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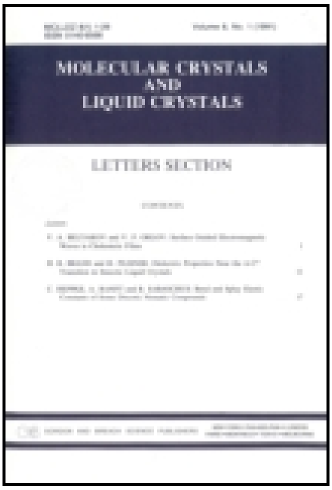

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Detection of Ethylenediamine Using a Fluorescent Probe in Solution and in a PMMA Matrix

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*Fluorescent 3′,6′-bis(octyloxy)-*p*-terphenyl-4,4′-dialdehyde* ***3*** *has been successfully synthesized via a Suzuki cross-coupling reaction of the corresponding dibromo compound with a boronic acid compound in the presence of palladium catalyst. The fluorescent probe molecule has aldehyde groups at both ends, which can be used as reactive sites for amines. Alteration of emission is expected by an interaction of* ***3*** *with amines, specifically ethylenediamine, which can be a measure of amine concentration. Moreover, uniform-sized poly(methyl methacrylate) (PMMA) particles were prepared to use as a probe matrix and* ***3*** *was incorporated in the PMMA particles during dispersion polymerization, which can be a sensitive and selective sensor platform for ethylenediamine.*

Keywords Sensors; fluorescence; fluorescent probe; aldehyde; amine sensing; dispersion polymerization; PMMA matrix

Introduction

Much research in biochemistry requires highly sensitive and selective analytical methods for the determination of amines such as amino acids, peptides, biogenic amines, and organic amines. Several techniques for the determination of amines have been investigated intensively in the literature including chromatography, electrophoresis, and fluorescence detection [1–5].

In particular, fluorometric analysis for accurate detection has attracted much attention in recent years. Fluorescent sensing and probing based on organic compounds represent unique classes of detection techniques, which feature simple methods for chemical or biological detection and analysis. Thus, fluorometric analysis requires highly sensitive and selective fluorescent probes. For these reasons, fluorescent probes demonstrate changes, such as enhancement or quenching of fluorescence, upon exposure to external stimuli [6–16].

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In this work, we report the synthesis of a fluorescent organic probe having aldehyde functional groups that are capable of reacting with amine groups in a target molecule. The synthesis was carried out via a palladium-catalyzed Suzuki cross-coupling reaction using the corresponding dibromo compound and a boronic acid. The fluorescent organic probe exhibited high sensitivity and selectivity for ethylenediamine (ED) among various organic amine compounds both in solution and in a PMMA matrix. Because of widespread use of primary amines including ED in pharmaceutical industries, polymer industries, and dye manufacturing, it is highly demanding to develop new and efficient detection techniques for aliphatic amines [17].

Experimental

Reagents and Instrumentation

Hydroquinone, potassium hydroxide, and potassium carbonate were purchased from Duksan. All other chemicals were purchased from Aldrich and used without further purification. ^{1}H NMR spectra were obtained with a Bruker DRX-300 spectrometer (Korea Basic Science Institute). The elemental analysis was performed with a CE Instruments EA-1110 elemental analyzer. FT-IR spectra were obtained using a Bruker Tensor 27 spectrometer. The particle images were observed by FE-SEM (Hitachi S-4800). UV-vis absorption spectra were recorded on a PerkinElmer Lambda 35 spectrometer. Photoluminescence spectra were obtained using a Varian Cary Eclipse equipped with a xenon lamp excitation source.

