were shown in Fig. S3 (Supporting Information). Single point energy calculations were carried out for BTEPy, TTF–COOH and BTEPy · 2TTF at the B3LYP/6-31+G* level with the corresponding B3LYP/6-31G* optimized geometries. Hydrogen bond energy was calculated and shown in Table S1 (Supporting Information). The hydrogen bond energy in the BTEPy · 2TTF ring-open form ($E_{\text{H-bond-O}}$) was calculated to be 0.4810 eV, and that in the ring-closed form ($E_{\text{H-bond-C}}$) was 0.4785 eV.

Absorption spectra of the BTEPy, TTF–COOH and BTEPy · 2TTF were investigated and shown in Fig. 2. Upon irradiation with light of 254 nm for 20 min, the colorless open-ring form BTEPy became purple ($\lambda = 558$ nm), which was due to the transformation of BTEPy by photocyclization into its closed form. BTEPy could be photochemically regenerated from its closed form by irradiation with light of 570 nm. Similarly, upon UV light irradiation at 254 nm for 20 min, BTEPy · 2TTF was also photoswitched to its closed form with the appearance of its characteristic absorption band at $\lambda_{1\max} = 374$ nm, $\lambda_{2\max} = 557$ nm. From Fig. 2b, no obvious difference in the spectra of the closed ring form between BTEPy and BTEPy · 2TTF was got. The absorption spectrum of BTEPy · 2TTF (ring open form) was approximately the sum of the absorption spectra

