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Switchable 2,3-dithienylmaleimide bonded to different fluorophores: synthesis and photochromic properties*

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Abstract: A series of photochromic diarylethene derivatives containing different fluorophores was synthesized by the Sonogashira coupling reaction and characterized by ^{1}H nuclear magnetic resonance (NMR), ^{13}C NMR and mass spectroscopy. Photochromic conversion of Cz-MS was observed and its structural change was confirmed by proton NMR. Switchable absorption and emission phenomena were observed for these molecules. These phenomena were attributed to the reversible photochromic fluorescence resonance energy transfer (pcFRET) process. The design of this novel photochromic system of Py-4MS enables information to be processed in a non-destructive manner. This overcomes the problem of the destructive nature of tracking photochromism using ultraviolet (UV)-vis spectroscopy.

Key words: Photochromic reaction, Diarylethene derivatives, Photochromic fluorescence resonance energy transfer (pcFRET)
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INTRODUCTION

Organic compounds designed for showing specific optoelectronic properties have recently attracted much attention because of their potential future applications, including organic light emitting diodes (OLED) (Lu *et al.*, 2000; Moorthy *et al.*, 2007) for large area, flat-panel, colour displays, fluorescent probes for biotechnology (Irie, 2000; Irie *et al.*, 2002) and dendrimers for light harvesting (Wang *et al.*, 2006). Besides these optoelectronic purposes, thermal stable and fatigue resistant photoswitchable molecules could potentially be used for erasable optical storage (Yamaguchi *et al.*, 2000; Feringa, 2001; Myles and Branda, 2002), where each bistable photochromic compound could represent '0' or '1' of a digital code (Liu *et al.*, 2003). Integration of several switchable units into a single molecule enabled the development of more complicated computational systems and generated further interest (Xiao *et al.*, 2005; Schafer *et al.*, 2007). Photochromic fluorescence resonance energy transfer (pcFRET) could be easily observed between the fluorescence donor and the photochromic acceptor. This provided a unique method for analyzing molecular conformation, association and separation in the 1~10 nm range by colorful imaging of objects ranging from single molecules to living cells (Jares-Erijman and Jovin, 2003; Giordano *et al.*, 2002). For this reason, a great number of photochromic compounds, including azobenzenes, fulgides and diarylethenes, have been developed (Hanazawa *et al.*, 1992; Loudwig and Bayley, 2006). Diarylethenes might be the most promising photochromic compounds owing to their unique photochromic properties, including the good thermal stability and high fatigue resistance of both isomers (Irie, 2000).

In our previous work, a carbazole and diarylethene based donor-acceptor (D-A) dyad was synthesized and its reversible optical property was investigated (Zhao *et al.*, 2007). Here, we report the synthesis of a series of photochromic compounds, in which 2,3-dithienyl-maleimide was introduced to the

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different fluorophores, carbazole and pyrene. Up to four photoswitchable units were integrated in a single molecule (Py-4MS) and an effective pcFRET was clearly observed.

EXPERIMENT

General method

Cyclohexane for ultraviolet (UV)-vis and emission spectroscopic measurements was redistilled. Commercially available reagents were used without further purification unless otherwise stated. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained on a Brucker AVANCE DMX500 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Electrospray ionization (ESI) mass spectra were obtained using a Brucker Daltonics Data Analysis 3.0 instrument. UV-vis spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Fluorescence spectra were recorded using a Shimadzu RF-5301PC spectrofluorophotometer.

Synthesis

1. 1-((4-(9H-carbazol-9-yl)phenyl)methyl)-3,4-bis(2,4,5-trimethylthiophen-3-yl)-1H-pyrrole-2,5-dione (Cz-MS)

Compound 2 (0.067 g, 0.2 mmol) was dissolved in anhydrous acetone (80 ml). 2,3-Dithienylmaleimide (MS) (0.07 g, 0.2 mmol) and K_2CO_3 (14.4 g, 100 mmol) were added to the acetone solution. The resulting mixture was refluxed for 24 h, then poured into H_2O (100 ml) under stirring. The mixture was extracted using diethyl ether. The combined ether solution was washed by brine and dried over anhydrous $MgSO_4$. After filtration, the volatile solvent was removed under reduced pressure. The residue was purified by preparative thin layer chromatography (hexane/methylene chloride). 50 mg Cz-MS (41% yield) was obtained. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 1.76 (s, 3H), 1.93 (s, 6H), 2.08 (s, 3H), 2.24 (s, 3H), 2.26 (s, 3H), 4.91 (m, 2H), 7.27 (m, 2H), 7.40 (s, 4H), 7.54 (d, 2H, J=7.5 Hz), 7.63 (d, 2H, J=7.5 Hz), 8.13 (d, 2H, J=7.5 Hz). ^{13}C-NMR ($CDCl_3$): δ 170.37, 170.27, 140.96, 137.42, 137.37, 137.16, 136.68, 136.44, 136.94, 132.06, 131.73, 130.85, 130.05, 127.75, 127.60, 127.64, 126.16, 123.60, 120.53, 120.20, 109.98, 41.85, 41.83, 14.75, 14.49, 13.63, 13.37, 13.34. Mass spectroscopy (ESI, m/z): 600 (34.48, M^+), 256 (100, p-$CzC_6H_4CH_2^+$).

