Nanohybrid material of bilateral switch based on diarylethene

Ying Zou, Shuzhang Xiao, Tao Yi,* Huijun Zhang, Fuyou Li and Chunhui Huang

Department of Chemistry & Laboratory of Advanced Materials, Fudan University, Shanghai 200 433, China

ABSTRACT: Air-stable hybrid organic–inorganic nanoparticles were prepared, comprising photochromic cationic diarylethene species intercalated in layered $MnPS_3$ by using a microemulsion method. The prepared hybrid material exhibited typical photochromic and fluorescent switch behavior similar to that in solution. Although its response to light was less sensitive, the hybrid material reduced the effect of solvents on its photochromism, and afforded a new approach to the application of molecular switch in solid. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: photochromism; diarylethene; $MnPS_3$; hybrid; fluorescence

INTRODUCTION

Photochromic materials are of great interest due to their applications in optical storage, memory devices, communication systems etc.[1] Most of the current researches are carried in solution, however, solvents usually affect the material's photochromic behavior. In order to explore the photochromic property used for solid-state applications and nanomemories, the materials are usually embedded in a solid matrix. Classical strategies include dispersion of the molecular species in organic polymers like Polymethylmethacrylate (PMMA),[2] hybrid inorganic–organic composites such as mesoporous silicates, clay, and layered intercalation compounds.[3]

Several years ago, Clement *et al*. found that photo-responsive organic cations could be intercalated in layered $MnPS_3$, affording hybrid intercalates that possessed various 'combined' properties.[4,5] When N-methylated pyrido-spiropyran cations were used, intercalation considerably stabilized the merocyanine (MC) form to such an extent that the MC form was no longer able to revert back to the spiropyran (SP) form in the absence of prolonged irradiation by visible light, which was ascribed to the formation of *J*-aggregates by the MC planar forms within the weak polar interlayer medium.[6] While nanoparticles of this material afforded a compromise between optical bistability and fast photo-response, SP embedded – in layered $MnPS_3$ – nanoparticles could undergo photochromism efficiently.[7]

As a thermal irreversible photochromic compound, diarylethene has attracted much interest due to its excellent fatigue-resistance.[1b,8] Diarylethenes have two conformations, which are in dynamic equilibrium; however, only the anti-parallel conformation can undergo photocyclization reaction. Thus the photocyclization quantum yield can be expected to be increased by enhancing the ratio of the anti-parallel conformation with inclusion of the molecules in a fixed cage. Irie *et al*. included diarylethene compounds in cyclodextrin cavity to study the effect of cyclodextrin on diarylethene's photocyclization quantum yield.[9] To improve diarylethene's photocyclization efficiency, a hybrid mesoporous silica material containing diarylethene was also investigated.[10] Herein, we prepared a cationic diarylethene **1** containing bispyridinium (Scheme 1) and intercalated it to the layer of an inorganic $MnPS_3$ nanomaterial at the first time by a bottom-up process. Both the photochromic behavior and fluorescent properties of **1,** and the hybrid nanomaterials were studied.

RESULTS AND DISCUSSION

Synthesis and characterization of $1/MnPS_3$ nanoparticles

One pot synthesis of $1/MnPS_3$ nanoparticles was carried out according to our previous procedure.[5f] Microemulsion was achieved by using inverse water containing micelles dispersed in cyclohexane in the presence of the Brij-97 surfactant. Two micelle solutions (20 ml organic

