

# Photo-cleavable perfluoroalkylated copolymers for tailoring the quantum dot thin films

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## 1. Materials

Benzil **1** (99.0%) was purchased from TCI. Hydroxylamine hydrochloride **2** (99%), isobornyl methacrylate (**IBMA**, technical grade), dichloromethane (anhydrous, 99.8%), tetrahydrofuran (THF, anhydrous, 99.9%), benzotrifluoride (BTF, anhydrous, 99%), butylated hydroxytoluene (BHT, 99%) were obtained from SigmaAldrich. 2,2-Azobisisobutyronitrile (AIBN) was purchased from Junsei Chemical and used after recrystallization from a mixture of MeOH and CHCl<sub>3</sub>. Sodium acetate trihydrate (Duksan, 98.5%), EtOH (Daejung, 99.9%), triethylamine (Acros organic, 99%), methacryloyl chloride (Angene International Limited, 95%) were used as received. 1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate (**FOMA**, 99%) were procured from Shanghai Heat-biochem Co., China. **FOMA** and **IBMA** were used after passing through a short column packed with Al<sub>2</sub>O<sub>3</sub>. Cyano-2-propyl dodecyl trithiocarbonate (CPDTC) was synthesized using a reported procedure.<sup>1</sup> Fluorous solvents, HFE-7200 (a mixture of ethyl nonafluoroisobutyl ether and ethyl nonafluorobutyl ether), HFE-7300 [1,1,1,2,3,4,5,6,6-decafluoro-3-methoxy-4-(trifluoromethyl)pentane], PF-7600 [1,1,1,2,3,3-hexafluoro-4-(1,1,2,3,3,3-hexafluoropropoxy)pentane], FC-770 (perfluoro *N*-alkyl morpholines) were supplied by 3M. Red (630 nm) and green (520 nm) emitting QDs (CdSe/ZnS) for multi-color QD patterning were purchased from PlasmaChem Germany.

[1. X. Zhang, Z. Yang, D. Xie, D. Liu, Z. Chen, K. Li, Z. Li, B. Tichnell and Z. Liu, *Des. Monomers Polym.*, 2018, **21**, 43-54.]

## 2. Equipment

<sup>1</sup>H Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 400 (400 MHz) spectrometer using the chemical shift of a residual protic solvent (CHCl<sub>3</sub> at  $\delta$  = 7.24 ppm) as a reference. Multiplicity of the signal was indicated as follows: s (singlet), br s (broad singlet), and m (multiplet). Size exclusion chromatography (SEC) was performed on a Younglin GPC system (YL9100, refractive index detector) by eluting AsahiKlin AK225G at 35 °C. Monodisperse poly(methyl methacrylate) (PMMA; molecular weight from 860 to 2,200,000; Shodex, Showa-Denko) was used as a reference standard for the SEC measurements. Differential scanning calorimetry (DSC; Pyris Diamond DSC, Perkin-Elmer) was used to measure the glass transition temperature ( $T_g$ ) of polymers at a heating/cooling rate of 10 °C min<sup>-1</sup> under a N<sub>2</sub> atmosphere during the heating/cooling/heating cycles. Thermogravimetric analysis (TGA, NETZSCH TG 209 F3 Tarsus) was carried out at a heating rate of 10 °C min<sup>-1</sup> under a N<sub>2</sub> atmosphere. The melting points of the monomers were measured using an IA9300 digital melting point apparatus from Electrothermal. UV irradiation was carried out using a spot-type UV-LED exposure apparatus (365 nm single wavelength) manufactured by SMT UV Technology, South Korea, and a MJB4 Mask Aligner (Hg light source with deep UV cut off) manufactured by SUSS MicroTec. Thin film thickness and surface profiles were obtained by using an Alpha-Step D-300 Stylus Profiler manufactured by KLA-Tencor. Scanning electron microscopy (SEM) images of the photo-patterned films were obtained using a Hitachi SU 8010. Photo patterned two-color quantum dot films were observed using a metallurgical-metallographic microscope during irradiation with the spot-type UV-LED. Oxygen plasma treatment was performed by CUTE-1MPR (Femto Science).

## 3. Synthesis

### Benzil monoxime (BMO) **3**

A solution of benzil **1** (4.31 g, 20.5 mmol), hydroxylamine hydrochloride **2** (1.40 g, 20.1 mmol), and sodium acetate trihydrate (3.0 g) in EtOH was heated to 90 °C and stirred for 3 h. After the reaction was complete according to thin layer chromatography (silica gel, EtOAc:hexane = 1 : 3), the solution was cooled to r.t. The organic layer was diluted with EtOAc (100 cm<sup>3</sup>) and washed twice with water (100 cm<sup>3</sup>). The organic layer was dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The crude product was precipitated in hexane to give benzilmonoxime (**BMO, 3**) as a white solid. (3.6 g, 78%); mp 161 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.24 (br s, 1 H, OH), 8.05–7.30 (m, 10 H, Ar-H).

