

Facile one-pot synthesis of a photo patternable anthracene polymer

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Abstract—A polycyclic aromatic compound, anthracene, was covalently connected through a methylene bridge via Friedel–Crafts alkylation reaction. Thus, a highly fluorescent anthracene polymer (PMA) linked by a methylene unit was prepared in one step to produce a conjugated–nonconjugated spacer-type polymer through its reaction with chloromethyl methyl ether (CME) and FeCl_3 at 0 °C. The resultant polymer was soluble in organic solvents and showed significantly higher fluorescence (quantum yield = 0.80) compared to monomeric anthracene, 9-methylanthracene, in chloroform solution. Fluorescent thin films of PMA as solid media were prepared with high film uniformity. The emission of the film was extinguished when the film was exposed to a UV source, due to the photodimerization of anthracene unit. A fluorescent gap electrode pattern was formed on the polymer film-forming average step depth of 8 nm and 14 nm, after 30 and 60 min irradiation with a UV light, respectively. The photo patternable fluorescent polymer afforded a convenient method of image formation and patterning.

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1. Introduction

The micro patterning of organic materials is of great importance for manufacturing functional materials and devices.¹ In particular, fluorescent patterning with π -electron conjugative polymers has recently attracted strong interest for possible applications in bio- and opto-electronics such as for a sensor, solar cell, and light-emitting diode. For such application and patterning, the preparation of patternable fluorescent polymers is an important issue because the resulting polymers could simply be processed into a thin film using solution processing. Here we take the advantages of patterning induced by photodimerization of fluorophore, which is effective for fabrication of patterns at a micrometer scale.

Among the fluorophores, anthracene is a promising building block for highly fluorescent $\pi\pi$ -electron-rich organic polymers² and valuable for the fabrication of organic semiconductors for organic transistor³ and stable blue emitting electroluminescent devices.⁴ Besides,

anthracene has been widely used as a signalling subunit for both cation and anion sensing, due to the commercial availability of a large variety of derivatives and the high fluorescence (quantum yield in acetonitrile is 0.36).⁵ To incorporate them in a solid medium, or link them as a polymer, electrochemical polymerization of anthracene has been attempted by several scientists.⁶ However, only few studies concerning direct polymerization of anthracene have been conducted and their patterning studies have not yet been studied much, possibly due to the formation of poorly soluble fully conjugated polymers. It is thus challenging to prepare polymers containing anthracene as a constitutional repeating unit with flexible bridging groups, to improve optical properties as well as thin film patterning process.

We report here the facile polymerization method of anthracene and formation of patterns on the film of a new main-chain anthracene polymer (PMA), in which anthracene is connected through methylene bridge.

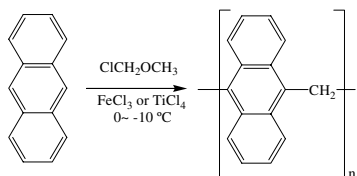
2. Results and discussion

2.1. Synthesis of an anthracene polymer

Methylene bridged anthracene polymer (PMA) was synthesized in 70% yield from anthracene via the

Keywords: Anthracene; Polymerization; Friedel–Crafts alkylation; Fluorescence; Thin film; Photodimerization; Pattern.

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Scheme 1. Synthesis of PMAn.

Friedel–Crafts alkylation,⁷ using chloromethyl methyl ether (CME)⁸ in the presence of FeCl_3 as summarized in Scheme 1. The weight average molecular weights (M_w) of the resulting polymer by GPC was 4950 with M_w/M_n of 2.78.

The ^1H NMR spectrum of PMAn showed a peak at 4.2 ppm characteristic of CH_2 bridging unit between anthracene rings. All the aromatic protons of PMAn were observed as multiplets at 7.44–8.52 ppm, corresponding to eight protons. In FT-IR spectrum, PMAn powder showed aromatic C–H and aliphatic CH_2 stretching bands centered at 3055 cm^{-1} and $2950\text{--}2850\text{ cm}^{-1}$, respectively, along with C=C (aromatic ring) vibrations at 1631 cm^{-1} and 1557 cm^{-1} . Thermo gravimetric analysis (TGA) indicated that the polymer is stable up to $300\text{ }^\circ\text{C}$. The char yield of PMAn was 43%, and its weight loss was 57% at $700\text{ }^\circ\text{C}$. Similarly, PMAn was also obtained when TiCl_4 was used as the acid catalyst, instead of FeCl_3 , under similar reaction conditions. The yield of 50% from the TiCl_4 reaction was slightly lower than that from FeCl_3 .

