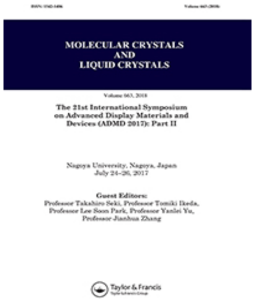

Molecular Crystals and Liquid Crystals

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# Synthesis of multifunctional monomers for patterning pixel define layer of organic light emitting diode

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**ABSTRACT**
Organic light emitting diode (OLED) is widely used as displays for small devices like cellular phone, tablet and wearable devices as well as large devices like TV. Photolithography utilizing black negative-tone photoresist is the vital process for patterning the black pixel define layer (PDL). In this work we report the syntheses of thermally-stable multifunctional monomers and evaluation of their contribution to the patterning of black PDL in OLED panel.

**KEYWORDS**
Multifunctional monomer; negative tone photoresist; organic light emitting diode; photolithography; pixel define layer

## 1. Introduction

It is well known that the visibility of organic light emitting diode (OLED) display is better than that of thin film transistor liquid crystal display (TFT-LCD), since OLED is self-emitting device while TFT-LCD has non-emitting mechanism [1, 2]. However, it is still necessary to increase the visibility of OLEDs, especially when used outdoors. The main reason for reduced outdoor visibility of the OLED is the reflection of ambient light from the OLED panel. So that the ¼ λ polarizing film is inserted and black matrix (BM) patterns are fabricated on top of the thin film encapsulation (TFE) layer of OLED panel [3∼5], as shown in Fig. 1.

The emission of separate red, green and blue light from the pixels of OLED becomes possible by fabrication of rectangular parallelepiped microstructures on the pixel define layer (PDL) of OLED panel. This process is currently carried out by the photolithographic method including coating of positive-tone photosensitive polyimide, UV exposure through the fine photomask followed by development with aqueous basic solution. The use of positive-tone photosensitive polyimide to make PDL pattern is not very effective in reducing the reflection of ambient light, since the color of polyimide PDL patteren is yellow to brown [6, 7]. In order to solve this problem a negative-tone photoresist containing black pigment was investigated in this work.

The black photoresist is composed of photoinitiator, photosensitizer, binder polymer, black pigment, dispersant and multifunctional monomer. The role of multifunctional monomer in the black photoresist is to make crosslinked structure in the UV light irradiated area of the spin coated black PDL. The multifunctional acrylate monomers such as pentaerythritol

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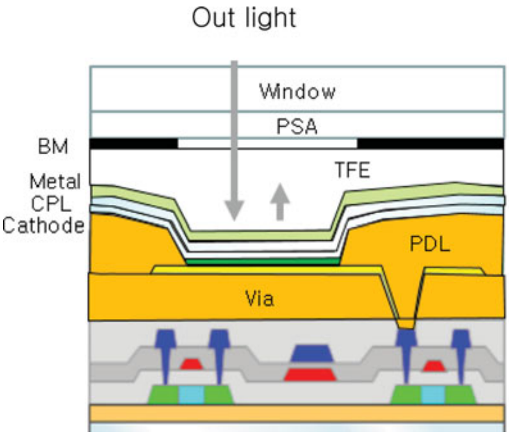


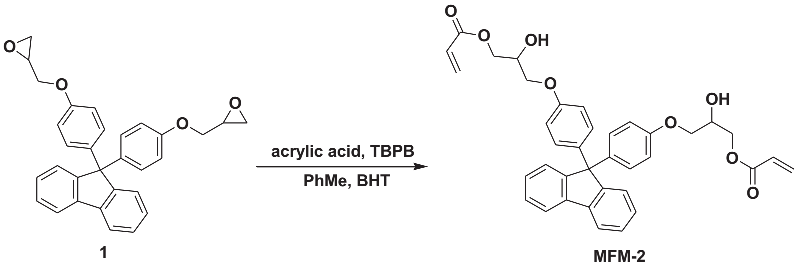
**Figure 1.** Illustration of PDL in OLED panel.

tetraacrylate (PETA) has been used for this purpose. However the thermal stability of the patterned black PDL is not high enough with the multifunctional monomer such as PETA. The black photoresist needs high thermal stability since the OLED panel fabrication processes after the patterning of black PDL require to withstand a temperature up to 300°C [8, 9]. We synthesized new multifunctional monomers and tested them in the photolithographic process for both good patterning and high thermal stability of the black PDL patterns in the OLED panel.

