JOURNAL OF
Materials
CHEMISTRY
Communication

A novel family of photochromic amorphous molecular materials based on dithienylethene

Hisayuki Utsumi, Daisuke Nagahama, Hideyuki Nakano and Yasuhiko Shirota*

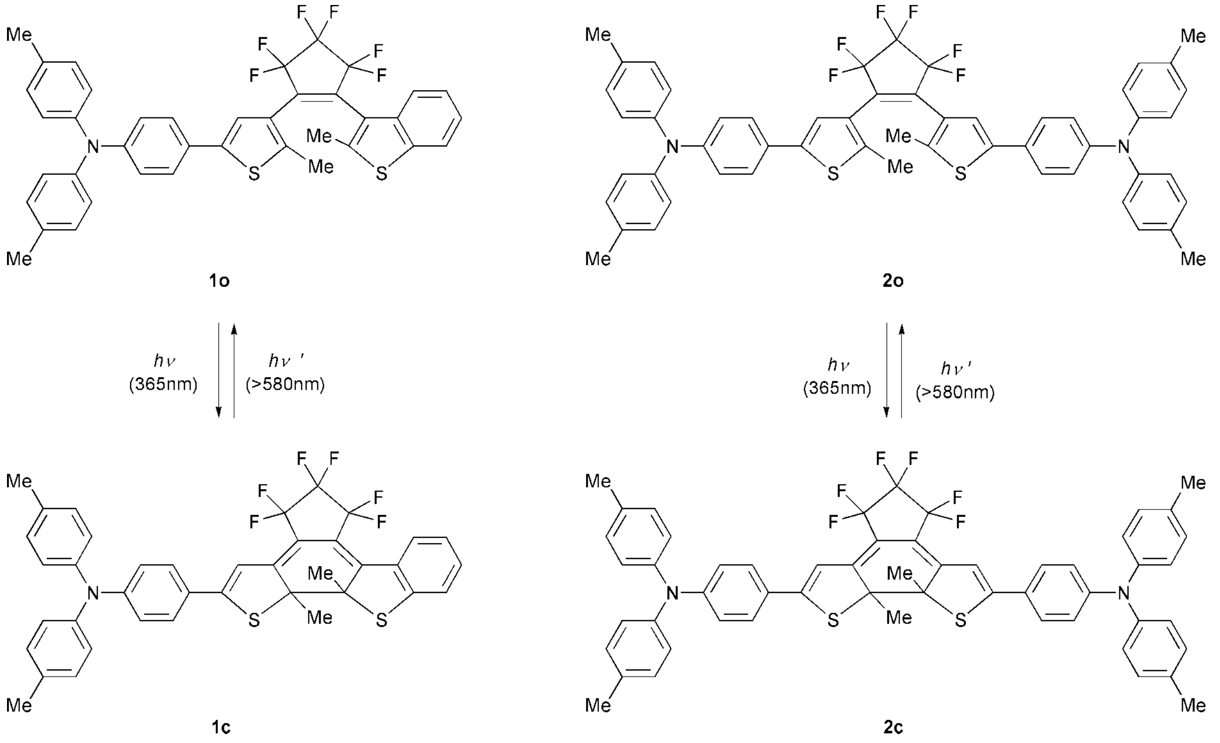
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka, 565-0871, Japan. E-mail: shirota@ap.chem.eng.osaka-u.ac.jp

Received 26th June 2000, Accepted 2nd August 2000
First published as an Advance Article on the web 19th September 2000

A novel family of photochromic amorphous molecular materials based on dithienylethene, 1-(5-{4-[bis(4-methylphenyl)amino]phenyl}-2-methylthiophen-3-yl)-2-(2-methylbenzo[*b*]thiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene (1o) and 1,2-bis(5-{4-[bis(4-methylphenyl)amino]phenyl}-2-methylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene (2o) with glass-transition temperatures of 66 and 94 °C, respectively, has been developed. Comparison of photochromic properties between 1o and 2o shows that the incorporation of two bulky triphenylamine moieties leads to higher conversion of photocyclisation in the amorphous film.

Photochromic materials have recently been attracting a great deal of attention because of their potential technological applications for optical recording for storage of information and optical switching. In applying photochromic materials for practical use, they may be used as solid films. There have been extensive studies on photochromic polymers and molecularly dispersed polymer systems, where low molecular-weight photochromic compounds are dispersed in polymer binders.[1–4] In contrast to polymers, low molecular-weight organic compounds usually do not form smooth, uniform films since they tend to crystallise readily. It is of interest and significance to create low molecular-weight organic photochromic compounds that readily form stable amorphous glasses above room temperature, which we refer to as “photochromic amorphous molecular materials”. They may constitute a novel class of photochromic molecular materials that form uniform amorphous thin films by themselves. They have an advantage that there is no dilution of photochromic chromophores relative to photochromic polymers and composite polymer systems, where low molecular-weight organic photochromic compounds may crystallise at high concentration. We have performed a series of studies on the creation of amorphous molecular materials[5,6] and developed a novel family of photochromic amorphous molecular materials containing an azobenzene moiety.[7,8]