In a control experiment, similar reactions without CME were carried out with anthracene and FeCl_3 . Although a brown color was developed from the reaction solution, >98% of anthracene was recovered. This result indicates that CME is a core component of the polymerization as an alkylating agent and suggests that polymerization proceeds through initial chloromethylation⁹ followed by Friedel–Craft alkylation.¹⁰

2.2. Optical properties of PMAn

PMAn was soluble in common organic solvents such as tetrahydrofuran, dichloromethane, chloroform, and chlorobenzene. The solubility of PMAn was higher than that of anthracene. This may be attributed to the attachment of a methylene spacer as a bridge between the anthracene rings. Anthracene and anthracene derivatives usually show three well-defined and shaped absorption bands between 330 and 400 nm, and the emission spectrum usually consists of well-defined and structured bands centered at ca. 415 nm. A PMAn solution in chloroform showed strong absorption peaks maximized at 380 nm (Fig. 1), which are originated from the anthracene unit.¹¹

The fluorescence properties of anthracene (An) and PMAn are compared in Figure 1b. The PMAn showed broad emission bands with a peak at 415 nm, which is similar to that of anthracene, suggesting that the methylene spacers do not significantly influence the electronic properties of the polymer in a solution.¹² The absorption and emission bands of PMAn were broader than those of anthracene, possibly due to the interchain interactions of the polymers and the broad distribution of different chain lengths of PMAn, as indicated by the value of M_w/M_n . Importantly, the emission intensity of PMAn was much higher than that of anthracene at the same concentration. The fluorescence quantum yield (ϕ_F) of PMAn in solution, excited at 366 nm, was determined as 0.80 using quinine sulfate as a reference ($\phi_F = 0.51$).¹³ The ϕ_F value of PMAn was comparable to that of 9,10-dimethylanthracene ($\phi_F = 0.93$),¹⁴ 9,10-bis (diisopropyl silyl)anthracene ($\phi_F = 0.9$),¹⁵ but it was much higher than that of 9-methyl anthracene (0.16) and anthracene polymers reported in the literature.^{14–17} Such a high fluorescence quantum yield in the polymer can be rationalized by considering that the covalently bound anthracene structure, bridged by methylene unit, prevents conformational disorder leading to nonradiative decay from the excited state.

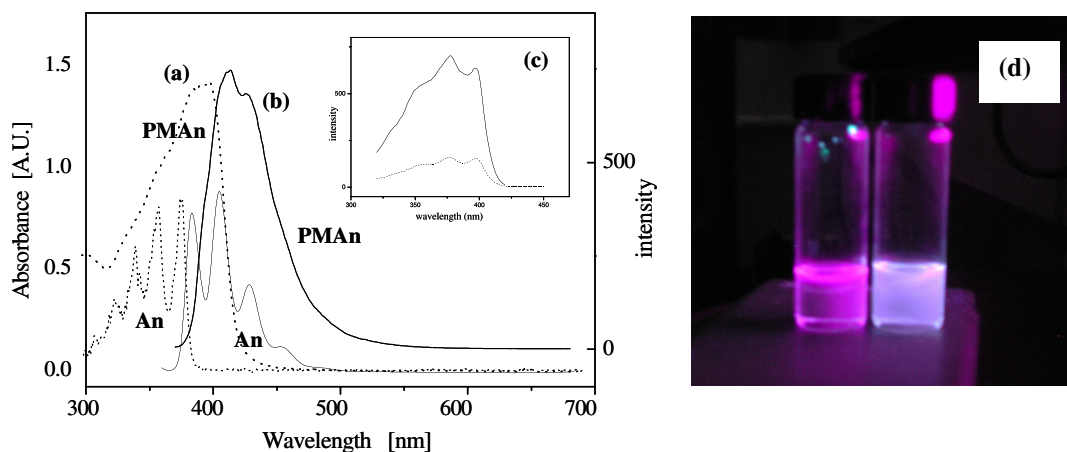


Figure 1. (a) Absorption (dotted lines) and (b) emission spectra (excited at 350 nm) of PMAn and anthracene (An) in a chloroform solution (solid lines). (c) Excitation spectra of PMAn in the same solution as (b) excited at 480 nm (solid) and 440 nm (dashed) lines. The concentration of the sample was 10^{-6} M in each solution. (d) Photographs of the solution of anthracene (left) and that of PMAn (right) in chloroform under UV exposure. The concentration of anthracene and PMAn in each solution was 10^{-7} M .