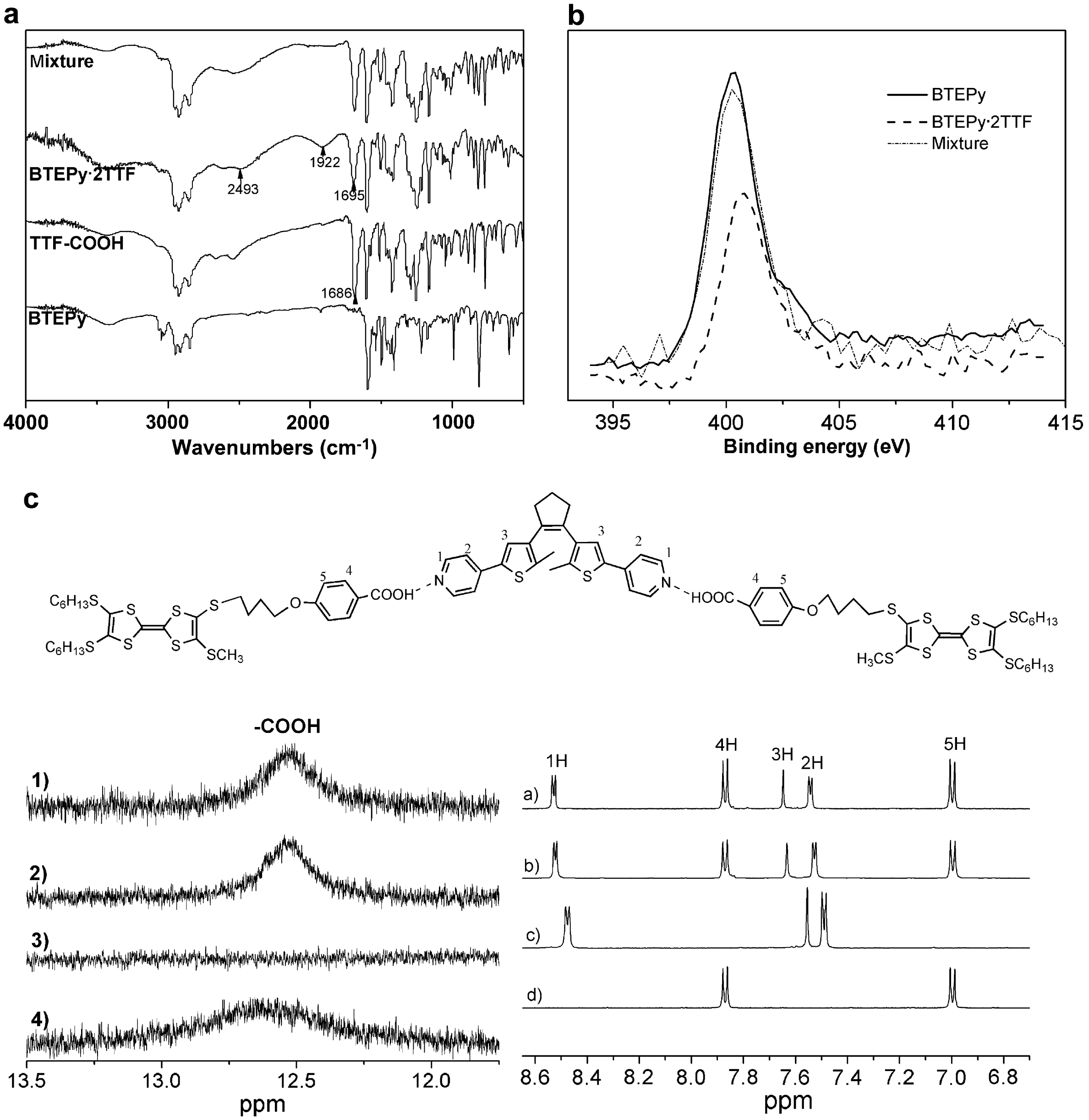

Fig. 1. Verification of the intermolecular hydrogen bond: (a) Room temperature FT-IR spectra of mixture (a mixture of powder BTEPy (open form): TTF = 1:2), self-assembled BTEPy · 2TTF (open form), TTF–COOH and BTEPy (open form); (b) *N* 1 s spectra (XPS) of BTEPy (open form), self-assembled BTEPy · 2TTF (open form) and mixture (a mixture of powder BTEPy (open form): TTF = 1:2); (c) Partial ^{1}H NMR spectra (in DMSO-d_6): line 1 and a are partial ^{1}H NMR spectra of BTEPy (open form): TTF–COOH = 1:3; line 2 and b are partial ^{1}H NMR spectra of BTEPy (open form): TTF–COOH = 1:2; line 3 and c are partial ^{1}H NMR spectra of BTEPy (open form); line 4 and d are partial ^{1}H NMR spectra of TTF–COOH.

of compounds BTEPy (ring-open form) and TTF–COOH (in Fig. 2a). The absorption position of the ring closed form was almost similar (in Fig. 2b). On the basis of the above results, it could be concluded that no strong electronic interaction existed between the TTF unit and the BTEPy unit in BTEPy · 2TTF.

The electrochemical studies of BTEPy · 2TTF were performed on VersaStar II electrochemical analyzer. The cyclic voltammograms of BTEPy · 2TTF in dichloromethane containing tetrabutylammonium hexafluorophosphate (0.1 M) before and after UV irradiation were shown in Fig. 3. Two conspicuous quasi-reversible redox waves for the open-ring isomer were observed at $E_{\mathrm{ox1}} = 0.65$ V and $E_{\mathrm{ox2}} = 0.99$ V (vs Ag/AgCl), and a small oxidation wave was at 1.3 V. After the solution of BTEPy · 2TTF was exposed to UV light (254 nm) for 30 min, the anodic potential E_{ox1} was shifted to the positive region by ca. 11 mV while the E_{ox2} was positively shifted by ca. 27 mV. The small oxidation wave at 1.3 V was shifted to 1.22 V, accompanied by the appearance of a small oxidation wave at 0.79 V.

To elucidate the electrochemical properties, the molecular orbital for the BTEPy · 2TTF both in its ring-open form and ring-closed form was analyzed for the B3LYP/6-31G$*$ optimized geometries. The HOMO (the Highest Occupied Molecular Orbital) and SOMO (the Second-highest Occupied Molecular Orbital) of the BTEPy · 2TTF (open form) were found to be mainly localized on the two TTF units with close energy of −4.907 eV and −4.914 eV (See Supporting information Table S3 and Fig. S4). This helped to explain the first couple at 0.65 V covered two unresolved oxidation processes, corresponding to two electrons almost simultaneously removed from the two TTF groups to form two TTF$^{\cdot+}$. The other two molecular orbitals on these two TTF units were also with the

