

## Luminescence Properties of Anthracene Chromophores in Cyclosiloxane-Based Hybrid Polymer Films

Ali Demirci,<sup>§</sup> Shunsuke Yamamoto,<sup>§</sup> Jun Matsui,<sup>†</sup> Tokuji Miyashita,<sup>§</sup> and Masaya Mitsuishi<sup>§\*</sup>

<sup>§</sup>Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan. <sup>†</sup>Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, 1-4-12 Kojirakawamachi, Yamagata 990-8560, Japan.

**ABSTRACT:** Luminescence properties of anthracene chromophores were investigated. Anthracene chromophores were incorporated in cyclosiloxane-based hybrid polymers through one-pot hydrosilylation reaction. Using four-armed cyclosiloxanes, divinyl-terminated siloxane monomers, and 9-vinylantracenes, anthracene-labeled hybrid polymers were prepared. Free-standing hybrid polymer films were prepared successfully by doctor-blade method and thermal treatment. The polymer films exhibit strong blue fluorescence from anthracene and its fluorescence lifetime was not influenced by the temperature, indicating that the movement of anthracene chromophores was restrained in cyclosiloxane-based hybrid polymer films.

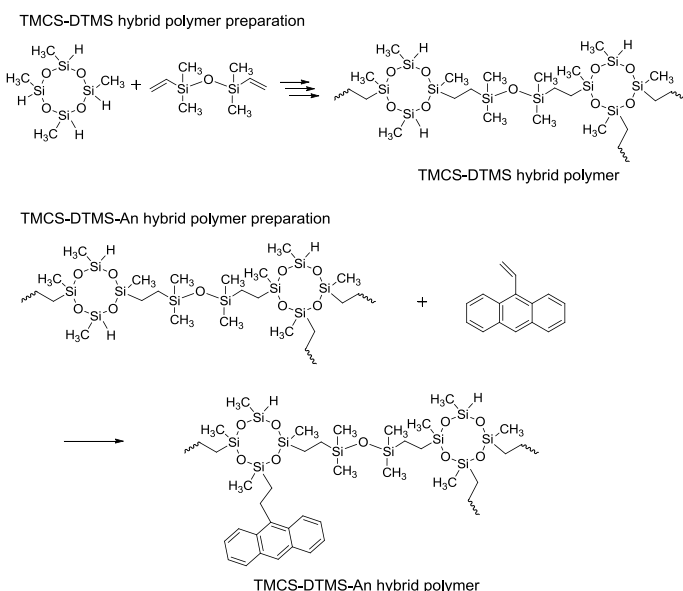
Organic photonics and electronics have attracted much attention.<sup>1,2</sup> The enrichment of organic materials is beneficial to developing organic optoelectronics device applications. The ease of preparation also makes the organic device applications more attractive. Anthracene and its derivatives are good examples of organic optoelectronic device applications such as organic light emitting diodes, organic thin-film transistors, and photovoltaic cells.<sup>3-6</sup>

Electronic devices consist of several electronic components. For example, organic light emitting diodes have electrodes, substrates, and emission layers including hole and electron transport layers. In terms of materials chemistry, both inorganic and organic materials are involved in the system. Metal oxides such as silica and titania are well known matrices for this demand. They serve as good insulating layers as well as optical transparent waveguides.<sup>7-9</sup>

Development of organic and inorganic hybrid materials preparation enables us to combine inorganic and organic components at the molecular level. In fact, luminescent chromophores are incorporated in inorganic matrices through sol-gel method.<sup>10,11</sup> Understanding the relationship between chromophores and the matrices will contribute the development of fundamentals and applications<sup>12</sup> of functional organic and inorganic hybrid materials.