2.3. UV Patterning of the fluorescent PMAAn film

Anthracene undergoes photodimerization under UV exposure,^{6,16,18,19} which can provide a solvent-free dry method of image formation and creation of patterns. Besides, Kuriyama and co-workers¹⁶ mentioned that polymethylphenylsilane–anthracene (PMPS-AN) could be photodecomposed to decrease the emission intensity of the polymer, which is applicable to photo patterning. The photodimerization of anthracene is reversible in solution, however, the reverse reaction of the conversion of dianthracene to mono anthracene is slow in a solid medium. Thus the dimerization is useful for photo patterning of anthracene containing film.

When the solutions of anthracene (An) and PMAAn in chloroform (10^{-7} M) were illuminated with a high-intensity UV lamp ($\lambda \geq 365$ nm), the fluorescence intensity of both samples was decreased (Fig. 2). Interestingly, the PMAAn solution showed faster decrease in the fluorescence intensity than that of the anthracene solution,

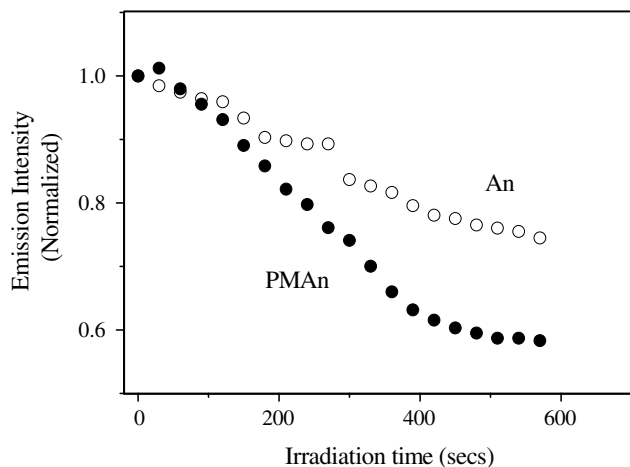


Figure 2. The intensity of the 430 nm fluorescence for the anthracene (An) and PMAAn solution under UV exposure at different irradiation time.

indicating that dimerization is faster in the solution of PMAAn (Fig. 2).

By taking advantage of the solubility of PMAAn in organic solvent, thin films of PMAAn could be prepared by a solution process using a spin-coater. Thin films having thickness of 50–1500 nm could be obtained, depending on the concentration of the polymer and spinning speed. Figure 3a shows average roughness of 3 nm for a 151 nm thick film as determined by an Alpha-step. The film coated on a quartz plate showed fluorescence with an emission maximum at ~540 nm as shown in Figure 3b. After 30 min of irradiation with a UV lamp ($\lambda \geq 365$ nm), the emission intensities from the film was significantly reduced as shown in Figure 3b. The FT-IR spectrum for the UV exposed film showed that the intensity for C=C (aromatic ring) vibrations at 1631 cm^{-1} and 1557 cm^{-1} were decreased, while those of aromatic C–H and aliphatic CH_2 stretching bands were not changed much (Fig. 4). The decrease in the intensity of the aromatic C=C vibration could be attributed to the loss of aromaticity in the benzene ring of the anthracene unit which is involved in the cyclo-addition, by the formation of dianthracene unit. In addition, UV spectrum of the UV exposed film showed a decrease in the optical density in the absorption region of anthracene and an increase in the absorption region of dianthracene (Fig. 4b). These results support that the anthracene units in PMAAn were dimerized by the UV exposure, which is coincident with the photo-dimerization of other anthracene derivatives.^{6,19}

Such a photodimerization of anthracene unit in the polymeric film led to pattern formation on PMAAn films by UV exposure. Thus, a PMAAn film (cast from 1 wt % chloroform solution) with 151 nm in thickness (3 nm average roughness) was illuminated with a UV source (intensity of 40 mW/cm^2) through a 0.1-mm-thick gap electrode mask. In this way, uniformly periodic patterns were formed on the PMAAn film in a large area. Figure 5a shows the patterned fluorescent image obtained from photo masked irradiation of PMAAn film for 30 min. It