Synthesis of 1,4-Bis(octyloxy)benzene (1)

Hydroquinone (10 g, 90.82 mmol), potassium hydroxide (20 g, 356.44 mmol), and DMSO (200 ml) were added to a 500 mL flask with a reflux condenser. Then 1-bromooctane (34.51 ml, 200 mmol) was added to the mixture. The reaction was carried out at 85°C for 4 h and then the mixture was poured into distilled water. The crude product was washed with ethanol, isolated by filtration and purified by recrystallization from ethanol to yield 13.2 g (44%) of **1**. ^{1}H NMR (300MHz, $CDCl_3$) $\delta_{\mathrm{ppm}} = 6.83$ (s, 4H), 3.93–3.89 (t, 4H), 1.81–1.71 (m, 4H), 1.47–1.40 (m, 4H), 1.32–1.29 (m, 16H), 0.92–0.87 (t, 6H).

Synthesis of 1,4-Dibromo-2,5-bis(octyloxy)benzene (2)

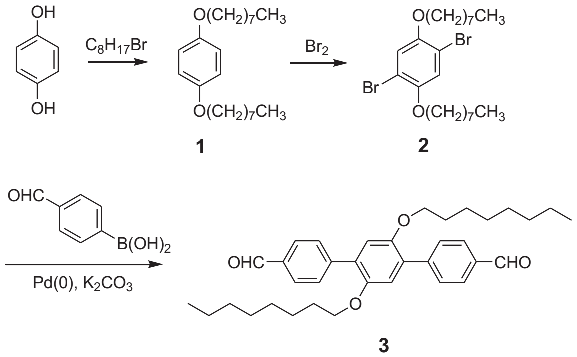
1 (6 g, 12.19 mmol) was dissolved in chloroform (20 ml) and placed in a 3-neck flask. A mixture of bromine (2 ml, 38.83 mmol) and chloroform (5 ml) was added to the flask dropwise at 0°C over 1 h. After 1 h, the temperature was increased to room temperature and the mixture was stirred for an additional 6 h and then quenched with $NaHSO_3$ solution (40 ml). The organic mixture was extracted with brine. The organic phase was dried over anhydrous $MgSO_4$, isolated by filtration, and concentrated with a rotary evaporator. The crude product was recrystallized from n-hexane to yield 5.73 g (65%) of **2**. ^{1}H NMR (300MHz, $CDCl_3$) $\delta_{\mathrm{ppm}} = 7.09$ (s, 2H), 3.98–3.93 (t, 4H), 1.85–1.76 (m, 4H), 1.53–1.44 (m, 4H), 1.33–1.30 (m, 16H), 0.92–0.88 (t, 6H)

Synthesis of 3′,6′-Bis(octyloxy)-p-terphenyl-4,4′-dialdehyde (3)

2 (2.86 g, 5.81 mmol) and 4-formylphenylboronic acid (2.06 g, 13.74 mmol) were added to a flask with a reflux condenser under argon atmosphere. Toluene (40 ml), THF (14 ml), and an aqueous solution of 2 M K_2CO_3 (3 ml) were added to the flask and then two drops of aliquat 336 and tetrakis(triphenylphosphine)palladium(0) (0.35 g, 0.3 mmol) was added to the flask. The mixture was stirred at 85°C for 48 h. The reaction mixture was cooled to room temperature and poured into methanol. The crude product was washed with water and recrystallized from ethanol to yield 1.39 g (44%) of **3**. ^{1}H NMR (300MHz, $CDCl_3$) δ_{ppm} = 10.1 (s, 2H), 7.96–7.94 (d, 4H), 7.79–7.77 (d, 4H), 7.02 (s, 2H), 3.98–3.93 (t, 4H), 1.75–1.66 (m, 4H), 1.38–1.25 (m, 20H), 0.90–0.86 (t, 6H). FT-IR (KBr pellet, cm^{-1}): 2916 (sp^3 C—H), 1701 (C=O), 1053 (C-O). Anal. Calc. for $C_{36}H_{46}O_4$: C, 79.67%; H, 8.54%. Found: C, 79.92%; H, 8.54%.