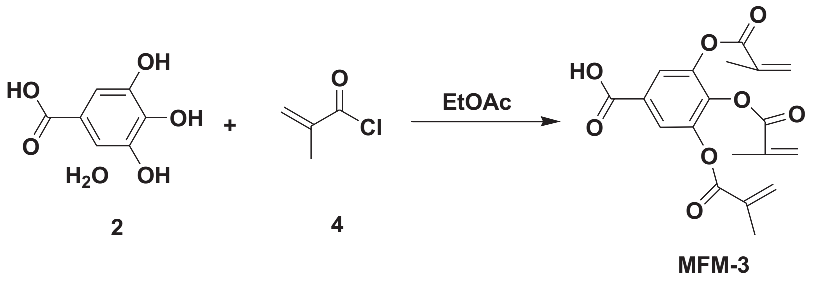
## 2. Experimental methods

In the syntheses of multifunctional monomers, common reagents and solvents were purchased and used without further purification. Synthesized compounds were characterized by $^1$H, $^{13}$C NMR (400 MHz FT-NMR Model: 400-MR DD2 Mag. Res. System at 298 K).

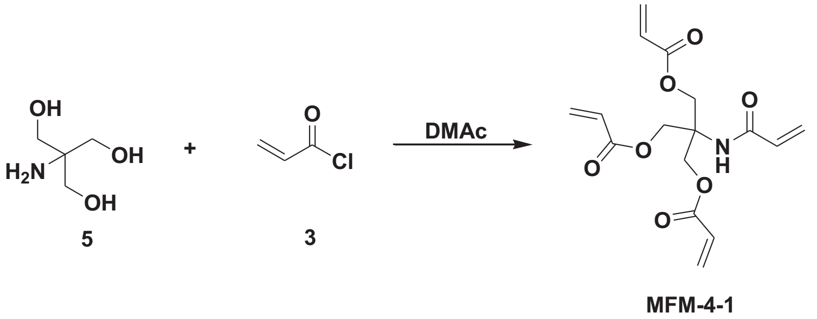
**Synthesis of MFM-2**. 9,9-Bis[4-(2-Glycidyloxyethyl)phenyl]fluorene (**1**, 1.3876 g, 3 mmol), acrylic acid (0.8647 g, 12 mmol), 2,6-di-tert-buthyl-4-methylphenol (**BHT**, 0.2644 g, 1.2 mmol) and tetrabutylphosphonium bromide (**TBPB**, 0.2036 g, 0.6 mmol) was added to 10 mL of toluene and stirred at 90°C for 7 hours. After cooling down, the reaction mixture was diluted with ethyl acetate and washed with saturated $NaHCO_{3(aq)}$. The organic layer was dried with anhydrous $Na_2SO_4$ and finally evaporated to dryness to afford **MFM-2**. Yield: 0.945 g, 52%. **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 7.82–7.84 (d, 2H), 7.32–7.44 (m, 8H), 7.20–7.16 (m, 4H), 6.83–6.91 (d, 4H), 6.48–6.52 (d, 2H), 6.18–6.25 (m, 2H), 5.89–5.94 (d, 2H), 4.21–4.56 (m, 8H).



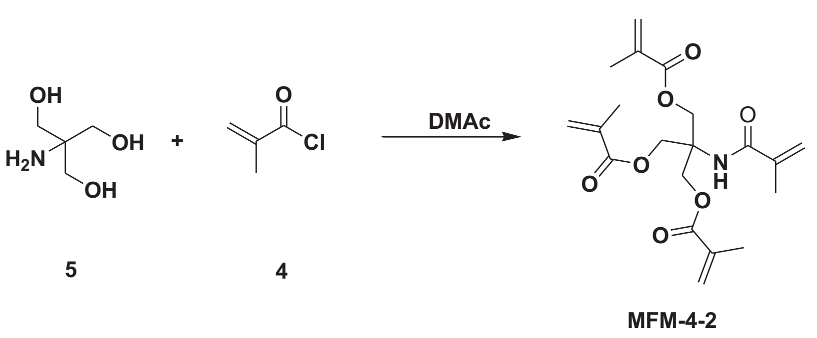
**Synthesis of MFM-3**. Acryloyl chloride (**3**, 2.4 mL, 30 mmol) was added to suspension of gallic acid monohydrate (**2**, 0.940 g, 5 mmol) in 5 mL EtOAc. The mixture was then stirred at 60°C for 4 hours before pouring into excess water. The organic layer was washed with saturated $NaHCO_{3(aq)}$, separated and dried with anhydrous $Na_2SO_4$, and finally evaporated to dryness to afford **MFM-3** as oil. Yield (not pure): 2.28 g, 137%. **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 12.52 (s, 1H), 7.55 (s, 1H), 5.89–6.32 (m, 6H).