Correspondence to: T. Yi, Department of Chemistry & Laboratory of Advanced Materials, Fudan University, Shanghai 200 433, China.
E-mail: yitao@fudan.edu.cn
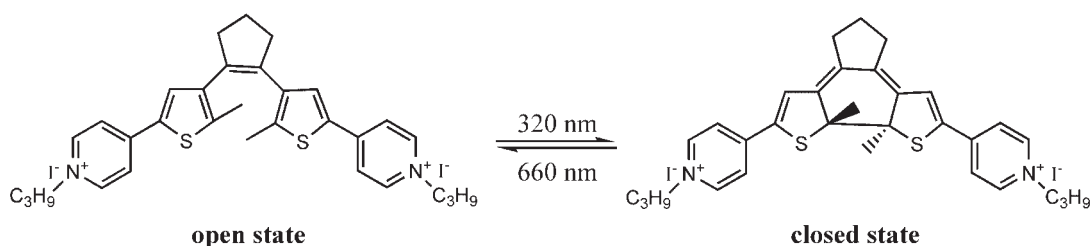
Scheme 1. Photochromism of **1**

phase respectively) were prepared separately, one containing 0.5 ml aqueous solution of $MnCl_2 \cdot 4H_2O$ (13.8 mg) and LiCl (5.9 mg), another containing an aqueous solution of $Na_4P_2S_6$ (11.9 mg in 0.5 ml H_2O). When the two micelle solutions were mixed under vigorous stirring, pale colored micelles formed within a few minutes. Then 0.5 ml methanol solution of **1** (6.6 mg) was added to the mixture and stirred for two hours in dark. The emulsion was subsequently broken by adding methanol. The yielded pale yellow powder was isolated by centrifugation, and then washed with methanol to remove the surfactant. The produced nanoparticles can be quantitively 'redissolved' in several organic mediums such as methanol, ethanol, and chloroform as well as in water.

Characterizations of 1/MnPS₃ nanoparticles

The IR spectrum of **1**/$MnPS_3$ nanoparticles reveals four sets of bands as shown in Fig. 1 (A). A medium band consisting of three components (612, 595, and 558 cm^{-1}), is similar to the band that appear in the same wavenumber region in the reported intercalated crystalline compounds, although the resolving is lower in the nanosystem.[6] This 'splitted' band is the signature of intercalated $MnPS_3$ systems and it has been assigned to the v (PS_3) asymmetric stretching band. A series of bands at 1630, 1558, 1511, 1465, 1430, and 1384 cm^{-1} are attributed to **1**. The above data indicate that the powder contains **1** intercalated in $MnPS_3$. The strong broad bands at 1091

and 1020 cm^{-1} reveal the presence of an important amount of 'phosphate species' whose formation is due to the hydrolysis of a fraction of the fragile $(P_2S_6)^{4-}$ anions. The broad band at 3400 cm^{-1} shows the presence of a large amount of water retained in the powder. Transmission electron microscopy (TEM) image (Fig. 1B) of the particles dispersed in methanol displays a rather homogeneous distribution of the prepared **1**/$MnPS_3$ sample, with the average diameter of 20 nm. Energy dispersive X-ray (EDX) analysis of all these samples yielded the expected Mn, P, and S stoichiometry.

Photochromism of 1

Although the electrochemical and photochemical properties of pyridine-functionalized diarylethene have been investigated by Lehn, Tian, Branda and Giraud *et al.*,[11] the fluorescent property of those compounds was rarely reported. Herein, we investigated both the absorption and emission change of **1** upon UV light irradiation. The photochromic behavior of **1** was studied in the solution of methanol and chloroform, as shown in Fig. 2. The absorption of the open form in the methanol were at 330 ($\varepsilon = 2.5 \times 10^4 \, dm^3 mol^{-1} cm^{-1}$) and 383 nm ($\varepsilon = 3.2 \times 10^4 \, dm^3 mol^{-1} cm^{-1}$). Upon UV irradiation, new absorption maxima appeared at 675 nm ascribed to the closed isomer with the photocyclic quantum yield of 85%. The very high photocyclic quantum yield indicated that **1** prefered an anti-parallel isomer in methanol solution since only anti-parrallel conformation could undergo
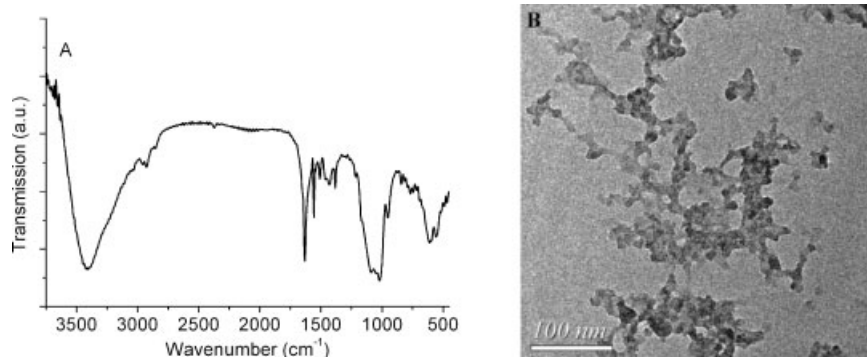