Dispersion Polymerization of Crosslinked PMMA and in situ Embedding of 3 (3@PMMA)

3 (0.02 g, 0.04 mmol), methyl methacrylate (5.4 ml, 70.42 mmol), and AIBN (50 mg, 0.3 mmol) were placed in a double-wall glass reactor. Poly(vinyl pyrrolidone) (PVP, 3 g) was dissolved in a mixture of water (24 ml) and methanol (96 ml). A portion of the PVP solution (52 ml) was added to the reactor and the mixture was stirred at 60°C. A crosslinking agent, ethylene glycol dimethacrylate (EGDMA, 1.8 ml, 6.89 mmol) and another portion of the PVP solution (26 ml) were added to the reactor dropwise over 2 h. The reaction proceeded for 24 h at 60°C. After the polymerization, the mixture was poured into excess methanol. The particles were obtained by centrifugation, washed with methanol, and, finally dried *in vacuo* to yield 1.53 g of **3**-embedded crosslinked PMMA particles with uniform size. Scheme 1. 1,4-Dibromo-2,5-bis(octyloxy)benzene **2** can be



Scheme 1. Synthetic route for probe molecule **3**.

Sensing of Organic Amine Compounds

Organic amine compounds such as triethylamine, aniline, 2-aminophenol, hexamethylenediamine, and ED were exposed to **3** in DMSO solutions (1.0×10^{-5} M). For the case of sensing with **3** in PMMA particles, organic amine compounds were added to the solutions of **3**-embedded PMMA (10 mg) dispersed in DMSO. In all cases, the resulting mixtures were analyzed after 24 h with UV-vis and fluorescence spectroscopy in a 10 mm quartz cuvette.

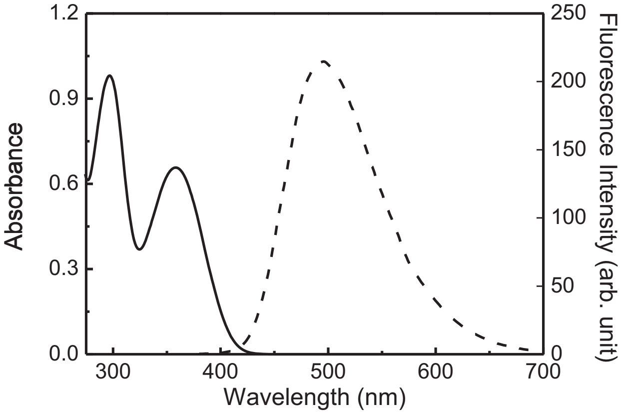
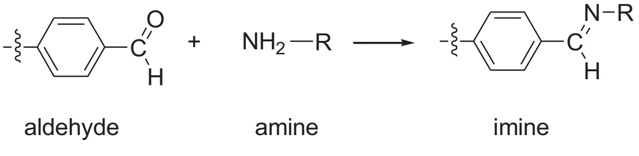


Figure 1. Absorption (solid) and (b) fluorescence (dashed) spectra of **3** in DMSO (1.0 × 10^{-5} M). Excitation corresponds to absorption maximum.

Results and Discussion

The synthetic route for amine-probing molecule **3** is demonstrated in synthesized from 1,4-bis(octyloxy)benzene **1** via bromination according to the literature procedures [18–21]. 3′,6′-Bis(octyloxy)-p-terphenyl-4,4′-dialdehyde **3** was synthesized by a palladium-catalyzed Suzuki cross-coupling reaction of **2** and 4-formylphenylboronic acid with a yield of 44%. The chemical structure of **3** was identified using ^{1}H NMR, IR, and elemental analysis, confirming the presence of aldehyde functional groups to be used for reaction with amines. The optical properties of **3** in DMSO solution (1.0 × 10^{-5} M) were investigated using absorption and fluorescence spectroscopy. As shown in Fig. 1, the probe molecule **3** has two absorptions at 297 and 358 nm and an emission band at 496 nm with bluish green emission.

