## *Supporting Information*

# Synthesis and Characterization of White-Light Luminescent End-Capped Polyimides Based on FRET and Excited State Intramolecular Proton Transfer

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## 1. Experimental Section

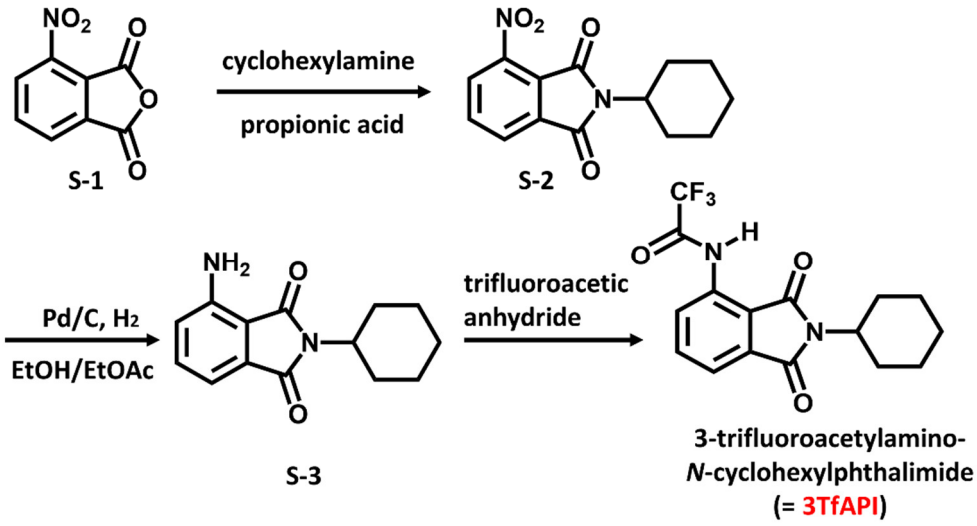
*Synthesis of 3-nitro-N−cyclohexylphthalimide (**S-2**)*. Briefly, 3-nitrophthalic anhydride (5.79 g, 30 mmol) was refluxed in a mixture of cyclohexylamine (4.46 g, 45 mmol) and propionic acid (50 mL) for 6.5 h. After cooling to a temperature of 20 °C, a faint brown solid that was reprecipitated by excess water, was filtered and dried. White, needle-like crystals were obtained by recrystallization from ethanol (yield, 82%). For $^1$H NMR (400 MHz, $CDCl_3$: $\delta$ [ppm] 1.25–1.39 (3H, br *m*, $CH_2$), 1.72–1.73 (3H, br *m*, $CH_2$), 1.86–1.87 (2H, br *m*, $CH_2$), 2.15–2.25 (2H, br *m*, $CH_2$), 4.15 (1H, *m*, N–CH), 7.90 (1H, *t*, *J* = 16.0 Hz, aryl), 8.08 (2H, *t*, *J* = 14.8 Hz, aryl) (**Figure S1**).

*Synthesis of 3-amino-N-cyclohexylphthalimide (**S-3**)*. Compound **S-2** (4.13 g, 15 mmol) was dissolved in a mixture of ethanol (50 mL) and ethyl acetate (95 mL), followed by the addition of 10% palladium on carbon (Pd/C, wetted with ca. 55% water) (0.917 g). This mixture was subsequently stirred at 20 °C under a hydrogen atmosphere for 1 d. The reaction solution was passed through Celite 535 to remove Pd/C, and the filtrate was concentrated using a rotary evaporator. The resulting solid was recrystallized from ethanol, and vivid yellow plate-like

crystals were obtained (yield, 76%). For $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ [ppm] 1.24–1.41 (3H, br *m*, $CH_2$), 1.66–1.73 (3H, br *m*, $CH_2$), 1.84–1.87 (2H, br *m*, $CH_2$), 2.13–2.23 (2H, br *m*, $CH_2$), 4.04 (1H, *m*, N-CH), 5.22 (2H, br *s*, NH), 6.82 (1H, *d*, *J* = 8.4 Hz, aryl), 7.10 (1H, *d*, *J* = 7.6 Hz, aryl), 7.38 (1H, *t*, *J* = 15.6 Hz, aryl) (**Figure S2**).