Figure 1. (A) IR spectrum of the prepared **1**/$MnPS_3$ nanoparticles; (B) TEM of the **1**/$MnPS_3$ nanoparticles dispersed in methanol. (Scale bar, 100 nm)
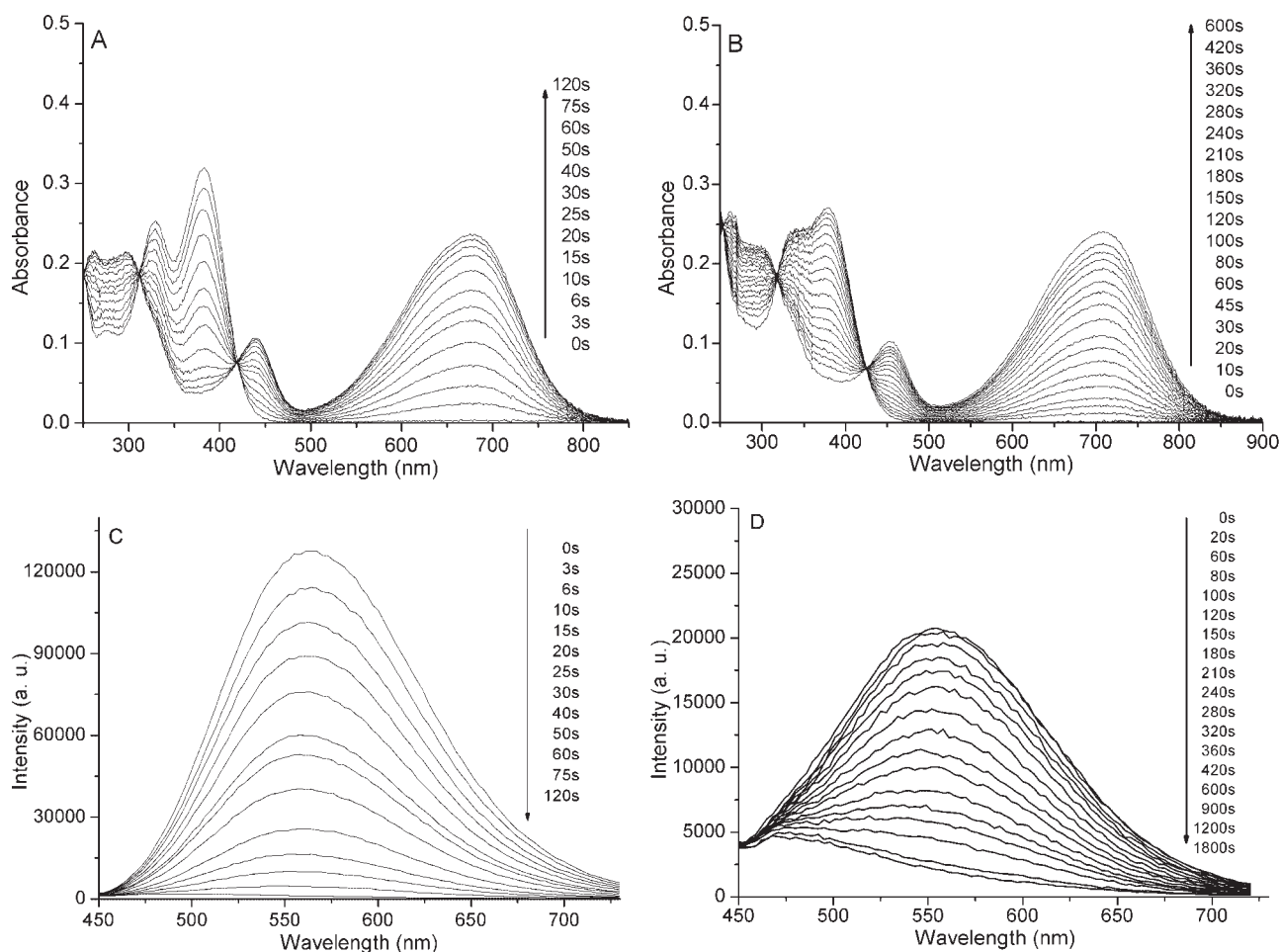
Figure 2. Absorption and fluorescent spectral change of **1** (1.0×10^{-5} mol/l) upon irradiation with 365 nm light in methanol (A: absorption; C: fluorescence) and chloroform solution (B: absorption; D: fluorescence) at room temperature

