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Positive and negative fluorescent imaging induced by naphthalimide polymers

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Two novel polymers with naphthalimide pendant groups have been prepared. In poly(2-methylacrylic acid 2-[6-(4-methylpiperazin-1-yl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinolin-2-yl]ethyl ester-*co*-methyl methacrylate) (copolymer **1**), an alkylated tertiary amine acts as an electron donor and quenches the fluorescence of the naphthalimide fluorophore *via* the photo-induced electron transfer (PET) process. Protonation of the alkylated tertiary amine by an acid generated by a photoacid generator (PAG) can switch off the PET path and the fluorescence of the naphthalimide fluorophore would be recovered and enhanced. For poly(2-methylacrylic acid 2-[6-(4-methylpiperazin-1-yl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinolin-2-yl]ethyl ester) (polymer **3**), protonation both of the aromatic amine and the alkylated amine by the acids generated from may result in significant fluorescence quenching and alter the fluorophore. When protonation processes occur, the fluorescence enhancement (×2) of copolymer **1** or the fluorescence quenching (×15) of polymer **3** would be applied to generate positive or negative fluorescent patterned images on their net films.

Introduction

The generation of patterned images in polymer films has become a central focus in fundamental and applied research areas, since the development of patterned functional images is of great importance in the electronics industry. The generation of functional images by selective immobilization of organic dyes in polymers films has been reported.[1–3] More recently, patterned functional images in polymer films have also been described,[4–8] in which quinizarin or pyridylbenzoxazole moieties were used as pendant groups. Naphthalimide derivatives are well known as brilliant greenish-yellow dyes for synthetic polymer fibers. They have in general higher fluorescent quantum yields.[9] As part of our efforts to produce functional images in polymer films, we now report the synthesis of the novel copolymer **1** and polymer **3** with naphthalimide pendant groups, and their use in the generation of fluorescent images. Although the idea of photo-induced fluorescent imaging by polymers is not novel, one important step forward in photo-induced fluorescent imaging with high contrast was achieved by the use of a naphthalimide derivative due to its high fluorescent quantum yield. Under a fluorescent microscope with weak UV light excitation (365 nm), no obvious decrease in the contrast of the image can be observed in our experimental system.

The design strategy for the molecule for fluorescent imaging is developed from the study of the photo-induced electron transfer (PET).[10,11] When an alkylated amine is linked to the 4-amino-position of the naphthalimide moiety, PET occurs from the nitrogen atom of the alkylated amine donor to the 4-amino-1,8-naphthalimide fluorophore through the piperazinyl ring and quenches the fluorescence of the 4-amino-1, 8- naphthalimide.[12–14] Switching off the PET path could be achieved by protonation of the alkylated amine donor. For this naphthalimide derivative, the alkylated amine electron donor can be protonated by reacting with an acid and the fluorescence of the naphthalimide fluorophore can be recovered. This kind of pH sensing fluorophore has been reported and used in solution.[15] However, for the application of patterned images the solid thin film should be used.

On the other hand, the color of 1,8-naphthalimide is dependent on the presence of a strong electron donating substituent linked to the 4-position of the naphthalimide ring.[16,17] If the electron-donating aromatic amine linked directly to the 4-position of the naphthalimide ring is replaced by an electron-withdrawing substituent, such as a nitro group, the fluorescence of the naphthalimide fluorophore of this naphthalimide derivative drastically decreases. When the aromatic amine in this naphthalimide derivative is protonated at much lower pH values, an electron-withdrawing effect, leading to fluorescence quenching, can also be induced chemically. Based on the previous research, we designed and have synthesized copolymer **1** and polymer **3** containing naphthalimide as the pendant group shown in Scheme 1. In copolymer **1**, the alkylated tertiary amine acts as the electron donor, PET occurs from the nitrogen atom of the tertiary amine to the naphthalimide fluorophore *via* hydrocarbon chain spacers and then quenches the fluorescence of the naphthalimide fluorophore. When copolymer **1** reacts with an acid, the tertiary amine will be protonated and the PET from the tertiary amine to the naphthalimide fluorophore will be inhibited. Then the fluorescence of the naphthalimide fluorophore will be recovered and even enhanced under some conditions. Photoacid generators are used to stop the PET process from the side chain in copolymer **1** in this work, which shows an increase of fluorescence (×2 in the solid film and nearly ×10 in the solution). However, for the naphthalimide homopolymer, that is, polymer **3**, there exist many more possibilities for both protonation on the alkylated amine and the aromatic amine due to the absence of diluting units (MMA), although the diprotonation of polymer **3** would be very incomplete. The electron-withdrawing effect of the protonated aromatic amine linked directly to the 4-positon of the naphthalimide ring

