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**Electric Supplementary Information**

# Elastic and Mechanofluorochromic Hybrid Films with POSS-Capped Polyurethane and Polyfluorene

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**Contents:**

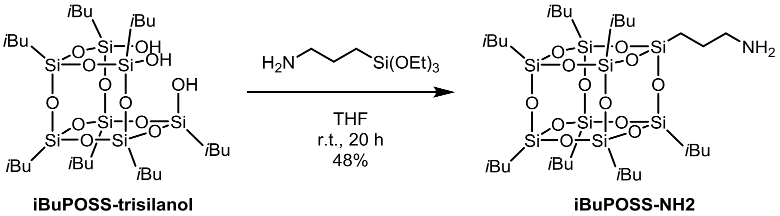
## General

$^1$H, $^{13}$C and $^{29}$Si NMR spectra were recorded on JEOL EX400 and AL400 instruments at 400, 100 and 80 MHz, respectively. Samples were analyzed in $CDCl_3$, and the chemical shift values were expressed relative to $Me_4Si$ as an internal standard. High-resolution mass spectra (HRMS) were obtained on a Thermo Fisher Scientific EXACTIVE spectrometer for atmospheric pressure chemical ionization (APCI). Scanning electron microscopy (SEM) recorded on JEOL JSM-6610A. The number-average molecular weight ($M_n$), the weight-average molecular weight ($M_w$) and PDI ($M_w/M_n$) of all polymers were estimated by the gel permeation chromatography (GPC) with a TOSOH G3000HXI system equipped with three consecutive polystyrene gel columns (TOSOH gels: a-4000, a-3000, and a-2500) and ultraviolet detector at 40 °C. The system was operated at a flow rate of 1.0 mL/min, with chloroform as an eluent. Polystyrene standards were employed for the calibration. UV−vis absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer, and samples were analyzed in $CHCl_3$ at room temperature. Fluorescence emission spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer, and samples were analyzed at room temperature. Absolute photoluminescence quantum efficiency ($\Phi_{PL}$) was recorded on a Hamamatsu Photonics Quantaurus-QY Plus C13534-01. The PL lifetime measurement was performed on a Horiba FluoreCube spectrofluorometer system; excitation was carried out using UV and visible diode lasers (NanoLED 375 nm). Thermogravimetric analysis (TGA) was recorded on a Seiko instrument inc. EXSTAR TG/DTA6000. Dynamic mechanical analysis (DMA) was recorded on a SEIKO DMS210. The uniaxial tensile test was conducted at the speed of 1 mm/min by using an Orientec Corporation TENSILON RTM-500.

## Material

Compounds POSS-trisilanol,[1] iBuPOSS[2] and PF[3] were synthesized according to the literatures. 3-Aminopropyltrimethoxysilane, tolylene-2,4-diisocyanate (TDI), dibutyltin dilaurate and 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene were purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. 1,6-Hexanediol (HDO), poly(tetramethylene oxide) (poly(tetramethylene glycol), PTMG, $M_n$ = 1,000, $n$ = 13.6), 2,2′-bipyridyl, 1,5-cyclooctadiene (COD), Ni(COD)$_2$, hexane, acetonitrile ($CH_3CN$) toluene, methanol and *N*,*N*-dimethylformamide (DMF) were purchased from Wako Pure Chemical Industries and used without further purification. Tetrahydrofuran (THF) was purchased from Wako Pure Chemical Industries and purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA) under Ar pressure. The perfluoroalkoxy alkane (PFA) dish (φ50 mm) were purchased from AS ONE Corporation.

**Synthesis of POSS-NH2**



The mixture of POSS-trisilanol (2.92 g, 3.69 mmol) and THF (15 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. Then, 3-aminopropyltrimethoxy silane (1.12 mL, 5.17 mmol) was added to the mixture via a syringe. The reaction was carried out at room temperature for 20 h with stirring. $CH_3CN$ (40mL) was added, and then white solid was afforded. The residue was washed by $CH_3CN$ several times to afford POSS-NH2 (1.55 g, 1.77 mmol, 48%) as a white solid.

$^1$H NMR ($CDCl_3$, 400 MHz) δ 3.52 (brs, -N*H*$_2$) 2.69−2.65 (t, *J* = 6.0 Hz, 2H, -C*H*$_2$NH$_2$), 1.90−1.80 (m, 7H, -C*H*-), 1.57−1.49 (m, 2H, -CH$_2$C*H*$_2$CH$_2$NH$_2$), 0.97−0.95 (m, 42H, -C*H*$_3$), 0.63−0.59 (m, 16H, Si-C*H*$_2$-) ppm; $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 44.8, 27.2, 25.7, 23.9, 22.5, 9.2 ppm. $^{29}$Si NMR ($CDCl_3$, 80 MHz) δ −67.2, −67.6, −67.8 ppm. HRMS (APCI) calcd. for $C_{31}H_{71}NO_{12}Si_8$ $[M+H]^+$: 874.3203, found: 874.3186. Elemental analysis calcd. for $C_{31}H_{71}NO_{12}Si_8$: C 42.57 H 8.18 N 1.60, found: $C_{31}H_{71}NO_{12}Si_8$: C 41.91 H 7.95 N 1.56.