photochromic reaction. Comparatively, two absorption peaks at 341 nm ($\varepsilon = 2.4 \times 10^4 \, dm^3 mol^{-1} cm^{-1}$) and 378 nm ($\varepsilon = 3.7 \times 10^4 \, dm^3 mol^{-1} cm^{-1}$) were observed in the open form of **1** in chloroform. The new absorption maximum was at 710 nm upon irradiation of 365 nm light with the photocyclic quantum yield of 78% in chloroform. Compared with the absorption in methanol, the absorbance maxima of **1** in the closed state red-shifted 35 nm in chloroform, with a smaller photocyclic quantum yield. In addition, the photocyclic reaction in chloroform is much slower and it needs 600 s to reach the photostationary state, whereas in methanol under the same condition, it takes only 120 s.

The fluorescence changes of **1** in methanol and chloroform were quite different (Figs. 2C and 2D). **1** exhibited yellowish green fluorescence centered at 564 nm in methanol, and its fluorescent quantum yield was measured to be 0.042, using Rhodamine B as reference. This fluorescence was efficiently quenched with the structure changing from the open state to the closed state upon 365 nm irradiation (0.3% remained). But in chloroform, it showed a weak emission at 555 nm with a much smaller fluorescent quantum yield (0.003),

indicating that the solvent affected the fluorescence in the photochromic process dramatically which has been illustrated before. [12] Although the emission can also be quenched by UV light, the efficiency was much lower with 10% of the fluorescence remained.

