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Short communication

A switching fluorescent photochromic carbazole−spironaphthoxazine copolymer

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Abstract

A switching, methacrylate fluorescent photochromic copolymer (PMMA−Cz−SPO) containing fluorescent, chromophoric carbazole (Cz) and spironaphthoxazine (SPO) moieties as pendant groups, has been synthesized. The compound displayed excellent photoregulation of luminescence change from the spirooxazine to the carbazole in both solution and solid film, imparted by alternate irradiation with UV and visible light. This may be attributed to the induced electron transfer between the carbazole donor and the spirooxazine acceptor. In addition, the fluorescence emission spectra showed remarkable concentration-dependence.

Keywords: Fluorescence; Photochromic; Spironaphthoxazine; Carbazole; Copolymer

1. Introduction

Organic photochromic materials attract much attention because of their numerous potential applications as optical devices, such as ultra-high-density optical information storage, variable-transmission filters and photoregulated molecular switches [1−5]. In particular, photoswitchable luminescence polymers are promising materials because bistable photoswitching of fluorescence emission is considered to be a promising signaling mode, not only since the fluorescence signals can be readily and sensitively recognized, but also because the small number of photons required for their excitation induce few side effects that could spoil digitised signals [6−12]. Spirooxazines (SPO) [13,14] are well-known photochromic compounds whose planar, oxazine ring structure is alterable upon exposure to UV−vis light or thermal stimulation. Two typical forms are a colorless spiro (Sp) form and a colored merocyanine (MC) form. A number of attempts to incorporate spirooxazine molecules into polymer systems have been reported [15,16].

Photochromism studies of spirooxazine in polymer matrices [17], liquid crystal polymers containing spirooxazine as mesophases [18], spirooxazine grafted, poly[2-ethynyl-pyridinum bromide] ionic conjugated polymer [19], poly[*N*,*N*-[(3-dimethylamino)propyl] methacrylamide [20] and other synthetic polymers [21,22] have recently been developed. However, photocontrollable fluorescent changes of spirooxazine are very scarce [23]; in particular, photoswitchable fluorescent photochromic spirooxazine polymers are virtually unknown.

This paper concerns the preparation and photochromism of a copolymer containing carbazole (Cz) and spironaphthoxazine (SPO) moieties in the pendant groups (PMMA−Cz−SPO) (as shown in Scheme 1), with particular focus on how the copolymer's photochromism affects their photoswitching fluorescence change properties.

The PMMA−Cz−SPO copolymer was prepared from the monomers **4** and **5** by radical polymerization (Scheme 2); the

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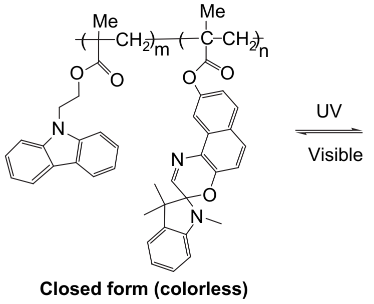


Scheme 1.

monomers were synthesized by reacting 2-(9*H*-carbazol-9-yl) ethanol (**1**) with methacryloyl chloride (**3**) for carbazole monomer (**4**), and 1,3,3-trimethyl-6′-hydroxyspiro-[2*H*]-indol-2,30-[3*H*]-naphtha[2,1-*b*][1,4] oxazine (**2**) with methacryloyl chloride (**3**) for spirooxazine monomer (**5**). The chemical structures of the intermediates **4** and **5** were characterized by ^{1}H NMR, MS; the PMMA–Cz–SPO copolymers were also determined by gel permeation chromatography (GPC) and ^{1}H NMR [24].

The discolored absorption spectra of the PMMA–Cz–SPO copolymer in THF solution are shown in Fig. 1. Upon irradiation with UV light, the PMMA–Cz–SPO copolymer exhibited photochromism, with a growth in intensity of the band at about 600 nm, corresponding to generation of the open form of the compound. The open form generated was thermally unstable and readily underwent thermal bleaching to the closed form. The inset shows absorption monitoring of cyclical, on and off photoconversions of PMMA–Cz–SPO copolymer in THF solution.