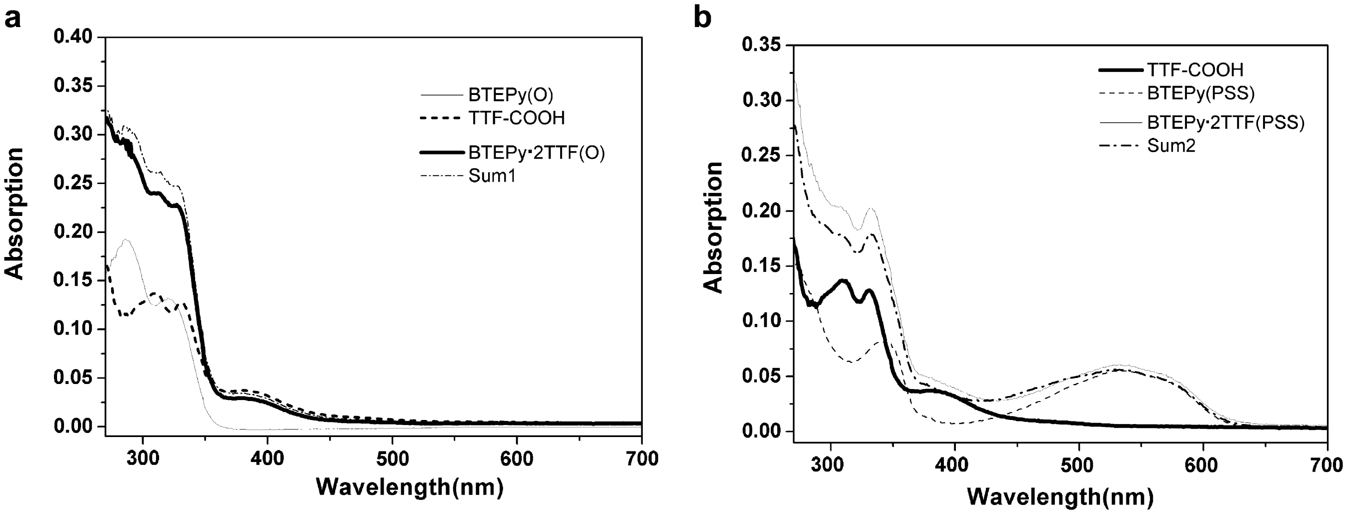

Fig. 2. Absorption spectra of TTF–COOH (2.0×10^{-5} mol L^{-1}), open form (O) of BTEPy (1.0×10^{-5} mol L^{-1}), open form (O) of BTEPy · 2TTF (1.0×10^{-5} mol L^{-1}) in THF, Sum of absorption spectra of TTF–COOH (2.0×10^{-5} mol L^{-1}) and open form (O) of BTEPy (1.0×10^{-5} mol L^{-1}), in (a). Absorption spectra of TTF–COOH (2.0×10^{-5} mol L^{-1}), photo-stationary state (PSS) of BTEPy (1.0×10^{-5} mol L^{-1}), photo-stationary state (PSS) of BTEPy · 2TTF (1.0×10^{-5} mol L^{-1}) in THF, Sum of absorption spectra of TTF–COOH (2.0×10^{-5} mol L^{-1}) and photo-stationary state (PSS) of BTEPy (1.0×10^{-5} mol L^{-1}), in (b).

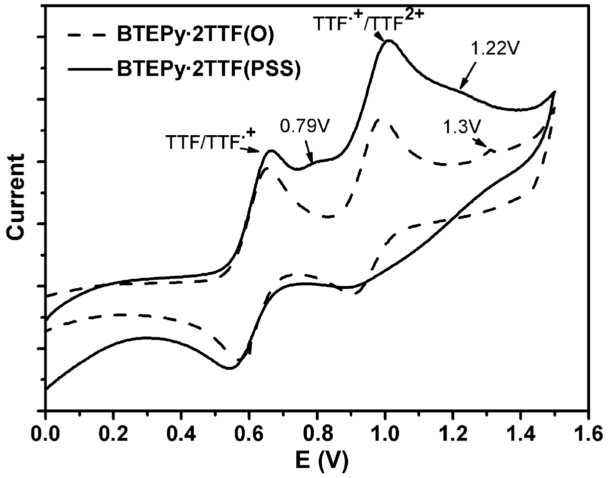

Fig. 3. Cyclic voltammograms of BTEPy · 2TTF in CH_2Cl_2 (5.0×10^{-4} mol L^{-1}) with a scan rate 50 mV s^{-1}.

similar energy of −6.191 eV and −6.196 eV (See Supporting information Table S3 and Fig. S5), which indicated that two more electrons were again almost simultaneously removed from the two $TTF^{\cdot+}$ at a higher potential (E_{ox2} = 0.99 V) to form two TTF^{2+}. Two conspicuous quasi-reversible redox waves for the closed-ring isomer were also ascribed to the formation of the two $TTF^{\cdot+}$ and two TTF^{2+}. Our calculation results indicated that HOMOs of both the ring-open and ring-closed isomers of BTEPy · 2TTF were mainly located on the TTF units, and the HOMO energy of the ring-open isomer (E_{HOMO} = −4.907 eV) was found to be higher than that of the ring-closed isomer (E_{HOMO} = −4.915 eV). The higher was the HOMO energy of the ring-open isomer, the lower its E_{ox}. This is consistent with our experimental results as discussed above.