Photochromism of 1/MnPS₃

The photochromic property of hybrid nanosystem **1/** MnPS₃ was studied in suspension. The absorption spectral changes of the nanoparticles dispersed in methanol and chloroform were recorded as seen in Fig. 3. The spectra of open isomer in methanol and chloroform were similar, with the absorption peaks at 381 and 328 nm in methanol, and 378 and 333 nm in chloroform. Upon UV irradiation a new absorption maxima of **1**/MnPS₃ appeared at 682 nm in methanol, a small red-shift compared with that of **1** in methanol solution, with the photocyclic quantum yield of 48%. While in chloroform, the maxima absorption band of the closed isomer of **1**/MnPS₃ appeared at 710 nm with
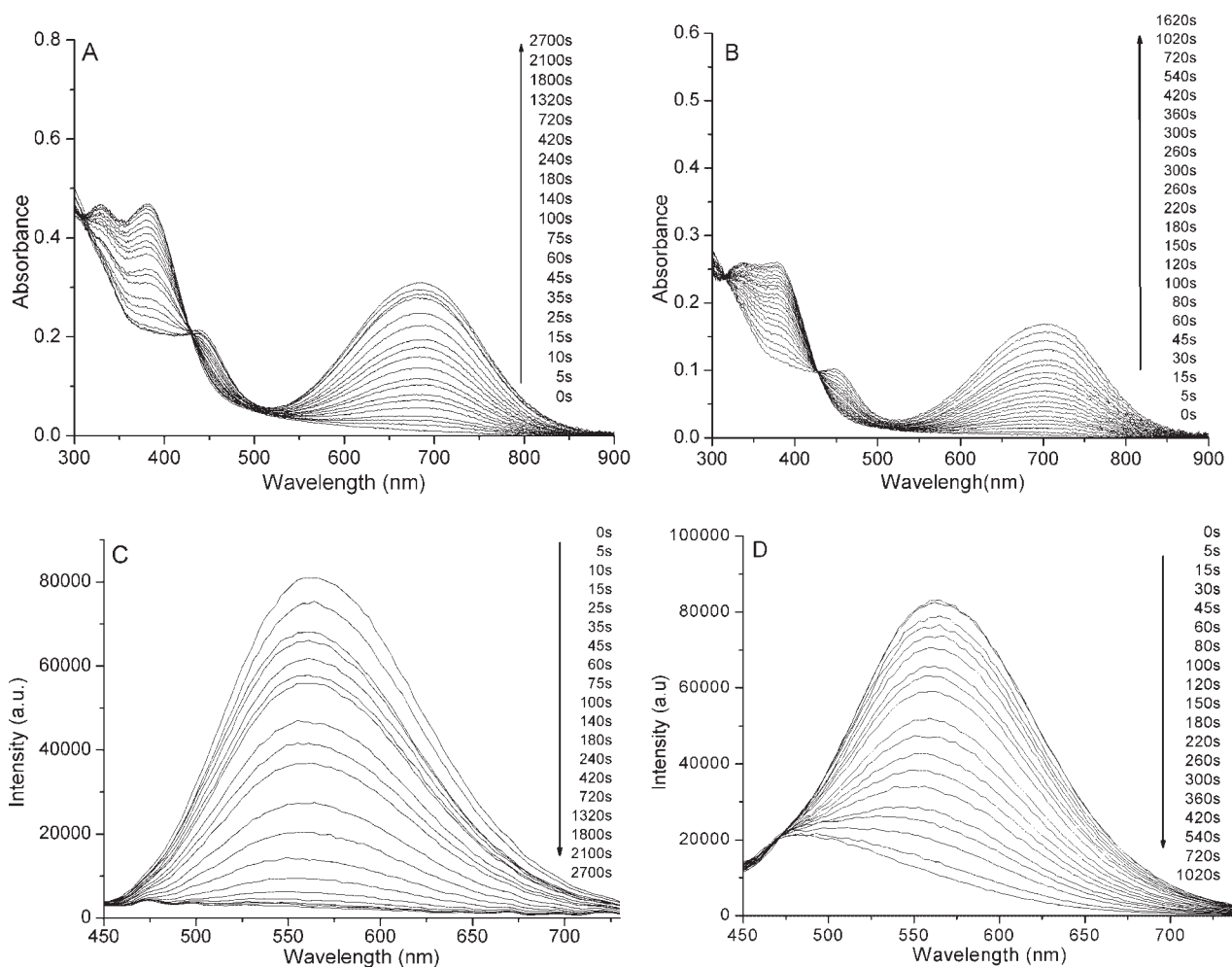
Figure 3. Absorption and fluorescent spectral change of **1**/MnPS$_3$ (1.4×10^{-5} mol/l of **1** in methanol) upon irradiation with 365 nm light (A: absorption; C: fluorescence); Absorption and fluorescent spectral change of **1**/MnPS$_3$ (1.0×10^{-5} mol/l of **1** in chloroform) upon irradiation with 365 nm light (B: absorption; D: fluorescence) at room temperature

almost no shift compared with that of **1** in chloroform solution. And its photocyclic quantum yield was measured to be 51%. The lower photocyclic quantum yield in hybrid material indicated that layered MnPS$_3$ structure could intercalate both parallel and anti-parallel conformations.