2. 1-(4-(pyren-1-ylethynyl)benzyl)-3,4-bis(2,4,5-trimethylthiophen-3-yl)-1H-pyrrole-2,5-dione (Py-MS)

Compound 6 (100 mg, 0.44 mmol), Compound 5 (500 mg, 0.88 mmol), cuprous iodide (10 mg, 0.05 mmol), dichlorobis (triphenylphosphine) palladium(II) (5 mg, 0.005 mmol), triphenylphosphine (5 mg, 0.02 mmol) and dry triethylamine 100 ml were placed in a 200 ml round bottle flask equipped with a Teflon™ covered magnetic stir bar. The solution was purged with nitrogen for half an hour, then refluxed under nitrogen for 8 h. The reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was purified through column chromatography (silica gel, hexane methylene chloride as eluent). 73 mg (25% yield) of Py-MS was obtained. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 1.74 (s, 3H), 1.90 (s, 6H), 2.06 (s, 3H), 2.24 (s, 3H), 2.27 (s, 3H), 4.84 (m, 2H), 7.49 (d, 2H, J=8.0 Hz), 7.69 (d, 2H, J=8.0 Hz), 8.01~8.24 (m, 8H), 8.65 (d, 1H, J=9.0 Hz). ^{13}C NMR ($CDCl_3$): δ 170.23, 170.14, 137.35, 137.16, 132.23, 131.48, 130.78, 129.83, 128.87, 128.59, 128.54, 128.41, 127.47, 126.46, 125.87, 125.81, 125.73, 124.75, 124.56, 123.26, 42.05, 14.67, 14.42, 13.55, 13.35, 13.32, 13.27. Mass spectroscopy (ESI, m/z): 659.9 (M^+).

3. Py-4MS was synthesized in a similar way.

20 mg (20% yield) of Py-4MS was obtained. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 1.74 (s, 12H), 1.91 (s, 24H), 2.06 (s, 12H), 2.24 (s, 12H), 2.27 (s, 12H), 4.84 (m, 8H), 7.49 (d, 8H, J=8.0 Hz), 7.70 (d, 8H, J=7.5 Hz), ^{13}C NMR ($CDCl_3$): δ 170.28, 170.19, 137.39, 137.19, 136.66, 136.43, 134.01, 132.38, 132.10, 131.17, 130.84, 130.02, 128.96, 128.72, 127.77, 127.63, 127.19, 124.32, 122.89, 119.14, 96.07, 88.25, 42.08, 29.96, 14.74, 14.49, 13.63, 13.41, 13.34.

RESULTS AND DISCUSSION

Synthesis

The synthesis of desired compounds is shown in Fig.1. MS was prepared by the reference method (Irie and Mohri, 1988). Intermediates **2** and **4** were prepared by bromination of their corresponding

