

# Reversible Self-Assembly of Entrapped Fluorescent Gelators in Polymerized Styrene Gel Matrix: Erasable Thermal Imaging via Recreation of Supramolecular Architectures

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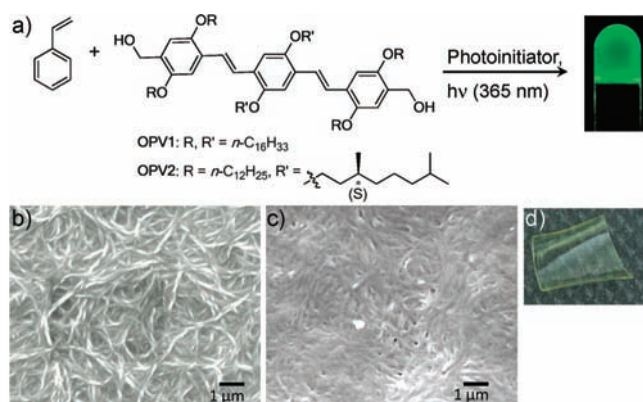
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Over the past three decades, supramolecular chemistry has matured from a conceptually marvelous scientific curiosity to a technologically relevant science encompassing the broad area of advanced materials.<sup>1,2</sup> Self-assembly of fluorescent molecules plays a central role in this area because of the inherent optoelectronic properties that are tunable by intermolecular interactions and external stimuli.<sup>3,4</sup> One of the applications of fluorescent molecular self-assemblies is in imaging.<sup>5,6</sup> The most striking advantage of fluorescence imaging is the prevention of photocopying and invisibility of the image under daylight. Herein we report a novel strategy for creating thermally writable, noncopyable, and erasable fluorescent images useful for secret documentation by using a fluorescent gelator entrapped in a polystyrene film prepared by gel-template-assisted polymerization.

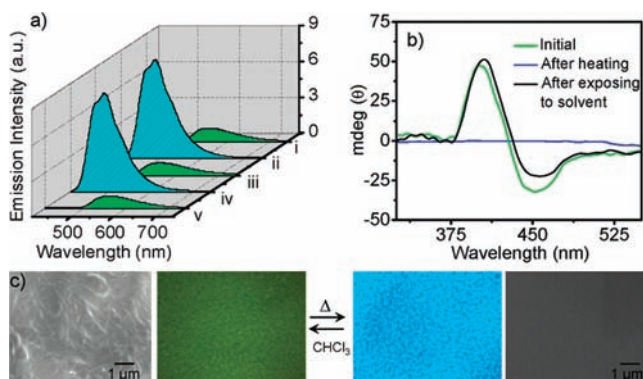
The oligo(*p*-phenylenevinylene) molecule **OPV1** reported earlier by us is an excellent gelator of nonpolar solvents.<sup>7,8</sup> Upon gelation, the strong blue fluorescence (450–500 nm) shifts to longer wavelength (550–650 nm) with significant quenching due to excited-state energy migration.<sup>8,9</sup> **OPV1** also forms a gel in styrene (1.1 mg/mL) with green emission [550–650 nm,  $\Phi_f = 0.19$ ,  $\tau_1 = 1.17$  ns (84%),  $\tau_2 = 3.08$  ns (16%)] that changes to a solution with blue emission (450–550 nm,  $\Phi_f = 0.69$ ,  $\tau = 1.63$  ns, monoexponential decay) upon heating.<sup>10</sup> Photopolymerization of the styrene gel using 365 nm light after adding a photoinitiator (2,2-dimethoxyphenylacetophenone, 0.1 wt %), resulted in a polystyrene (PS) monolith.<sup>11</sup> The polymerization was stopped when the molecular weight ( $M_w$ ) reached  $\sim 95\,000$  g/mol with a glass transition temperature ( $T_g$ ) of 107–109 °C. Scanning electron microscopy (SEM) images before and after polymerization showed the formation of supramolecular tapes with widths of 10–200 nm and lengths of micrometers that are trapped in the PS matrix (Figure 1b,c).

A film was prepared by dissolving the **OPV1**–PS in chloroform and drop-casting over a glass plate; this film appeared transparent with a pale-yellow color (under daylight) after the solvent was removed under vacuum at room temperature (Figure 1d). Upon excitation at 365 nm, the film showed a green fluorescence [550–650 nm,  $\Phi_f = 0.19$  (determined by the calibrated integrating sphere method),  $\tau_1 = 1.24$  ns (81%),  $\tau_2 = 2.88$  ns (19%)].<sup>10</sup> When the film was heated above the glass transition temperature of PS (110 °C) for a short period of time (2–5 s), an intense blue emission [450–550 nm,  $\Phi_f = 0.78$ ,  $\tau = 1.66$  ns (100%)] was obtained.<sup>10</sup> Upon exposure of the polymer film to chloroform vapor for 1 min, the green fluorescence [ $\Phi_f = 0.19$ ,  $\tau_1 = 1.24$  ns (81%),  $\tau_2 = 2.88$  ns (19%)] was regained.<sup>10</sup> This could be repeated for several cycles, indicating a reversible process [Figure 2a(i–v)]. Fluorescence microscopy and SEM images of the **OPV1**–PS film after heating and exposure to chloroform vapor are shown in Figure 2c.