1/MnPS$_3$ in suspension of methanol had fluorescent emission at about 564 nm and this emission was quenched (3% remained) under UV light irradiation, similar with that happened in the methanol solution of pure **1**. The fluorescent quantum yield of **1**/MnPS$_3$ was only 0.005, much lower than sole compound **1** in dilute solution. In chloroform, the suspended **1**/MnPS$_3$ maintained the fluorescence at 565 nm with the fluorescent quantum yield of 0.006, which was almost the same with that in methanol. Under UV light irradiation, 90% of the fluorescence of **1**/MnPS$_3$ could be quenched. It is clearly that the hybrid material was able to undergo photochromism under UV light with the fluorescence quenched by converting the open form to the closed form. Different with pure **1** whose fluorescence was strongly depended on

the solvents, the influence of solvent on the fluorescence of diarylethene in the hybrid system was effectively reduced.

The Effect of MnPS$_3$ on Photochromic Process of 1

As pointed out above, both the photochromic process and fluorescence of **1** depended on the polarity of the solvent in dilute solution. In methanol, **1** responds to light rapidly, and reached photo-stationary-state (PSS) in 2 min under 365 nm light (Fig. 4). However, **1** in chloroform responds to UV light slowly, and it needed almost 10 min to reach equilibrium. What's interesting was that **1**/MnPS$_3$ reached PSS after 17 min irradiation suspended in both methanol and chloroform. This indicated that solvents had little effect on photochromism of the hybrid material as illustrated above. However, the sensitivity of these hybrid materials, even in nanosize, was lower than those molecules in dilute solutions. Similar phenomenon was
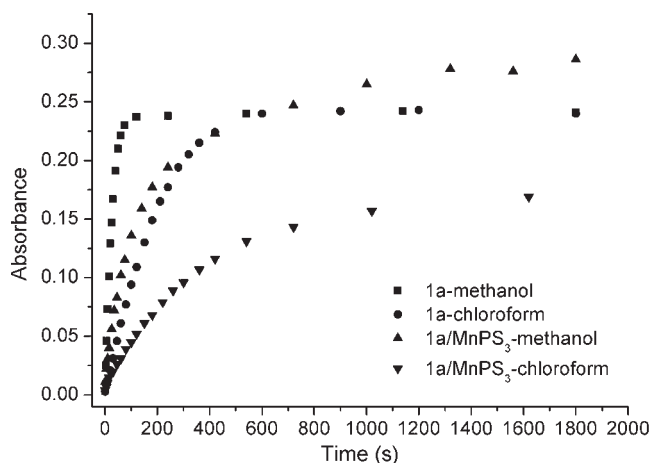
Figure 4. Absorption change (at maximum absorption of closed isomers) as a function of time under 365 nm light irradiation

observed from closed isomer to the open form. It takes 4 h for **1** to convert from PSS to open isomer in methanol solution; while it needs 8 h for the same process of **1/ MnPS₃**. It is surely that MnPS₃ layered structure reduced the sensitivity of diarylethene to light because it embodied **1** inside to debase the light intensity.

On the other hand, the thermal stability seems better in hybrid material. When the closed form of cationic diarylethene in methanol was placed in the dark by 24 hour, the absorption maxima reduced 8.5%, while 8.1% conversion was observed once the cationic diarylethene was intercalated into MnPS₃.

CONCLUSIONS

We obtained hybrid nanophotochromic materials by intercalating cationic diarylethene into layered MnPS₃ using a microemulsion method. From the investigation of the photochromism and fluorescent properties of the hybrid material suspension, we found that the hybrid nanomaterials exhibited an effective switch, giving obvious signal outputs both in absorption and fluorescent properties, similar to the pure diarylethene in solution. However, the solvent's effect on the optical properties which usually happened in the solution, was effectively obstructed by the inorganic-organic hybrid materials at a large extent. This may have more practical applications on nanomemories.