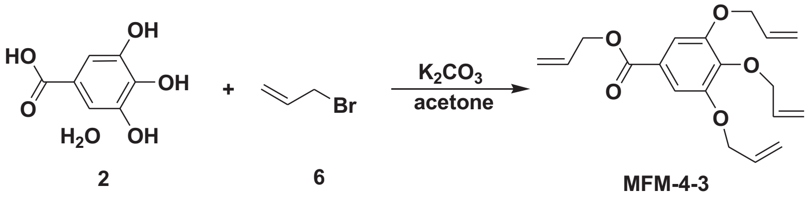
**Synthesis of MFM-4-1**. Acryloyl chloride (**3**, 8.0 mL, 100 mmol) was added into 20 mL dimethyl acetamide (DMAc) solution of trisaminomethane (**5**, 1.21 g, 10 mmol) at RT. The mixture was then stirred at 60°C for 4 hours before pouring into excess water. The oil was extracted with dichloromethane, dried with anhydrous $Na_2SO_4$, and finally evaporated to dryness to afford **MFM-4-1** as oil. Yield (not pure): 5.514 g, 82%. **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 6.41–6.46 (d, 6 H), 6.12–6.23 (d, 2H), 6.22–6.27 (d, 6H), 5.88–5.90 (d, 2H), 5.65–5.68 (s, 6H), 4.62 (d, 12H).



**Synthesis of MFM-4-2**. Methacryloyl chloride (**4**, 6.0 mL, 60 mmol) was added into 10 mL DMAc solution of trisaminomethane (**5**, 1.21 g, 10 mmol) within 10 min and the mixture was stirred at RT for 18 hours. After pouring into excess water, the oil was extracted with dichloromethane, dried with anhydrous $Na_2SO_4$, and finally evaporated to dryness to afford **MFM-4-2** as oil. Yield: 2.7 g, 69%. **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 6.52–6.62 (d, 1H), 6.12–6.23 (d, 3H), 5.62–5.70 (d, 3H), 5.30–5.39 (d, 1H), 4.61 (s, 6H), 1.93–1.94 (d, 12H).



**Synthesis of MFM-4-3**. Allyl bromide (6.914 mL, 80 mmol) in 15 mL of acetone was added dropwise to suspension of gallic acid monohydrate (**2**, 1.881 g, 10 mmol) and $K_2CO_3$ (13.8 g, 100 mmol) in acetone within 30 min. After stirring overnight at reflux, the mixture was filtered and the solid was washed with acetone. The mother liquid was evaporated to dryness and the residue was purified by silica-gel column chromatography (eluent: EtOAc/hexane = 1/20) to afford **MFM-4-3**. Yield: 721 mg, 22%. **$^1$H NMR** ($CDCl_3$, 400 MHz): $\delta$ 7.31 (s, 2H), 6.03–6.12 (m, 4H), 5.17–5.46 (m, 8H), 4.79–4.82 (d, 2H), 4.61–4.66 (d, 6H).



## 3. Results and discussions

A typical formulation of a negative-tone black photoresist is shown in Table 1. In this photoresist propylene glycol monomethyl ether acetate (PGMEA) was used as common solvent to dissolve or mix all the components of the black photoresist. This was because the black millbase (LT-1, from SKC htm Korea, 23% solid in PGMEA) containing lactam black pigment was prepared to a well dispersed state (average partical size 50 nm) in PGMEA. If any one component in black photoresist is not completely soluble in PGMEA, it could make micro-coagulums, which will lead to saw-toothed pattern of black PDL.

The photolithographic process was as following. The black photoresist was spin coated on the wafer ($Si/SiO_2$ 200 nm) with a stepwise speed of 300 rpm/5 sec, 500 rpm/5 sec, and 5,000 rpm/50 sec. After soft bake at 120°C for 100 sec, the dry black photoresist thin film was exposed to UV irradiation (120 $mJ/cm^2$) through the photomask. After hard bake at 120°C for 100 sec, the black PDL thin film was developed with AZ-300 MIF developer (tetramethylammonium hydroxide 2 wt% in water, Bayer Co., Germany) for 120 sec followed by water rinsing and drying with $N_2$ gun.