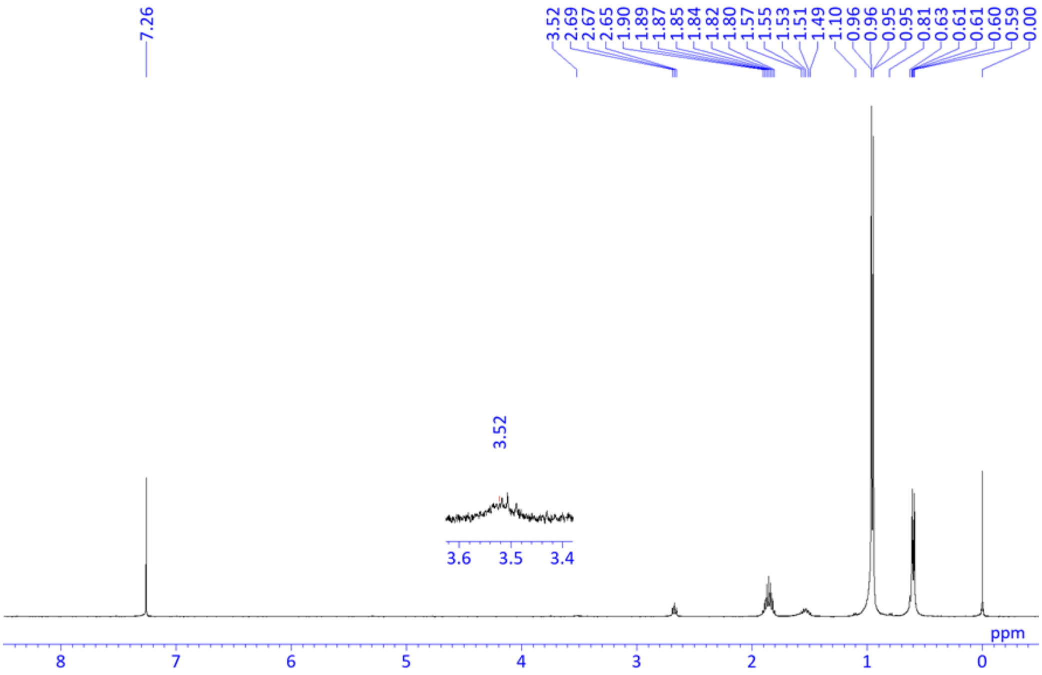


**Chart 1.** $^{1}$H NMR spectrum of iBuPOSS-NH2.

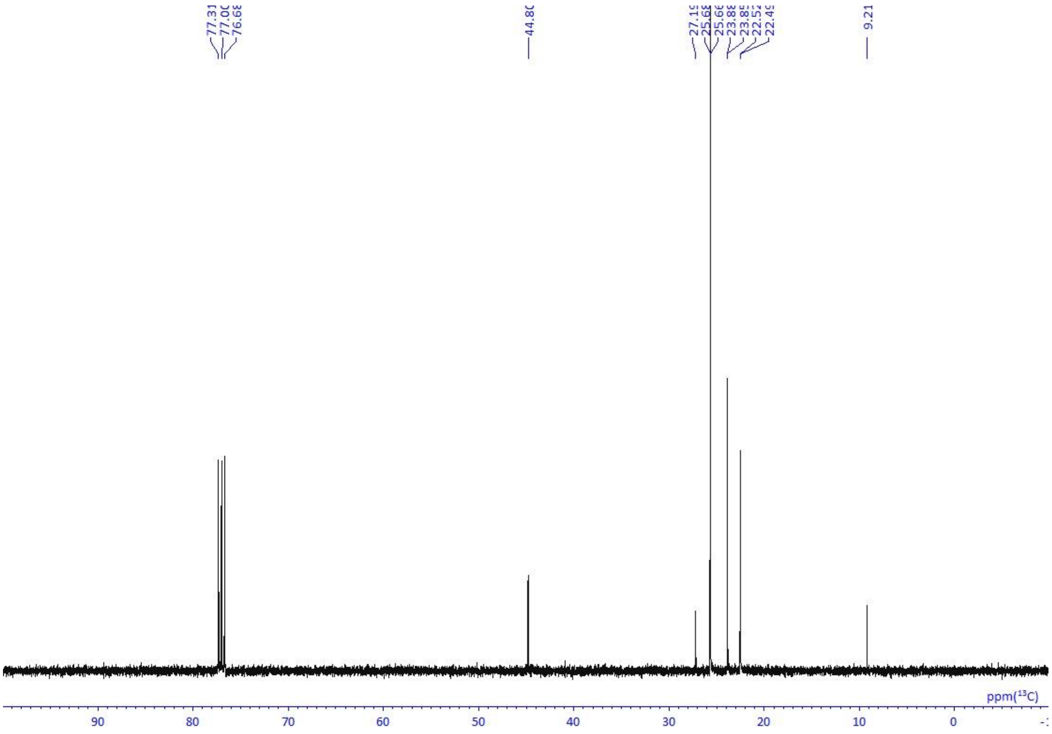


**Chart 2.** $^{13}$C NMR spectrum of iBuPOSS-NH2.

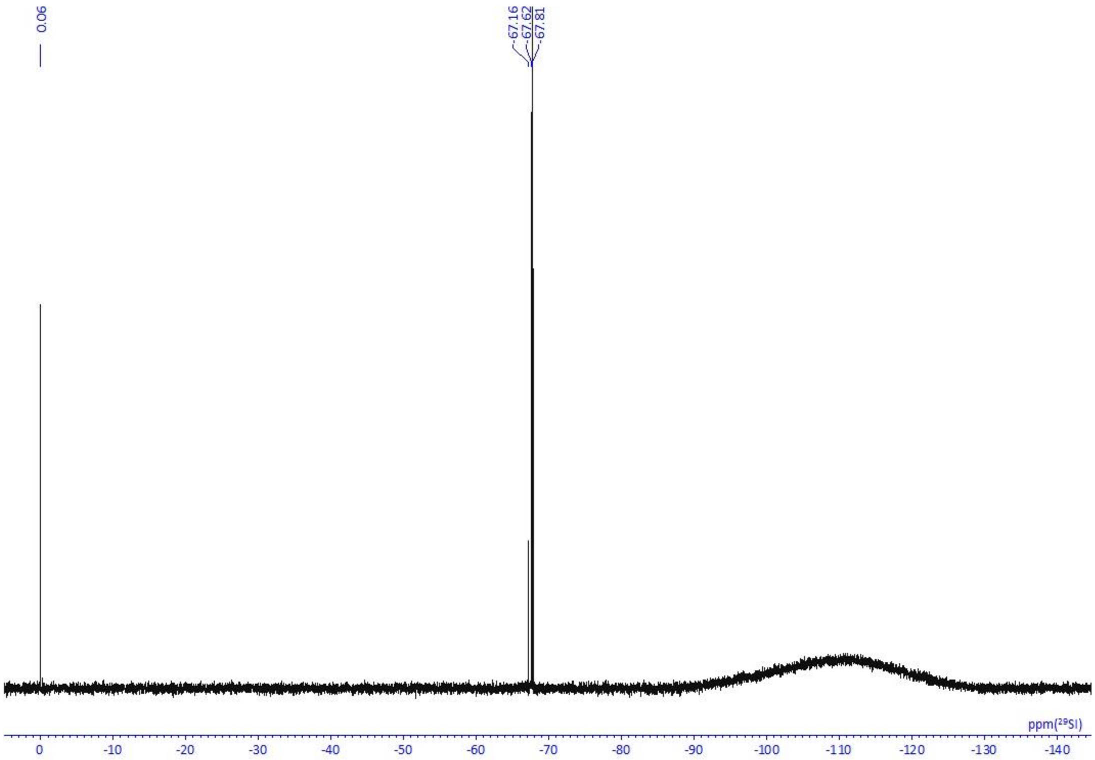
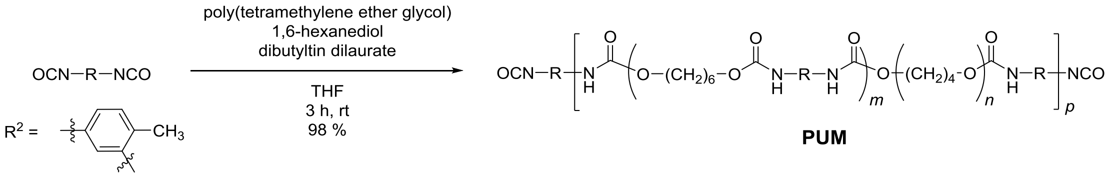


**Chart 3.** $^{29}$Si NMR spectrum of iBuPOSS-NH2.

## Synthesis of PUM



The mixture of HDO (0.25 g, 2.1 mmol), PTMG (0.30 g, 0.3 mmol), dibutyltin dilaurate (15 $\mu$L) and THF (4 mL) was placed in a round-bottom flask equipped with a magnetic stirring bar. Then TDI (0.51g, 3.0 mmol) in THF (2 mL) was added to the mixture via a syringe and the reaction was carried out at 50 °C for 3 h under Ar pressure. The resulting solution was poured into a beaker containing 150 mL of hexane, and white precipitates were afforded. The solvents were removed by filtration to afford PUM (1.05 g, 98%). According to the $^1$H NMR, the peak of hydroxyl group (2.28 ppm) disappeared. Therefore, it was presumed that all the alcohol was consumed and all ends of polyurethane chains were converted into isocyanate groups.

$^1$H NMR ($CDCl_3$, 400 MHz) δ 7.74 (brs, 54H, aryl-*H* ), 7.26 (brs, 54H, aryl-*H*), 7.04 (brs, 54H, aryl-*H*), 6.55 (brs, 54H, -CON*H*CO-), 4.14 (brs, 95H, $-OCH_2-$), 3.76−3.73 (t, 14H, *J* = 6.0 Hz, $-OCH_2-$), 3.41 (brs, 163H, $-OCH_2-$), 2.17 (brs, 109H, $-CH_3$), 1.87−1.84 (m, 14H, $-OCH_2CH_2-$), 1.65-1.62 (m, 272H, $-OCH_2CH_2-$), 1.40 (brs, 95H, $-OCH_2CH_2CH_2-$) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 153.9, 136.8, 136.1, 130.6, 114.5, 70.6, 70.1, 65.2, 64.9, 31.5, 28.6, 26.5, 26.2, 25.8, 25.4, 25.4, 22.6, 17.0, 16.7, 14.1 ppm.