### Benzilmonoxime methacrylate (BMOMA) **5**

**BMO** (3.00 g, 13.3 mmol), Et<sub>3</sub>N (2.7 g, 27 mmol), and BHT (1.0 mg) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 cm<sup>3</sup>) and cooled to 0 °C. Methacryloyl chloride **4** (2.78 g, 26.6 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) was added dropwise to the cooled solution. The reaction mixture was allowed to warm up to r.t. and stirred for 4 h. After the reaction was complete according to thin layer chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>: hexane =

2:1), the reaction was quenched with the addition of an aqueous HCl solution, and the organic layer was recovered and washed twice with water (100 cm<sup>3</sup>). The organic layer was dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The crude product was recrystallized three times from EtOH to give a white crystalline solid, benzilmonoxime methacrylate (**BMOMA**, 2.2 g, 56%); mp. 158 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.00–7.36 (m, 10 H, Ar-H), 5.72 (s, 1 H, C=CH<sub>2</sub>), 5.42 (s, 1 H, C=CH<sub>2</sub>), 1.70 (s, 3 H, CH<sub>3</sub>).

#### Copolymerization of PFB-X (X= 1, 2, 3), PFBI and PFI

**FOMA** (1.18 g), **BMOMA** (0.20 g), AIBN (5.6 mg), CPDTC (23.5 mg), THF (1.5 cm<sup>3</sup>), and BTF (1.5 cm<sup>3</sup>) were added to a 25 cm<sup>3</sup> Schlenk tube. It was sealed and degassed via three freeze-pump-thaw cycles using liquid N<sub>2</sub> under reduced pressure and finally purged with N<sub>2</sub>. The solution was stirred magnetically at 80 °C for 12 h. The solution was poured into MeOH, and the precipitate was filtered and dried under reduced pressure to yield **PFB-1** (1.1 g, 80%) as a pale yellow powder; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub> + CF<sub>2</sub>Br<sub>2</sub>):  $\delta$  = 8.08–7.28 (m), 4.25 (br s), 2.48 (br s), 2.17–0.49 (m). **PFB-2** and **PFB-3** were polymerized using the same method of **PFB-1** except the monomer feed; for **PFB-2**, **FOMA** (1.18 g), **BMOMA** (0.4 g), and for **PFB-3**, **FOMA** (1.18 g), **BMOMA** (0.6 g).

In the case of **PFBI**, **FOMA** (5.00 g), **BMOMA** (0.85 g), **IBMA** (1.42 g), AIBN (23.8 mg), CPDTC (0.1 g), THF (7 cm<sup>3</sup>) and BTF (7 cm<sup>3</sup>) were added to a 50 cm<sup>3</sup> Schlenk tube. The reaction procedure was the same as that of **PFB-1**. The yield of **PFBI** was 87% (6.3 g); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub> + CF<sub>2</sub>Br<sub>2</sub>):  $\delta$  = 8.04–7.30 (m), 4.57–4.00 (m), 2.45 (br s), 2.18–0.48 (m).

In the case of **PFI**, **FOMA** (2.0 g), **IBMA** (0.45 g), AIBN (9.5 mg), CPDTC (40 mg), and BTF (2 cm<sup>3</sup>) were added to a 25 cm<sup>3</sup> Schlenk tube. The reaction procedure was the same as that for **PFB-1**.

## 4. Lithographic evaluation

### Photopatterning of PFB-X (X = 1, 2, 3)

**PFB-X** [10% (w/v) over the coating solvent] were dissolved in PF-7600. The solution was spin-coated on a Si substrate at 1000 rpm (200 rpm s<sup>-1</sup>) for 60 s to form **PFB-1**, **PFB-2**, or **PFB-3** film. The substrate was baked at 80 °C for 3 min and exposed to UV light through a photomask. Suitable exposure doses were 2.4 J cm<sup>-2</sup>, 4.0 J cm<sup>-2</sup>, and 0.6 J cm<sup>-2</sup> for **PFB-1**, **PFB-2**, and **PFB-3**, respectively. The substrates were then washed in a mixed solvent of FC-770 and HFE-7300 (10:1 by volume for **PFB-1** and 4:1 by volume for **PFB-2**) for 120 s and in a mixture of FC-770 and HFE-7200 (1 : 3 by volume for **PFB-3**) and rinsed with FC-770.