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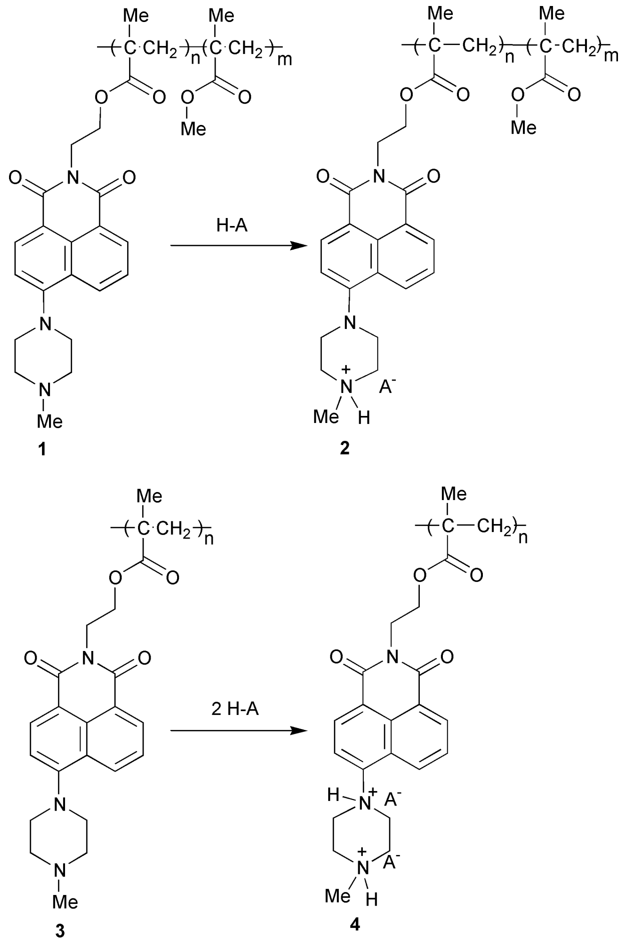


Scheme 1 The reaction of copolymer **1** and polymer **3** with the acids (H–A).

(shown as structure **4** proposed in Scheme 1) will lead to fluorescence quenching. Photoacid generators are also used here to protonate and alter the fluorophore in polymer **3**, which results in an obvious decrease of the fluorescence (decrease near 15 times in the net film). The difference between copolymer **1** and polymer **3** is the presence of the diluting MMA units in copolymer **1**. If the acid-induced fluorescence recovering or quenching is significant and occurs in selected areas, positive or negative fluorescent images with a high contrast will be obtained.

Numerous photoacid generators (PAG) are used in chemical amplification resist systems for high resolution patterning with high sensitivity.[18–20] A PAG molecule can be converted to a strong acid upon absorption of a photon. The rate of the photochemical reaction is fast and is governed by the quantum efficiency of the particular acid generator and exposure energy. In this work, copolymer **1** and polymer **3** were combined with PAG to make thin films and subjected to UV exposure through photo-masks for positive or negative fluorescence images. The synthesis route to monomer **7** is shown in Scheme 2.

