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Reversible near-infrared fluorescence switch by novel photochromic unsymmetrical-phthalocyanine hybrids based on bisthienylethene†

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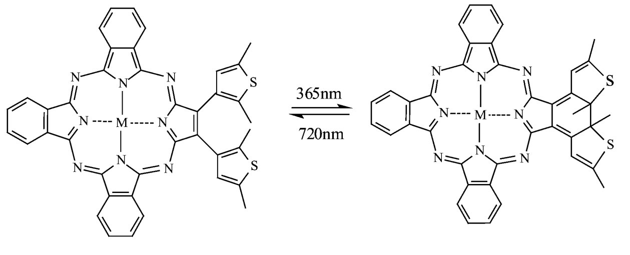
Received (in Cambridge, UK) 22nd January 2002, Accepted 3rd April 2002
First published as an Advance Article on the web 15th April 2002

A novel family of photochromic hybrids, 2,3-bis(2,5-dimethyl-3-thienyl) unsymmetrical-phthalocyanines (BTE-uPcs), which show a photoregulating fluorescence switch in the near-infrared spectral region were synthesized by a concise route.

Photochromic compounds,[1] especially 1,2-bisthienylethene (BTE) derivatives,[2,3] are of interest for numerous potential applications, such as erasable memory media and optical switching, owing to their excellent thermal-stability, fatigue-resistance and easily monitoring using UV-Vis spectroscopy. The application of BTEs for erasable memory media requires that both photochromic states be detected in the readout event in a facile and non-invasive manner. UV-Vis spectroscopy is by far the most common detection method used today. However, there is the same absorption that induces the ring-opening and ring-closing reactions of the photochrome sometimes. Recording changes in luminescence is a promising alternative for non-destructive readout. Branda's group and Irie's group[4] described supramolecular photochromic switches based on BTE. As the authors point out the luminescence changes of the systems can be used to achieve non-destructive readout.

The fact that phthalocyanines exhibit fluorescence in the infrared region and the possibility of photo-regulation of fluorescence of phthalocyanine by photochromism prompted us to design phthalocyanine–bisthienylethene hybrids with attractive functionality for non-destructive information processing. In the present work, novel 2,3-bis(2,5-dimethyl-3-thienyl) unsymmetrical-phthalocyanines hybrids (BTE-uPcs) were synthesized and confirmed according to the typical and efficient synthetic method described in the literature.[5,6] To the best of our knowledge, they are the first family of unsymmetrical-phthalocyanine hybrids containing a photochromic moiety (shown in Scheme 1). They have high solubility in common organic solvents, such as, DMSO, $CHCl_3$, CH_2Cl_2 and EtOH because of peripheral bisthiophenes. Uniform thin films can be obtained by the spin-coating technique. The relationship between the fluorescence intensity of the BTE-uPcs and the photo-switch states (open and closed ring of the bisthienylethene) is clearly illustrated and provides a new candidate for information process.



Fluorescent
(M= Mg, 1a; M= Zn, 3a)

Non-fluorescent
(M= Mg, 1b; M= Zn, 3b)

Scheme 1 The photochromism of unsymmetrical-phthalocyanine hybrids based on bisthienylethene.

The electronic absorption spectra of BTE-uPcs were shown in Fig. 1. The BTE-uPcs clearly show a splitting of the Q-band, due to the lowered C_{2v} symmetry. The splitting (not shown in the figure) in metal-free H_2BTE-uPc (**2a**†) is particularly large compared with the metal-containing BTE-uPcs (**1a**, **3a**) for its much lower symmetry. BTE-uPcs have very large absorption coefficient values in $CHCl_3$ (1.33×10^5 $M^{-1}cm^{-1}$ at 678 nm for **1a**) which was another important characteristic required urgently to be improved for the high sensitivity of photonic devices.