The cyclic voltammetry of BTEPy (open form) showed two oxidation waves at 1.0 V and 1.3 V (See Supporting information Fig. S2). Therefore, in the cyclic voltammetry of BTEPy · 2TTF (ring-open form) the oxidation wave at 1.0 V belonging to the BTEPy unit was superposed with the second redox wave ($TTF^{\cdot+}/TTF^{2+}$) at E_{ox2} = 0.99 V (vs Ag/AgCl). The HOMO and SOMO energies of BTEPy in closed form (HOMO: −4.859 eV and SOMO: −6.083 eV) were higher than those in the open form (HOMO: −5.709 eV and SOMO: −6.145 eV). As a result, oxidation waves of the BTEPy in the closed form were at lower potentials compared with those of BTEPy in the open form, leading to the appearance at 0.79 V of the originally covered oxidation wave (at 1.0 V for open form) of BTEPy. Interestingly, after irradiation with the light (>540 nm), the initial cyclic voltammograms were almost restored. This can be employed to construct a molecular switch with UV/visible light as inputs and electrochemical signal as outputs.

TTF exhibits two reversible one-electron oxidation processes, corresponding to $TTF/TTF^{\cdot+}$ and $TTF^{\cdot+}/TTF^{2+}$ redox reactions, respectively. Thus, the transformation of TTF into $TTF^{\cdot+}$ and TTF^{2+} can be achieved by electrochemical oxidations. TTF units in the molecule could be transformed into $TTF^{\cdot+}$ by application of an oxidation potential at +0.75 V (vs Ag/AgCl) and the formation of TTF^{2+} could be obtained by sequential oxidation at +1.1 V (vs Ag/AgCl). Furthermore, both $TTF^{\cdot+}$ and TTF^{2+} could be reduced to the neutral TTF after applying a reduction potential at −0.1 V (vs Ag/AgCl). The absorption spectra of BTEPy · 2TTF (5×10^{-5} M in dry CH_2Cl_2) and those after electrochemical redox were shown in Fig. 4. After applying an oxidation potential at +0.75 V (vs Ag/AgCl) for 1 h,

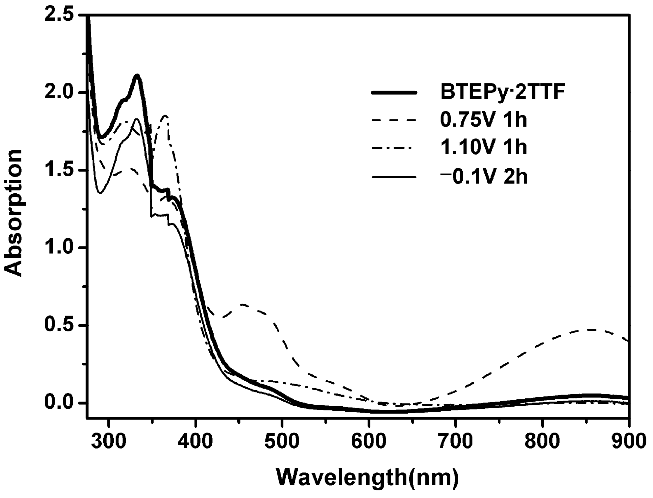

Fig. 4. Absorption spectra of BTEPy · 2TTF (open form) in CH_2Cl_2 (5.0×10^{-5} mol L^{-1}) after applying different potentials.

new absorption bands at 456 nm and 851 nm appeared, and the absorption at 321 nm (due to neutral TTF) decreased. The absorption band at 456 nm was attributed to $TTF^{\cdot+}$ and that at 851 nm was ascribed to π-dimer (TTF_2^{2+}) [34]. Sequential application of an oxidation potential at +1.1 V (vs Ag/AgCl) for another 1 h, the absorption bands at 456 nm and 851 nm almost disappeared and the absorption band at 362 nm appeared which was attributed to TTF^{2+}. Then, by the application of a reduction potential at −0.1 V (vs Ag/AgCl) for 2 h, the absorption band at 362 nm was decreased, indicating the reduction of TTF^{2+} to the neutral TTF.

4. Conclusions

In summary, we designed a novel supramolecular photoswitch built from bisthienylethene-pyridine (BTEPy) and carboxyl attached tetrathiafluvalene (TTF–COOH) via intermolecular hydrogen bond. The formation of the intermolecular hydrogen bond was verified by FT-IR, XPS, ^1H NMR and theoretical calculation. The supramolecular self-assembly BTEPy · 2TTF in THF could be triggered between the colorless ring-open and colored ring-closed forms by alternating irradiation with UV and visible light. A molecular switch with UV/vis light as inputs and electrochemical signals as outputs was obtained since the oxidation potential of self-assembled complex BTEPy · 2TTF could be reversibly modulated by alternating UV and visible light irradiation. Moreover, by applying different potentials, absorption spectra showed distinct absorption bands which might be used for further application.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2008.02.091.

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