Experimental

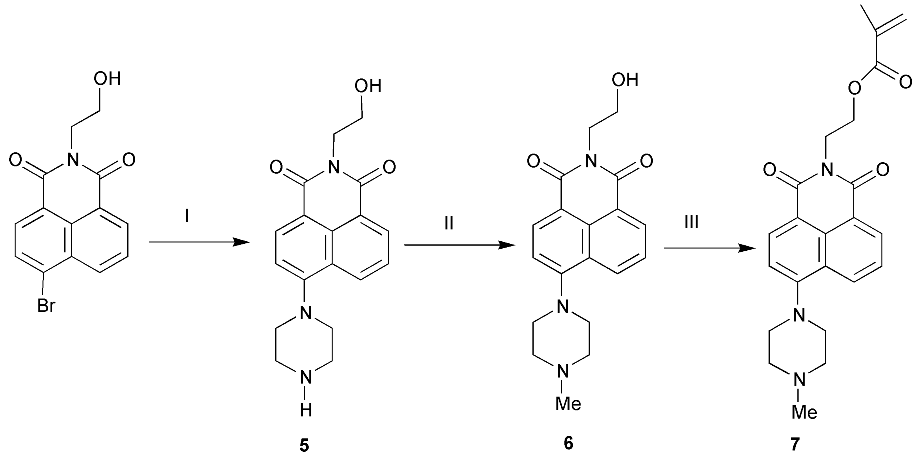
^{1}H NMR spectra were obtained using a Bruker AM 500 spectrometer. Mass spectra (MS) were recorded on a MA1212 instrument using standard conditions (EI, 70 eV). UV–Vis spectra were recorded on a Varian Cary 500 spectrophotometer. Fluorescence spectra were recorded on a Hitachi-850 spectrophotometer. The fluorescent patterned micrograph images were taken by an Olympus BH-2 fluorescent microscopy. The starting compound 6-bromo-2-(2-hydroxyethyl)-benzo[*de*]isoquinoline-1,3-dione was prepared based on the known method.[12,21,22]

Preparation of 2-(2-hydroxyethyl)-6-(piperazin-1-yl)benzo[*de*]-isoquinoline-1,3-dione (5)

6-Bromo-2-(2-hydroxyethyl)benzo[*de*]isoquinoline-1,3-dione 5 g (15.7 mmol) and piperazine hydrate 5.1 g (26.3 mmol) in 20 mL methoxyethanol were vigorously stirred and heated to reflux for 3 h. The mixture was allowed to stand overnight at room temperature. The yellow solid obtained was filtered. 4 g (yield 75%) pure crystals were obtained by recrystallization from aqueous ethanol. Mp 225–226 °C. ^{1}H NMR (DMSO-d$_6$) δ(ppm): 8.47 (m, 2H), 8.40 (d, J = 8.10 Hz, 1H), 7.81 (dd, J = 8.26 Hz, J = 7.44 Hz, 1H), 7.32 (d, J = 8.25 Hz, 1H), 4.14 (d, =NCH$_2$-, 2H), 3.60 (t, -CH$_2$-O-, 2H), 3.15 (s, -N(CH$_2$)$_2$-, 4H), 3.02 (s, -N(CH$_2$)$_2$-, 4H). Anal. Calcd. for $C_{18}H_{19}N_3O_3$: C 66.45, H 5.89, N 12.91. Found: C 66.63, H 5.81, N 12.78 %.

Preparation of 2-(2-hydroxyethyl)-6-(4-methylpiperazin-1-yl)-benzo[*de*]isoquinoline-1,3-dione (6)

0.3 g paraformaldehyde (amount equivalent to 10 mmol formaldehyde) was added to a solution of **5** (1.5 g, 4.6 mmol) in 10 mL formic acid (88%), with stirring at 80 °C and stirring was continued for 20 h. Then all solvent was removed under vacuum, and to the residue, 20 mL 3 M hydrochloric acid was added, and the solution was refluxed for 1 h. Sodium carbonate powder was added carefully, and a yellow solid was obtained. 1.2 g (yield 78%) pure crystals were obtained by recrystallization from ethanol. Mp 217–219 °C. MS-EI *m*/*z* 339 (M$^+$). ^{1}H NMR (D$_2$O) δ(ppm): 7.65 (m, 2H), 7.54 (d, J = 7.98 Hz, 1H), 7.13 (dd, J = 7.74 Hz, J = 7.76 Hz, 1H), 6.68 (d, J = 8.04 Hz,



Scheme 2 The synthesis of **7** (monomer). *Reaction conditions*: I: piperazine hydrate–methoxyethanol, II: paraformaldehyde and formic acid, III: methacryloyl chloride, triethylamine (TEA)–dichloromethane.