We report here the synthesis and photochromic properties of a novel family of photochromic amorphous molecular materials based on dithienylethene, 1-(5-{4-[bis(4-methylphenyl)amino]phenyl}-2-methylthiophen-3-yl)-2-(2-methylbenzo-[*b*]thiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene (**1o**) and 1,2-bis(5-{4-[bis(4-methylphenyl)amino]phenyl}-2-methylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene (**2o**) (Scheme 1). Dithienylethene derivatives have recently received attention as promising photochromic materials with thermal stability and excellent fatigue-resistant properties.[9–14] Recently synthesised



Scheme 1

DOI: 10.1039/b005067i

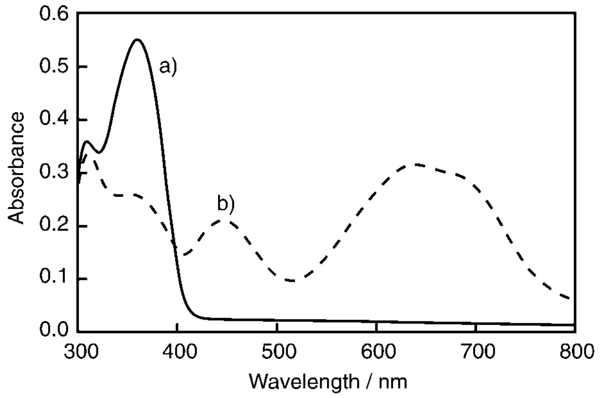


Fig. 1 Electronic absorption spectral change of **2o** amorphous film. a) before photoirradiation. b) photostationary state upon irradiation with 334 and 365 nm light.

1,2-bis[2,4-dimethyl-5-(4-*tert*-butylphenyl)thiophen-3-yl]-3,3,4,-4,5,5-hexafluorocyclopentene has been shown to form an amorphous glass.[15]

Compound **1o** was synthesised by lithiation of 5-{4-[bis(4-methylphenyl)amino]phenyl}-3-bromo-2-methylthiophene (**3**) (3.5 g, 7.8 mmol) followed by reaction with 1-(2-methylbenzo-[*b*]thiophen-3-yl)-2,3,3,4,4,5,5-heptafluorocyclopentene (3.0 g, 8.8 mmol), prepared by the reaction of 3-lithio-2-methylbenzo[*b*]thiophene with 1,2,3,3,4,4,5,5-octafluorocyclopentene. Compound **2o** was synthesised by lithiation of **3** (5.4 g, 12 mmol) followed by reaction with 1,2,3,3,4,4,5,5-octafluorocyclopentene (1.2 ml, 8.9 mmol). Compounds **1o** and **2o** were purified by silica-gel column chromatography, followed by recrystallisation from THF–ethanol and toluene–hexane to give 1.8 g (yield 33%) and 2.5 g (yield 45%), respectively. They were identified by various spectroscopic methods, mass spectrometry, and elemental analysis.[16]

Both **1o** and **2o** were found to readily form stable amorphous glasses when the melt samples were left to stand in air, as evidenced by differential scanning calorimetry (DSC), X-ray diffraction, and polarising microscopy. The glass-transition temperatures (T_gs) and melting points are 66 and 158 °C for **1o** and 94 and 207 °C for **2o**, as determined by DSC. The amorphous glasses of these two materials are very stable, no crystallisation phenomenon being observed upon heating above their T_gs. Compounds **1o** and **2o** form uniform amorphous films by spin coating.

Compounds **1o** and **2o** were found to exhibit photochromism in their amorphous films as well as in solution. Fig. 1 shows the electronic absorption spectral change of an amorphous film of **2o** prepared by spin coating from benzene solution (*ca.* 6.6×10^{-3} mol dm^{-3}). Upon irradiation with 334 and 365 nm light (1.6 mW cm^{-2}) from a 500 W super-high-pressure mercury lamp in air, the band with a maximum at around 360 nm gradually decreased and new absorption bands with maxima at around 442 and 635 nm together with a shoulder at *ca.* 675 nm appeared due to the transformation of **2o** into **2c** by photocyclisation, and the system finally reached a photostationary state. The backward ring-opening reaction of **2c** to regenerate **2o** took place on irradiation with visible light (>580 nm) from a 500 W xenon lamp. A similar spectral change was also observed for the amorphous film of **1o**. The photocyclised compound **2c** was isolated from a benzene solution irradiated with 334 and 365 nm light using HPLC (eluent: methanol–acetone (3 : 1)), and purified by recrystallisation from THF–ethanol. Compound **2c** was also found to readily form an amorphous glass with a T_g of 104 °C. Both **1c** and **2c** were characterised by electronic absorption and ^{1}H NMR spectroscopy.[17]