### Image contrast measurement of PFBI

A 10% (w/v) **PFBI** solution in PF-7600 was spin-coated on a Si substrate (1000 rpm, 500 rpm s<sup>-1</sup>, duration: 50 s) and it was baked at 80 °C for 3 min. The **PFBI** film thickness was 405 nm. The substrate was irradiated with 365 nm UV-LED light at increasing irradiation doses from 100 mJ cm<sup>-2</sup> to 6,000 mJ cm<sup>-2</sup>. The exposed film was dipped

into HFE-7300 for 2 min, rinsed with FC-770, and the remaining film thickness was measured with a surface profiler. Dose-to-clear was approximately 2,300 mJ cm<sup>-2</sup>.

### **5. Multi-color QD film patterning**

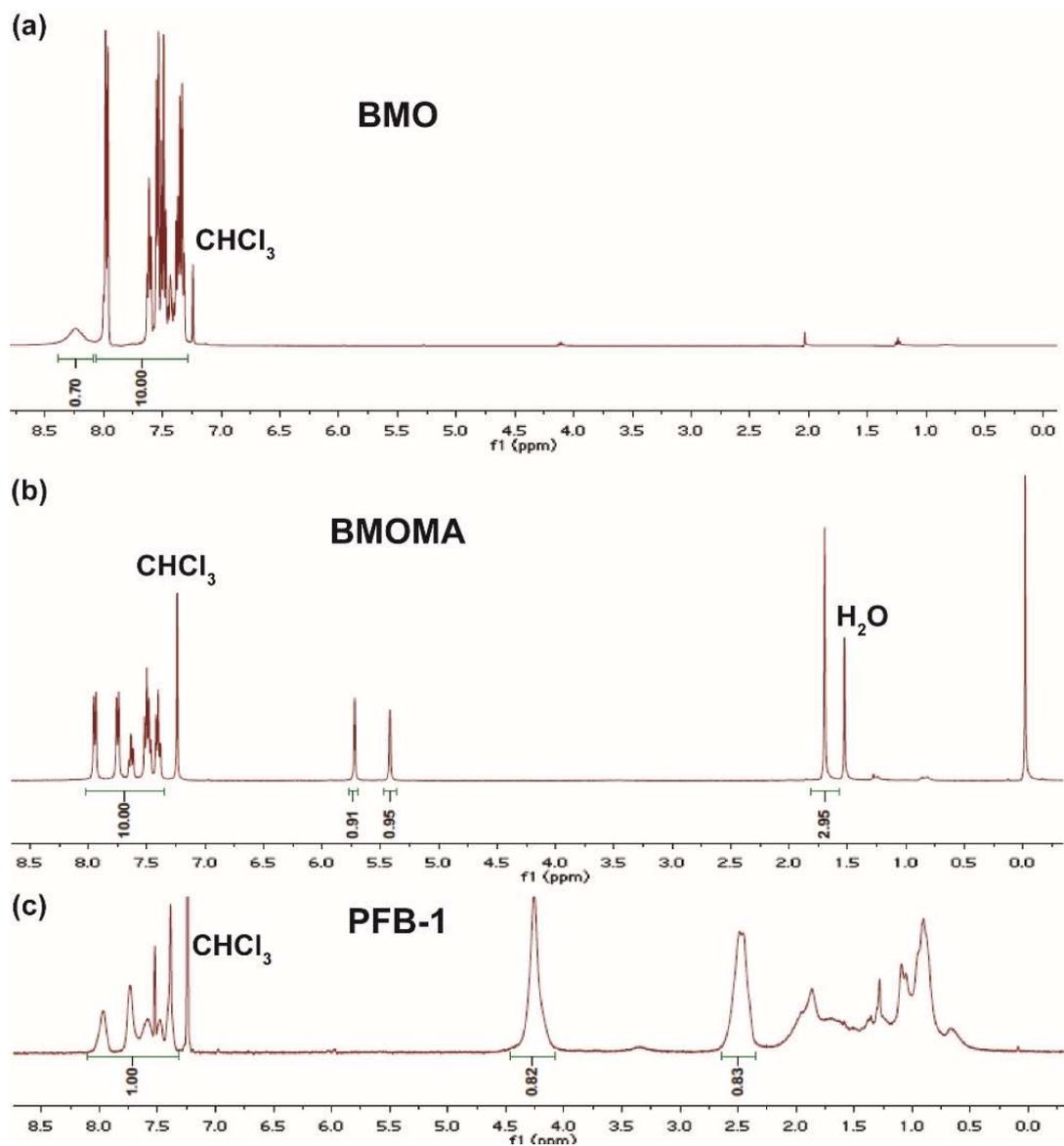
A 20% (w/v) **PFBI** solution in PF-7600 was spin-coated on a Si substrate (1000 rpm, 200 rpm s<sup>-1</sup>, duration: 50 s) and it was baked at 80 °C for 3 min. The film thickness was 1.4 μm. UV irradiation was performed using an MJB4 aligner with a dose of 2.3 J cm<sup>-2</sup>, and the irradiated substrate was immersed into HFE-7300 for 7 min and rinsed with FC-770 to form a stencil. The thickness of the 60 μm x 180 μm elliptical pattern was approximately 1.2 μm. The 1<sup>st</sup> red emitting CdSe/ZnS QD solution in hexane (10 mg cm<sup>-3</sup>) was spin-coated (4000 rpm, acceleration: 4000 rpm s<sup>-1</sup>, duration: 40 s) on the substrate and baked at 80 °C for 5 min. The QD-deposited **PFBI** substrate was baked at 180 °C for 10 min and cooled to r.t. and washed in HFE-7300 for 10 min to lift-off the stacked film of the stencil and QD. The patterning of the 2<sup>nd</sup> green emitting QDs (10 mg cm<sup>-3</sup>) in hexane was conducted repeatedly following the same procedure as the 1<sup>st</sup> QDs. The thickness of the resulting 1<sup>st</sup> and 2<sup>nd</sup> QD films were 30 and 25 nm, respectively.