We successfully obtained optically transparent, robust, free-standing hybrid polymer films based on cyclosiloxane monomers.<sup>13</sup> Using four-armed cyclosiloxanes (1,3,5,7-tetramethylcyclotetrasiloxane (TMCS) in Scheme 1) as a building block, we prepared chemically soluble and processable linear hybrid polymers. Because of multifunctionality of TMCSs, hybrid polymers make it possible to undergo crosslinking through multi-step thermal treatment. The salient benefits of cyclosiloxane-based polymers are the following: (1) multifunctional cyclosiloxane groups allow various types of functionalization through covalent chemical bonding; and

### Scheme 1. One-pot synthesis of TMCS-DTMS-An hybrid polymer.



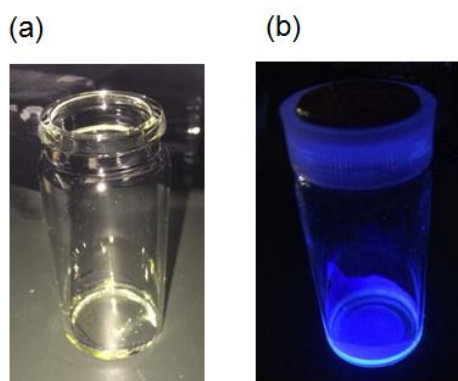
(2) the reaction proceeds in a one-pot process. Subsequent purification is another benefit of hybrid polymers to remove unreacted monomers and catalysts.

Herein we prepared anthracene-labeled hybrid polymers through one-pot, two-step hydrosilylation reaction (Scheme 1). At the first step, the TMCS-DTMS polymer was synthesized using the one-pot hydrosilylation reaction of TMCS with di-vinyl terminated 1,3-divinyltetramethylsiloxane (DTMS) monomer. To avoid gelation in hydrosilylation of four functional TMCS monomers, the total monomer concentration in solution was set at 1 mol/L, and the monomer ratio of TMCS and DTMS was adjusted as 1 : 1. At the second step, 9-vinyl anthracene chromophores were incorporated in TMCS-DTMS hybrid polymers through one-pot hydrosilylation reaction. Anthracene containing TMCS-DTMS polymers (TMCS-DTMS-An hybrid polymers) were reprecipitated in acetonitrile and then stirred with active-carbon to remove Pt-catalyst and low-molecular-weight compounds. Colorless and liquid-viscous TMCS-DTMS-An hybrid polymers were obtained. TMCS-DTMS-An hybrid polymers were chemically soluble in toluene, chloroform, and tetrahydrofuran. The weight-average molecular weight ( $M_w$ ) and polydispersity index (PDI) of the polymer were determined as  $\sim 2 \times 10^4$  and  $\sim 3$ , respectively. To confirm the hydrosilylation reaction between residual Si-H groups and anthracene comonomers, we

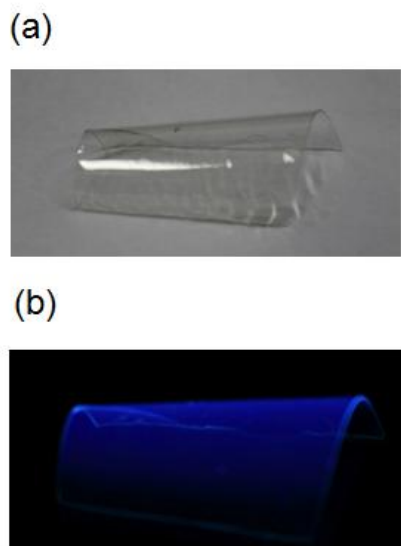
\*To whom correspondence should be addressed.

E-mail: masaya@tagen.tohoku.ac.jp

varied the molar ratio of 9-vinylanthracene to the residual Si-H groups from 1.4 to 9.6 mol%. Using  $^1\text{H}$  NMR, the integral ratio of the Si-H and  $\text{CH}=\text{CH}_2$  to Si- $\text{CH}_3$  was examined with the integral ratio of the anthracene protons to Si-H and  $\text{CH}=\text{CH}_2$  before and after the second-step functionalization. Results show that the vinyl peaks at 5.6–6.8 ppm disappeared in  $^1\text{H}$  NMR spectra when the mixing ratio of 9-vinylanthracene to residual Si-H groups was set at 1.4 %, 2.8 %, and 5.6 %, but that the vinyl peaks still remained at 9.6 %. This means that the maximum amount of residual Si-H groups of the TMCS-DTMS polymer, which can react with 9-vinylanthracene, is 5.6 %. In other words, 94 % of the Si-H groups still remain after introducing anthracene moieties into the TMCS-DTMS hybrid polymers.