Compounds **1a** and **3a** were found to exhibit photochromism in $CHCl_3$ (shown in Fig. 1, Scheme 1 and the ESI). Upon irradiation of the solution of **1a** and **3a** with 365 nm light, the absorption band with a maximum of 678, 653, 353 nm for **1a** and 676, 650, 351 nm for **3a** gradually decreased and new absorption bands with a maximum at around 803, 724 nm for compound **1** (Mg(BTE-uPc)) and 803, 725 nm for compound **3** (Zn(BTE-uPc)) appeared in the presence of an isosbestic point due to the transformation of **1a** and **3a** to **1b** and **3b** by photocyclization. The splitting of the Q-band absorption of BTE-uPcs due to the lowered symmetry of the macrocyclic core disappears with photocyclization. As seen from Scheme 1, the ring-closed forms (**1b** and **3b**) show very similar structural configurations of typical phthalocyanine. The unsymmetrical trend for **1b** and **3b** decreases with photocyclization. The photostationary state upon irradiation with 365 nm light was attained within different irradiation times (9 h for **1a** and 1.5 h for **3a**). The backward ring-opening reaction of compounds **1b** and **3b** to regenerate compound **1a** and **3a** took place on irradiation with light of 724 nm. Compound **2** (H_2(BTE-uPc)) shows no photochromic process in solution. After prolonged UV irradiation the cyclization of **2a** was not observed until the complete photo-degradation of the compound. It is expected that in the open-ring form, excitation energy transfer from the excited states of the bisthienylethene moiety to the phthalocyanine unit is indeed likely. It might decrease the quantum yield of photo-cyclization, which may be a reason to explain why the free base phthalocyanine hybrid **2a** is not photochromic. But this is only one of the presumptions, further work is necessary

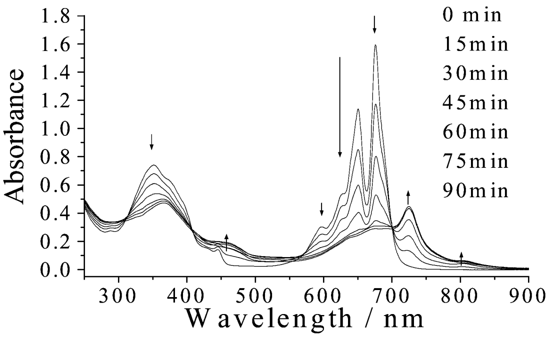


Fig. 1 Absorption spectra of compound **3a** in $CHCl_3$ (1.3×10^{-5} M) and the changes in absorption of **3a** under different irradiation time by light of 365 nm.

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† Electronic supplementary information (ESI) available: experimental details, synthetic and spectroscopic data. See http://www.rsc.org/suppdata/cc/b2/b200718e/

DOI: 10.1039/b200718e

on. The photochemical decomposition of **1** and **3** is too small to detect after one cycle of photochromism. The fatigue resistance of these compounds in their thin films is being measured by a recyclic photochromic process. Both BTE-uPCs isomers in the solid state were thermally stable to store in the dark for more than two months at rt similar to typical phthalocyanines and BTEs.[2*a*,6,7]

