Supporting Information for

A new fluoropolymer having triazine rings as a dielectric material: synthesis and properties †

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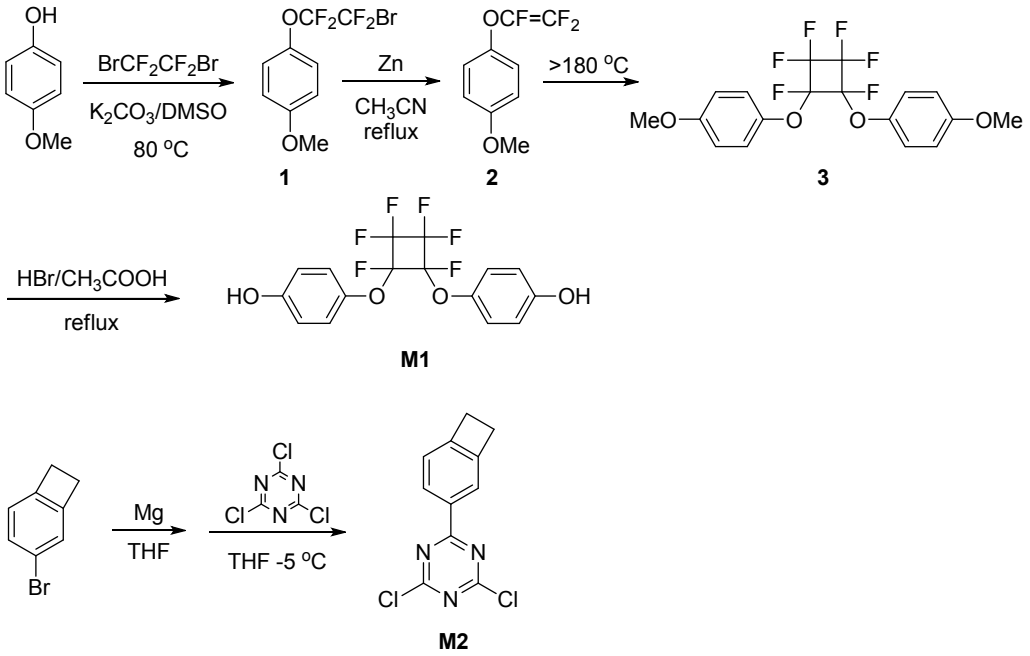
Synthesis of monomers M1 and M2



Scheme S1. Procedure for the synthesis of monomers **M1** and **M2**.

Regents: Cyanuric chloride and 4-methoxyphenol were purchased from Admas-Beta Reagents (Shanghai) Co., Ltd. Zinc powder was activated by washing with 0.1 M hydrochloric acid followed by drying at 150 °C in vacuum for 3 h before use. 1,2-Dibromotetrafluoroethane was purchased from Top Fluorochem Co., Ltd., China and used as received.

Compounds **1**, **2**, and **3** were prepared according to the previously reported route[1].

*Synthesis of **M1*** (see Scheme 1): a mixture of compound **3** (13.48 g, 33.02 mmol), hydrobromic acid (100 mL, 40 wt%) and acetic acid (150 mL) was heated to reflux and kept at the temperature for 12 h. After being cooled to room temperature, the mixture was neutralized with aqueous NaOH (5M), and the solvents were evaporated under reduced pressure. The residue was re-dissolved in acetone and the obtained solution was poured into

water to give **M1** as a gray precipitate in a yield of 94.6%. ^{1}H NMR (400 MHz, acetone-d_6, ppm): δ 8.74 ~ 8.34 (s, 2H, Ar-OH), 7.25 ~ 6.95 (d, 2H, Ar-H), 6.95 ~ 6.59 (d, 2H, Ar-H). ^{13}C NMR (100 MHz, acetone-d_6, ppm): δ 156.21, 155.98, 145.98, 145.69, 121.09, 120.78, 117.00, 116.93. ^{19}F NMR (376 MHz, acetone-d_6, ppm): δ -128.02, -129.66, -129.80, -130.07, -130.26, -130.29, -130.32, -130.66, -130.67, -130.99, -131.00, -131.33, -131.62, -131.92, -132.21, -132.80. Anal. Calcd. For $C_{16}H_{10}F_6O_4$: C, 50.54; H, 2.65; F, 29.98. Found: C, 50.44; H, 2.79; F, 29.31. HRMS (EI, m/z) Calcd. for (M^+) $C_{11}H_8N_3Cl_2^+$ = 380.0483. Found 380.0485.