1H), 3.73 (t, =NCH_2-, 2H), 3.55 (t, -CH_2O-, 2H), 3.08 (s, -$N(CH_2)_2(CH_2)_2N$-, 8H), 2.65 (s, -CH_3, 3H). Anal. Calcd. for $C_{19}H_{21}N_3O_3$: C 67.24, H 6.24, N 12.38. Found: C 67.37, H 6.21, N 12.30%.

Preparation of 2-methylacrylic acid 2-[6-(4-methylpiperazin-1-yl)-1,3-dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinolin-2-yl]ethyl ester (monomer 7)

2-(2-Hydroxyethyl)-6-(4-methylpiperazin-1-yl)benzo[*de*]isoquinoline-1,3-dione **6** (5.0 g, 14.7 mmol) was dissolved in dichloromethane (100 mL), methacryloyl chloride (3.1 g, 29.4 mmol) and TEA (5.0 mL, 35.9 mmol) were added. The mixture was stirred at room temperature for 15 h, poured into 300 mL of water, the organic layer was separated and the water layer was extracted with 4 × 50 mL of dichloromethane. The combined dichloromethane extracts were washed with water and dried with anhydrous magnesium sulfate. The solvent was removed under vacuum, and 5.0 g yellow residue of **7** was obtained with a yield of 83.2%. Recrystallization twice from ethanol afforded yellow crystals. Mp 169–171 °C. MS (EI) *m*/*z* $[M+1]^+$ 408 (10.9%), $[M]^+$ 40 7 (26.7%). ^1H NMR (500 MHz, $CDCl_3$) δ(ppm): 8.59 (d, 1H, J = 7.27 Hz), 8.53 (d, 1H, J = 8.04 Hz), 8.41 (d, 1H, J = 8.38 Hz), 7.70 (dd, 1H, J = 7.84 Hz, J = 7.87 Hz), 7.24 (d, 1H, J = 8.12 Hz), 6.05 (s, 1H), 5.50 (s, 1H) , 4.55 (t, -CH_2-, 2H), 4.48 (t, -CH_2-, 2H), 3.34 (s, -$N(CH_2)_2$-, 4H), 2.80 (s, -$N(CH_2)_2$-, 4H), 2.48 (s, NCH_3, 3H), 1.87 (m, -CH_3, 3H). Elemental analysis calcd. for $C_{23}H_{25}N_3O_4$ (407.46): C 67.80, H 6.18, N 10.31. Found: C 67.60, H 6.14, N 10.27%.

Preparation of copolymer 1 and polymer 3

A solution containing monomer **7** (0.5 g, 1.2 mmol), methyl methacrylate (MMA 3.0 g, 30 mmol), 2,2′-azoisobutyronitrile (AIBN 100 mg) and 1-methylpyrrolidin-2-one (NMP, 5 mL) in an ampoule was subjected to repeated freeze–thaw cycles before the ampoule was heated at 70 °C for 40 h. After polymerization, the product was precipitated by addition of methanol and dried. For the determination of the polydispersity, ^1H NMR and the UV spectroscopic analyses, copolymer **1** was purified and extracted in a Soxhlet apparatus with methanol for 48 h and dried to give copolymer **1** (3.1 g, 88.6%) as a yellow powder. Copolymer **1** has a weight-average molecular weight (GPC) of 93 700 with a polydispersity of 1.96. ^1H NMR and UV spectroscopic analyses confirmed the 1 : 14 ratio of naphthalimide monomer to MMA monomer in **1**. Polymerization of monomer **7** without methyl methacrylate according to the same procedure of copolymer **1** gave polymer **3** as a yellow powder (yield 78%). Polymer **3** has a weight-average molecular weight (GPC) of 4500 with a polydispersity of 2.13.

Results and discussion

Absorption and fluorescence properties

In order to confirm that the fluorescence recovery and the fluorescence quenching can be induced by protonation of the alkylated amine or both the alkylated amine and the aromatic amine in these naphthalimide derivatives, the luminescent properties of polymer **3** in tetrahydrofuran (THF) for different proton concentrations were investigated. The naphthalimide absorption bands of polymer **3** were blue-shifted upon protonation by perchloric acid (data listed in Table 1).