With these chemical features and optical characteristics of **3** in mind, reaction-based detection of various organic amine compounds was investigated. As already reported, primary amines react rapidly with aldehyde to form imine compounds (see the equation below). Thus, a probe molecule containing aldehydes that are connected with a conjugated system can react with amines to form the imine compounds, which, in turn, alter the emission property of the probe molecule.



As shown in Fig. 2a, several organic amine compounds with different structures were exposed to **3** in DMSO solution. It was found that ED can interact with **3**, accompanied by an emission that was blue-shifted from 496 nm to 436 nm. Other amine compounds did not alter the emission of **3**, because ED had two more reactive primary amines compared with the other amines. The emission color change can be observed with the naked eye, as shown in Fig. 2b. It seems that this phenomenon was caused by shortening of the conjugation length, which was induced by reaction of the amine groups of ED and aldehyde groups of **3**. For this reason, a blue-shift of the emission was observed with a slight increase in emission intensity.

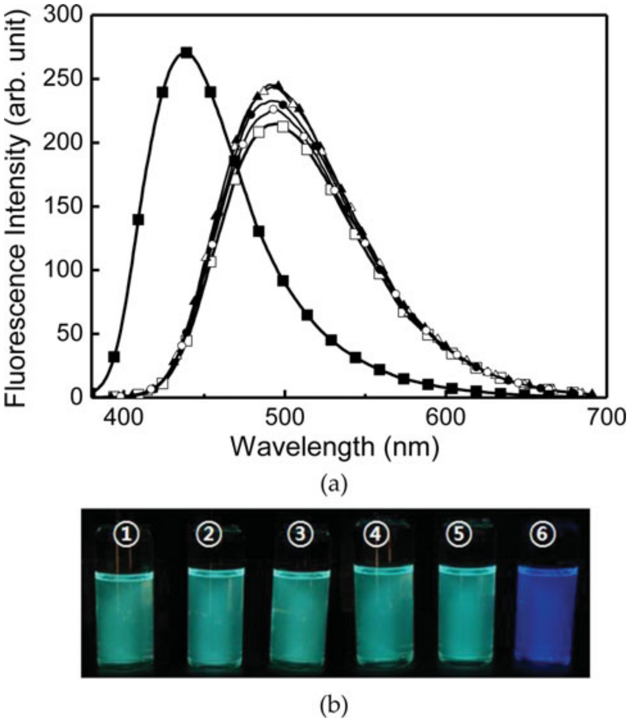
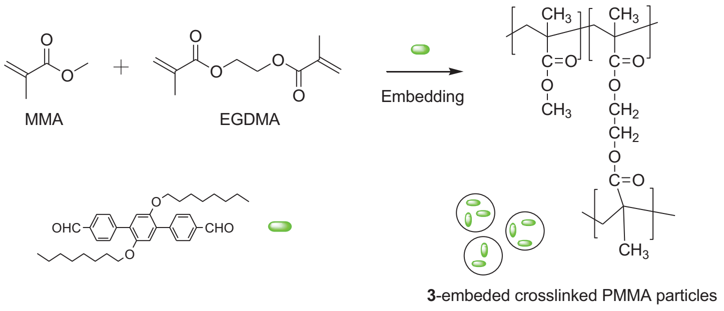


Figure 2. (a) Fluorescence spectra and (b) photograph of **3** (1.0×10^{-5} M) after addition of organic amine compounds (10 equiv) in DMSO. (□,①: **3**; ▲,②: **3** + triethylamine; △,③: **3** + aniline; ◆,④: **3** + 2-aminophenol; ◇,⑤: **3** + hexamethylenediamine; ■,⑥: **3** + ethylenediamine).