EXPERIMENTAL

Measurements

UV-visible spectra were obtained with a Shimadzu 2550 spectrometer (Japan). Edinburgh 900 spectrometer was used for fluorescence spectra. Infrared spectra of

powders were obtained at room temperature on an IR PRESTIGE-21 spectrometer using KBr pellets. TEM was recorded by JEOL JEM 2011 (Japan) operated at 200 KV attached with an energy dispersive X-ray analysis. Samples were prepared by evaporating a drop of solution on a carbon (Agar) grid. Irradiations were carried out on both dispersed colloid sample and thin films using a CHF-XM550W power system (China). Visible light was generated by a 500 W Xe lamp with a standard band-pass filter 550 AF10 (Omega). Irradiations in the UV region were affected at 365 nm.

The photocyclic quantum yield was measured by the following method: $Y = (A_O - A_T)/A_O$, here A_O means the absorption value of the open form at the irradiation wavelength and A_T means the absorption of the molecules at PSS at the irradiation wavelength.

The fluorescent quantum yield means the ratio (amount of emissive photons /amount of absorbed photons): $Q_S = Q_R(I_S\ A_R\ n_S^2)/(I_R\ A_S\ n_R^2)$. [13] Here Q means the fluorescent quantum yield; I referred to the fluorescent integrated area; A is the absorption value at the excitation wavelength; and n is the refractive index of the solvent. (subscript R is the reference and subscript S is the sample)

SYNTHESIS

1. 1, 2-bis (2-methyl-5-(N-propylpyrid-4-yl)-thien-3-yl)-cyclopentene (1)

The material of 1,2-bis (2-methyl-5-(pyrid-4-yl)-thien-3-yl) cyclopentene (BTEPy) was synthesized according to the previous report and characterized by ¹H NMR. [14] 0.24 ml (2.5 mmol) $CH_3CH_2CH_2I$ was added to 0.5 g (1.2 mmol) BTEPy in 20 ml dry acetonitrile in dark. The solution was stirred at 70 °C for 24 h. Then the solvent was evaporated in vacuum and washed with ether. Filtration of the mixture afforded a yellow solid of **1** with 90% yield. ¹H NMR (400 MHz, CD_3OD, 25 °C): δ (p.p.m.) 1.01 (t, $J = 7.2$, 6 H), 2.02 (m, 4H), 2.10 (s, 6H), 2.19 (m, 2 H), 2.94 (t, $J = 7.2$, 4 H), 4.47 (t, $J = 7.2$, 4 H), 7.97 (s, 2 H), 8.13 (d, $J = 6.8$, 4 H), 8.75 (d, $J = 7.2$, 4 H).

REFERENCES

1. (a) Fan MG, Yu LH, Zhao W. In *Organic Photochromic and Thermochromic Compounds (Topics in Applied Chemistry)*, Crano JC, Guglielmetti R (eds). Plenum Press: New York, 1999; 141–206. (b) Irie M. *Chem. Rev.* 2000; **100**: 1685–17161.; (c) Feringa BL. *Molecular Switches*. Wiley-VCH: Weinheim, 2001.
2. (a) Levitus M, Talhavini M, Negri RM, Atvars TDZ, Aramendia PF. *J. Phys. Chem. B* 1997; **101**: 7680–7686; (b) Levitus M, Aramendia PF. *J. Phys. Chem. B* 1999; **103**: 1864–1870; (c) Berkovic G, Krongauz V, Weiss V. *Chem. Rev.* 2000; **100**: 1741–1754; (d) Jiang GY, Wang S, Yuan WF, Jiang L, Song YL, Tian H, Zhu DB. *Chem. Mater.* 2006; **18**: 235–237.
3. (a) Biteau J, Chaput F, Boilot JP. *J. Phys. Chem.* 1996; **100**: 9024–9031; (b) Benard S, Rivière E, Yu P, Nakatani K, Delouis