*Synthesis of 3-trifluoroacetylamino-N-cyclohexylphthalimide (**3TfAPI**)*. Compound **S-3** (0.50 g, 2.0 mmol) and sodium hydrogen carbonate (0.17g, 2.0 mmol) were added to 1,4-dioxane (4 mL), and trifluoroacetic anhydride (0.35 mL, 2.5 mmol) was added dropwise with stirring, after which the mixture was stirred for 30 min. The reaction solution with excess water was filtered and dried. White needle-like crystals were obtained by recrystallization from *n*-hexane (yield, 65%). For $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ [ppm] 1.25–1.42 (3H, br *m*, $CH_2$), 1.55–1.90 (5H, br *m*, $CH_2$), 2.09–2.22 (2H, br *m*, $CH_2$), 4.09 (1H, *m*, N-CH), 7.63 (1H, *d*, aryl), 7.75 (1H, *t* aryl), 8.68 (1H, *d*, aryl), 10.55 (1H, br *s*, NH) (**Figure S3**).
HRMS (FAB) m/z $[M + H]^+$ calcd for $C_{16}H_{15}N_2O_3F_3$ 341.1113; found 341.1119.
Anal. Calced for $C_{16}H_{15}N_2O_3F_3$: C, 56.47; H, 4.44; N, 8.23; O, 14.10; F, 16.75. Found: C, 56.85; H, 4.19; N, 8.23; O+F, 30.73.