The emission of **3** gradually changed as the concentration of ED increased, as shown in Fig. 3a. As the concentration of ED increased, both a decrease in the fluorescence intensity at 496 nm and a subsequent increase in the emission at 436 nm were observed. As ED (2.0×10^{-5} M) was added to **3**, very small decrease in fluorescence intensity was observed as well as emission shift to shorter wavelength, implying that the reaction between aldehyde groups in **3** and amines took place. The changes in emission were saturated at around 24 h, presumably because of the characteristics of the reaction-based system.



Scheme 2. Crosslinked PMMA embedded with **3** during dispersion polymerization.

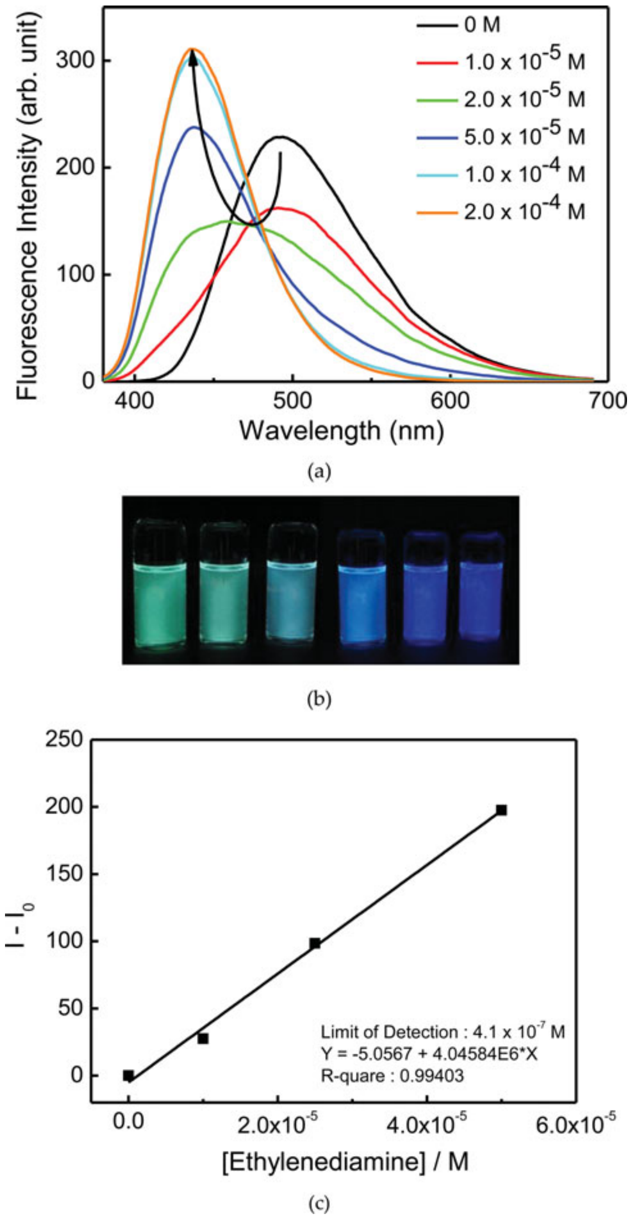


Figure 3. (a) Fluorescence spectra and (b) photographs of **3** (1.0×10^{-5} M) as a function of ethylenediamine concentrations (from left to right: 0; 1.0×10^{-5}; 2.0×10^{-5}; 5.0×10^{-5}; 1.0×10^{-4}; 2.0×10^{-4} M) in DMSO. (c) Change of fluorescence intensity of ($I–I_o$). I_o and I correspond to the intensity at 436 nm before and after addition of ethylenediamine, respectively.