When the proton concentration increased to about 1 × 10^{-2} mol L^{-1} (the concentration changes from A to D shown in Fig. 1), the alkylated amine of polymer **3** is protonated, then the fluorescence of the naphthalimide fluorophore was enhanced about seven times. The maximum emission wavelength of the naphthalimide was blue-shifted about 8 nm. This is attributed to the "switching off" of the PET path from the alkylated amine to the naphthalimide fluorophore. Further protonation (the proton concentration changes from D to G shown in Fig. 1) of the aromatic amine at much lower pH value resulted in the fluorescence quenching of the naphthalimide fluorophore to about 1/34 of its original level, as shown in Fig. 1. Based on the photophysical behavior of 1,8-naphthalimide derivatives studied previously by Samanta[23] and others including ourselves,[9,12,17] the absorption and fluorescence spectra of the diprotonated structure **4** proposed in Scheme 1 should shift much more into the blue. However, the experimental measurements here for the reference systems listed in Table 1 did not support the prediction above as proposed in Scheme 1. This means the diprotonation of polymer **3** is very incomplete. This can also be expected because the first protonation site is so close to the second site. Additionally, the aromatic amine is quite substantially conjugated to the imide, which reduces its basicity even further. In fact, the spectra of polymer **3** in high proton concentration solution should be the sum of that of diprotonated and monoprotonated species. The fluorescence intensity of the mixed system under these condition was too weak to determine exactly its maximum peak. The very broad fluorescent spectral band shown in Fig. 1 still shows the maximum peak at 510 nm (though not exact), which might quite likely result from the monoprotonated species. In order to confirm the structure **4** proposed in Scheme 1, the difficult purification and characterisation experiments should be further pursued and are in progress.

Table 1 Absorption and fluorescence emission spectra data of polymer **3** for different proton concentrations ($\lambda^{ab}{}_{max}$/nm, 10^{-4} M in THF; $\lambda^{flu}{}_{max}$ /nm, 10^{-4} M in THF, excited at the maximum absorption wavelength; room temperature. Rhodamine B was used as quantum yield standard and its fluorescence quantum yield was defined as 1.00. Perchloric acid was the proton source.)

Proton concentration/mol L^{-1}	$\lambda^{ab}{}_{max}$/nm ($\log\varepsilon$/dm^3 mol^{-1} cm^{-1})	$\lambda^{flu}{}_{max}$/nm (φ_f)
1 × 10^{-7}	398.0 (3.94)	519.6 (0.11)
1 × 10^{-5}	397.0 (3.92)	517.8 (0.12)
1 × 10^{-3}	383.0 (3.85)	511.9 (0.71)
1 × 10^{-2}	383.0 (3.82)	511.7 (0.78)
0.1	381.0 (3.84)	511.0 (0.38)
1	380.0 (3.89)	510.7 (0.21)
5	379.5 (3.93)	510.2 (0.023)

Photoacid -induced fluorescence enhancement for copolymer 1

The absorption spectrum of copolymer **1** in THF has a maximum absorption wavelength at 394 nm that is attributed to the typical band of 4-amino-1,8-naphthalimide moieties.[9] To investigate the possible formation of polymer **2** and the fluorescence recovery by acid-induced chemical transformation, a

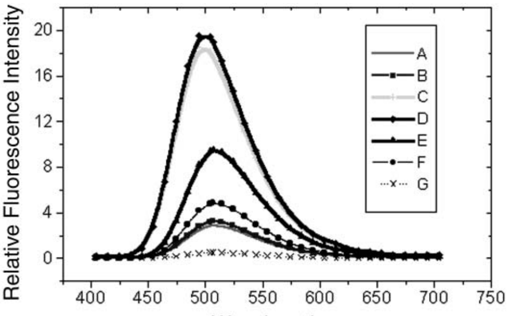


Fig. 1 Fluorescence spectra of polymer **3** in THF for different proton concentrations: (A) 1 × 10^{-7} (B) 1 × 10^{-5} (C) 1 × 10^{-3} (D) 1 × 10^{-2} (E) 0.1 (F) 1 (G) 5 mol L^{-1}. Perchloric acid is the proton source.