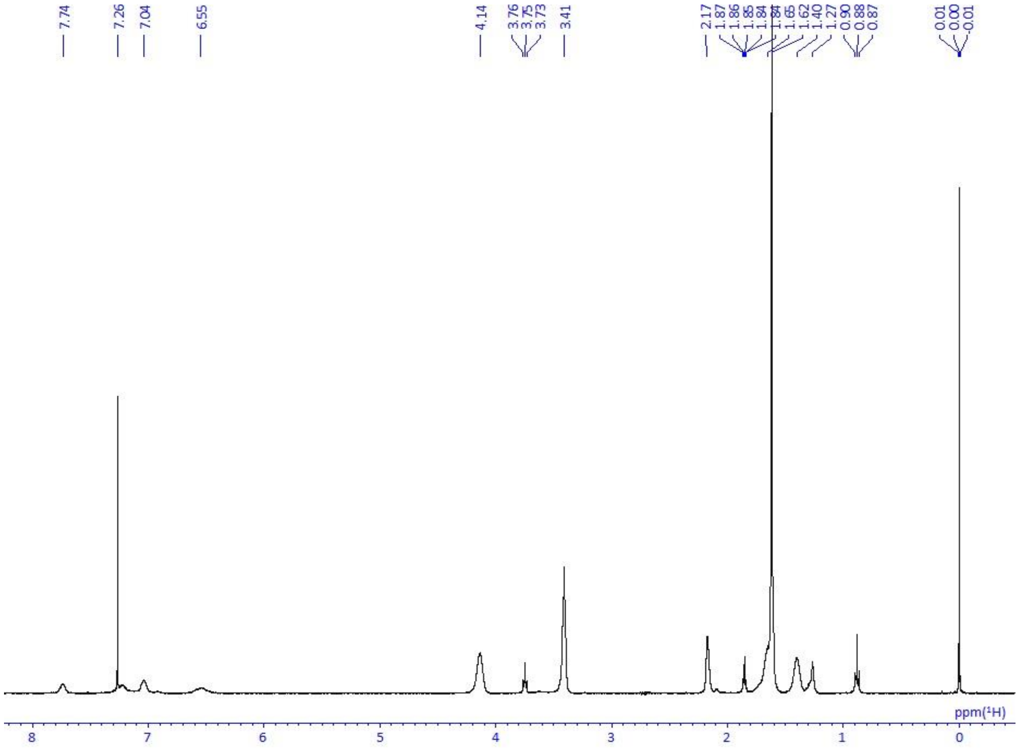


**Chart 4.** $^1$H NMR spectrum of PUM.

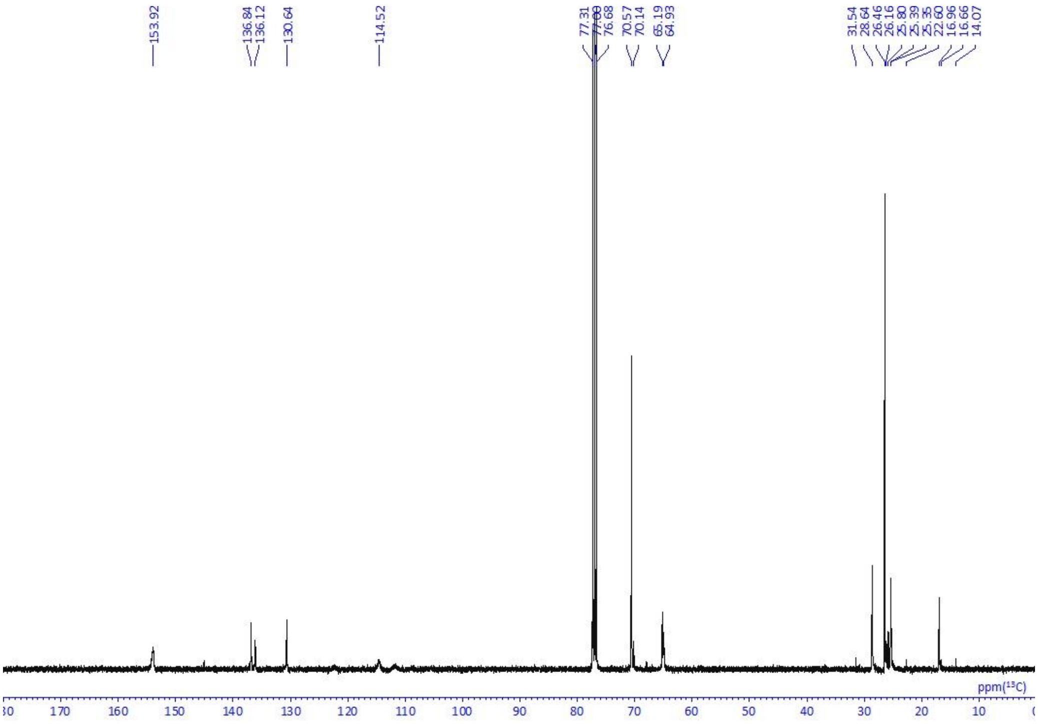
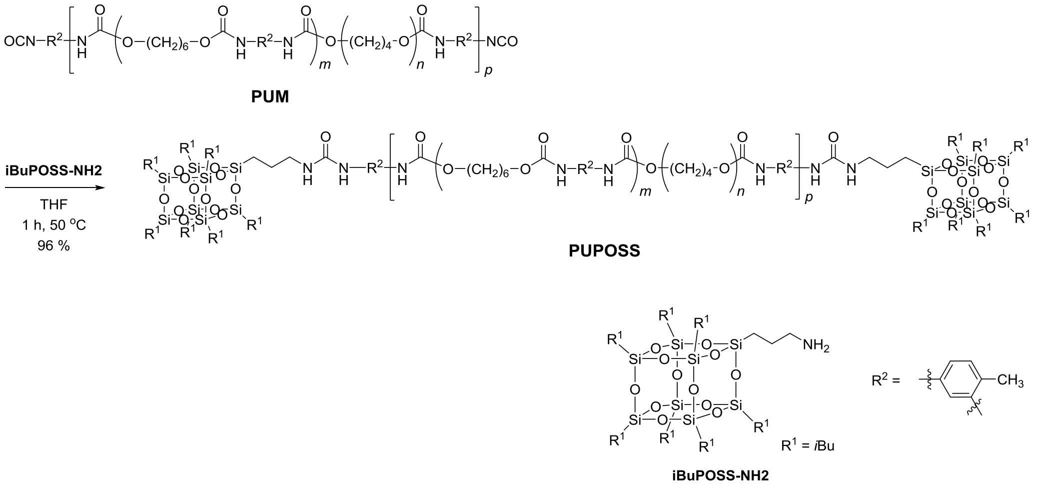


**Chart 5.** $^{13}$C NMR spectrum of PUM.

### Synthesis of PUPOSS



PUPOSS was obtained by almost the same procedure as PUM. Before reprecipitation by pouring into the hexane, POSS-$NH_2$ (0.13 g, 0.15 mmol) in THF (2 mL) was added to the mixture. Then the reaction was carried out at 50 °C for 1 h. The resulting solution was poured into a beaker containing 150 mL of hexane, white precipitates were afforded and the solvents were removed by filtration to afford PUPOSS (1.14 g, 96%).

$^1$H NMR ($CDCl_3$, 400 MHz) δ 7.73 (brs, 54H, aryl-*H*), 7.21 (brs, 54H, aryl-*H*), 7.03 (brs, 54H, aryl-*H*), 6.55 (brs, 54H, -CON*H*CO-), 4.13 (brs, 95H, -OC$H_2$-), 3.76−3.73 (t, 14H, $J$ = 6.0 Hz, -OC$H_2$-), 3.41 (brs, 163H, -OC$H_2$-), 2.17 (brs, 109H, -C$H_3$), 1.87−1.84 (m, 14H, -OC$H_2$C$H_2$-), 1.66−1.61 (m, 272H, -OC$H_2$C$H_2$-), 1.40 (brs, 95H, -OC$H_2$C$H_2$C$H_2$-), 0.96−0.95 (m, 33H, -C$H_3$), 0.61−0.59 (m, 11H, -C$H_2$-) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 153.9, 136.9, 136.2, 130.7, 114.7, 70.6, 70.2, 67.9, 65.2, 65.0, 31.6, 30.9, 28.7, 26.5, 26.2, 25.8, 25.7, 25.6, 25.4, 25.4, 23.8, 22.6, 22.5, 17.0, 14.1 ppm. $^{29}$Si NMR ($CDCl_3$, 80 MHz) δ −67.3, −67.6, −67.8 ppm.