### **6. Solubility test of O<sub>2</sub> plasma-treated PFBI and PFI films**

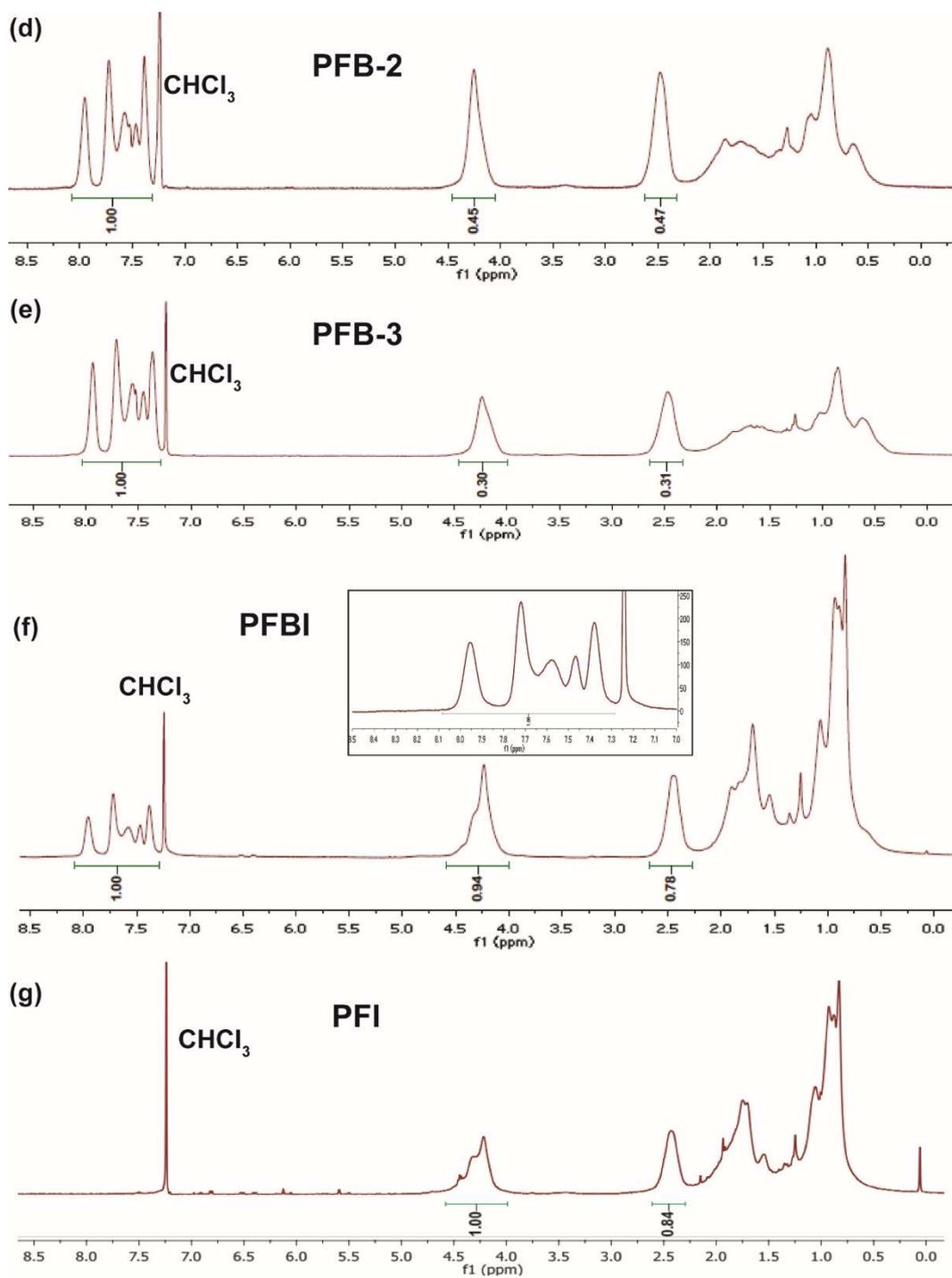
The thicknesses of the starting **PFBI** and **PFI** films were 1.3 μm and 360 nm, respectively. An isotropic O<sub>2</sub> plasma treatment was conducted on both films for 60 s (2 sccm, 50 W, 50 kHz). After treatment, both films were immersed into PF-7600 for 30 min. The remaining thickness of both films was measured in every 5 min.