Synthesis of ***M2*** (see Scheme 1): a solution of 4-bromobenzocyclobutanene (29.60 g, 162.66 mmol) in tetrahydrofuran (70 mL) was added dropwise to a mixture of magnesium turnings (5.80 g, 238.58 mmol) and tetrahydrofuran (30 mL) at 40 °C. After addition, the resulting mixture was stirred for additional 3 h and cooled to room temperature under nitrogen atmosphere. A benzocyclobutanene-based Grignard reagent was thus obtained, which was then added dropwise to a solution of cyanuric chloride (20.00 g, 108.45 mmol) in tetrahydrofuran (200 mL) at about -5 °C. The reaction mixture was stirred for additional 12 h at the temperature, treated with saturated NH_4Cl aqueous solution (200 mL), and extracted with dichloromethane. The organic layers were combined, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum. The obtained residue was purified by flash column chromatography to give **M2** as white crystals in a yield of 78.8%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.44~8.38 (d, 1H, Ar-H), 8.20~8.14 (s, 1H, Ar-H), 7.22~7.16 (d, 1H, Ar-H), 3.31~3.18 (t, 4H, Ar-C_2H_4). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 175.59, 171.87, 154.44, 146.80, 131.48, 129.61, 123.93, 123.26, 30.29, 29.44. Anal. Calcd. for $C_{11}H_7N_3Cl_2$: C, 52.41; H, 2.80; N, 16.67; Cl, 28.13. Found: C, 52.22; H, 2.89; N, 16.70; Cl, 28.47. HRMS (DART,

m/z) Calcd. for (M^+H^+) $C_{11}H_8N_3Cl_2^+$ = 252.0095. Found 252.0090.

Characterization of polymer P1:

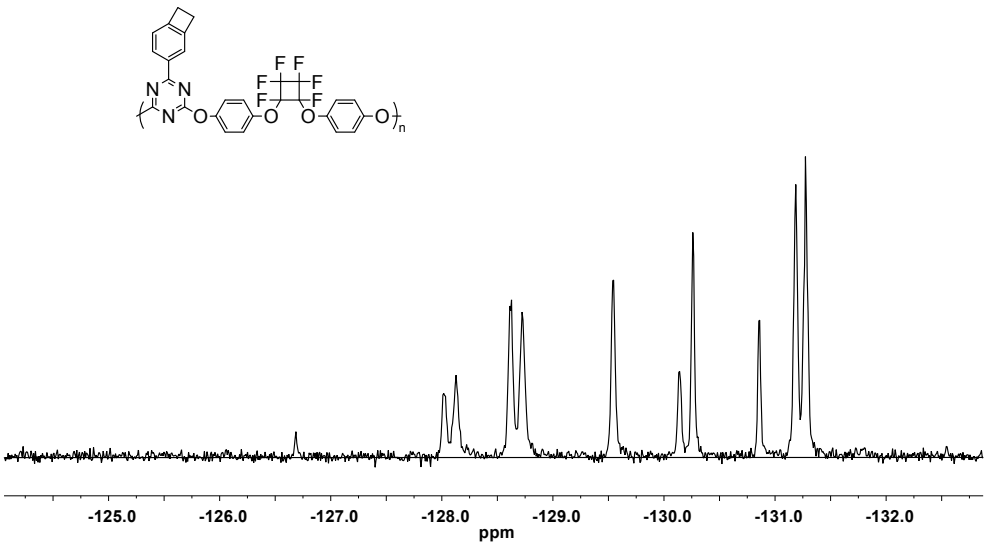


Fig. S1 ^{19}F NMR spectrum of **P1** (376 MHz, $CDCl_3$).