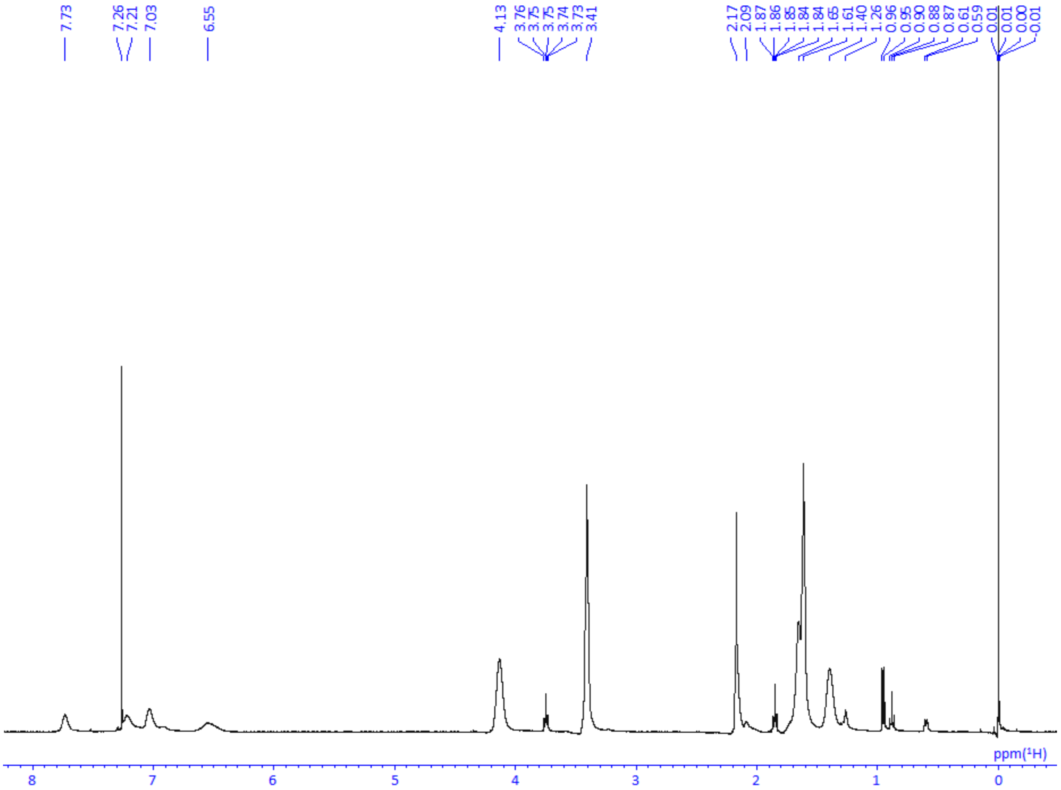


**Chart 6.** $^1$H NMR spectrum of PUPOSS.

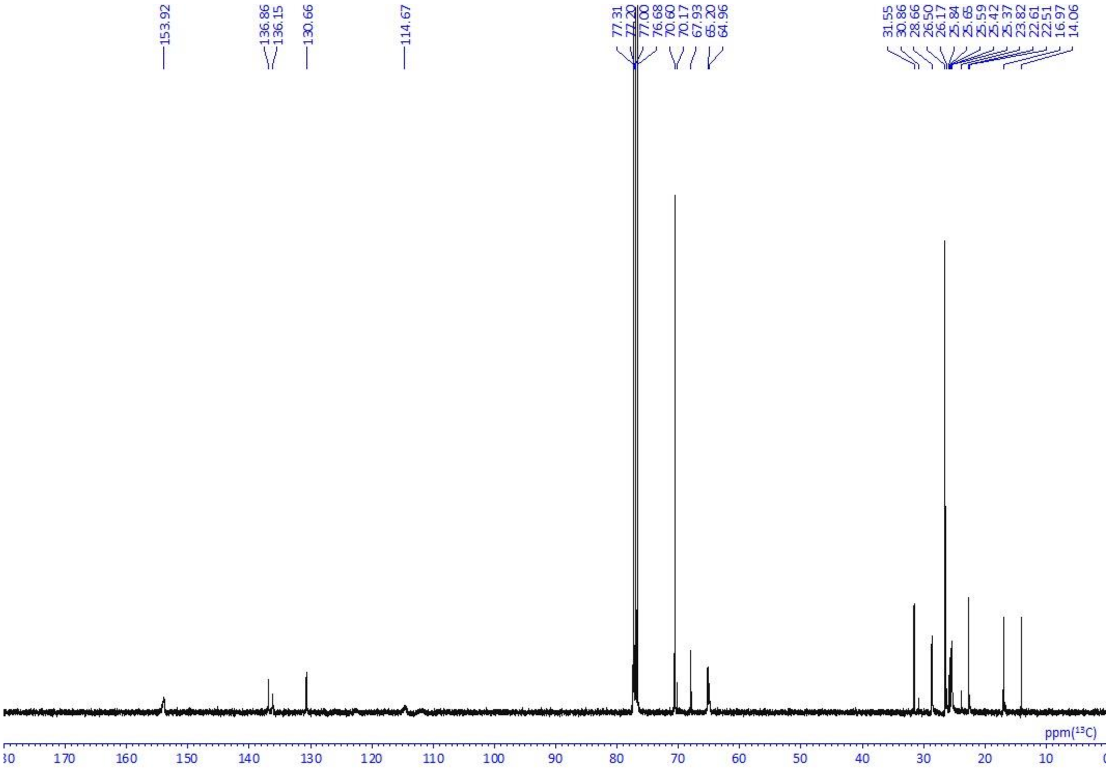


**Chart 7.** $^{13}$C NMR spectrum of PUPOSS.

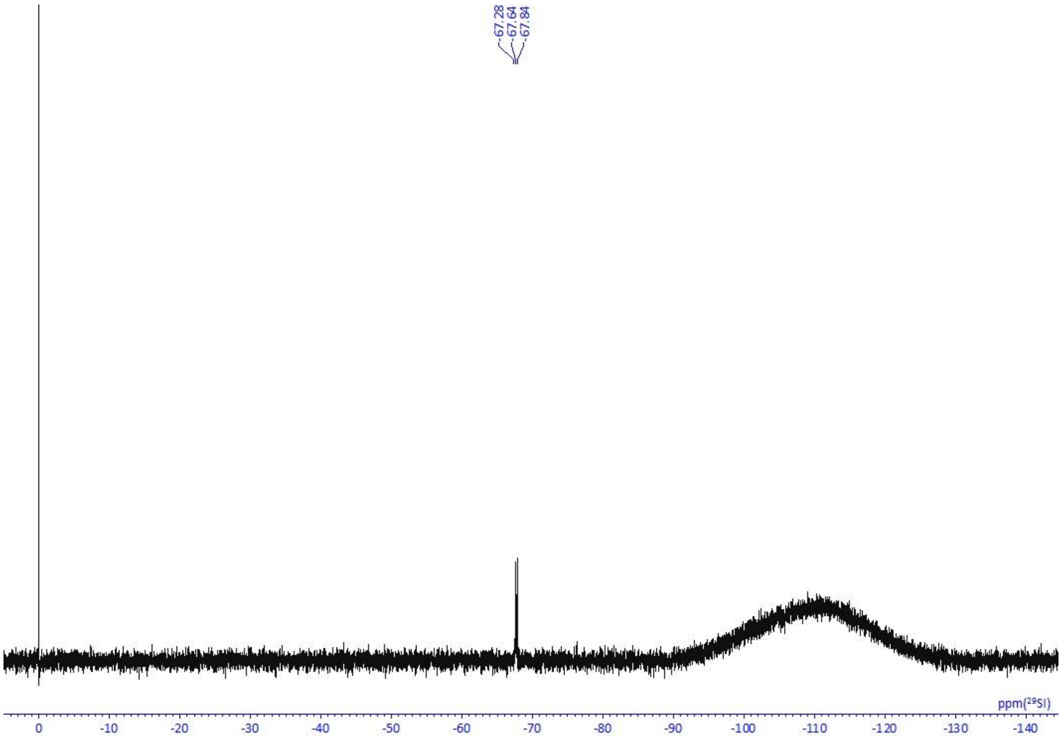
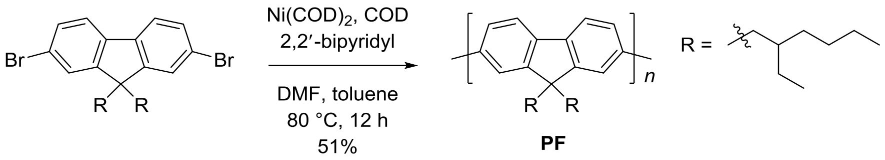


**Chart 8.** $^{29}$Si NMR spectrum of PUPOSS.

**Synthesis of PF**



The solution containing 1,5-cyclooctadiene (COD) (1.06 mL, 8.6 mmol), $Ni(COD)_2$ (1.60 g, 5.8 mmol), and 2,2′-bipyridyl (1.06 g, 6.8 mmol) in 53 mL of anhydrous DMF was placed in a round-bottom flask equipped with a magnetic stirring bar and stirred at 60 °C for 30 min under Ar. Then 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene (1.50 g, 2.7 mmol) in 5 mL of anhydrous toluene was added. The reaction was stirred at 80 °C for 12 h in the dark. A small amount of chloroform was added to the reaction mixture and the products were reprecipitated into methanol. The Ni reagent was quenched by concd. HCl and the yellow solid was collected by filtration. The solid was dissolved in a small amount of chloroform and the products were reprecipitated into methanol. The light yellow solid were afforded and the solvents were removed by filtration to afford PF (549 mg, 51%).

$^1$H NMR ($CDCl_3$, 400 MHz) δ 7.80 (brs, 2H, aryl-*H*), 7.66 (brs, 4H, aryl-*H*), 2.12 (brs, 2H, -C*H*-), 0.94 (18H, alkyl-*H*), 0.68 (8H, alkyl-*H*), 0.60 (6H, alkyl-*H*) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 151.2, 140.2, 126.1, 123.0, 119.8, 55.1, 44.5, 34.8, 34.2, 34.1, 28.3, 27.1, 22.8, 14.0, 14.0, 10.4 ppm.