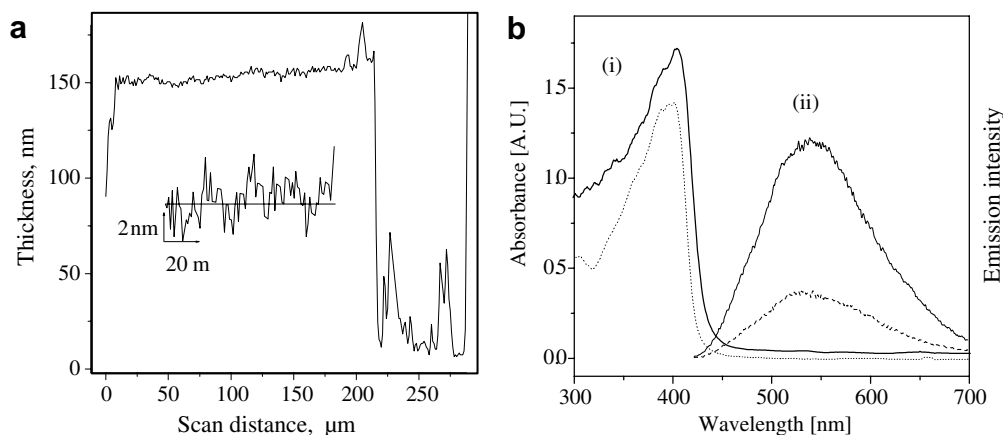


Figure 3. (a) Thickness and roughness of the PMAAn film deposited on a quartz from a surface profiler. (b) Absorption spectrum of the PMAAn film compared to that of the PMAAn in solution (dotted) (i); and emission spectra of the PMAAn film before (solid) and after (dotted) UV exposure for 3 min (ii).

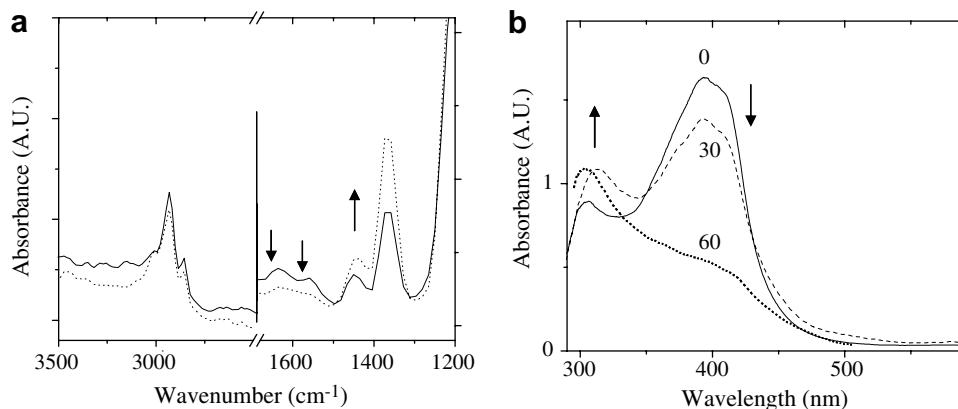


Figure 4. (a) FT-IR spectra for PMAn film before irradiation (solid line) and after irradiation with a UV light for 30 min (dotted line). (b) UV spectral change of PMAn film: before irradiation (solid line) and after irradiation with a UV light for 30 min (dotted line) and 60 min (dashed line).

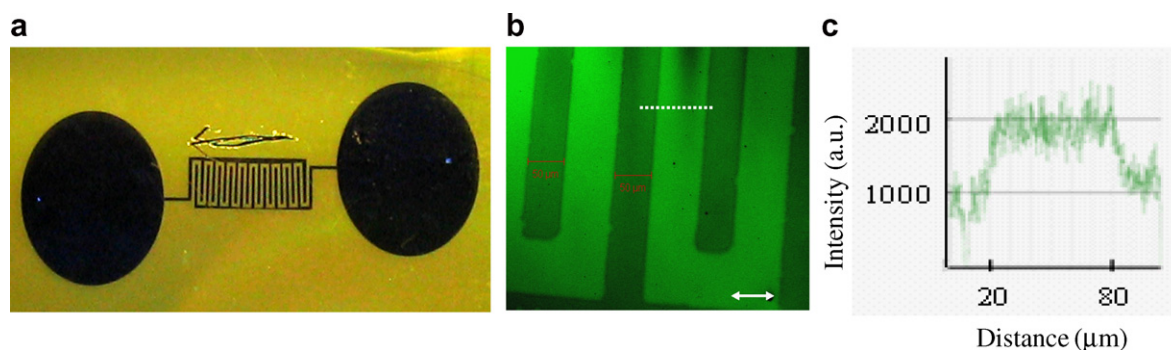
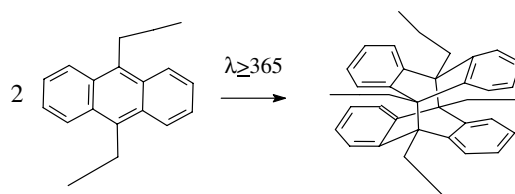