## 2. Figures and Table




**Scheme S1.** Synthesis route of 3-trifluoroacetylamino-*N*-cyclohexylphthalimide (**3TfAPI**).

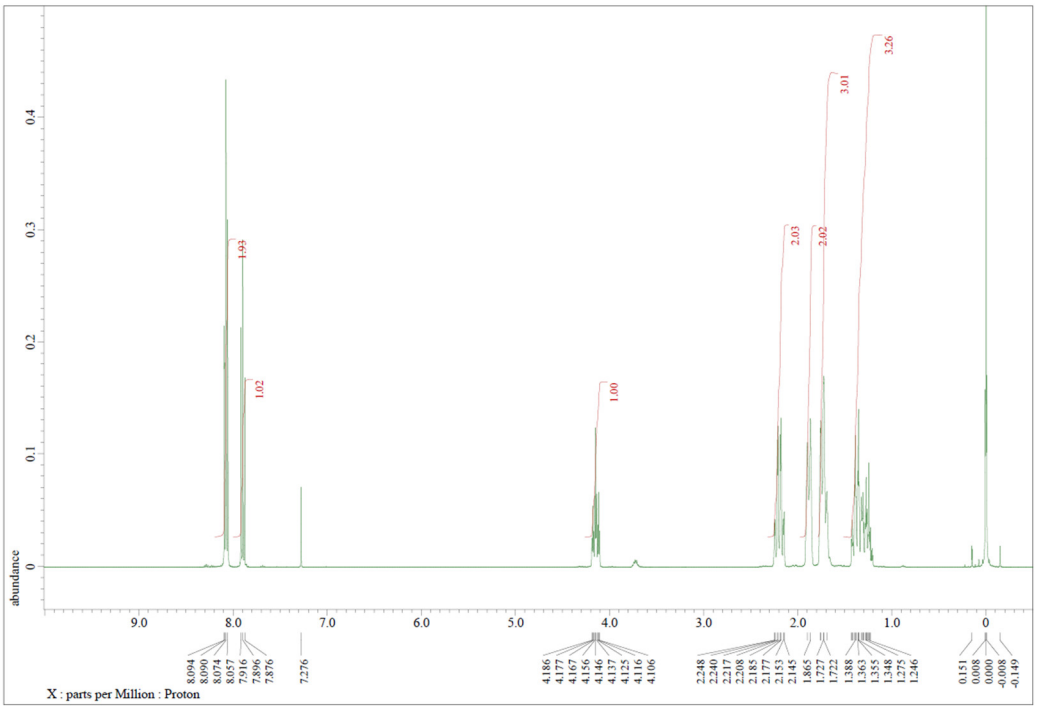



**Figure S1.** $^{1}$H NMR spectrum of 3-nitro-*N*-cyclohexylphthalimide (**S-2**).