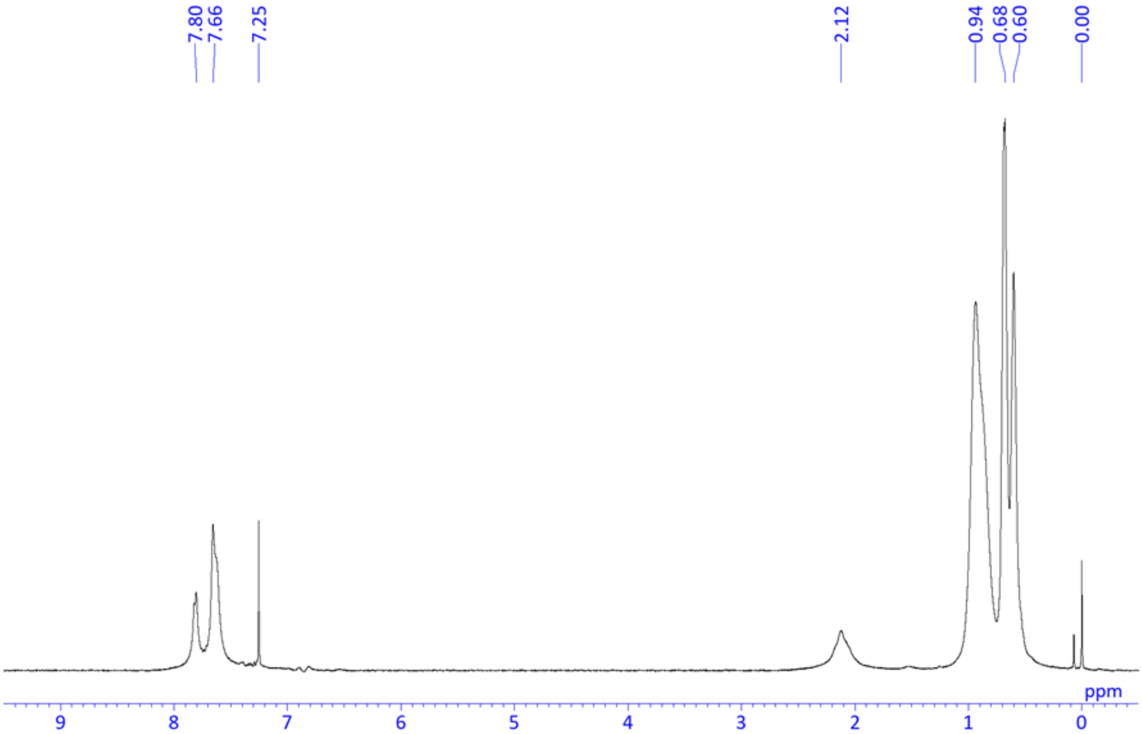


**Chart 9.** $^{1}$H NMR spectrum of PF.

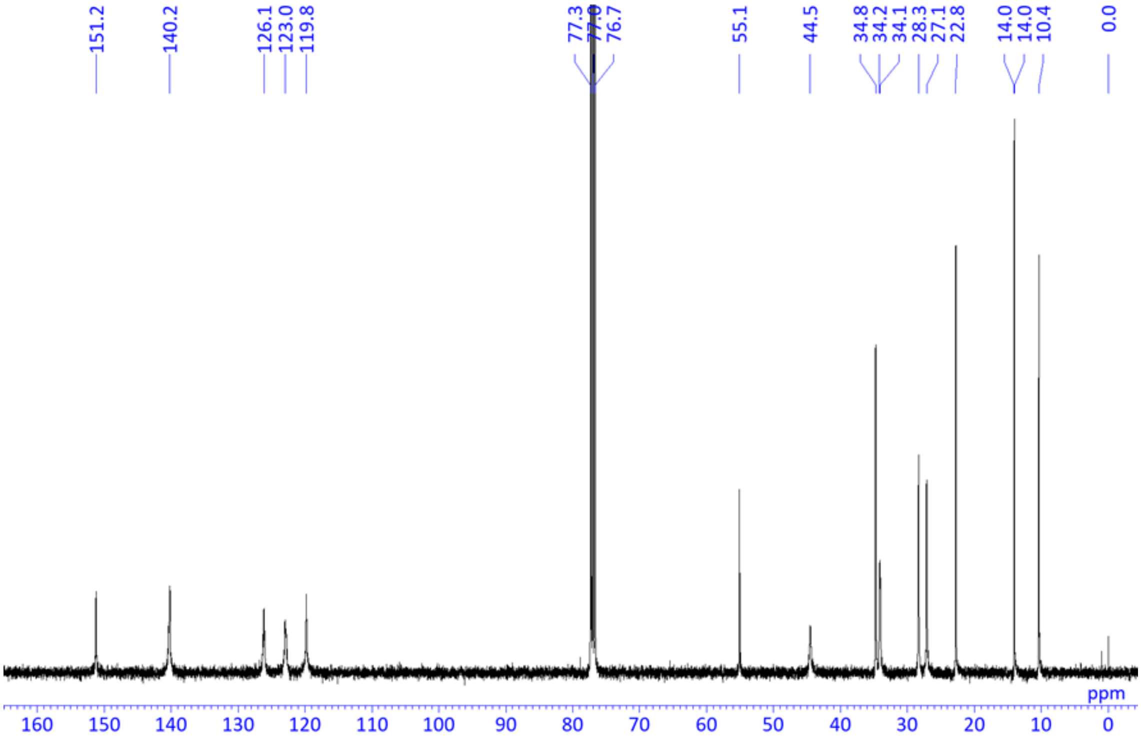
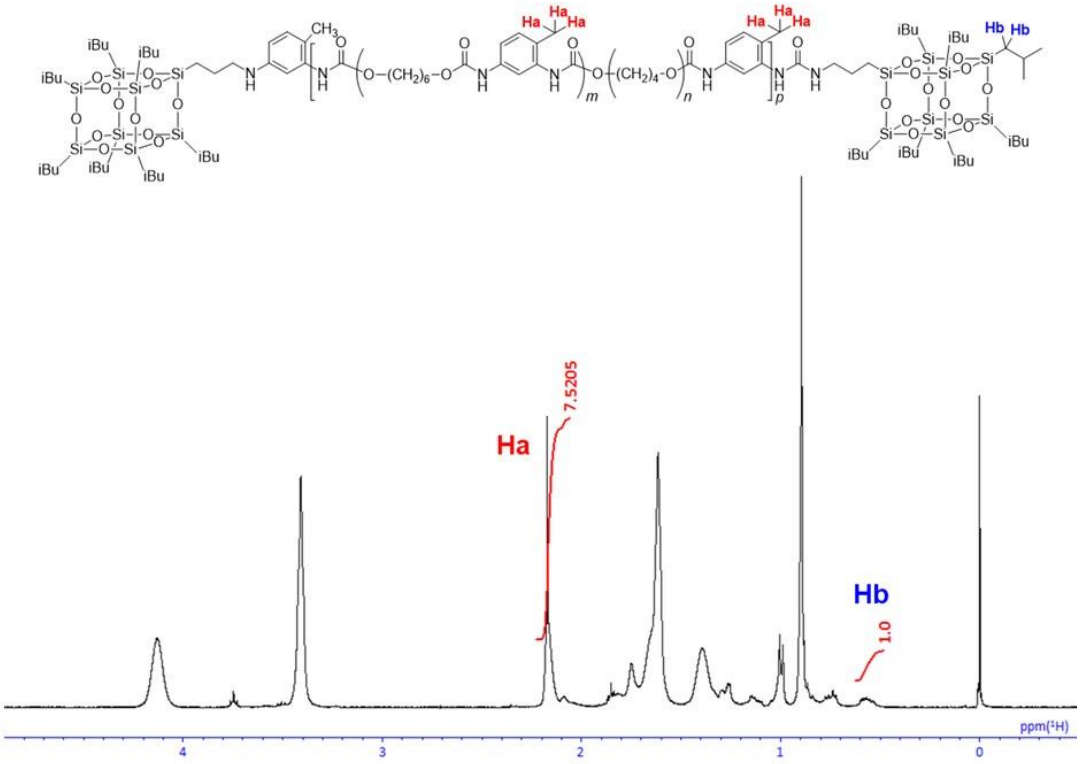


**Chart 10.** $^{13}$C NMR spectrum of PF.

## Calculation of POSS introduction rate in PUPOSS



$$\begin{aligned} M_{\text{repeating unit}} &= 174 \times 8 + 118 \times 7 + 1000 \times 1 \\ &= 3218 \end{aligned}$$

$$M_{\text{n}} / M_{\text{repeating unit}} = 6.8$$

$$\begin{aligned} \text{Ha} : \text{Hb} &= (6.8 \times 8 \times 3) : (2 \times x \times 14) \\ &= 7.5 : 1.0 \end{aligned}$$