Table 1 Quantum yields for the photocyclisation reaction by irradiation with 365 nm monochromatic light ($\Phi_{o\rightarrow c}$) and the backward photochemical ring-opening reaction by irradiation with 600 nm monochromatic light ($\Phi_{c\rightarrow o}$), and the molar ratio of the photocyclised molecules to the total molecules at the photostationary state upon irradiation with 334 and 365 nm light (Y_{pss})

System	$\Phi_{o\rightarrow c}$	$\Phi_{c\rightarrow o}$	Y_{pss}
1, benzene solution	0.79	0.015	1.00
1, amorphous film	0.33	0.010	0.36
2, benzene solution	0.61	0.001	0.98
2, amorphous film	0.33	0.001	0.77

Table 1 summarises quantum yields for the photocyclisation ($\Phi_{o\rightarrow c}$) and the backward photochemical ring-opening reaction ($\Phi_{c\rightarrow o}$), together with the molar ratio of the photocyclised molecule to the total amount of the starting and photocyclised molecules at the photostationary state (Y_{pss}). Compounds **1o** and **2o** exhibited relatively high $\Phi_{o\rightarrow c}$ in solution (0.79 for **1o** and 0.61 for **2o**) compared with the values reported for other dithienylethene derivatives in solution (mostly in the range from 0.3 to 0.5),[9] although the highest value (0.86) has been reported for a dithienylethene-backbone photochromic polymer.[18]

It is noteworthy that the quantum yield for the photocyclisation ($\Phi_{o\rightarrow c}$) in the amorphous film is approximately a half of that in solution for both **1o** and **2o**. It is known that dithienylethene derivatives have two conformers, "antiparallel" (ap) conformer having two thienyl moieties with C_2 symmetry and "parallel" (p) conformer containing two thienyl moieties with mirror symmetry, and that only the former undergoes photocyclisation reaction.[9,10] It is thought that no transformation takes place between the two conformers in the solid state and hence, the photocyclisation quantum yield in the solid state is decreased due to the presence of the p-conformer which does not undergo photocyclisation. In addition, intermolecular interactions in the solid state may cause enhanced radiationless deactivation, leading to lower quantum yields in the amorphous film than in solution. Also noteworthy is that the Y_{pss} value of the amorphous film of **2o** is double that of **1o**. This result suggests that the population of the ap-conformer in the amorphous film of **2o** is larger than that of **1o**. It is suggested that the steric effect due to the two bulky triphenylamine moieties is responsible for this difference. The CPK models of these two molecules show that while both the ap- and p-conformers of **1o** and the ap-conformer of **2o** permit free rotation around the C–C bond connecting the thienyl and triphenylamine moieties, this rotation is restricted for the p-conformer of **2o** because of steric crowding. Therefore, the ap-conformer is suggested to be more populated for **2o**. Irradiation of an amorphous film of the photocyclised compound **2c** with light of the wavelength longer than 580 nm produced **2o** with the photoactive antiparallel conformer due to the photochemical ring-opening reaction with a $\Phi_{c\rightarrow o}$ of 0.001. The **2o** compound thus produced underwent the photocyclisation to give **2c** with a $\Phi_{o\rightarrow c}$ of 0.41.

In summary, a novel class of photochromic amorphous molecular materials based on dithienylethene, **1o** and **2o**, has been created. These novel dithienylethene derivatives were found to readily form stable amorphous glasses and uniform amorphous films by spin coating, exhibiting photochromism in solution and in the amorphous film. Comparison of photochromic behavior between **1o** and **2o** in their amorphous films suggests that the introduction of two bulky triphenylamine moieties increases the population of the ap-conformer of the molecule, leading to higher conversion of the photocyclisation reaction. The present study presents a new guideline for the molecular design of photochromic amorphous molecular materials based on dithienylethene.

Notes and references

1 K. Horie and I. Mita, *Adv. Polym. Sci.*, 1989, **88**, 79.

2 H. Dürr and H. Bouas-Laurant, *Photochromism, Molecules and Systems*, Elsevier, Amsterdam, 1990.

3 C. B. McArdle, *Applied Photochromic Polymer Systems*, Blackie & Son Ltd, New York, 1992.

4 K. Ichimura, *Organic Photochromic and Thermochromic Compounds*, Vol. 2, Eds. J. C. Crano and R. J. Guglielmetti, Plenum Press, New York and London, 1999, p. 9.