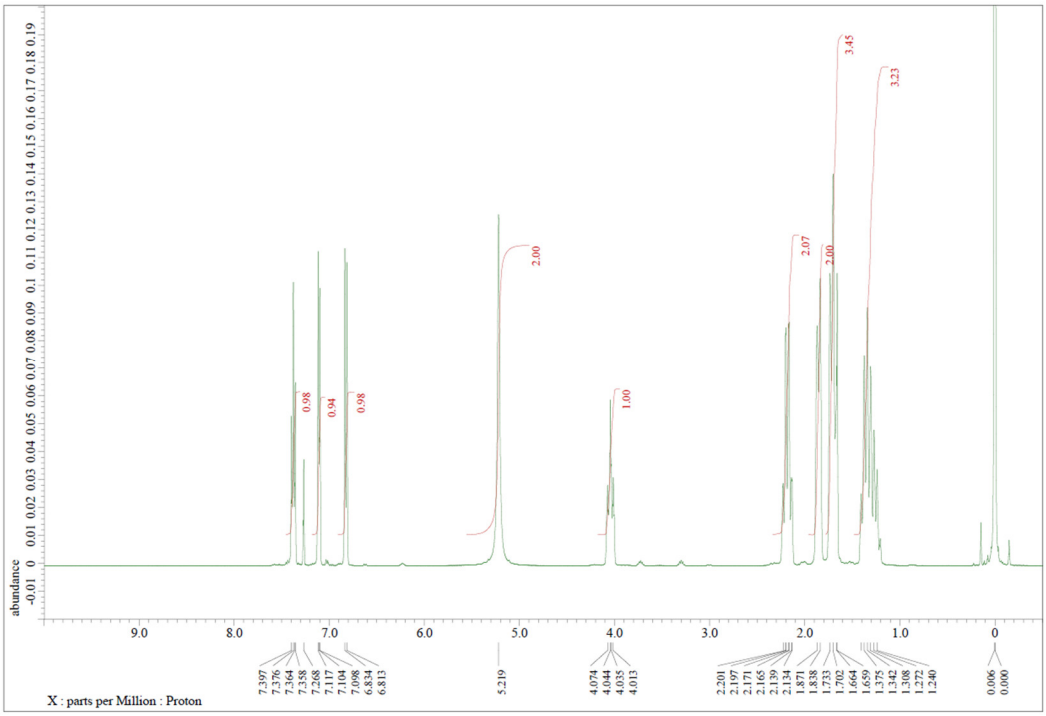



**Figure S2.** $^{1}$H NMR spectrum of 3-amino-*N*-cyclohexylphthalimide (**S-3**).

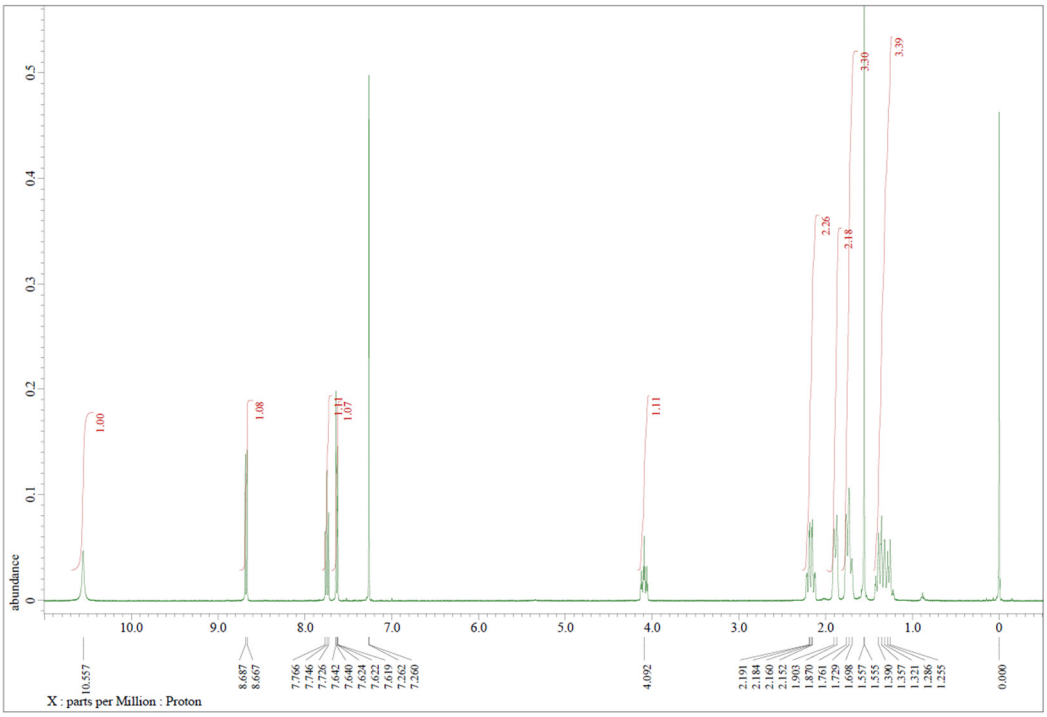
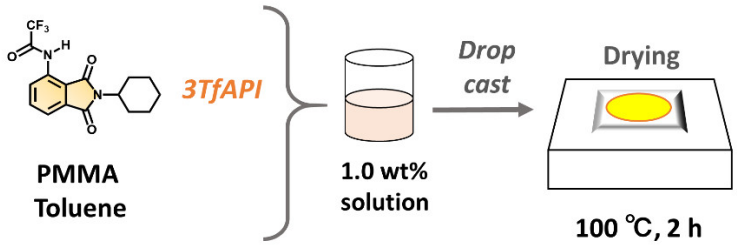