$$x = 78\%$$

**Figure S1.** Calculation of POSS introduction rate based on a $^{1}$H NMR spectrum of PUPOSS.

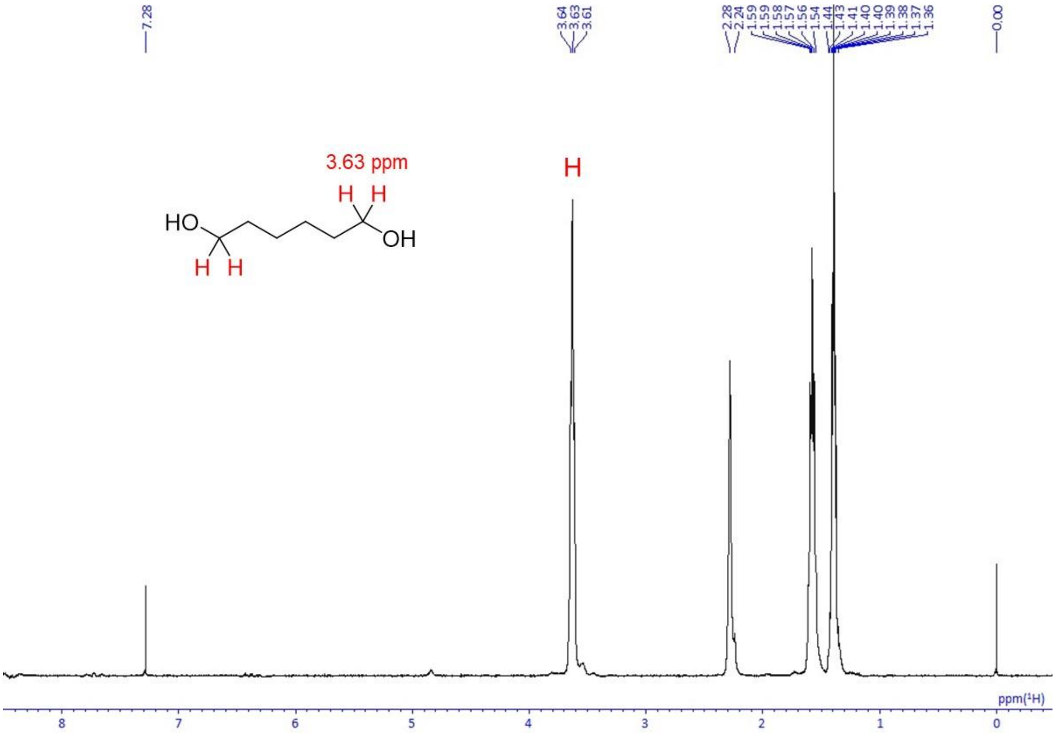


**Figure S2.** $^1$H NMR spectrum of HDO.

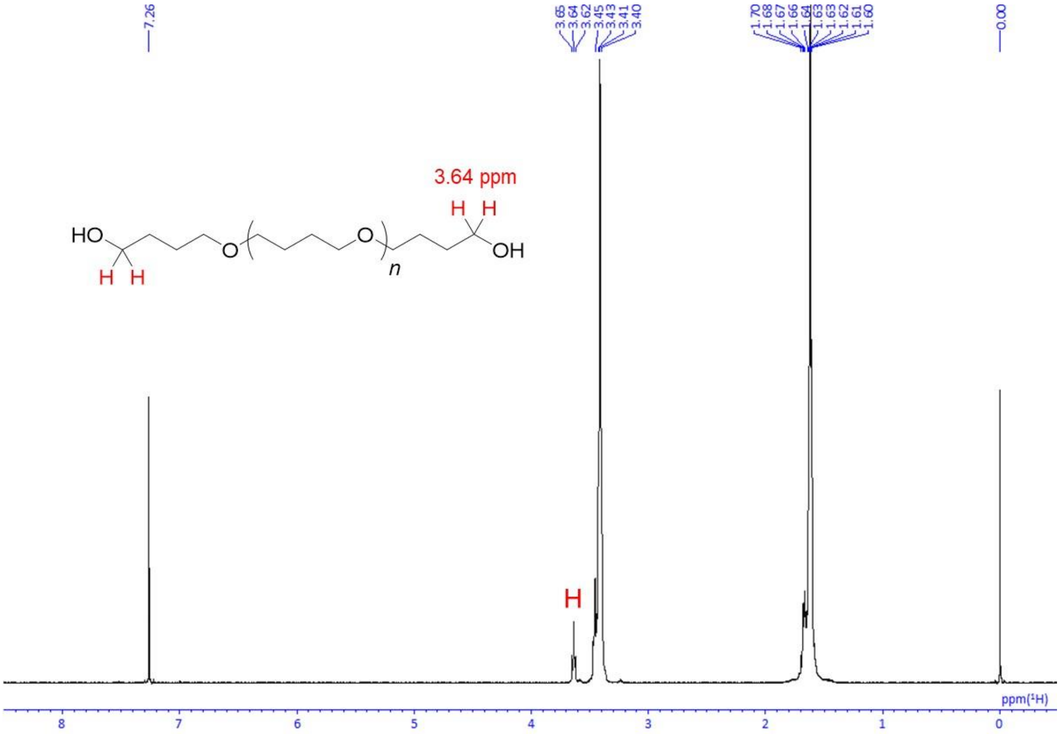


**Figure S3.** $^1$H NMR spectrum of PTMG.

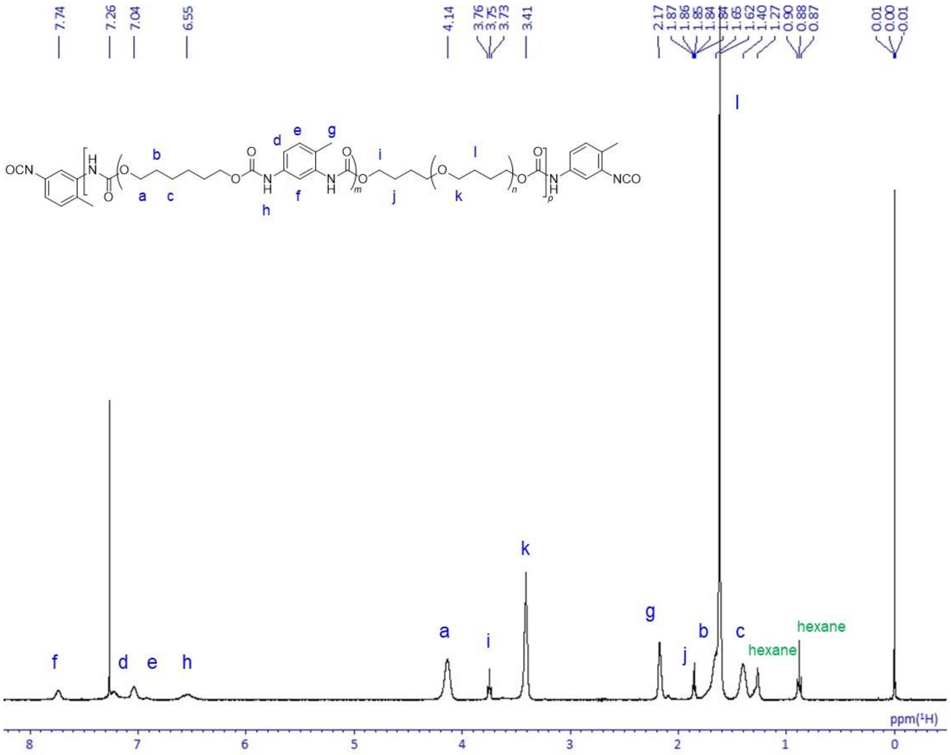


**Figure S4.** Identification of chemical shifts of protons in $^1$H NMR spectrum of PUM.

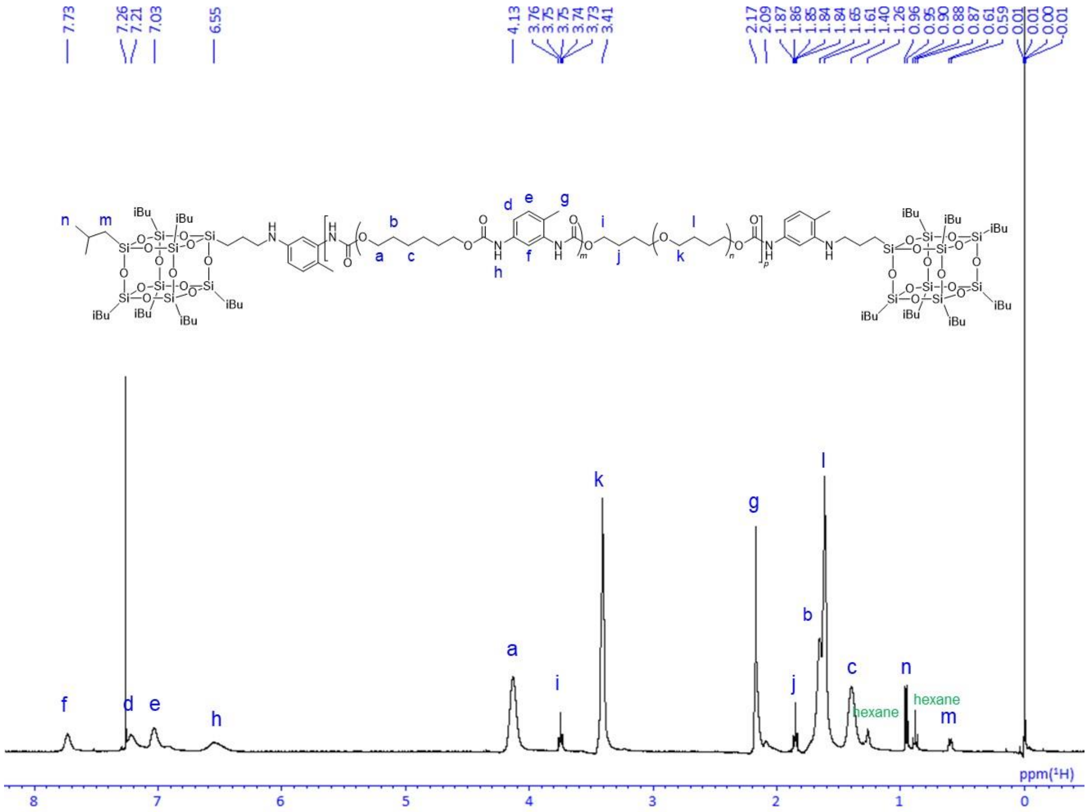


**Figure S5.** Identification of chemical shifts of protons in $^1$H NMR spectrum of PUPOSS.

### Preparation of PF/PUPOSS and PF/PUM

The mixtures (4 mL) containing the PUPOSS or PUM (300 mg) and PF (1.5 mg) in THF were stirred at room temperature for 1 h. The resulting solution was dropped on the perfluoroalkoxy alkane (PFA) dish (φ50 mm) and dried for 12 h under ambient condition to afford self-standing hybrid films, PF/PUPOSS or PF/PUM. The amounts of PF were 0.5 wt%. By the same procedure, films not-containing PF were also prepared.

### Preparation of PF/iBuPOSS/PUM

The mixtures (4 mL) containing PUM (300 mg), PF (1.5 mg) and iBuPOSS (18 mg: the amount of iBuPOSS was the same as that of POSS units in PUPOSS in THF were stirred at room temperature for 1 h. The resulting solution was dropped on the PFA dish (φ50 mm) and dried for 12 h under ambient condition to afford self-standing hybrid films, PF/iBuPOSS/PUM. The amounts of PF and iBuPOSS were 0.5 and 6 wt%. By the same procedure, films not containing PF were also prepared.

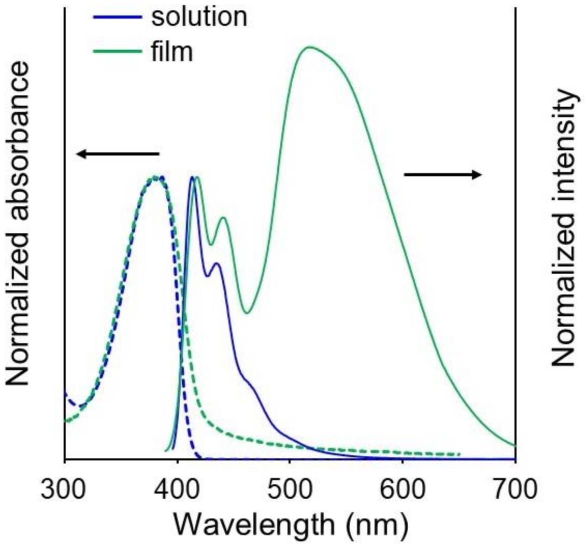


**Figure S6.** UV–vis absorption (dotted line) and PL spectra (solid line) of PF in chloroform ($1.0 \times 10^{-5}$ M per repeating units) and a film state with the excitation light at 375 nm.