### **7. Lift-off test of the O<sub>2</sub> plasma-treated stencil and QD stacked film**

A stencil of **PFBI** was prepared by the same multi-color QD film patterning procedure. An O<sub>2</sub> plasma treatment was carried out for 60 s onto the stencil, and blanket UV exposure (8 J cm<sup>-2</sup>) using MJB4 mask aligner was performed. The red CdSe/ZnS QD solution in hexane was then spin-coated onto the stencil film and the substrate was baked at 80 °C for 5 min. The QD-deposited substrate was baked at 180 °C for 20 min, cooled to r.t., dipped in PF-7600 for 20 minutes, and sonicated for 5 s to lift off the QDs.



**Fig. S1**  $^1\text{H-NMR}$  of monomers [(a) **BMO**, (b) **BMOMA**], and polymers [(c) **PFB-1**, (d) **PFB-2**, (e) **PFB-3**, (f) **PFBI** and (g) **PFI**]. (Continued)



**Fig. S1**  $^1\text{H-NMR}$  of monomers [(a) **BMO**, (b) **BMOMA**], and polymers [(c) **PFB-1**, (d) **PFB-2**, (e) **PFB-3**, (f) **PFBI** and (g) **PFI**]. The inset image is a magnification of benzil parts in (f).

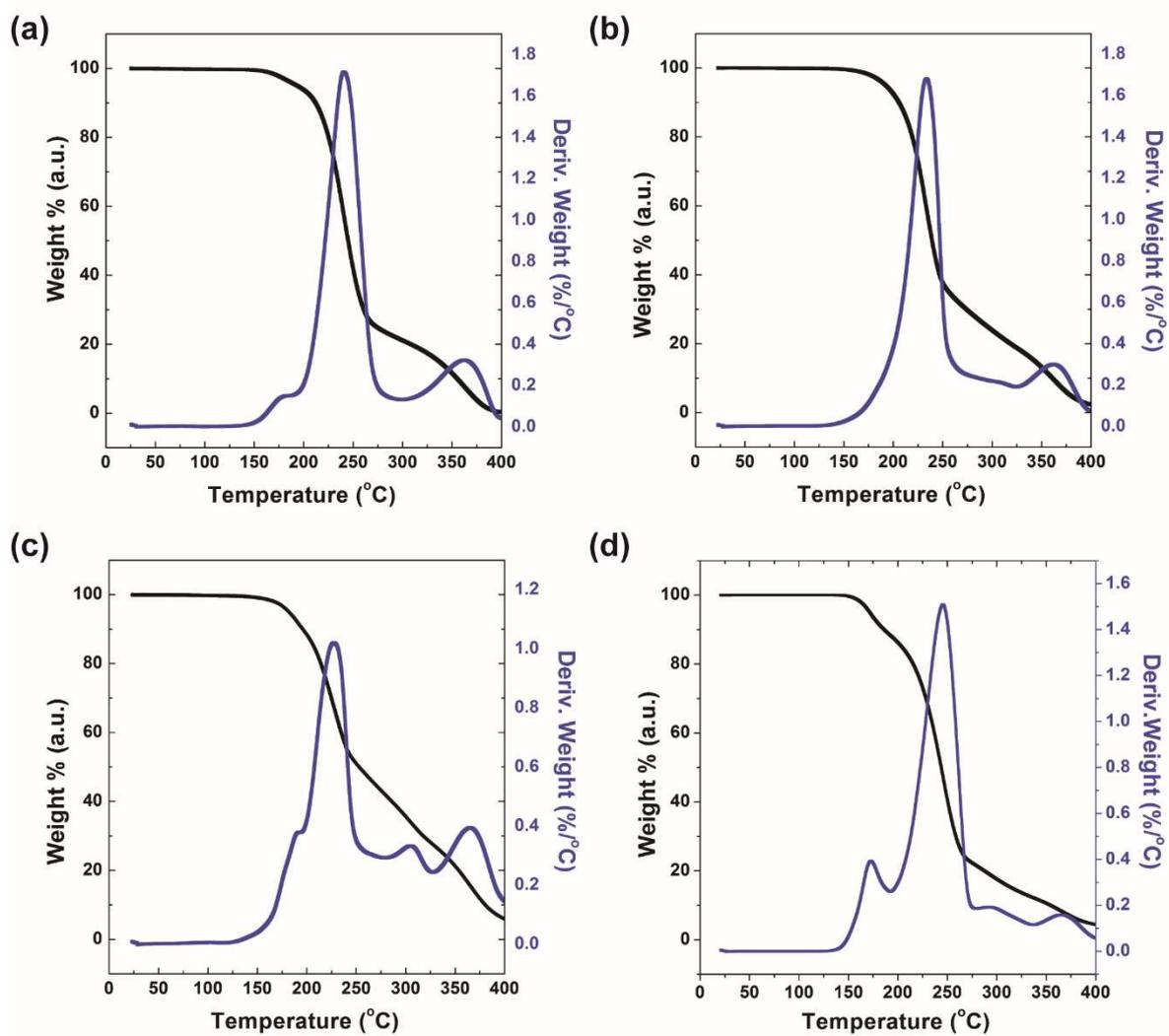


Fig. S2 TGA results of (a) PFB-1, (b) PFB-2, (c) PFB-3 and (d) PFBI.

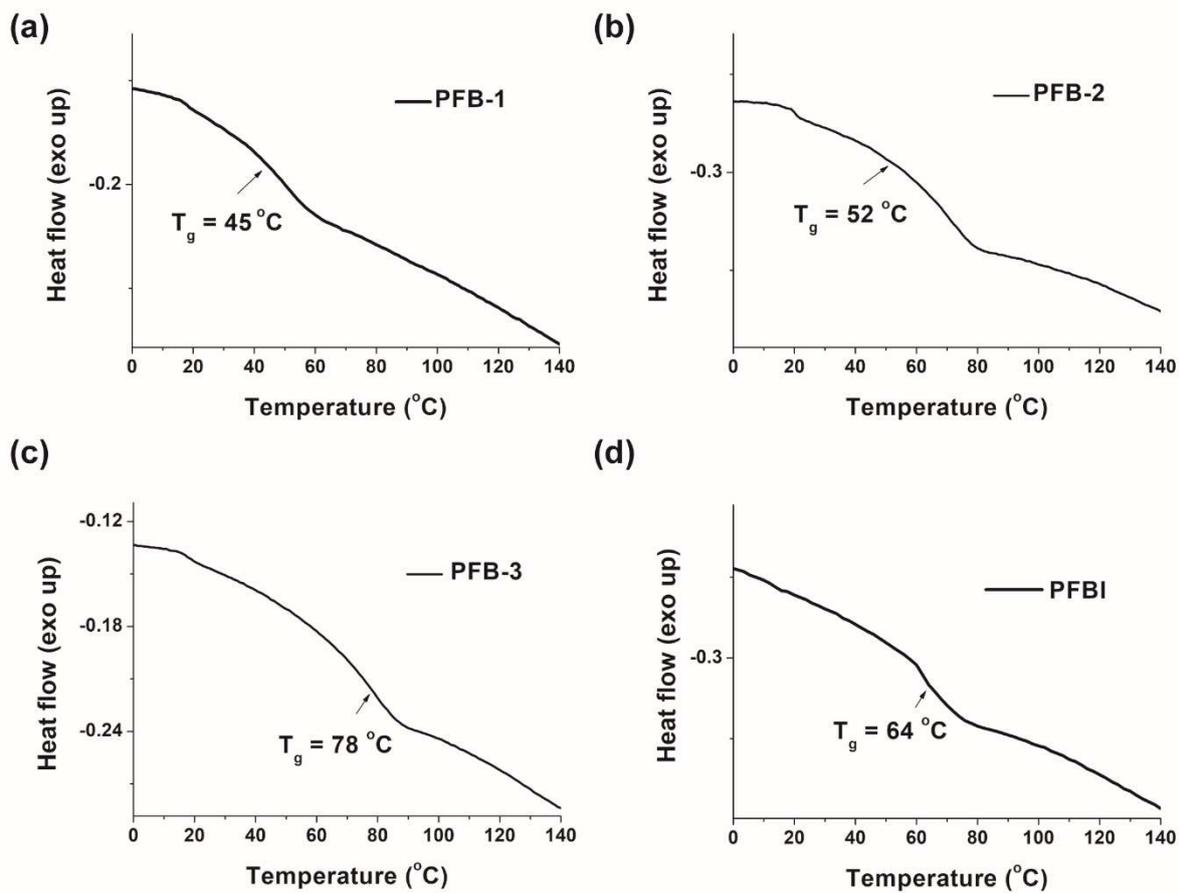


Fig. S3 DSC results of (a) PFB-1, (b) PFB-2 and (c) PFB-3 and (d) PFB-I.