Compound **1a** and **3a** exhibited relatively high photocyclization quantum yields $f_{\text{O-C}}$ in solution (27%, 40% for **1a** and **3a** calculated according to the methods used in ref. 8 and Ref. 4*c* respectively). Since the BTE open form exists in parallel and antiparallel states, only the antiparallel is photochromic, the cyclization yield cannot exceed 0.5.[2] In addition, excitation energy transfer from the excited open-ring form to the phthalocyanine unit is considered to suppress further increase of quantum efficiency of the photo-cyclization. The quantum yields for the backward photochemical ring-opening reaction ($f_{\text{C-O}}$) are 17% and 23% for **1b** and **3b**, respectively. Fluorescence of compounds **1a** and **3a** were observed by excited in UV-region, the emission peak shifted to red with 25 nm compared to the Q-band. The emission spectrum of **3a** is shown in Fig. 2. The fluorescence quantum yields (relative to the standard of Rhodamine 6G) were measured as 17.5%, 11.4% (excited at 365 nm) and 3.5%, 1.4% (excited at 445 nm) for compounds **1a** and **3a**, respectively. The fluorescence of the hybrids **1a** and **3a** result from two sources (*i.e.* the open ring form of bisthienylethene and the phthalocyanine core) and greatly depends on the open and closed ring states of bisthienylethene. In the open ring form, the hybrid BTE-uPcs display significant fluorescence intensity around 701 nm. When irradiated by light of 365 nm the photocyclization reaction was carried out, the non-fluorescent closed ring forms were produced. Meanwhile, the intramolecular energy transfer from the phthalocyanine core to the ring-closed form of the BTE unit also quenches the fluorescence of the phthalocyanine although it has a small quantum yield.[6] It is difficult at present to determine which process, energy transfer, photoinduced electron transfer or all of them occur and contribute to the dramatic change in fluorescence. The intramolecular energy transfer from the Pc unit to the closed-ring form of BTE is indeed likely. If the photoinduced electron transfer from the Pc unit to the closed-ring form of BTE occurs, this process would also quench the fluorescence of Pc core, consequently it increases the emission contrast of the two switch states. The back irradiation by light of 724 nm regenerated the open ring form of bisthienylethene and recovered the original emission spectrum. The intensity of the fluorescence of the hybrids BTE-uPcs can be conveniently regulated by alternate additional irradiation at 365 nm and 724 nm.

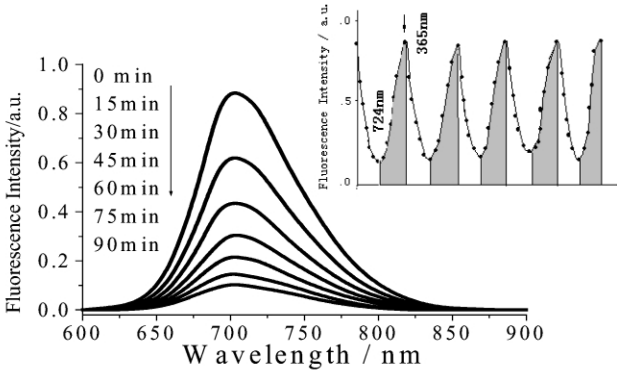

Fig. 2 The emission spectra of **3a** (excited at 445 nm) and its changes when **3a** was transformed to **3b** (irradiated by another UV light of 365 nm) over different times. Insert: modulated emission intensity at a peak of 703 nm (excited at 445 nm at rt) of a chloroform solution of compound **3** (1.3×10^{-5} M) during alternating irradiation at 365 nm (unshaded areas) and 724 nm (shaded areas).

When luminescence is used as a detection method for the application of erasable memory media, however, an important condition must be met additionally. That is, the wavelengths of light used to produce the luminescence (excited wavelengths) and the resulting emission wavelengths must reside outside the spectral regions where the photochromic reactions are induced.[4] If BTE-uPcs emit by excitation at the B-band where the cyclization reaction results in photochemical interconversion of the photochrome, this would limit the use in data processing application. In fact, these drawbacks can be circumvented by excitation of the hybrids BTE-uPcs with 445 nm (at which the photochemical interconversion of two states was inactive in either direction), although with relative weak fluorescence. The open ring forms of **1a** and **3a** emit at 703 nm which is a wavelength insensitive to the photo-recyclization and cannot induce recyclization of **1b** and **3b**, although the emission spectrum slightly overlaps with the UV-Vis absorption spectrum of **1a** and **3a**. There exists proportional dependence between the content of the closed ring form and the luminescence intensity in the present system. The emission intensity (excited at 445 nm) of **1a** and **3a** can be modulated by photochemical regulation between open and closed forms (shown in the insert figure in Fig. 2) providing a non-destructive readout method.

In summary, a novel family of unsymmetrical-phthalocyanine hybrids with a photochromically active bisthienylethene moiety has been synthesized by a concise route. The near infrared fluorescence of BTE-uPcs, which is excited at the region that is inactive to induction of photocyclization and recyclization, can be adjusted by irradiation with UV and visible light. The phenomena are useful for application to the non-destructive readout capabilities of optical memory media.

The authors acknowledge the support NSFC/ China (29986001 and 29836150) and Education Committee of Shanghai.

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