**Table S1.** Spectroscopic data of PF

| | $\lambda_{abs}$ (nm) | $\lambda_{PL}$ (nm)[a] | $\Phi_{PL}$ (%)[b] | $\tau$ (ns) | $\chi^2$ |
|---|---|---|---|---|---|
| solution | 387 | 414, 434 | 69 | 0.45 | 1.17 |
| film | 380 | 418, 441, 517 | 48 | <0.1, 8.7 | −, 1.20 |

[a] Excited at 375 nm. [b] Determined as an absolute value.

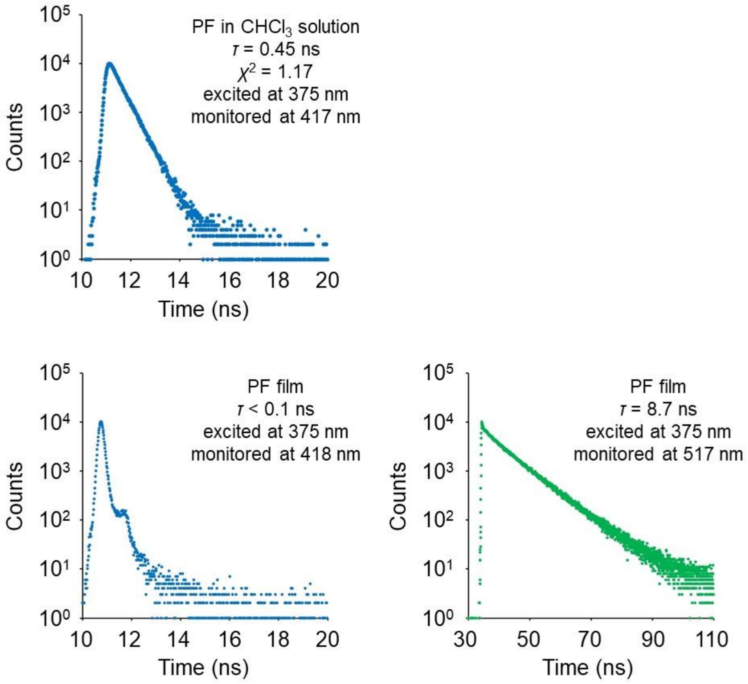


**Figure S7.** PL lifetime decay curves of **PF** both in chloroform ($1.0\times10^{-5}$ M) and film at room temperature (excited at 375 nm with a LED laser).

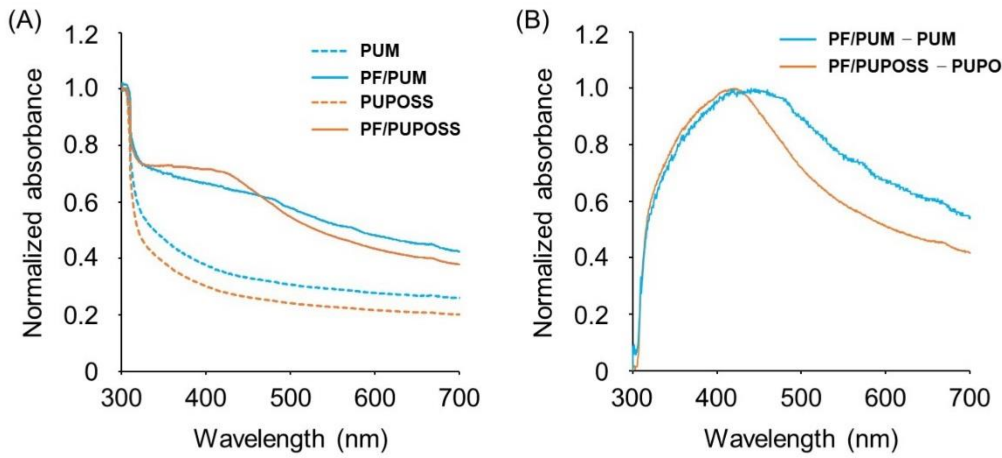


**Figure S8.** UV–vis absorption spectra of hybrid films. (A) Normalized spectra of hybrid films and (B) absorbance difference spectra of hybrid films.

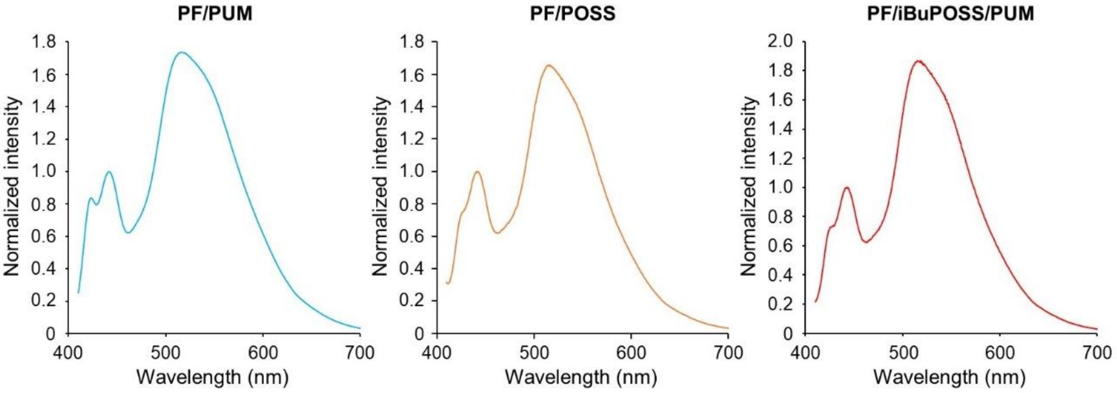


**Figure S9.** PL spectra of the hybrid films.

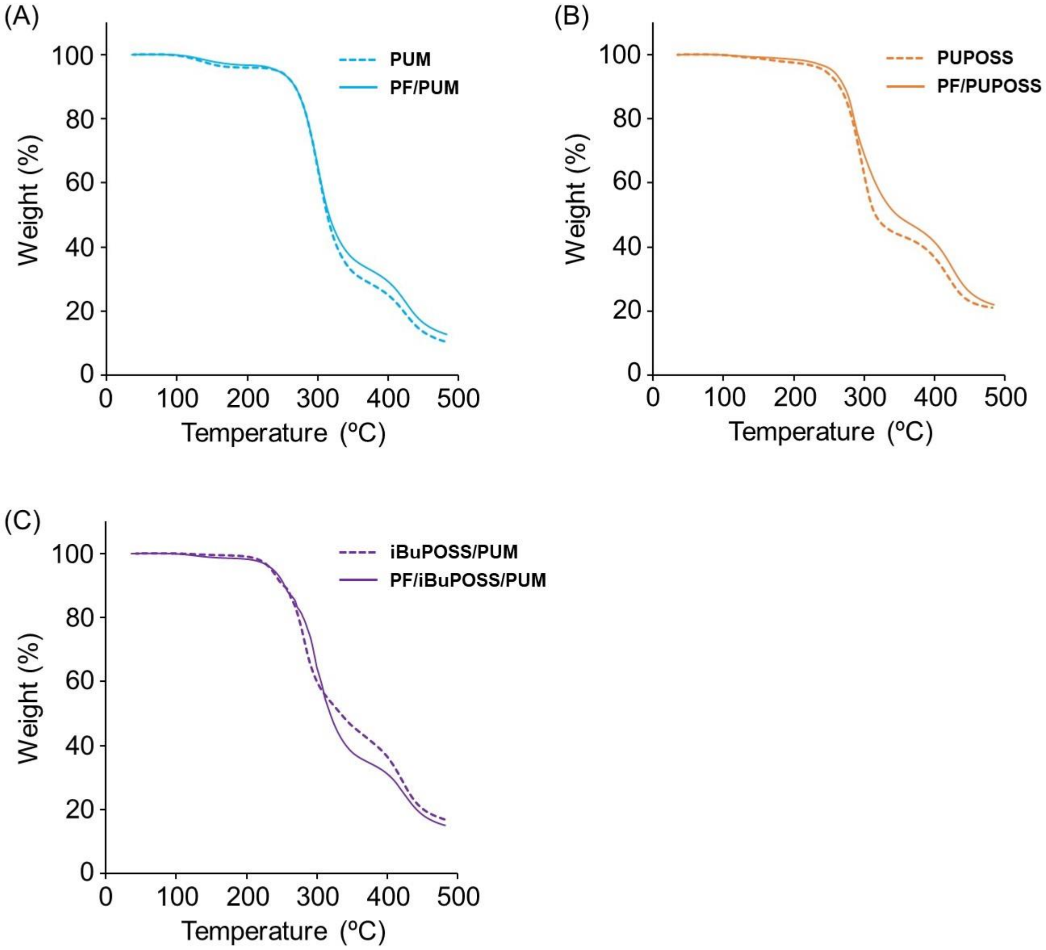


**Figure S10.** TGA curves of hybrid films of (A) **PUM** and **PF/PUM**, (B) **PUPOSS** and **PF/PUPOSS**, (C) **iBuPOSS/PUM** and **PF/iBuPOSS/PUM** under $N_2$ (scan rate, 10 °C $\mathrm{min}^{-1}$).