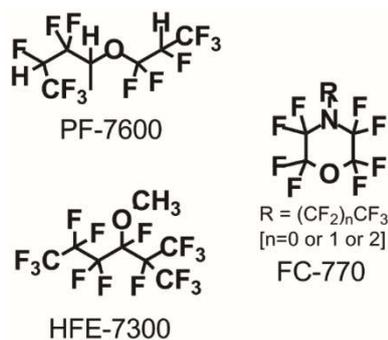
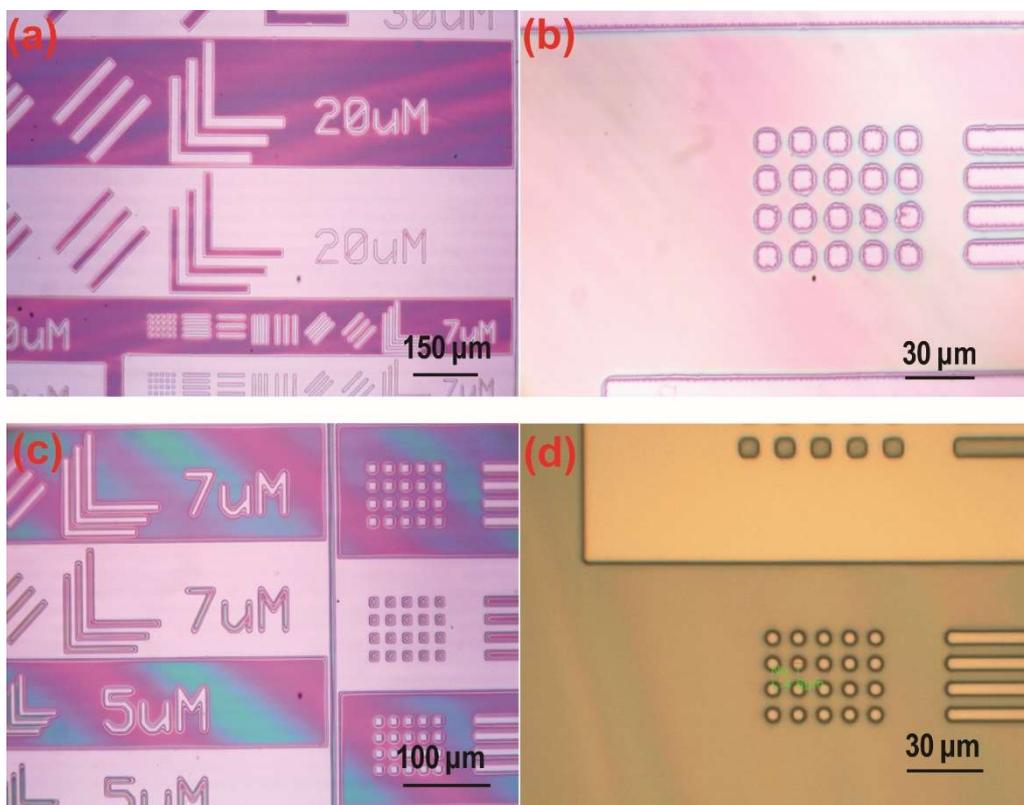
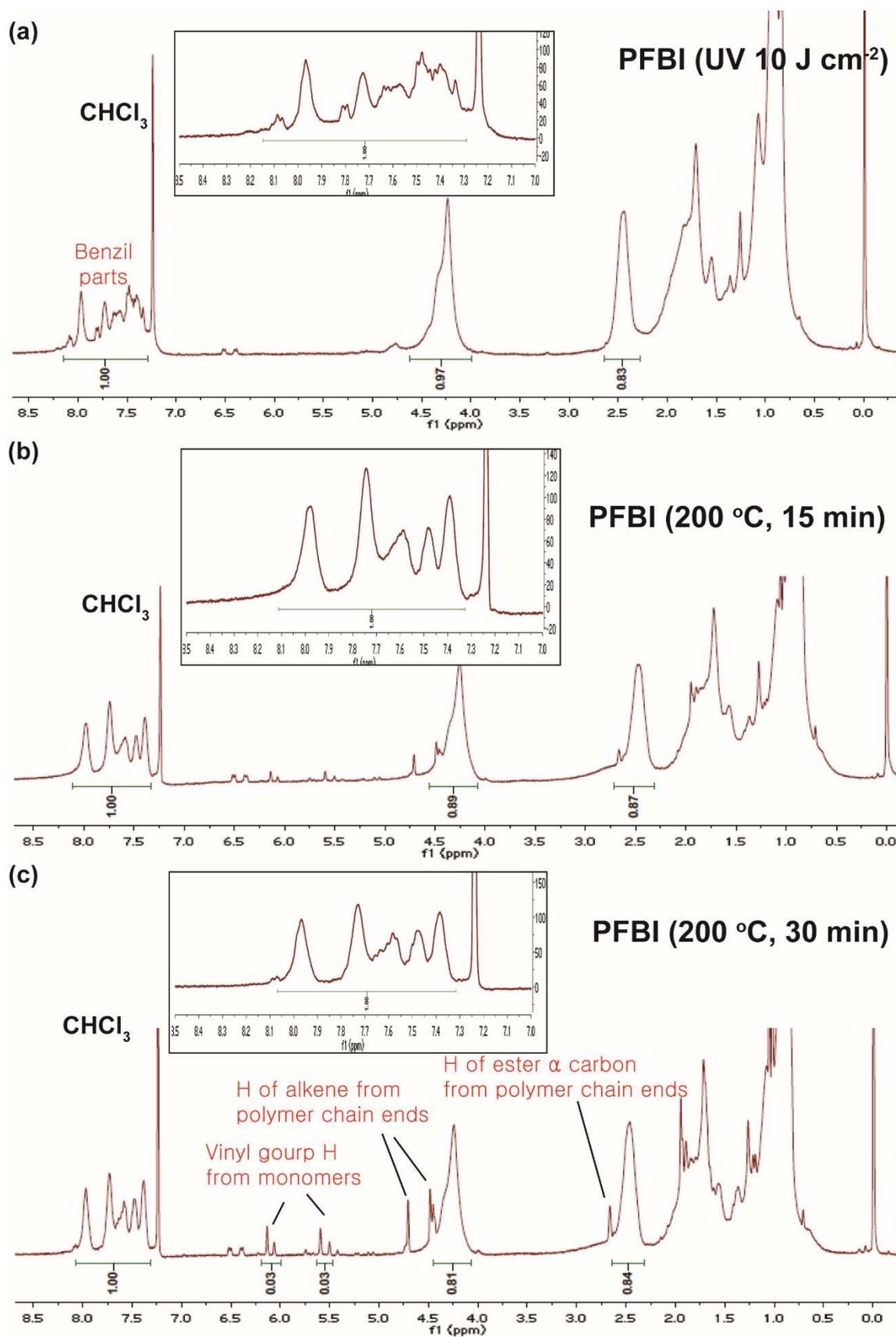