5 Y. Shirota, T. Kobata and N. Noma, *Chem. Lett.*, 1989, 1145.

6 Y. Shirota, *J. Mater. Chem.*, 2000, **10**, 1 and references cited therein..

7 Y. Shirota, K. Moriwaki, S. Yoshikawa, T. Ujike and H. Nakano, *J. Mater. Chem.*, 1998, **8**, 2579.

8 T. Ujike, K. Moriwaki, H. Nakano and Y. Shirota, *J. Photopolym. Sci. Technol.*, 1998, **11**, 33.

9 M. Irie and M. Mohri, *J. Org. Chem.*, 1988, **53**, 803.

10 K. Uchida, Y. Nakayama and M. Irie, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1311.

11 S. L. Gilat, S. H. Kawai and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1993, 1439.

12 M. Irie, O. Miyatake, K. Uchida and T. Eriguchi, *J. Am. Chem. Soc.*, 1994, **116**, 9894.

13 M. Irie, K. Sakemura, M. Okinaka and K. Uchida, *J. Org. Chem.*, 1995, **60**, 8305.

14 A. Fernández-Acebes and J.-M. Lehn, *Chem. Eur. J.*, 1999, **5**, 3285.

15 T. Kawai, N. Fukuda, D. Gröschl, S. Kobatake and M. Irie, *Jpn. J. Appl. Phys.*, 1999, **38**, L1194.

16 **1o**: ^{1}H NMR (benzene-d_6, 600 MHz): δ (ppm) = 1.65 (s, 3H), 1.97 (s, 3H), 2.10 (s, 6H), 6.91 (d, 4H, $J = 8.3$ Hz), 6.92 (t, 1H, $J = 8.0$ Hz), 7.00 (d, 2H, $J = 8.9$ Hz), 7.05 (t, 1H, $J = 8.0$ Hz), 7.05 (d, 4H, $J = 8.3$ Hz), 7.15 (d, 2H, $J = 8.9$ Hz), 7.18 (s, 1H), 7.30 (d, 1H, $J = 8.0$ Hz), 7.64 (d, 1H, $J = 8.0$ Hz). $\lambda_{\max}$ (benzene) (log ε): 302 nm (4.4), 357 nm (4.5). MS (*m*/*z*) 689 (M^+). Found: C, 67.83; H, 4.26; N, 2.04%. Calcd for $C_{39}H_{29}NF_6S_2$: C, 67.91; H, 4.24; N, 2.03%.; **2o**: ^{1}H NMR (benzene-d_6, 600 MHz): δ (ppm) = 1.72 (s, 6H), 2.11 (s, 12H), 6.92 (d, 8H, $J = 8.4$ Hz), 7.04 (d, 4H, $J = 8.6$ Hz), 7.07 (d, 8H, $J = 8.4$ Hz), 7.25 (d, 4H, $J = 8.6$ Hz), 7.28 (s, 2H). $\lambda_{\max}$ (benzene) (log ε): 304 nm (4.6), 362 nm (4.8). MS (*m*/*z*) 911 (M^+). Found: C, 72.41; H, 4.94; N, 3.12%. Calcd for $C_{55}H_{44}N_2F_6S_2$: C, 72.51; H, 4.87; N,3.07%.

17 **1c**: ^{1}H NMR (benzene-d_6, 600 MHz): δ (ppm) = 1.99 (s, 3H), 2.00 (s, 3H), 2.09 (s, 6H), 6.64 (s, 1H), 6.71 (t, 1H, $J = 7.4$ Hz), 6.73 (t, 1H, $J = 7.4$ Hz), 6.82 (d, 1H, $J = 7.4$ Hz), 6.86 (d, 2H, $J = 8.9$ Hz), 6.91 (d, 4H, $J = 8.9$ Hz), 7.00 (d, 4H, $J = 8.6$ Hz), 7.09 (d, 2H, $J = 8.9$ Hz), 7.99 (d, 1H, $J = 7.4$ Hz). $\lambda_{\max}$ (benzene) (log ε): 303 nm (4.5), 455 nm (4.1), 580 nm (4.5).; **2c**: ^{1}H NMR (benzene-d_6, 600 MHz): δ (ppm) = 2.09 (s, 6H), 2.19 (s, 12H), 6.67 (s, 2H), 6.89 (d, 4H, $J = 8.9$ Hz), 6.91 (d, 8H, $J = 8.2$ Hz), 7.02 (d, 8H, $J = 8.2$ Hz), 7.12 (d, 4H, $J = 8.9$ Hz). $\lambda_{\max}$ (benzene) (log ε): 300 nm (4.6), 442 nm (4.4), 635 nm (4.6). MS (*m*/*z*) 911 (M^+). Found: C, 72.28; H, 4.94; N, 2.95%. Calcd for $C_{55}H_{44}N_2S_2$: C, 72.51; H, 4.87; N,3.07%.

18 F. Stellacci, C. Bertarelli, F. Toscano, M. C. Gallazzi, G. Zotti and G. Zerbi, *Adv. Mater.*, 1999, **11**, 292.