thin polymer film containing copolymer **1** (80 wt %) and a photoacid generator (triphenylsulfonium hexafluoroantimonate (TPSHFA),[18,19,24] 20 wt%) was prepared on a quartz plate by spin-coating from THF solution. At the same time, a reference solution was prepared by dissolving 9.3 mg copolymer **1** and 3.1 mg TPSHFA in 50 mL THF (the naphthalimide segment in copolymer **1** of this solution is equivalent to 1×10^{-4} M of monomer **7** in THF). The solution was irradiated with UV light (254 nm) for 10 min. The solid film was irradiated for 30 seconds followed by post-exposure baking (PEB) at 120 °C for 60 seconds. The UV irradiation results in the fluorescence enhancement of the 4-amino-1,8-naphthalimide fluorophore by more than 10 times in the solution and two times in the film and about 5 nm blue-shift of the maximum emission wavelength (Table 2 and Fig. 2b). The naphthalimide absorption bands of polymer **2** in the solution and in net film are also blue-shifted about 5 nm compared to those of copolymer **1** (Table 2 and Fig. 2a). The results demonstrate that the strong acid (presumably hydrogen fluoride (HF) and hydrogen hexafluoroantimonate ($HSbF_6$)), which was generated by irradiation of the photoacid generator, protonates the alkylated tertiary amine linking with the 4-amino-1,8-naphthalimide fluorophore through the piperazinyl ring, and switches off the PET path from the tertiary amine to the 4-amino-1,8-naphthalimide. Then the fluorescence of the 4-amino-1,8-naphthalimide fluorophore is obviously recovered and enhanced.

Table 2 Absorption and fluorescence emission spectra data of copolymer **1** containing TPSHFA in THF and in net film with thickness of about 1.0 μm before UV irradiation and after UV irradiation

	In THF		In net film	
Copolymer **1**	Before irradiation (SB)	After irradiation (SA)	Before irradiation (FB)	After irradiation (FA)
λ^{ab}_{max}/nm	394.9	390.1	398.8	393.0
λ^{fl}_{max}/nm	523.9	519.1	521.8	517.0
(Intensity)	(5.1)	(47.7)	(23.3)	(54.6)

Photoacid-induced fluorescence quenching for polymer 3

A solution in THF and a polymer film containing polymer **3** and TPSHFA were prepared as for those of copolymer **1**. The naphthalimide segment concentration of polymer **3** in THF is the same as that of copolymer **1**. A thin polymer film containing polymer **3** and TPSHFA was prepared in the same way as that of copolymer **1** except that chloroform was selected as the solvent. The solution and the polymer film were irradiated as described above. The absorption and emission data are listed in Table 3 and shown in Fig. 3. The naphthalimide absorption bands of the structure **4** shown in Scheme 1 in THF and in the net film are blue-shifted about 15 nm and 13 nm compared to those of polymer **3**, respectively. The UV irradiation results in the fluorescence quenching of the naphthalimide fluorophore in the THF solution by more than two times. The fluorescence of the naphthalimide fluorophore is not so obviously quenched because the acids generated by the PAG may be diluted by the THF solvent, and part of the aromatic amines linked directly to the 4-position of the naphthalimide ring may not be protonated. However, the fluorescence of the naphthalimide fluorophore of polymer **3** in the net film was

Table 3 Absorption and fluorescence emission spectra data of polymer **3** containing TPSHFA in THF and in net film with thickness of about 1.0 μm before UV irradiation and after UV irradiation (254 or 365 nm)

	In THF		In net film	
Polymer **3**	Before irradiation (SB)	After irradiation (SA)	Before irradiation (FB)	After irradiation (FA)
λ^{ab}_{max}/nm	393.2	378.0	398.0	385.0
λ^{fl}_{max}/nm	515.5	495.0	520.5	505.4
(Intensity)	(3.4)	(1.5)	(11.5)	(0.75)