Figure 5. (a) Photograph of a gap electrode pattern on a PMAn film by UV exposure for 30 min (diameter of the circle = 0.3 cm). (b) A confocal macroscopic image of the gap electrode pattern of (a). The scale bar in (b) corresponds to 50 μm . (c) The intensity of fluorescence at the wavelength of 500 nm probed at a patterned region in the white dotted bar of (b).

consists of bright (UV shaded) and dark area (UV exposed for 30 min). The film shows uniformity in the whole area and homogeneity in their fluorescence intensity as examined by a confocal microscope. Figure 5b shows the patterned area where the gap between dark and bright region corresponds to the mask gap. Figure 5c shows the intensity of fluorescence at the wavelength of 500 nm probed at a patterned region in the white dotted bar of Figure 5b. The intensity of the 488 nm fluorescence in the UV exposed area is $\sim 50\%$ compared to UV shaded area. Besides, the resulting fluorescence intensity of step pattern distance corresponds to 50 μm which depicted in Figure 5a and b.

During the photodimerization of anthracene, the larger van-der Waals inter-molecular spacing (distance $>3.4 \text{ \AA}$) between the anthracene units is replaced by the smaller intra-molecular covalent bond (C–C 1.54 \AA), as shown in Scheme 2 for $4\pi+4\pi$ cycloaddition as an example. Thus photodimerization of anthracene results in volume shrinkage and generates thickness variation along the pattern. Indeed the average depth of the periodic pattern was determined as $\sim 8 \text{ nm}$ (5% shrinkage) by an Alpha-step profilometer from the above pattern. The average step depth of the pattern was 14 nm from the film of 101 nm thickness. The pattern formed on the PMAn film did not show any indication of decomposition



Scheme 2. Photodimerization of anthracene polymers.

under ambient condition. When the film was irradiated for 1 h, the depth becomes larger as compared in Figure 6c. Such an optical and physical step formation by the photodimerization of anthracene from the polymer film could be extended for the preparation of various fabrication and fluorescent imagings as a dry patterning process.

In conclusion, we have synthesized and characterized a new highly fluorescent anthracene polymer (PMAn) using the Friedel–Crafts alkylation reaction. This polymer showed good solubility, thin film-forming ability and patternability. The absorption and emission spectra showed that the active chromophores in the polymer are anthracene. The fluorescence quantum efficiency of PMAn in solution was 0.8, which is higher than that of the monomeric anthracene analogue in solution and

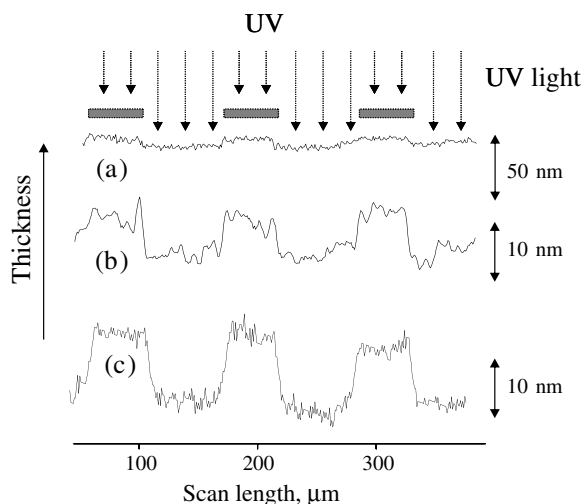


Figure 6. (a) Depth of the pattern formed from the PMAn film exposed to UV lamp under the photomask for 30 min (thickness of the film = 151 nm, same film used for Fig. 5). (b) Expanded scale in y axis of (a). (c) Depth of the pattern formed from the PMAn film exposed to UV for 1 h (thickness of the film = 101 nm).

much higher than that of other anthracene polymers reported in the literature. The PMAn film could be patterned with UV light, resulting in fluorescent pattern with a pattern depth of 8–14 nm depending on exposure time. Further works based on anthracene polymer are in progress to explore in fluorogenic sensors and switches.