Figure 3b shows photographs of the continuous transformation in emission color from green to blue. Figure 3c shows that the linear correlation between the change in fluorescence intensity at 436 nm and the concentration of ED ($R = 0.994$). The limit of detection (LOD, 3σ/slope) was found to be 4.1×10^{-7} M, as estimated according to a previously reported

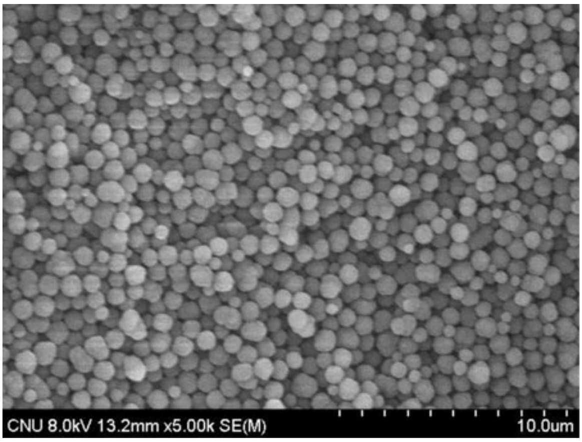


Figure 4. SEM image of crosslinked PMMA particles embedded with **3** (**3**@PMMA).

method [22, 23]. Thus, it can be concluded that the probe molecule **3** has good sensitivity as well as selectivity toward ED.

Using the probe molecule **3** in the solid state, versatile detection applications can be carried out. A possible approach can be accomplished using PMMA particles as the host matrix. As shown in Scheme 2, **3** was incorporated into the PMMA matrix during

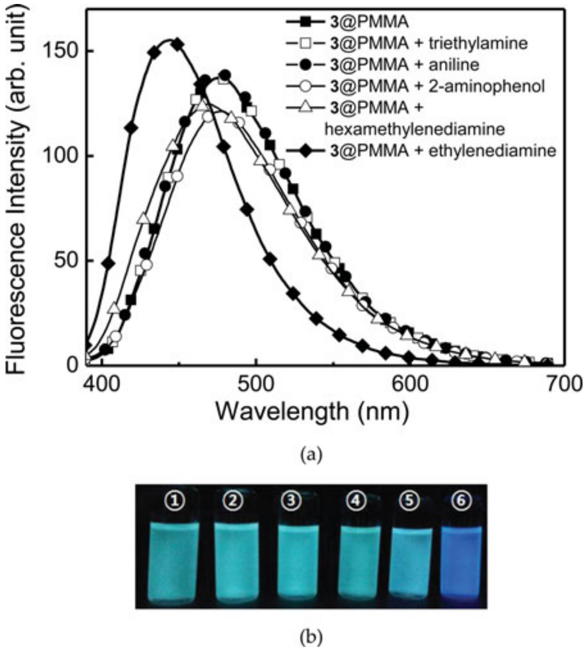
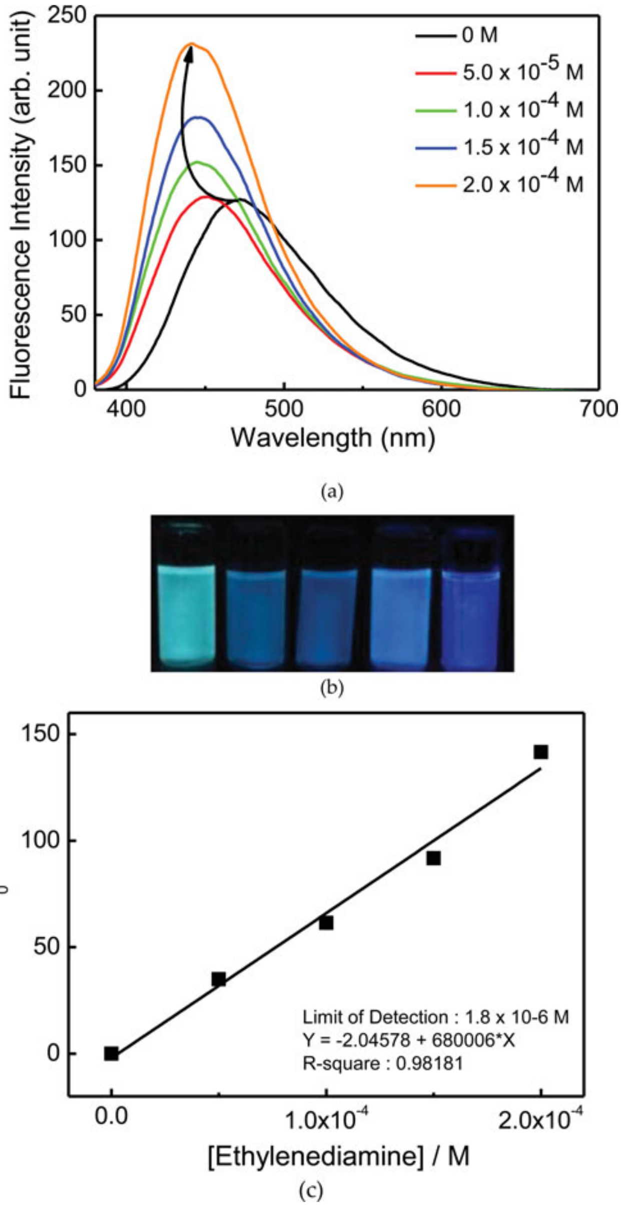