**Figure S3.** $^{1}$H NMR spectrum of 3-trifluoroacetylamino-*N*-cyclohexylphthalimide (3TfAPI).




**Scheme S2.** Preparation scheme for polymethyl methacrylate (PMMA) dispersion thin film.

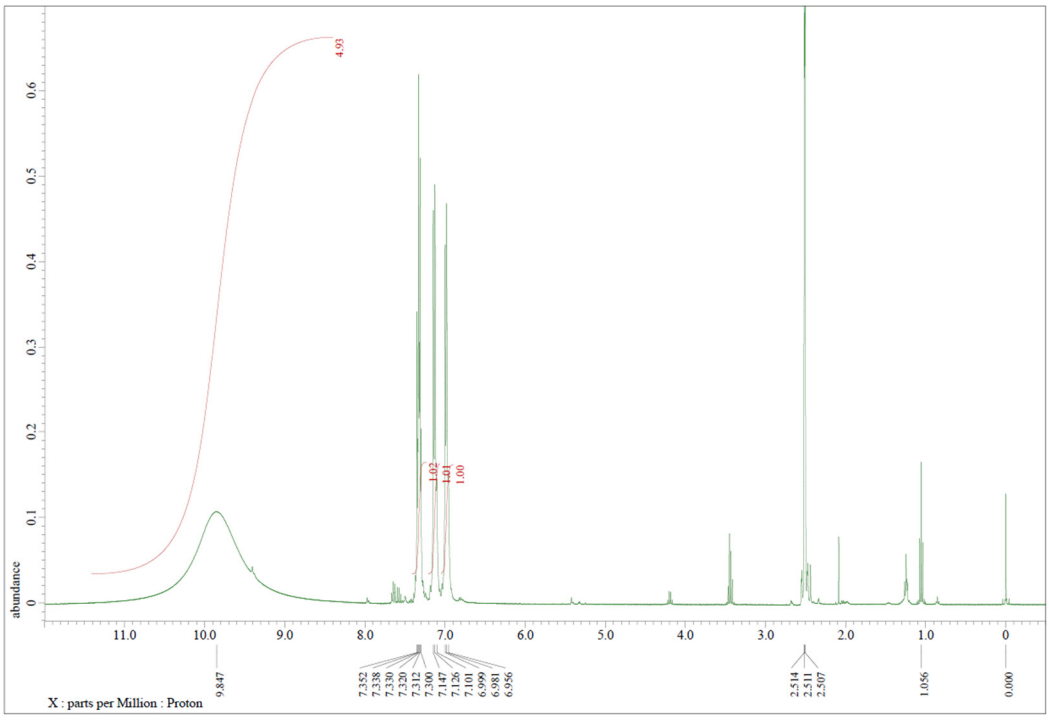



**Figure S4.** [1]H NMR spectrum of 3-aminophthalic acid hydrochloride (**2**).

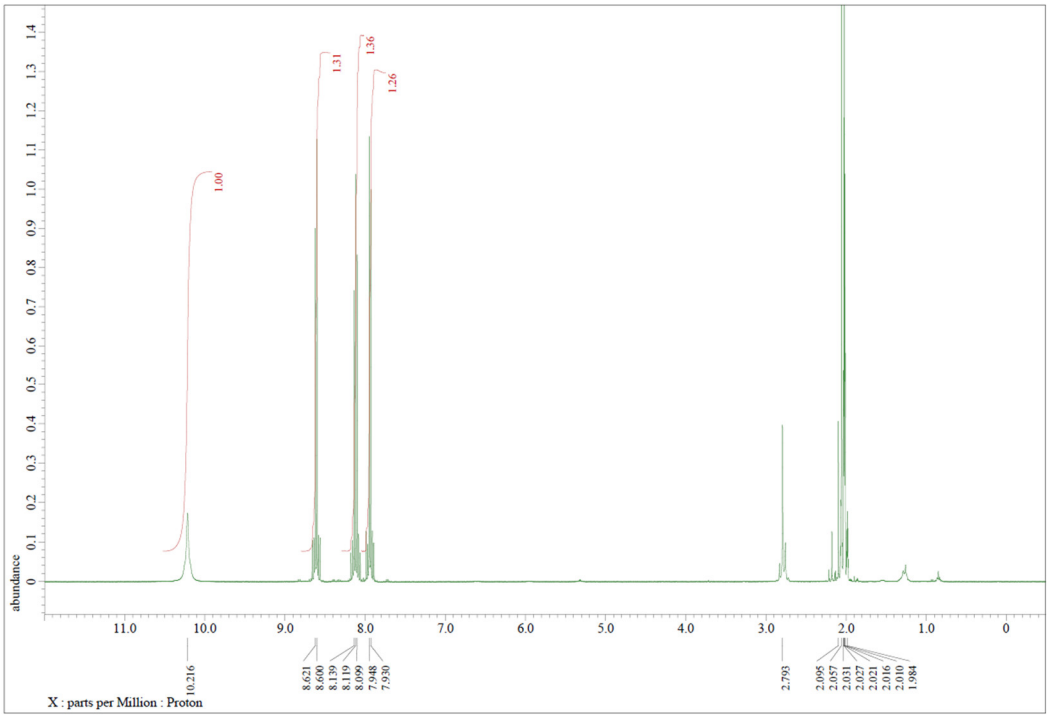



**Figure S5.** [1]H NMR spectrum of 3-trifluoroacetylaminophthalic anhydride (3TfAPA).

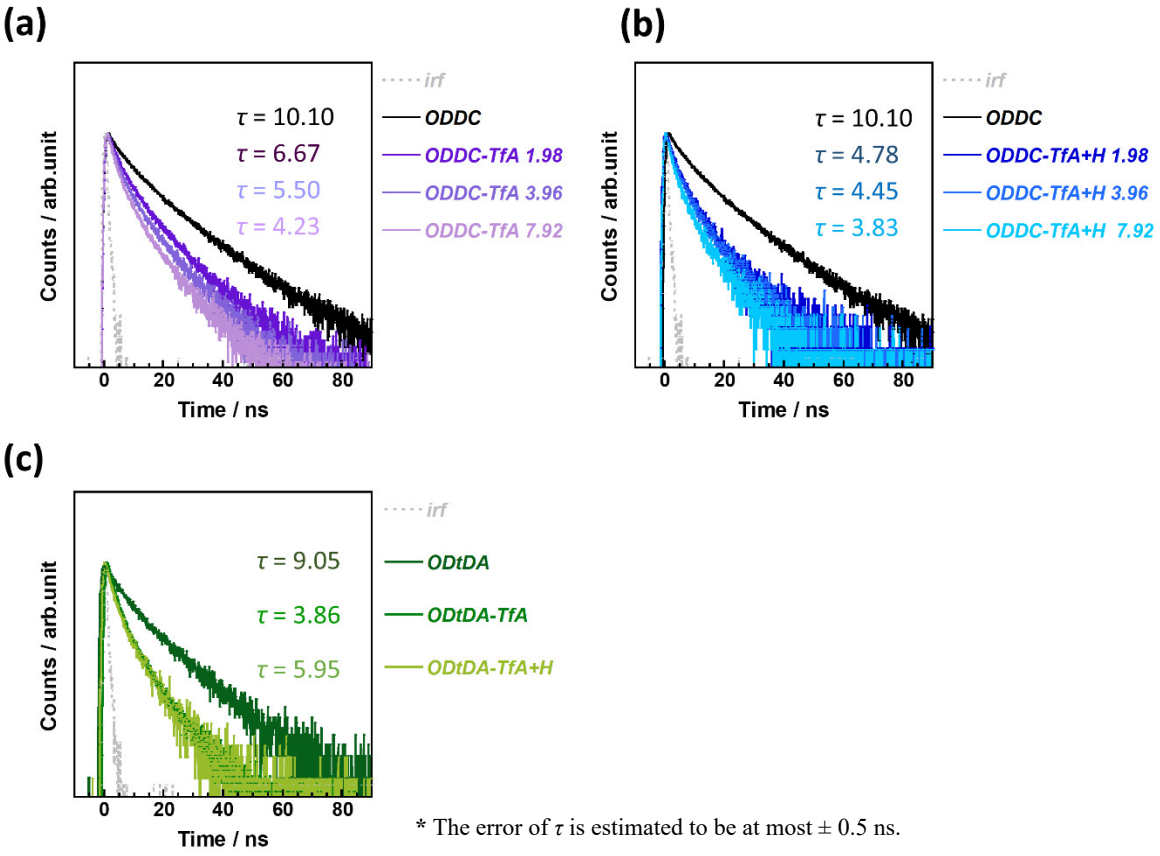