The PMMA–Cz–SPO copolymer in solid film showed similar photochromic behaviour to that in solution (Fig. 2). The absorption band had a λ_{max} at 600 nm and was observed immediately after 50 s irradiation with UV light, which demonstrated that it exhibited excellent photochromic properties. Moreover, the intensity of the absorption band at λ_{max} decreased gradually during the discoloration process. The inset shows cyclical on and off photoconversions of PMMA–Cz–SPO copolymer in film measured at λ_{max}.

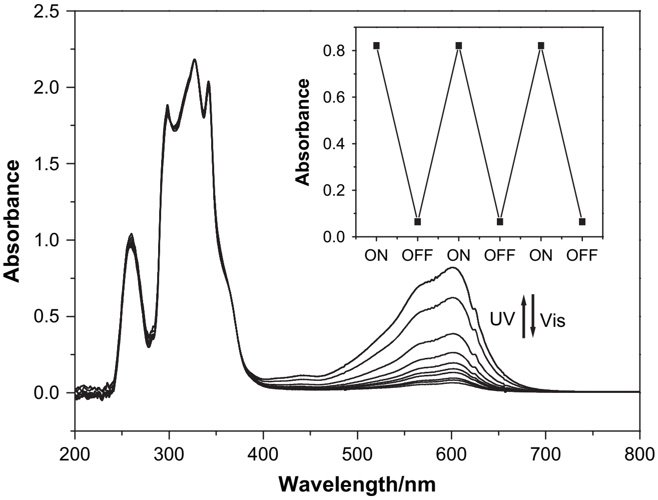
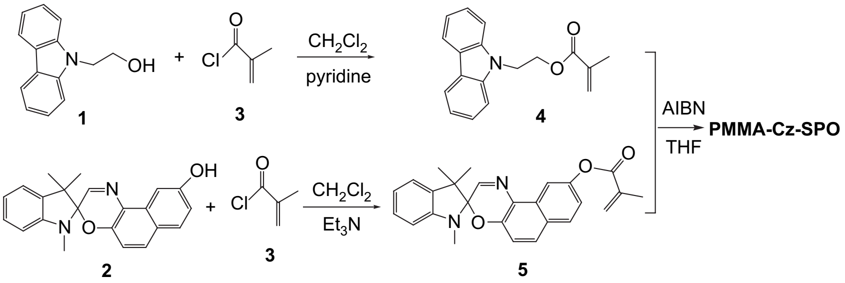


Fig. 1. UV–vis absorption spectral change of PMMA–Cz–SPO copolymer in THF solution (2.5 × 10^{-4} M) upon irradiation with UV and visible light. The inset shows absorption monitoring of cyclical on and off (by alternative irradiation with UV and visible light) photoconversions of PMMA–Cz–SPO copolymer (at λ_{max} 600 nm).

The copolymer exhibited photoluminescence at 348 nm and 364 nm in THF solution at room temperature when excited at 320 nm. The fluorescence intensity of the copolymer decreased with change from the ring-closed form to the open-ring form as a result of irradiation with UV light (Fig. 3). The original photoluminescence was recovered within 5 s by irradiation with visible light. The inset in Fig. 3 shows a cycling experiment in which the maximum emission of PMMA–Cz–SPO in THF solution was monitored upon alternate irradiation with UV and visible light.

Fig. 4 shows the fluorescence spectral changes of PMMA–Cz–SPO in solid film using an excitation wavelength at 342 nm; broad emission in the range 400–550 nm with a λ_{em} around 450 nm was observed. Upon irradiation with UV light, the fluorescent intensity of PMMA–Cz–SPO gradually decreased and was almost completely quenched, suggesting an increase in photoinduced electron transfer (PET) between the carbazole units and the photoinduced



Scheme 2.