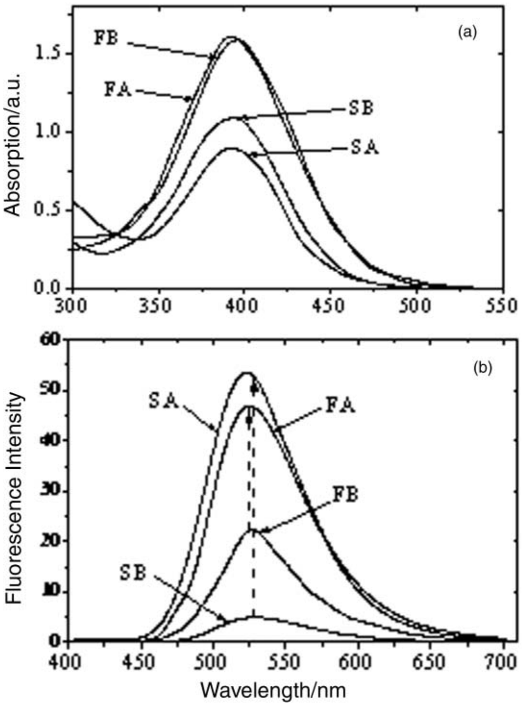


Fig. 2 The absorption (a) and fluorescence emission spectra (b) of copolymer **1** containing TPSHFA. SB (in THF before UV irradiation), SA (in THF after UV irradiation), FB (in net film before UV irradiation), FA (in net film after UV irradiation).

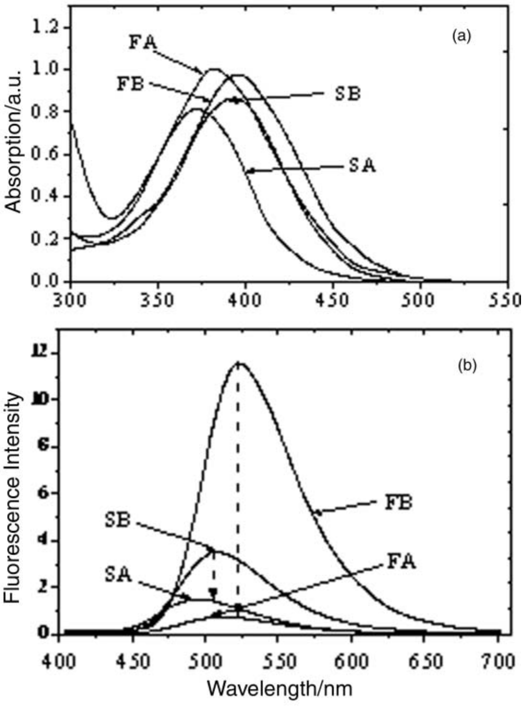


Fig. 3 The absorption (a) and fluorescence emission spectra (b) of polymer **3** containing TPSHFA. SB (in THF before UV irradiation), SA (in THF after UV irradiation), FB (in net film before UV irradiation), FA (in net film after UV irradiation).

quenched to less than one-fifteenth of the original level. (Fig. 3b) The naphthalimide maximum emission wavelength of structure **4** in the solution and in the net film were also blue-shifted about 20 nm and 15 nm compared to that of polymer **3**, respectively.

Fluorescent imaging

The final phase of the current work is the formation of patterned fluorescent images with copolymer **1** and polymer **3**. According to the design strategy for fluorescent imaging, the fluorescence recovery in the specific areas requires generation of acid. Polymer films containing copolymer **1** and TPSHFA on a quartz plate or polymer **3** and TPSHFA on a silicon wafer were irradiated with a light of 254 nm for 30 s followed by a PEB step at 120 °C for 60 seconds through photo-masks. As shown in Fig. 4, excited by an UV light (365 nm, 20 mJ cm^{-2}), fluorescent image patterns appeared under fluorescence microscopy. The fluorescence of copolymer **1** was enhanced by photochemically generated acid and afforded positive fluorescent images in the solid film (Fig. 4a). Experiments to improve the resolution of the positive fluorescent images generated by copolymer **1** and the TPSHFA in solid film are in progress. Because a few aromatic amine units in copolymer **1** will inevitably not be protonated, and this may result in some fluorescence quenching, fluorescent imaging with a high resolution using copolymer **1** is still a challenge. An important additional reason for the small fluorescence increase ($\times 2$) of copolymer **1** is because PET is slow within the solid polymer matrix (as opposed to polar liquid solvents where dipole orientation occurs faster to stabilize the charge separated state).[15] The experiments by Wasielewski[11,25] and Fabbrizzi[26] demonstrated this by freezing solvents to stop PET and to distinguish between PET and electronic energy transfer (EET). In fact, the MMA units protect the arylamine units from further protonation simply by dilution in copolymer **1**, since the proton concentration generated by PAG in the film is constant, whereas the degree of protonation in polymer **3** cannot be controlled in the absence of the MMA units' diluting effect under the same proton concentration, and thus either the selective enhancement or suppression of the fluorescence can be obtained easily.