**Figure S6**. Time-resolved fluorescence decay curves for the end-capped PIs; (a) **ODDC-TfA** and (b) those doped with 0.5 ~ 1.0 eq. $H_2SO_4$ prepared with variable *r* values (*r* = 0, 1.98, 3.96, 7.98). (c) **OD*t*DA-TfA** and that doped with 0.5 eq. $H_2SO_4$ prepared with *r* = 0 and 14.8.

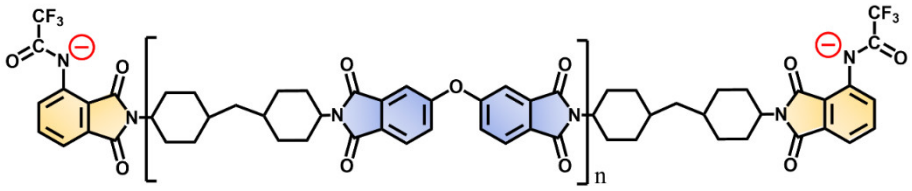


**Figure S7.** Chemical structure of the anion form of **ODDC-TfA**.

**Table S1.** Detailed International Commission on Illumination (CIE) coordinates for each end-capped PI (**ODDC-TfA**, **OD*t*DA-TfA** and those doped with $H_2SO_4$ (0.5 ~ 1.0 eq.) prepared with variable *r* values (*r* = 1.98, 3.96, 7.98, 14.8)).