JF. *Chem. Mater.* 2001; **13**: 159–162; (c) Schaudel B, Guermeur C, Sanchez C, Nakatani K, Delaire JA. *J. Mater. Chem.* 1997; **7**: 61–65; (d) Wirnsberger G, Scott BJ, Chmelka BF, Stucky GD. *Adv. Mater.* 2000; **12**: 1450–1454; (e) Andersson N, Alberius P, Örtegren J, Lindgren M, Bergström L. *J. Mater. Chem.* 2005; **15**: 3507–3513; (f) Sasai R, Ogiso H, Shindachi I, Shichi T, Takagi K. *Tetrahedron* 2000; **56**: 6979–6984; (g) Sasai R, Itoh H, Shindachi I, Shichi T, Takagi K. *Chem. Mater.* 2001; **13**: 2012–2016.
4. (a) Lacroix PG, Clément R, Nakatani K, Zyss J, Ledoux I. *Science* 1994; **263**: 658–660; (b) Clément R, Lacroix PG, Ohare D, Evans J. *Adv. Mater.* 1994; **6**: 794–797.
5. (a) Lacroix PG, Nakatani K. *Adv. Mater.* 1997; **9**: 1105–1108; (b) Clément R. In *Hybrid Organic-Inorganic Composites (ACS Symposium Series 585)*, Mark JE, Lee YC, Bianconi P (eds). American Chemical Society: Washington, DC, 1995; 29–42 (c) Coradin T, Clément R, Lacroix PG, Nakatani K. *Chem. Mater.* 1996; **8**: 2153–2158; (d) Lacroix PG, Malfant I, Bénard S, Yu P, Rivière E, Nakatani K. *Chem. Mater.* 2001; **13**: 441–449; (e) Bénard S, Yu P, Audière JP, Riviere E, Clément R, Guilhem J, Tchertanov L, Nakatani K. *J. Am. Chem. Soc.* 2000; **122**: 9444–9454; (f) Yi T, Clement R, Haut C, Catala L, Gacoin T, Tancrez N, Ledoux I, Zyss J. *Adv. Mater.* 2005; **17**: 335–338.
6. Benard SLeaustic ARivière EYu PClement R *Chem. Mater.* 2001; **13** 3709–3716
7. Zhang HJ, Yi T, Li FY, Delahaye E, Yu P, Clement R. *J. Photochem. Photobio. A* 2007; **186**: 173–177.
8. Tian H, Yang SJ. *Chem. Soc. Rev.* 2004; **33**: 85–97.
9. (a) Takeshita M, Choi CN, Irie M. *Chem. Commun.* 1997; 2265–2266; (b) Takeshita M, Kato N, Kawauchi S, Imase T, Watanabe J, Irie M. *J. Org. Chem.* 1998; **63**: 9306–9313; (c) Takeshita M, Yamada M, Kato N, Irie M. *J. Chem. Soc. Perkin Trans* 2000; **2**: 619–622.
10. Okada H, Nakajima N, Tanaka T, Iwamoto M. *Angew. Chem. Int. Ed.* 2005; **44**: 7233–7236.
11. (a) Gilat SL, Kawai SH, Lehn JM. *Chem. Eur. J.* 1995; **1**: 275–284; (b) Corodetsky B, Samachetty HD, Donkers RL, Workentin MS, Branda NR. *Angew. Chem. Int. Ed.* 2004; **43**: 2812–2815; (c) Baron R, Onopriyenko A, Katz E, Lioubashevski O, Willner I, Wang S, Tian H. *Chem. Commun.* 2006; 2147–2149; (d) Giraud M, Leaustic A, Charlot MF, Yu P, Cesario M, Philouze C, Pansu R, Nakatani K, Ishow E. *New. J. Chem.* 2005; **29**: 439–446.
12. (a) Irie M, Sayo K. *J. Phys. Chem.* 1992; **96**: 7671–7674; (b) Yamaguchi T, Irie M. *Chem. Lett.* 2004; **33**: 1398–1399; (c) Miyasaka H, Nobuto T, Murakami M, Itaya A, Tamai N, Irie M. *J. Phys. Chem. A* 2002; **106**: 8096–8102.
13. Huang CH, Li FY, Huang YY. *Ultrathin Films for Optics and Electronics*. Pekin University Press: 2001; 196–197.
14. Qin B, Yao RX, Zhao XL, Tian H. *Org. Biomol. Chem.* 2003; **1**: 2187–2191.