The black PDL pattern in Fig. 2(a) shows that the black photoresist sample PT-1 containing acrylate type multifunctional monomer (PETA) gave sharp pattern of black PDL. The black

**Table 1.** Formulation of black photoresist for PDL patterning.

| Compnents/Photoresist | | PT-0 | PT-1 | PT-2 | PT-3 | PT-4 | PT-5 |
|---|---|---|---|---|---|---|---|
| Photoinitiator | Irgacure 754 | 1 | 1 | 1 | 1 | 1 | 1 |
| | Irgacure TPO | 6 | 6 | 6 | 6 | 6 | 6 |
| Photosensitizer | Darocur ITX | 2 | 2 | 2 | 2 | 2 | 2 |
| Binder Polymer (30 wt% in PGMEA) | SR-6300 (SMS Co., Korea) | 35 | 35 | 35 | 35 | 35 | 35 |
| Multifunctional Monomers | PETA | 8 | | | | | |
| | MFM-2 | | 8 | | | | |
| | MFM-3 | | | 8 | | | |
| | MFM-4-1 | | | | 8 | | |
| | MFM-4-2 | | | | | 8 | |
| | MFM-4-3 | | | | | | 8 |
| Dispersant | BYK-9076 | 1 | 1 | 1 | 1 | 1 | 1 |
| Black Millbase (23 wt% in PGMEA) | LT-1 (SKC htm. Co., Korea) | 42 | 42 | 42 | 42 | 42 | 42 |
| Solvent | PGMEA | 5 | 5 | 5 | 5 | 5 | 5 |
| Total | wt% | 100 | 100 | 100 | 100 | 100 | 100 |
| Thermal Stability | 1 wt% loss temp. (TGA) | 282 | — | — | 304 | — | — |

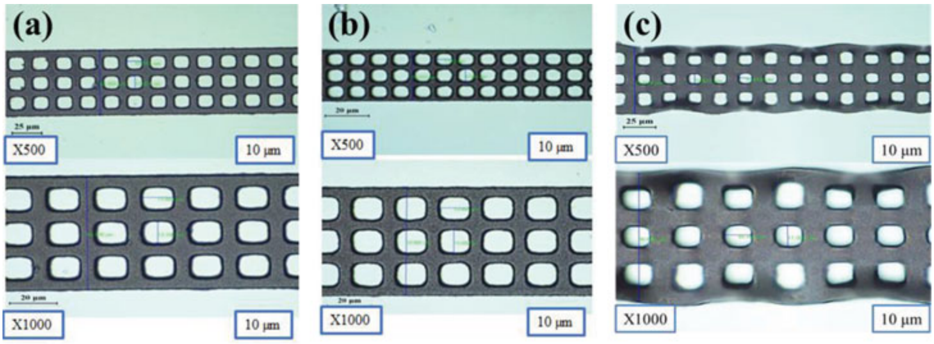


**Figure 2.** The optical microscope images of black PDL patterns obtained with **(a)** PT-0, **(b)** PT-3, **(c)** PT-4 photoresists.

photoresist sample PT-3 also showed good black PDL pattern as shown in Fig. 2(b). However other photoresist samples failed to give acceptable PDL patterns. The analyses were as following; PT-1 photoresist had **MFM-2** monomer with two acrylates ($f = 2$) so that it could not give enough photo-crosslinking under 120 mJ/cm$^2$ UV exposure density. Similarly, PT-2 also had $f = 3$ multifunctional monomer (**MFM-3**). Although PT-3, 4, 5 samples had all four acrylate groups ($f = 4$) in the multifunctional monomers, only PT-3 resulted in good black PDL pattern. This could be explained by the structures of the multifunctional monomers. The multifunctional monomers **MFM-4-2** had methacrylates compared to acrylates in **MFM-4-1** thus causing steric hindrance in photo-crosslinking reaction due to the methyl group (Fig. 2(c)). The **MFM-4-3** monomer had allylic group which could cause autoinhibition reaction, a well-known phenomenon in the free radical polymerization, in the photo-crosslinking process.

## 4. Conclusion

In this work 5 multifunctional monomers (with $f = 2, 3, 4$) were used to make black photoresists and tested in photolithographic patterning of black PDL for OLED panel. Of the multifunctional monomers the one with four acrylate groups (**MFM-4-1**) gave sharp black PDL pattern, which could be explained by effective photo-crosslinking reaction with the highest double bond number density based on unit mass of multifunctional monomers.

It was also noted that the thermal stability of black photoresist PT-3 was higher than that of PT-0 with PETA as multifunctional monomer. This seemed to be due to more effective crosslinking reaction caused by the higher double bond number density of **MFM-4-1** than that of PETA monomer which has higher molecular weight than **MFM-4-1**.

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## Competing interests

The authors declare that they have no competing interests.

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