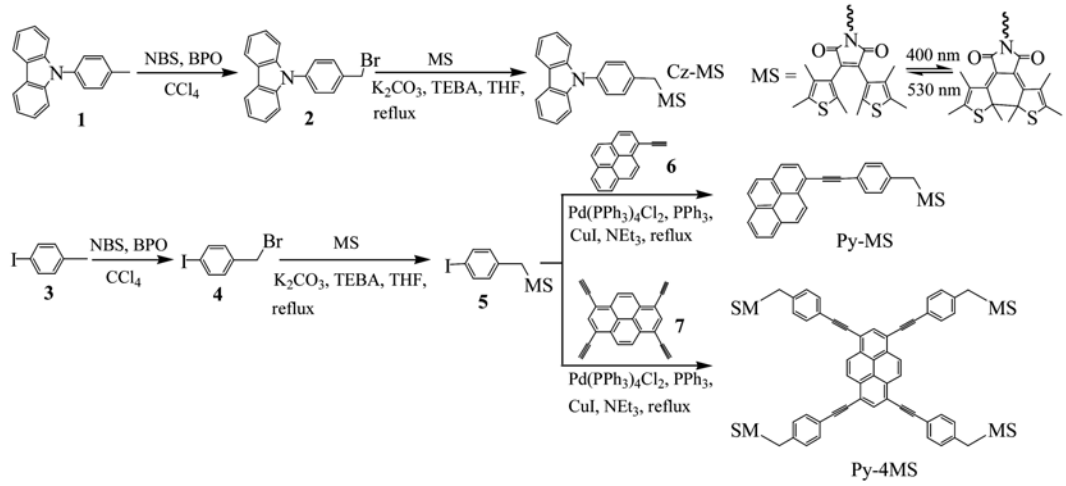


Fig.1 Synthetic route to MS, Cz-MS, Py-MS and Py-4MS

precursors. Treatment of intermediates **2** and **4** with MS in an alkalescence condition gave Cz-MS and intermediate **5**, respectively. Finally, the Pd/Cu-catalyzed Sonogashira coupling reaction of 1-ethynylpyrene **6** and 1,3,6,8-tetraethynylpyrene **7** with intermediate **5** yielded Py-MS and Py-4MS, respectively. These compounds were purified by silica-gel column chromatography, and their molecular structures were verified by ^{1}H NMR and ^{13}C NMR spectroscopy and ESI MS measurement as follows.

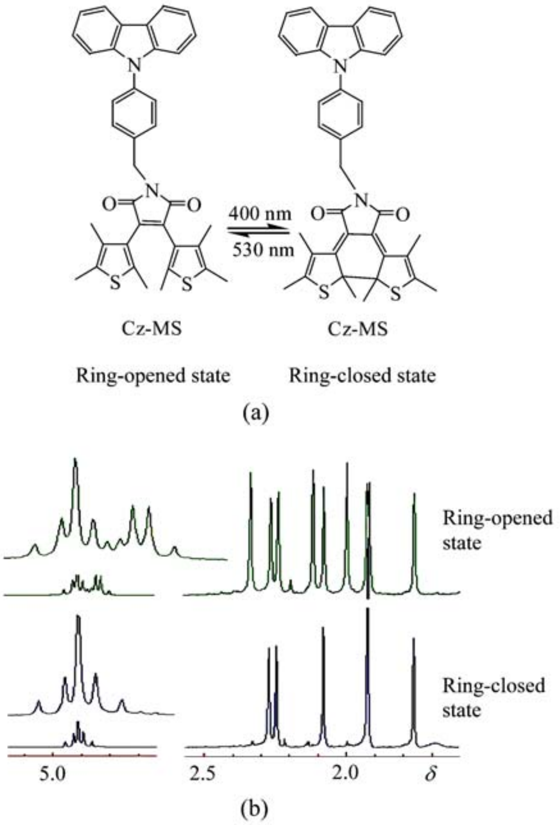


Fig.2 (a) Structural change of Cz-MS; (b) ^{1}H NMR indicating ring-closing process of Cz-MS

Photochromic conversion analysis by proton NMR

Photochromic conversion of Cz-MS is shown in Fig.2. Its structural change was confirmed by proton NMR. In the ring-opened state of Cz-MS, five peaks (δ1.76 (s, 3H), δ1.93 (s, 6H), δ2.08 (s, 3H), δ2.24 (s, 3H), δ 2.26 (s, 3H), assigned to six methyl groups) were observed in ring-opened state. One of them was the coincidental overlap of two methyl groups based on the integration. Six methyl groups arose from two forms, parallel and anti-parallel, in this state. Two different methylene groups were simultaneously observed in the spectrum, corresponding to parallel and anti-parallel. The methylene group for the parallel form was a singlet (δ4.90) owing to its enantiotopic nature, while the methylene group for the anti-parallel form was a doublet of a doublet (δ4.94, 4.91 and δ4.88, 4.85) owing to its diastereotopic nature (Fig.2b, bottom). The coupling constant for the diatereotopic protons was found to be 15 Hz. Moreover, two carbonyl peaks (δ170.28, 170.37) were identified as parallel and anti-parallel, respectively, using ^{13}C NMR. After irradiation at 400 nm for 6 h in CDCl$_3$, three new peaks (δ1.99, 2.11, 2.33, assigned for methyl groups of the ring-closed state (Cz-MS)) were introduced (Fig.2b, top). Two coincidental methyl groups (δ1.93) were split into two peaks (δ1.924, 1.917). Consequently, a new doublet of a doublet (δ4.86, 4.83 and δ4.82, 4.79) for the arising methylene group was seen resulting from the diastereotopic protons in the ring-closed state. Furthermore, when this dark solution was exposed to 530 nm for 6 h, a clear yellowish solution was regenerated and the structure of the solute was shown to be the original ring-opened state of Cz-Ms by its ^{1}H NMR spectrum. As a result, we concluded that the ring-opened and the ring-closed states of Cz-Ms could be successfully inter-transferred through alternative irradiation at 400 nm and 530 nm for a certain period, respectively.