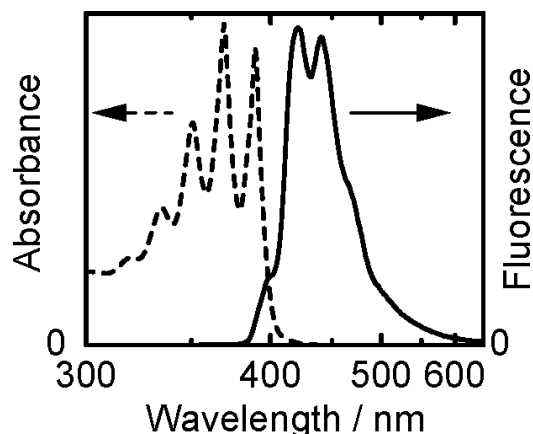


**Figure 1.** Photos of TMCS-DTMS-An hybrid polymers: (a) without and (b) with UV-light illumination. The mole content of 9-vinylanthracene is 5.6 %.



**Figure 2.** Photos of free-standing TMCS-DTMS-An hybrid polymer film: (a) without and (b) with UV-light illumination.

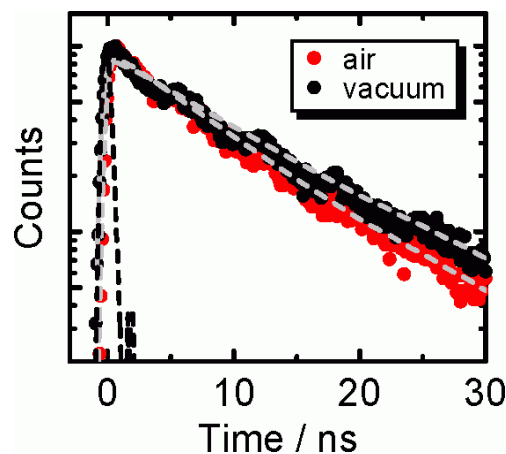
TMCS-DTMS-An hybrid polymer is transparent and viscous liquid; the polymer emits the blue light under UV irradiation (Fig. 1). TMCS-DTMS-An hybrid polymer was spread on a Kapton<sup>TM</sup> film by doctor-blading. Then the film was heated in air from room temperature to 60°C, then 100°C, 150°C, 200°C and finally 220°C. Residual Si-H groups undergo hydrolysis and self-condensation at air conditions: TMCS-DTMS-An hybrid polymers crosslink themselves and make a free-standing TMCS-DTMS-An hybrid polymer film.



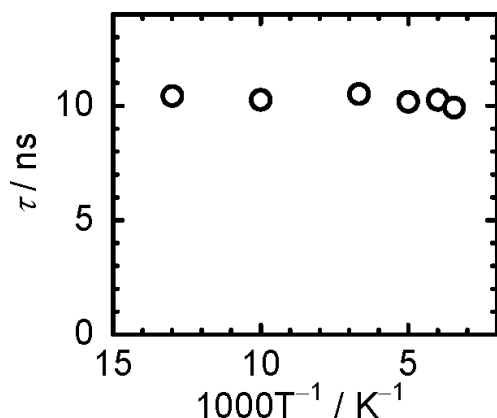
**Figure 3.** UV-Vis absorption and fluorescence spectra of TMCS-DTMS-An hybrid polymer film on cover glass substrate. Excitation wavelength is 340 nm.

A robust, flexible, and optically transparent TMCS-DTMS-An hybrid polymer (5.6% An content) film was obtained (Fig. 2). The film exhibits uniform fluorescence emission, indicating that anthracene chromophores tightly bound to the TMCS-DTMS hybrid polymer chains. Figure 3 shows UV-Vis absorption and fluorescence spectra of the TMCS-DTMS-An hybrid polymer film. The strong absorption band is seen at 350 nm. Compared with the fluorescence spectrum of TMCS-DTMS-An hybrid polymer film in the previous report,<sup>13</sup> no emission band appears at 390 nm, which corresponds to 0-0 band transition. This is because of the reabsorption<sup>14</sup> of anthracene chromophores in the TMCS-DTMS-An hybrid polymer film. Usually anthracene excimer is observed with broad structureless emission band at high concentration, however, the luminescence spectrum has no remarkable broad emission band at longer wavelength region. Anthracene chromophores are likely to be located uniformly in the TMCS-DTMS-An hybrid polymer film.