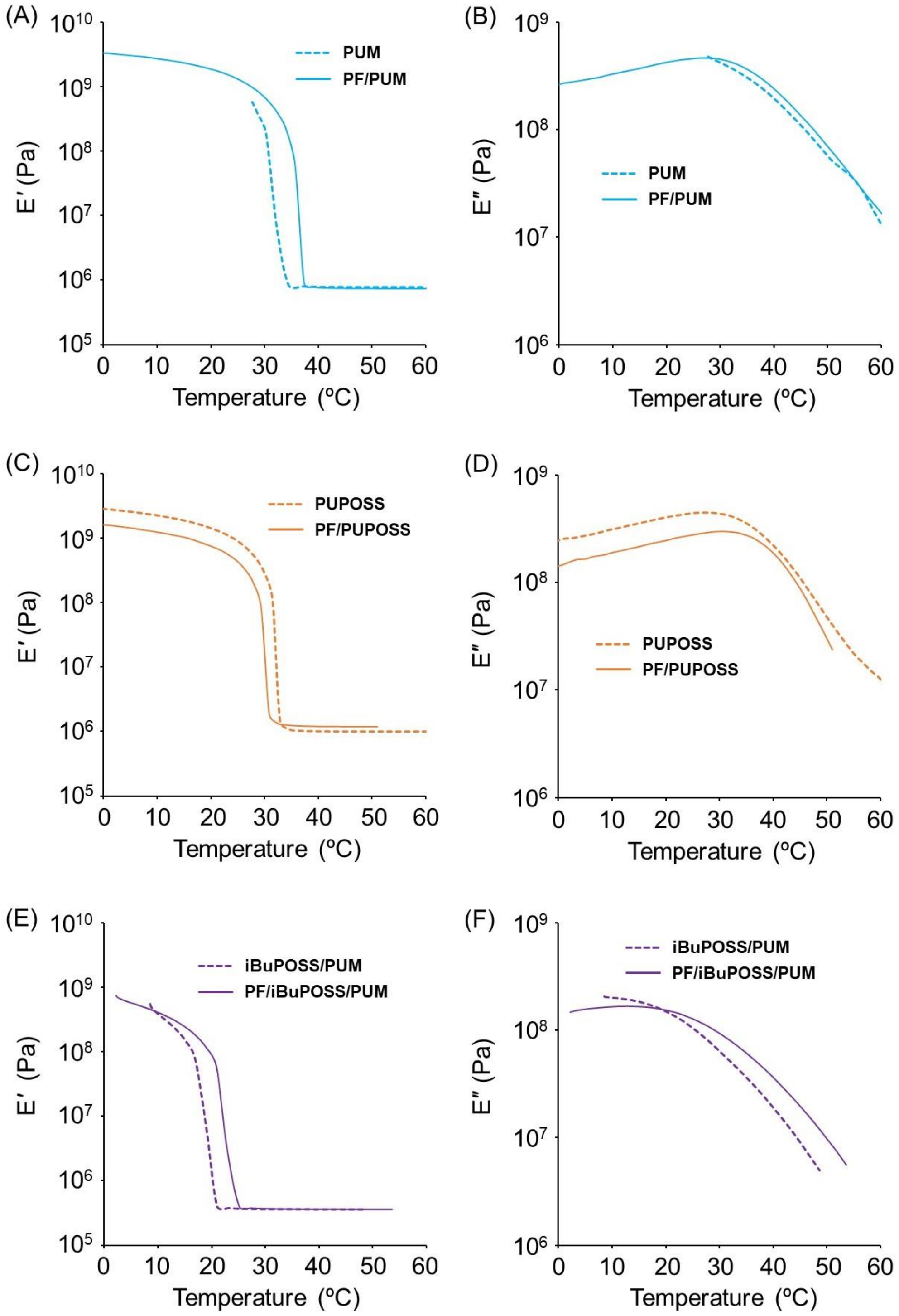


**Figure S11.** DMA curves of hybrid films of (A) storage modulus and (B) loss modulus of **PUM** and **PF/PUM**, (C) storage modulus and (D) loss modulus of **PUPOSS** and **PF/PUPOSS**, (E) storage modulus and (F) loss modulus of **iBuPOSS/PUM** and **PF/iBuPOSS/PUM** under air (scan rate, 4 °C $\text{min}^{-1}$, frequency, 1 Hz).

**Table S2.** Storage moduli and glass transition temperatures of hybrid films

|  | PF content (wt%) | $E'$ (MPa)[a] | $E''$ (MPa)[a] | tan $\delta$[a] | $T_g$ (°C) |
|---|---|---|---|---|---|
| PUM | 0 | 0.79 | 203 | 257 | 34 |
| PF/PUM | 0.5 | 0.78 | 240 | 308 | 37 |
| PUPOSS | 0 | 1.02 | 223 | 219 | 35 |
| PF/PUPOSS | 0.5 | 1.20 | 188 | 157 | 34 |
| iBuPOSS/PUM | 0 | 0.36 | 19 | 53 | 25 |
| PF/iBuPOSS/PUM | 0.5 | 0.36 | 36 | 100 | 20 |

[a] Measured at 40 °C.

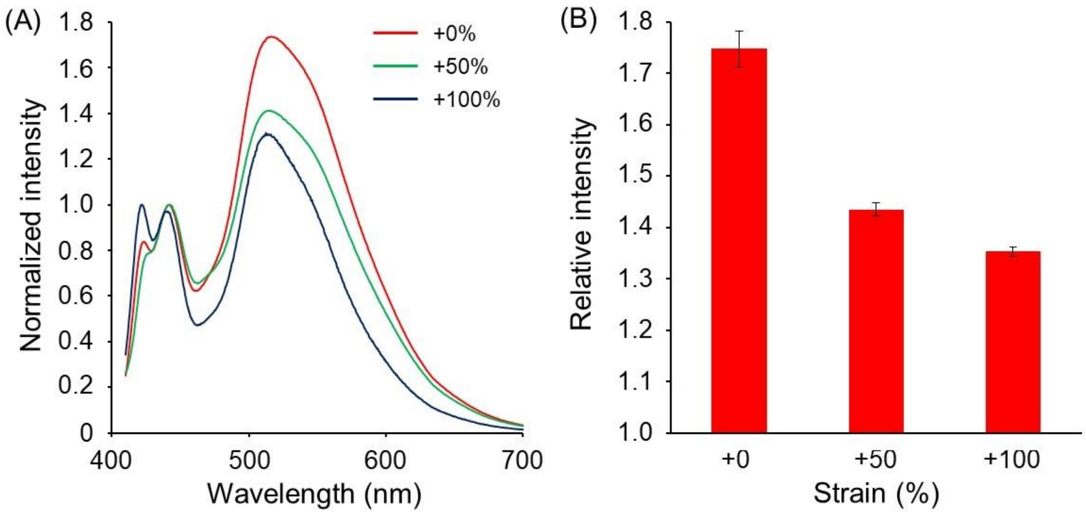


**Figure S12.** (A) PL spectra of **PF/PUM** at each strain. The spectra are normalized at the peak top wavelength of blue emission. (B) Relative intensity at the peak top wavelength of excimer emission at each strain. The error bar is calculated from four times experiments.

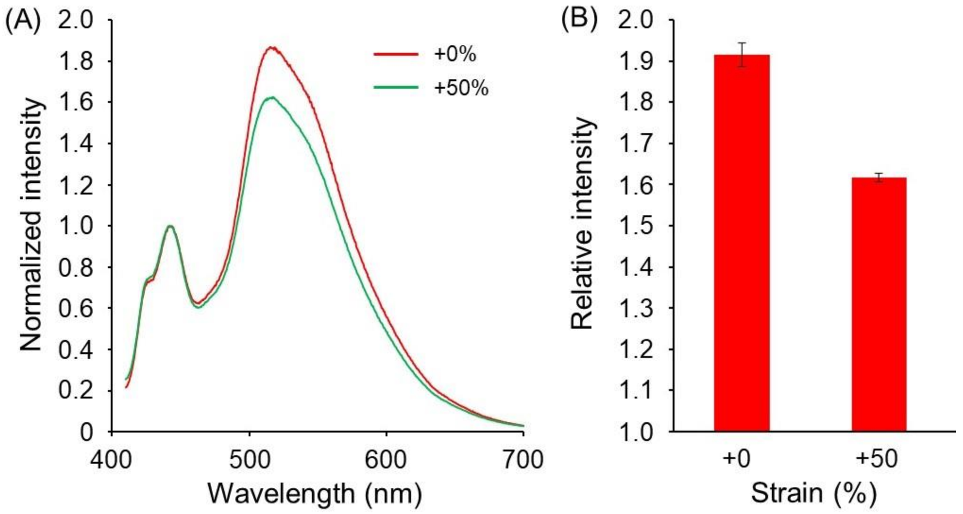


**Figure S13.** (A) PL spectra of **PF/iBuPOSS/PUM** at each strain. The spectra are normalized at the peak top wavelength of blue emission. (B) Relative intensity at the peak top wavelength of excimer emission at each strain. The error bar is calculated from four times experiments.

## References

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2. K. Tanaka, S. Adachi and Y. Chujo, *J. Polym. Sci. Part A: Polym. Chem.*, 2009, **47**, 5690−5697.

3. K. Ueda, K. Tanaka and Y. Chujo, *Polym. J.*, 2016, **48**, 1133−1139.