Figure 5. (a) Fluorescence spectra and (b) photographs of crosslinked PMMA particles (10 mg) embedded with **3** after addition of organic amine compounds (1.0×10^{-4} M) in DMSO. (■,①: **3**; □,②: **3** + triethylamine; •,③: **3** + aniline; ○,④: **3** + 2-aminophenol; △,⑤: **3** + hexamethylenediamine; ♦,⑥: **3** + ethylenediamine).



(a)

(b)

(c)

Figure 6. (a) Fluorescence spectra and (b) photographs of **3**-doped PMMA particles (10 mg) as a function of ethylenediamine concentration (from left to right: 0; 5.0×10^{-5}; 1.0×10^{-4}; 1.5×10^{-4}; 2.0×10^{-4} M) in DMSO. (c) Change of fluorescence intensity of ($I–I_o$). I_o and I correspond to the intensity at 436 nm before and after addition of ethylenediamine, respectively.

dispersion polymerization of PMMA and crosslinking agent EGDMA. The crosslinked PMMA particles were found to be uniform and spherically-shaped with a diameter of about 750 nm, as shown in the SEM images (Fig. 4). **3** embedded in the crosslinked PMMA (**3**@PMMA) showed emission at 476 nm, which was blue-shifted compared with the emission in the solution.

Upon exposure to various organic amine compounds, **3**@PMMA was responsive only to ED, similar to the case of detection in solution (Fig. 5a). Thus, a blue-shift of emission (476 nm to 445 nm) with a slight increase in emission of **3**@PMMA was observed, in which other organic amine compounds did not induce noticeable changes. An emission color change can be clearly observed under UV irradiation (Fig. 5b).

It should be noted that **3**@PMMA particles showed a blue-shift and increased fluorescence intensity change as the concentration of ED increased (Fig. 6a), and an intensified blue emission was observed (Fig. 6b). The LOD can be calculated via the relationship of emission intensity of **3**@PMMA ($R = 0.98$) and the concentration of ED (Fig. 6c) and was found to be 1.8×10^{-6} M, which shows a less sensitive detection compared with the detection in solution, presumably because of a possible difficulty in the penetration of ED through PMMA.

Conclusion

We have synthesized an organic fluorescent probe **3** having aldehyde functional groups that are capable of reacting with amine groups. The emission changes of **3** were investigated upon exposure to various amines in DMSO solution. **3** exhibited a response to ED in terms of blue-shifted emission, in which the intensity was proportional to the concentration of ED. Moreover, when **3** was embedded in crosslinked PMMA particles, it showed an alteration in emission color similar to the case in the solution. It seems that amine groups in ED played an important role in the reaction with aldehyde groups in **3** and, in turn, the altered conjugation produced a blue-shift in the fluorescence.

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