The information on fluorescence lifetime provides the details of the vicinity of anthracene chromophores. Figure 4 shows time-resolved fluorescence decay curves of the TMCS-DTMS-An hybrid polymer film. The fluorescence decay curves were obtained using a time-correlated single-photon counting system. The film was put in a optical cryostat (Optistat DN-V2, Oxford instruments plc). A pico-second pulsed Nd:YAG laser (355 nm, Leopard SS-10, Continuum) was used as an irradiation source and fluorescence was detected using a streak camera system (C4334, Hamamatsu Photonics) through optical fiber. As seen in Fig. 4, fluorescence from anthracene chromophores decays single-exponentially. The fluorescence decays



**Figure 4.** Time-resolved luminescence decay curves of TMCS-DTMS-An hybrid polymer films at room temperature.



**Figure 5.** Fluorescence lifetime of anthracene chromophores in the TMCS-DTMS-An hybrid polymer film as a function of reciprocal of temperature.

faster in air than in vacuum. Decay curves were fit with single-exponential function. The fluorescence lifetimes in air and in vacuum at room temperature were determined as 8.14 (ns) and 9.92 (ns), respectively. These lifetimes are longer than those of 9-vinylanthracene (5.53 ns) and anthracene (5.32 ns),<sup>15</sup> but are comparable to that of 9-ethylanthracene in toluene (9.2 ns).<sup>16</sup> Molecular oxygen is well known as an efficient quencher for aromatic hydrocarbons,<sup>17</sup> however, anthracene chromophores in the TMCS-DTMS-An hybrid polymer film are less sensitive to oxygen. The result indicates that cyclosiloxane-based hybrid polymers, i.e., TMCS-DTMS hybrid polymers serve as "solid" matrices.

Interestingly, the fluorescence lifetime is independent of surrounding temperatures (Fig. 5). The temperature was controlled from 77 K to room temperature. TMCS-DTMS-An hybrid polymer has flexible dimethylsiloxane units, however, the thermal crosslinking makes the TMCS-DTMS-An hybrid polymer be frozen even in room temperature. The increase in siloxane linkage from  $\text{RSiO}$  to  $\text{RSiO}_{1.5}$  or  $\text{RSiO}_2$  makes the film more rigid. For that reason, no significant change in the fluorescence lifetime was observed in the TMCS-DTMS-An hybrid polymer film.

In conclusion, the reactivity of anthracene monomers with TMCS-DTMS hybrid polymers was investigated. Residual Si-H groups of TMCS-DTMS hybrid polymers allow the hydrosilylation reaction with vinyl-terminated monomers, however, only 6 % of the residual Si-H groups underwent substituting with anthracene groups. The steric hindrance and reactivity of 9-vinylanthracene are the reason for the limitation. The result does not mean that the residual Si-H groups have the reaction limit. In fact all the Si-H groups can undergo hydrolysis and self-condensation under thermal treatment. In that sense, the substitution efficiency depends on the type of functional groups. The work on this issue is now in progress.

Luminescence properties of anthracene chromophores in TMCS-DTMS-An hybrid polymer films were also examined. No excimer emission band was observed in the fluorescence spectrum, indicating that anthracene chromophores are distributed uniformly in the TMCS-DTMS-An hybrid polymer film. The fluorescence lifetime was kept almost constant from 77 K to room temperature. The result reflects the hardness of crosslinked TMCS-DTMS-An hybrid polymer films, which restrains the molecular motion of covalently-bound anthracene moieties. Clear and homogeneous fluorescence was obtained from cyclosiloxane-based hybrid polymer films. Anthracene chromophores were incorporated in silsesquioxane<sup>12,18</sup> and silica matrices.<sup>19</sup> Cyclosiloxane-based hybrid polymers also afford high performance such as thermal stability ( $\sim 300^\circ\text{C}$ ) and robustness, which is beneficial to organic optoelectronic device applications.

**KEYWORDS:** Anthracene, Cyclosiloxane, Hybrid, Fluorescence

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