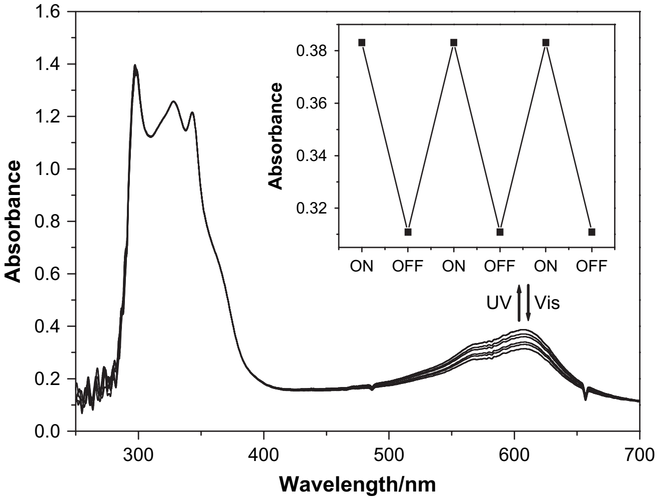


Fig. 2. UV–vis absorption spectral change of PMMA–Cz–SPO copolymer in film (casting film from toluene solution) upon irradiation with visible light. The inset shows absorption monitoring of cyclical on and off (by alternative irradiation with UV and visible light) photoconversions of PMMA–Cz–SPO copolymer (at λ_{max} 600 nm).

spirooxazine isomers [12]. Upon irradiation with visible light, the original emission spectra were regenerated.

Fig. 5 shows a cycling experiment in which the maximum emission of PMMA–Cz–SPO film was monitored upon alternate irradiation with UV and visible light.

The concentration-dependence of fluorescence excitation spectra was also measured in THF solution at room temperature (Fig. 6). The fluorescence emission spectra showed remarkable concentration-dependence, fluorescence intensity rapidly increasing with increase in concentration. These results indicate that molecular aggregation and fluorescence increase may occur as a result of concentration increase [25].

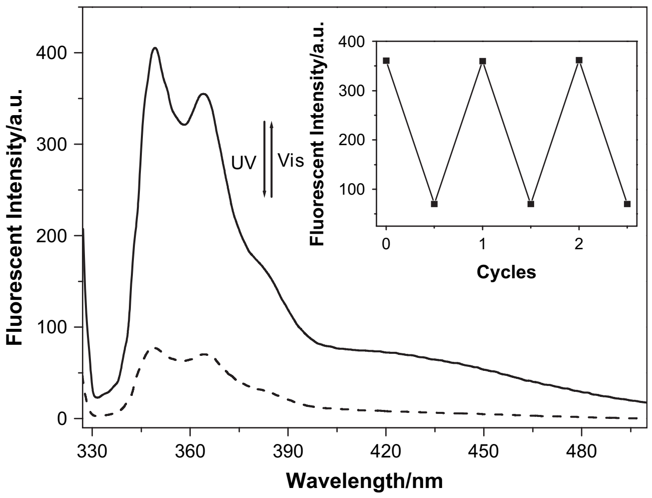


Fig. 3. Fluorescence emission spectral change of PMMA–Cz–SPO copolymer in THF solution (5.0×10^{-4} M) upon irradiation with UV light at room temperature. The inset figure shows the fluorescence monitoring of cycles on and off (by alternative irradiation with UV and visible light) photoconversion of PMMA–Cz–SPO copolymer in THF solution (5.0×10^{-4} M) at 0 °C (excited at 320 nm, $\lambda_{em} = 348$ nm).

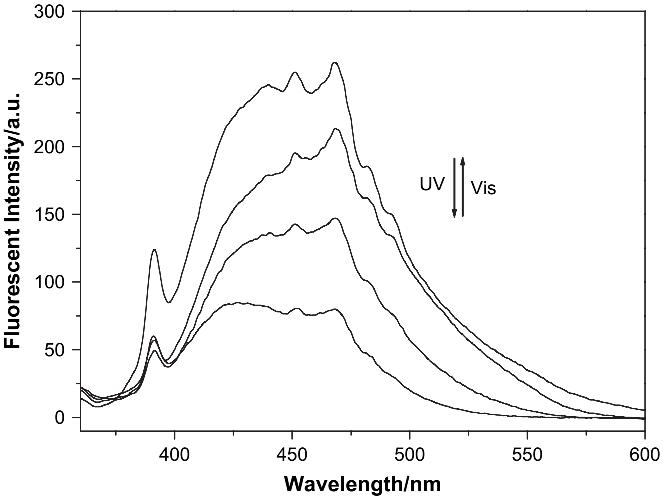


Fig. 4. Fluorescence emission spectral change of PMMA–Cz–SPO copolymer in film (casting film from toluene solution) upon irradiation with UV light at room temperature (excited at 342 nm).

2. Conclusions

A photochromic carbazole–spironaphthoxazine copolymer has been synthesized, which offers potential as a photoregulated fluorescent molecular switches in all-photon mode molecular devices. The luminescence of the carbazole chromophore was effectively regulated by toggling between the two isomers of the spirooxazine subunit in solid film, which can be attributed to changes in PET between the carbazole and each form of the spirooxazine photochrome. In addition, the fluorescence emission spectra showed remarkable concentration-dependence.