3. Experimental methodology

3.1. Materials

Anthracene (Aldrich), 9-methyl anthracene (Aldrich), chloromethyl methyl ether (CME), titanium(IV) chloride in toluene (Aldrich), ferric(III) chloride (Aldrich), anhydrous dichloromethane (Aldrich), methyl alcohol (Duksan chemicals, Korea) and other chemicals were purchased and used as received.

3.2. Polymerization of anthracene with CME

In a three-neck round bottomed flask with magnetic bar arrangement, anthracene (1.06 g, 6 mmol) was dissolved in anhydrous dichloromethane (50 mL) at 0 to -10 °C followed by drop-wise addition of CME (1.5 mL, 18 mmol) under nitrogen atmosphere. The mixture was stirred for 20 min at 0 °C and then the solution of FeCl_3 (0.6 mmol, 4 mmol) in CH_2Cl_2 was added drop by drop to the reaction mixture at 0 °C under a nitrogen atmosphere. After completion of the addition, the reaction mixture was stirred at ambient temperature in a nitrogen atmosphere attached with a water condenser. During addition of FeCl_3 , the reaction mixture turns to green. After stirring for 48 h at ambient temperature, the reaction mixture was washed with distilled water several times. The organic phase was dried with MgSO_4 and concentrated by a rotary evaporator. The mixture was

poured into excess of methanol to afford yellow colored solids. Filtration followed by recrystallization from methanol yielded yellow sponge solids of PMAn with 70% isolation yield. GPC(THF): $M_w = 4950$ ($M_w/M_n = 2.78$), FT-IR: 780 cm^{-1} ($\nu_{\text{C-O-C}}$, stretch), $1450\text{--}1350$, 1631 , and 1577 cm^{-1} (anthracene unit), $2995\text{--}2850\text{ cm}^{-1}$ (aliphatic CH_2 stretch), and 3051 cm^{-1} (aromatic C–H stretch); $^1\text{H NMR}$ (CDCl_3 , ppm): CH_2 (s, attached to aromatic carbon, 4.2 ppm), 7.44–8.52 ppm (m, 8H, aromatic protons of anthracene). A similar reaction was carried out with titanium(IV) chloride to yield a 50% anthracene polymer: GPC (THF): $M_w = 2178$ ($M_w/M_n = 1.59$).

3.3. Instruments and film characterization

^1H spectrum was determined on a Bruker ARX-400 spectrometer. FT-IR spectra were obtained from a Bio-Rad Digilab Division FTS-80. The average molecular weight of the polymer was characterized by gel permeation chromatography (GPC) (model: Waters R-401 ALC/GPC) with THF as an eluent and polystyrene standard for calibration. UV spectra were obtained from a Guided Wave model 260 (Guided Wave, Inc., USA). Fluorescence was measured with luminescence spectrometer (Perkin–Elmer, Model LS55). The molar concentrations of the anthracene polymer (PMAn) in the UV and emission spectra were based on the monomeric unit, methylene anthracene ($\text{CH}_2\text{-C}_{14}\text{H}_9$), to compare the spectral properties of the monomer (anthracene). The thickness of the PMAn film was determined via an Alpha-step profilometer (Tencor Instruments, Alpha-step IQ) with an accuracy of 1 nm. For the spectroscopic measurements, the PMAn films on quartz plates were prepared by spin coating the PMAn in chloroform solution. The thin films were dried in vacuo at 50 °C to remove the residual solvent. The thickness of the film was $1.5\text{ }\mu\text{m}$ for the UV–vis and fluorescence measurement (Figure 3b). The polymer films were illuminated with a high-intensity UV lamp (Spectroline, USA, 40 mW/cm^2), model ENF-260/FE for the pattern experiments through a photomask. The pattern in the PMAn film was examined by a digital camera (Model: Canon Power Shot A640) under UV exposure (10 mW) and a confocal microscope (Carl Zeiss, Inc., LSM 510 META) under the excitation at 405 nm.

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