Absorption and emission measurement

400 nm and 530 nm irradiation can be used for ring-closing and ring-opening interconversions of 2,3-dithienylmaleimide (Yamaguchi *et al.*, 2000). In the case of Cz-MS in cyclohexane solution, the absorption peak at 377 nm became higher and a new characteristic peak at 528 nm appeared when it was continuously exposed to irradiation at 400 nm for 30 min (Fig.3). When the ring-closed state of Cz-MS was irradiated at 530 nm for a while, a reversible absorption phenomenon was observed and the structure changed to the ring-opened state. Similar reversible absorption spectra were observed using a different fluorophore (pyrene) (Fig.4).

When the switchable molecules Py-MS and Py-4MS were exposed to 400 nm for the ring-closing reaction for a certain period of time, there was an increase in intensity in both their absorption spectra but different changes occurred in their emission spectra. Increasing absorptions of Py-4MS at 374 nm, 437 nm, 467 nm, and 528 nm were clearly observed by UV-vis spectrometry (Fig.4b). There were also slight increases in absorption of Py-MS at 364 nm and 437 nm. Meanwhile, the emission intensities of Py-4MS at 482 nm and 514 nm (excited at 400 nm), that originated from the conjugated 1,3,6,8-tetrakis(phenylethynyl)pyrene core, gradually decreased during the ring-closing process (Fig.5). However, the emission spectrum of Py-MS remained the same (Fig.4a).

We suppose that this different phenomenon was attributed to the pcFRET mechanism. Emissions of tetrakis(phenylethynyl)pyrene at 482 nm and 514 nm

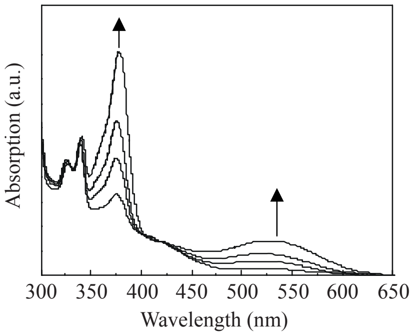
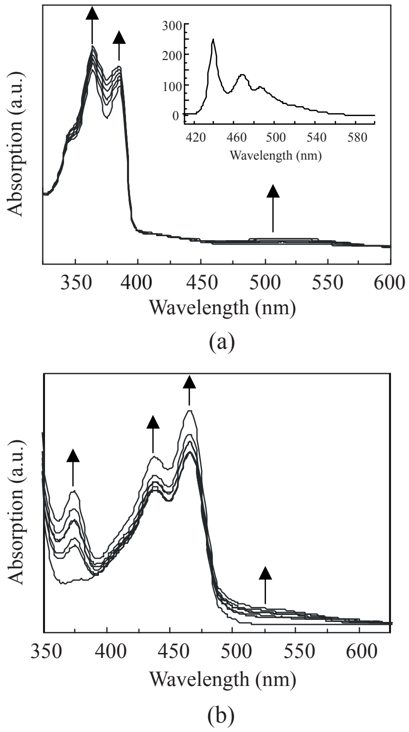


Fig.3 Absorption spectral change of Cz-MS in dilute cyclohexane upon irradiation with 400 nm light



(a)

(b)

Fig.4 Absorption spectral change of (a) Py-MS and (b) Py-4Ms in dilute cyclohexane upon irradiation with 400 nm light

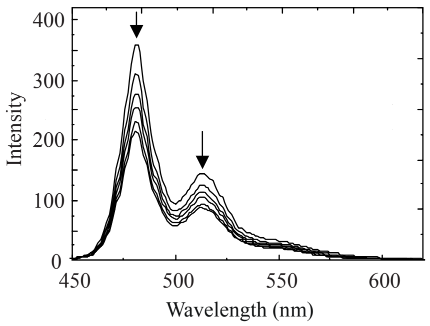


Fig.5 Varied emission spectra indicating pcFRET of Py-4MS in dilute cyclohexane, upon irradiation with 400 nm light

partially overlapped the absorption ranges of the ring-closed state of the photochromic acceptor, but not the absorptions of its ring-opened state. Thus, when the molecule was in the ring-opened state, the pcFRET process from pyrene to molecular switch was not operating. When the molecule was exposed to 400 nm for a while, the pericyclic reaction occurred and the pcFRET process was activated. Emission of tetrakis(phenylethynyl)pyrene was successfully absorbed by the photo-switchable acceptor. The decreased emission intensity was a good indicator (Fig.5). However, there was no overlap between the absorption of the photochromic acceptor and the emission of 1-(phenylethynyl)pyrene, which emitted light at 420 nm. So emission intensities of Py-MS did not change even after a long exposure to irradiation at 400 nm. Therefore, a suitable overlap between the donor's emission and the acceptor's absorption was the key issue for a successful pcFRET process.

CONCLUSION

A series of photo-switchable compounds bonded with different fluorophores was synthesized. The molecules showed reversible changes in absorption spectra. The ring-closed state was confirmed by proton NMR and the decreasing intensity of Py-4MS was explained by the operation of a pcFRET mechanism.

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