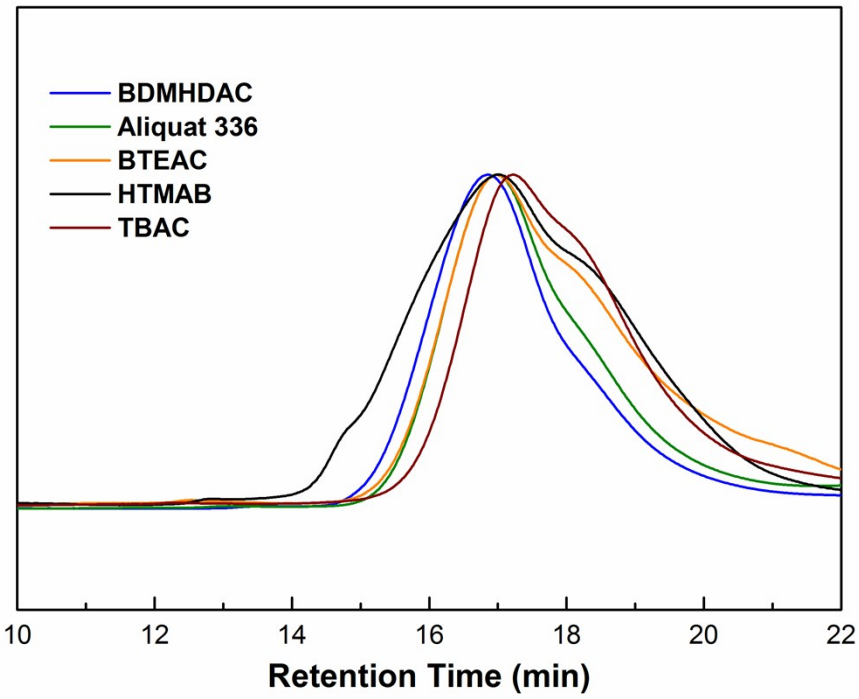


Fig. S2 GPC curves of the effect of the structure of PTC on polymerization

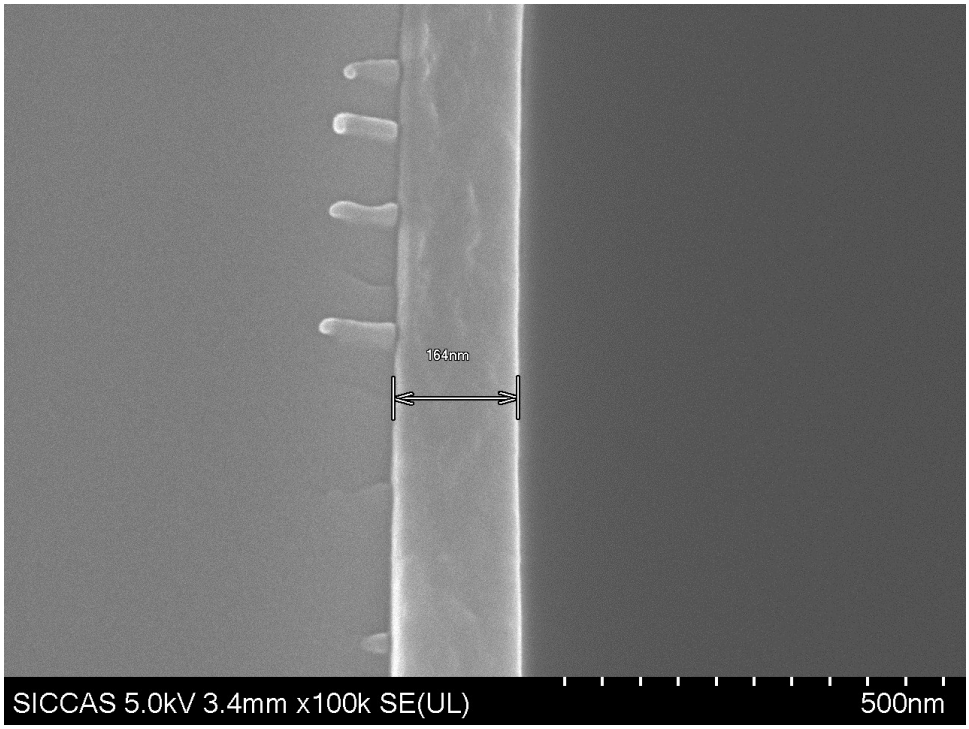


Fig. S3 SEM image of the section plane of cured **P1** film on wafer for the measurement of dielectric constants and dissipation factors.

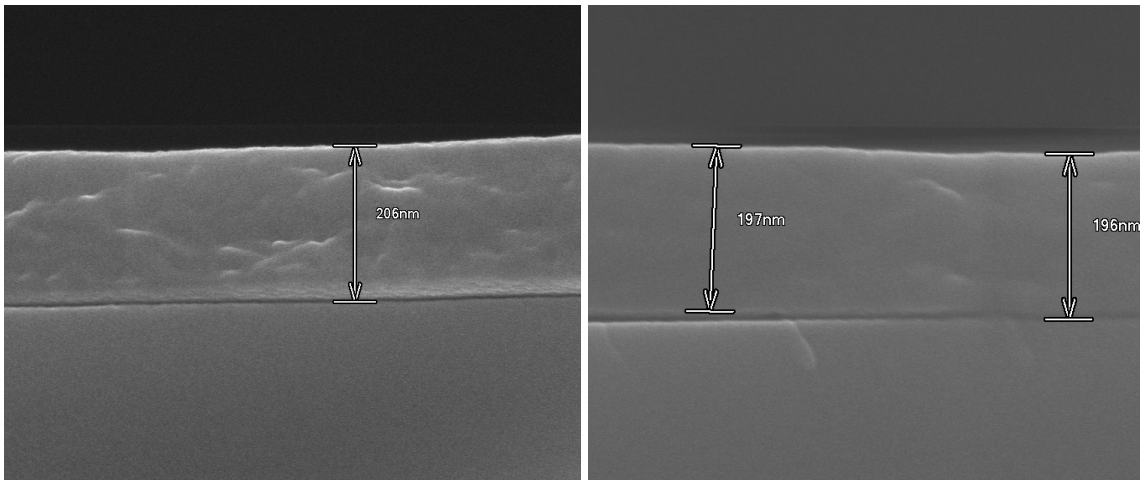


Fig. S4 SEM images of the section plane of cured **P1** film (left) and PPE film (right) on wafers for the measurement of dielectric strength.

References

1. Q. Fang , J. Zhou, Y. Luo, J. Wang, K. Jin and Y. Wang, Chinese Patent, CN104311401, 2015.