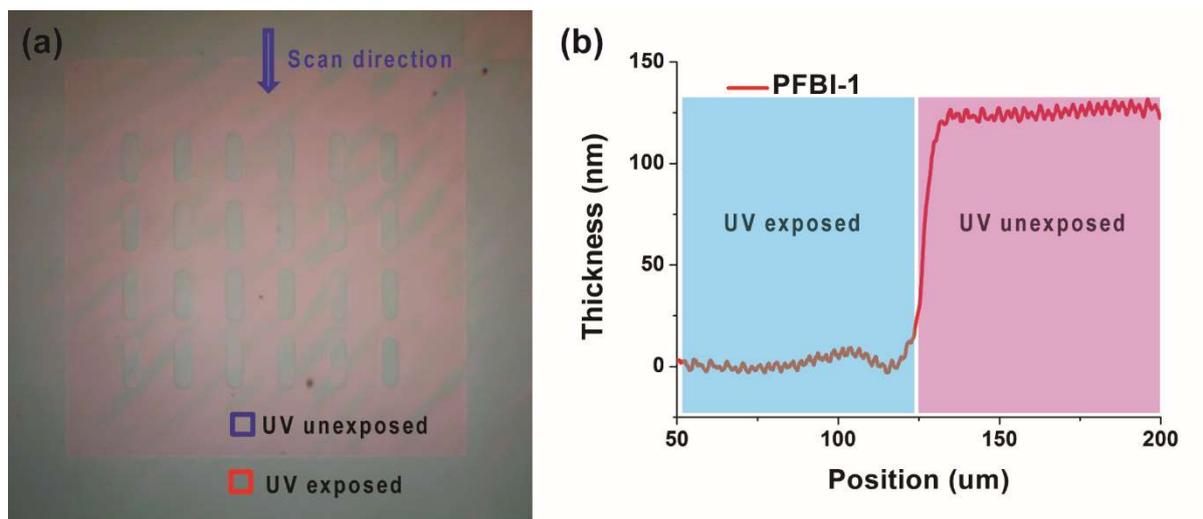
Fig. S4 Chemical structure of fluoruous solvents used in the study.



**Fig. S5** Optical microscopic images of (a) PFB-1, (b) PFB-2, (c) PFB-3 and (d) PFBI pattern film.



**Fig. S6** <sup>1</sup>H-NMR of PFBI after (a) UV and (b) 200 °C, 15 min and (c) 30 min treatment. The inset images are a magnification of benzil parts.



**Fig. S7** (a) A photograph of the latent image of a PFBI film after UV exposure and baking at 80 °C for 1 min. (b) PFBI film thickness difference with or without exposure in the latent image (a).