| Polyimide (PI) | *r* | CIE coordinates |
|---|---|---|
| **ODDC-TfA** | 1.98 | (0.198, 0.174) |
| | 3.96 | (0.225, 0.218) |
| | 7.92 | (0.252, 0.258) |
| **$H_2SO_4$- doped ODDC-TfA (0.5~1.0 eq.)** | 1.98 | (0.221, 0.192) |
| | 3.96 | (0.255, 0.244) |
| | 7.92 | (0.301, 0.327) |
| **OD*t*DA-TfA** | 14.8 | (0.212, 0.230) |
| **$H_2SO_4$-doped OD*t*DA-TfA (0.5 eq.)** | 14.8 | (0.307, 0.347) |

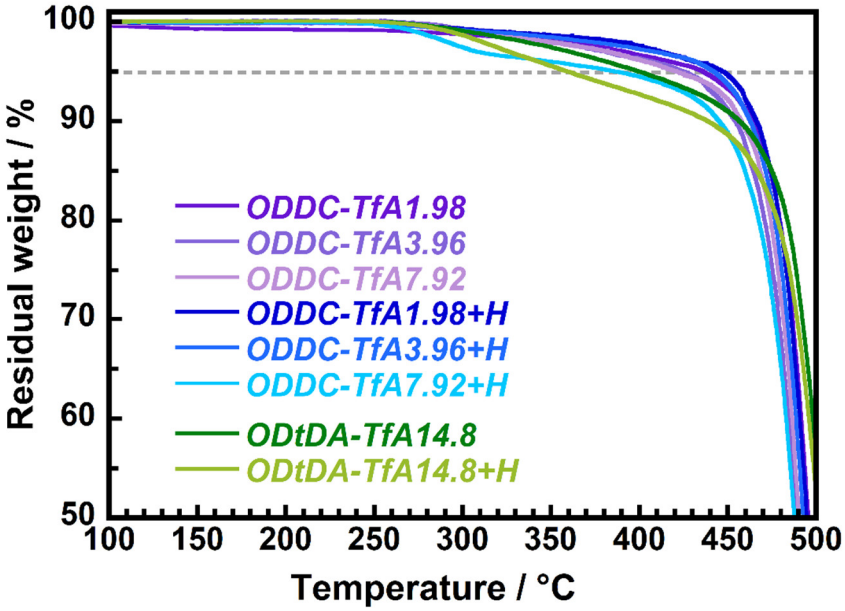



**Figure S8.** Thermogravimetric curves measured by thermogravimetric analysis (TGA) for the end-capped PIs (**ODDC-TfA**, **OD*t*DA-TfA** and those doped with 0.5 ~ 1.0 eq. $H_2SO_4$ prepared with variable *r* values (*r* = 1.98, 3.96, 7.98, 14.8)).

**Table S2.** 5% weight loss temperatures ($T_d^5$) for each end-capped PI (**ODDC-TfA**, **OD*t*DA-TfA** and those doped with $H_2SO_4$ (0.5 ~ 1.0 eq.) prepared with variable *r* values (*r* = 1.98, 3.96, 7.98, 14.8)).

| Polyimides (PIs) | *r* | $T_d^5$ (°C) |
|---|---|---|
| **ODDC-TfA** | 1.98 | 436 |
| | 3.96 | 425 |
| | 7.92 | 423 |
| **$H_2SO_4$- doped ODDC-TfA (0.5~1.0 eq.)** | 1.98 | 447 |
| | 3.96 | 442 |
| | 7.92 | 387 |
| **OD*t*DA-TfA** | 14.8 | 400 |
| **$H_2SO_4$-doped OD*t*DA-TfA (0.5 eq.)** | 14.8 | 360 |