In analogy to our previous reports on gelation of OPVs,<sup>8</sup> the above fluorescence change could be attributed to the reversible self-

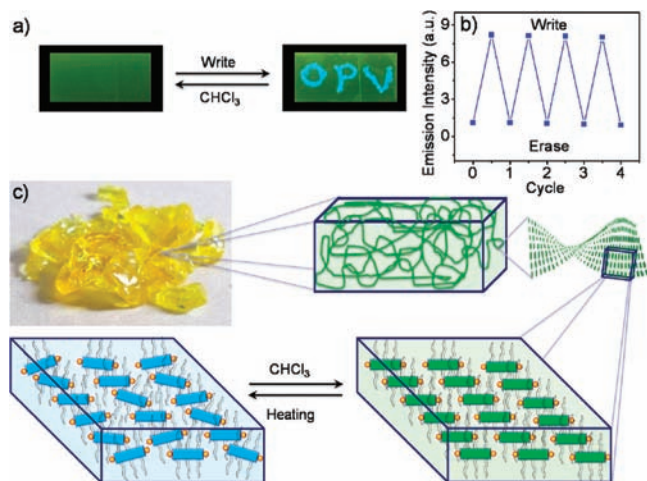


**Figure 1.** (a) Photopolymerization of a fluorescent gel of **OPV1** ( $1 \times 10^{-3}$  M) in styrene. (b, c) SEM images of **OPV1**–styrene xerogel (b) before and (c) after irradiation. (d) Transparent pale-yellow film of the polymerized **OPV1**–styrene gel under daylight.



**Figure 2.** (a) Fluorescence spectra of the **OPV1**–PS film ( $\lambda_{ex} = 390$  nm): (i) initial state, (ii) after heating to 110 °C, (iii) after exposure to chloroform vapor, (iv) after the second heating, and (v) after the second exposure. (b) CD spectra of the **OPV2**–PS film under different conditions. (c) Fluorescence and SEM images of the **OPV1**–PS film (left) before and (right) after heating.

assembly of **OPV1** in the PS matrix, as is clear from the SEM images in Figure 2c. To further establish this argument, we prepared a PS film with a chiral gelator, **OPV2**. Circular dichroism (CD) spectra of the **OPV2**–PS film exhibited a bisignate Cotton effect corresponding to the  $\pi$ – $\pi^*$  band with a zero crossing close to the absorption maximum at 400 nm, indicating a helical sense of the self-assembly. The absence of a CD signal after the film was heated suggests the disruption of the helical self-assembly.<sup>12</sup> Upon exposure to chloroform vapors, the CD signal was regained, indicating that the helical self-assembly was recreated (Figure 2b). The emission and CD signals could also be regenerated with vapors



**Figure 3.** (a) OPV1–PS film after thermal writing and erasing upon exposure to 365 nm UV light. (b) Fluorescence responses of the OPV1–PS film over four continuous cycles of writing and erasing. (c) Cartoon representation of the solvent-vapor-assisted reversible self-assembly of OPV1 in PS.

of CH<sub>2</sub>Cl<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, THF, and CCl<sub>4</sub>, whereas acetone, hexane, CH<sub>3</sub>OH, ethyl acetate, toluene, chlorobenzene, and dichlorobenzene did not show any considerable fluorescence regeneration effect.<sup>10</sup>

The reversible fluorescence color change of the OPV1–PS film was utilized to create images visible only under UV exposure (see the Supporting Information for a movie showing thermal writing and erasing).<sup>10</sup> Figure 3a shows an image that was thermally written using a soldering pen. The image was found to be stable over a temperature range of 10–50 °C and under sunlight.<sup>10</sup> The image could be erased by exposing the film to chloroform vapor for 1 min. The writing and erasing could be done several times without much loss of the intensity of the emission, as shown in Figure 3b. Since the background and the image were both fluorescent, the image could not be photocopied, thereby preventing duplication of the document.

The mechanism of the rewritable imaging involves the reversible self-assembly of OPVs in the PS film. When heated above  $T_g$ , the film softens, and the thermal energy induces breakage of the initially formed OPV self-assembly with green emission into individual molecules with strong blue emission. Upon exposure to chloroform vapors, the film allows the reassembly of the OPV molecules, regenerating the green emission. Since chloroform is a good solvent of PS, the polymer film is softened by the solvent vapors, which allows the gelator molecules to recreate the self-assembly. Exposure of the OPV–PS film to the solvent vapors creates a situation similar to a high concentration of OPVs in the solvent. For an efficient reassembly, it is important to use a solvent with a high vapor pressure that is also a good solvent for the PS film, at the same time facilitating the self-assembly of OPVs. Chlorinated solvents with high vapor pressures are suitable for this purpose.

The novelty of the described gelation-assisted template polymerization approach is apparent from the fact that a composite film of OPV1 dispersed in a commercial PS ( $M_w = 88\,500$  g/mol) by a simple mixing did not work well. In this case, the film was nontransparent, and the reversible fluorescence changes were inefficient.

In conclusion, we have demonstrated gelation-assisted trapping of fluorescent supramolecular architectures in a polymer film and its application in erasable thermal imaging. Since the fluorescence of the unimaged area is weak and that of the imaged area is strong, high-contrast imaging can be achieved. Solvent-vapor-assisted recreation of self-assembly in a polymer matrix and its demonstration in rewritable, noncopyable fluorescent imaging opens a new window for the application of fluorescent molecular gelators.

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**Supporting Information Available:** Details of the preparation of the polymer composite; differential scanning calorimetry, absorption and emission, spectral changes, quantum yields, fluorescence lifetimes, gelation, and solvent effect; and a movie file showing the thermal writing and erasing (AVI). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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