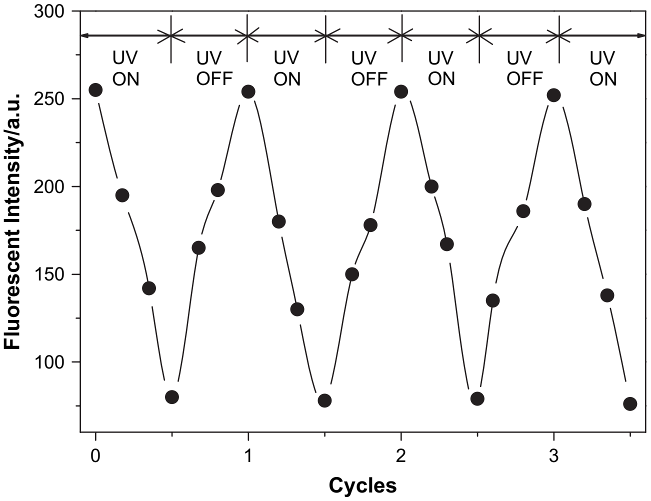


Fig. 5. Fluorescence monitoring of cycles on and off (by alternative irradiation with UV and visible light) photoconversion of PMMA–Cz–SPO copolymer in film at room temperature (excited at 342 nm, $\lambda_{em} = 452$ nm).

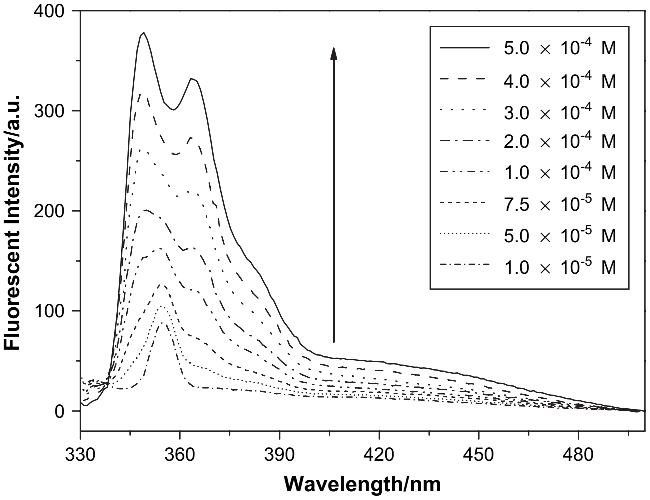


Fig. 6. Fluorescence emission spectral change of PMMA–Cz–SPO copolymer in different concentrations in THF solutions at room temperature (excited at 320 nm).

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[24] The analytical data agree with the proposed structure for compound **4**: yield: 3.9 g, 73%; m.p. 76.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.1 (d, $J = 7.52$ Hz, 2H), 7.46 (m, 4H), 7.24 (m, 2H), 5.93 (s, 1H), 5.49 (s, 1H), 4.63 (t, 2H, N–CH_2), 4.53 (t, 2H, O–CH_2), 1.80 (s, 3H, CH_3). MS: $m/z = 279$. Compound **5**: yield: 2.54 g, 85%; m.p. 143 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.26 (s, 1H), 7.76 (d, $J = 9.0$ Hz, 1H), 7.70 (s, 1H), 7.65 (d, $J = 9.0$ Hz, 1H), 7.16 (m, 1H), 7.08 (d, $J = 7.52$ Hz, 1H), 7.00 (d, 1H), 6.90 (m, 1H), 6.58 (d, 1H), 6.41 (s, 1H), 5.79 (s, 2H), 2.76 (s, 3H), 2.10 (s, 3H), 1.56 (s, 3H, CH_3), 1.34 (s, 3H, CH_3). FAB-MS, $m/z = 412$. The PMMA–Cz–SPO copolymer: yield: 110.0 mg, 80%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.28 (br), 7.90 (br), 6.85–7.30 (br), 6.4 (br), 4.3 (br), 3.64 (m), 2.51 (br), 1.6–1.22 (m). GPC M_n: 5437, M_w: 8161, M_p: 5841, M_w/M_n: 1.50.

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