The fluorescence of polymer **3** was significantly quenched by photochemically generated acid and afforded finely resolved negative fluorescent images with 5 μm resolution (Fig. 4b). The 2.5 μm negative lattice pattern was seen on the fluorescent imaging pattern with 5 μm resolution, but clear photography cannot be obtained because of the limitation of our fluorescent microscope. The fluorescent images were obtained after irradiation by a strong UV light (254 nm, 200 mJ cm^{-2}) for 30 seconds followed by a post-exposure bake step at 120 °C for 60 seconds. Without the heating of the polymer film under strong UV irradiation, fluorescent images will not be obtained. That is, the reading of the images with a weak UV light (365 nm, 20 mJ cm^{-2}) under fluorescent microscopy will not lead to the fluorescence quenching and the contrast of the images will not change, at least within the time of the imaging. In the research reported in ref. 6, the benzoxazole chromophore of the polymer reported by the authors has the same absorption band around 320–400 nm; the same method was used for the formation of patterned fluorescent images. The fluorescent images reported here were also obtained successfully by similar methods. We have done another experiment to prove that the fluorescent quenching by illumination with UV light was not a serious problem for reading images. One important step forward in photo-induced fluorescent imaging with high contrast is achieved by use of a naphthalimide derivative due to its high fluorescent quantum yield. After 10 min exposure under a fluorescent microscope with an UV light (365 nm), a decrease in the contrast of the image cannot be observed in our experimental system. Of course, an additional important reason for the high image contrast is because the fluorescence of the fluorophore in polymer **3** was obviously quenched within the solid film.

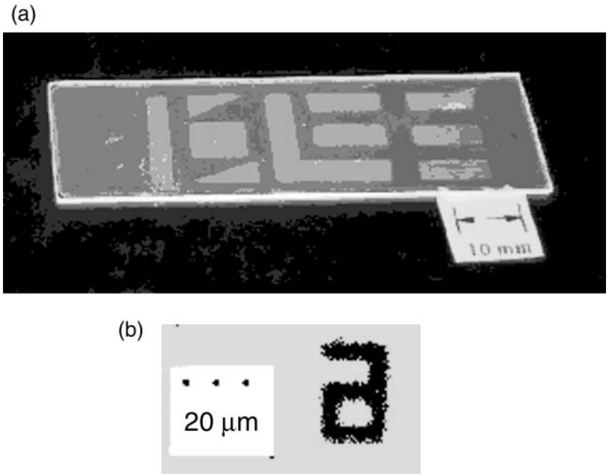


Fig. 4 Fluorescent image patterns obtained with a 1.0 μm thick film containing copolymer **1** (80 wt%) and TPSHFA (20 wt%) on a quartz plate (a); polymer **3** (80 wt%) and TPSHFA (20 wt %) on a silicon wafer (b) after UV irradiation (254 nm) for 30 seconds followed by PEB step at 120 °C for 60 seconds through different photo-masks. The pattern areas are portions exposed through the photo-mask.

Conclusions

Two novel polymers with naphthalimide pendant groups have been prepared. The MMA units in copolymer **1** protect the arylamine units from further protonation simply by dilution, whereas the degree of protonation in polymer **3** cannot be controlled without the MMA units' diluting effect under the same proton concentration. Thus either the selective enhancement or suppression of the fluorescence can be obtained easily. When the protonation occurs induced by an acid, the fluorescence enhancement of copolymer **1** and the fluorescence quenching of polymer **3** were investigated. These two polymers were applied successfully to generate positive or negative fluorescent patterned images, when their films were exposed to 254 nm UV light for 30 seconds and baked post-exposure at 120 °C for 60 seconds. The two polymers were shown to have good film forming properties. The negative fluorescent patterned images generated by polymer **3** showed a resolution of 5.0 μm under our current experimental conditions.

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