

Supporting Information

Direct arylation of fluoroarenes toward linear, bent-shaped and branched π -conjugated polymers: Polycondensation and post-polymerization approaches

Shotaro Hayashi,* Yuki Togawa, Yoshihisa Kojima, Toshio Koizumi*

Address, 1-10-20 Hashirimizu, Yokosuka, Kanagawa 239-8686, Japan. Fax: +81 46 844 5901; Tel: +81 46 841 3810 ext 3592; E-mail: shayashi@nda.ac.jp, tkoizumi@nda.ac.jp.

Synthesis of 2-Bromo-6-octyloxynaphthalene

2-bromo-6-naphthol (2.23 g, 10 mmol), 1-bromooctane (2.32 g, 12 mmol) and K_2CO_3 (2.07 g, 15 mmol) were dissolved in acetone (50 mL), the mixture was stirred under refluxing and a nitrogen atmosphere for 12 hours. The product was filtered to remove K_2CO_3 , and then acidified by diluted hydrochloric acid. After rotary evaporation, the residue was treated with water and extracted with chloroform. The organic layer was collected and dried over anhydrous $MgSO_4$, and then concentrated. The product was purified by column chromatography on silica gel with a mixture of hexane as eluent. The pure compound was obtained as a white solid. Yield: 93% (3.12 g). 1H NMR (300 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.59 (m, 2H), 7.46 (d, $J = 5.7$ Hz, 1H), 7.14 (d, $J = 9.0$ Hz, 1H), 7.06 (s, 1H), 4.03 (t, $J = 9.1$ Hz, $J = 12.9$ Hz, 2H), 1.85 (m, 2H), 1.5-1.2 (br, 10H), 0.88 (br, 3H). ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 157.44, 133.11, 129.92, 129.62, 129.51, 128.39, 128.31, 120.08, 116.86, 106.54, 68.12, 31.82, 29.36, 29.24, 29.20 26.01, 22.65, 14.08. Anal. Calcd. for ($C_{18}H_{23}BrO$): C, 64.48; H, 6.91. Found: C, 64.45; H, 6.93.

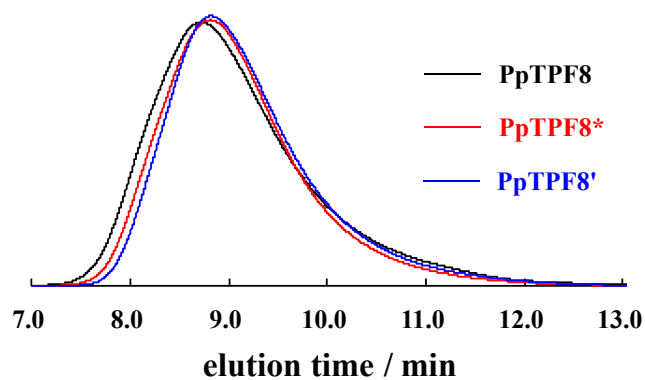


Figure S1. GPC trace of PpTPF8s.

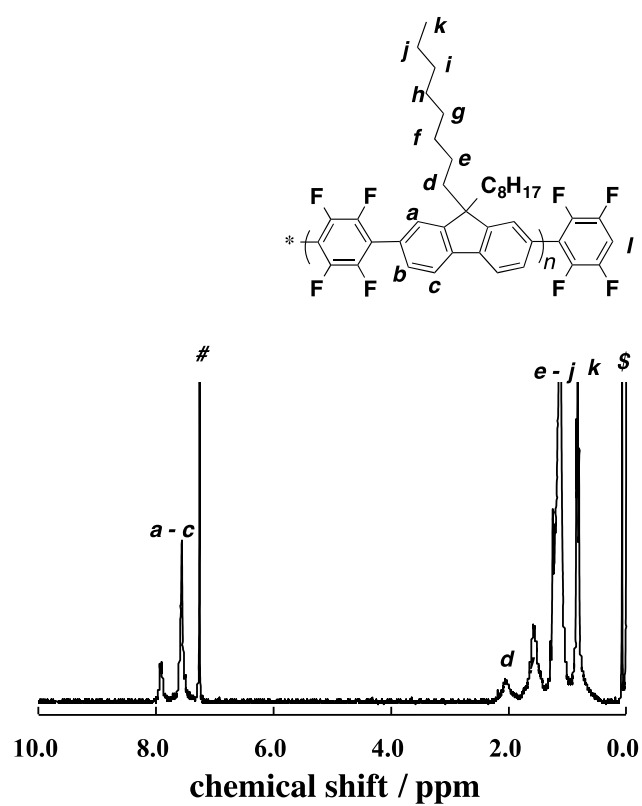


Figure S2. ^1H NMR spectrum of PpTPF8. #: CHCl_3 . !: H_2O . \$: TMS.

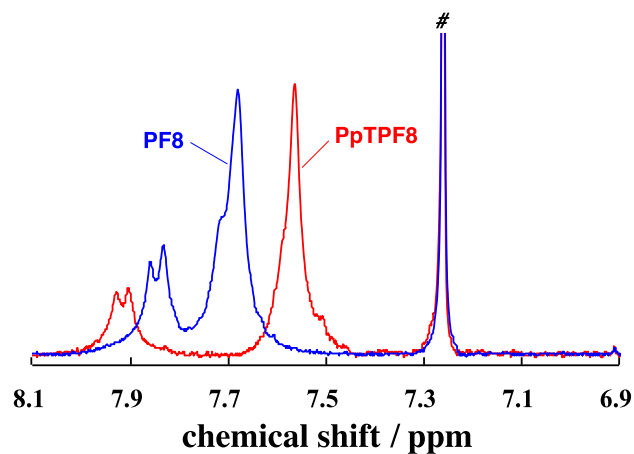


Figure S3. ^1H NMR spectra of **PpTPF8** (red line) and **PF8** (blue line). #: CHCl_3 .

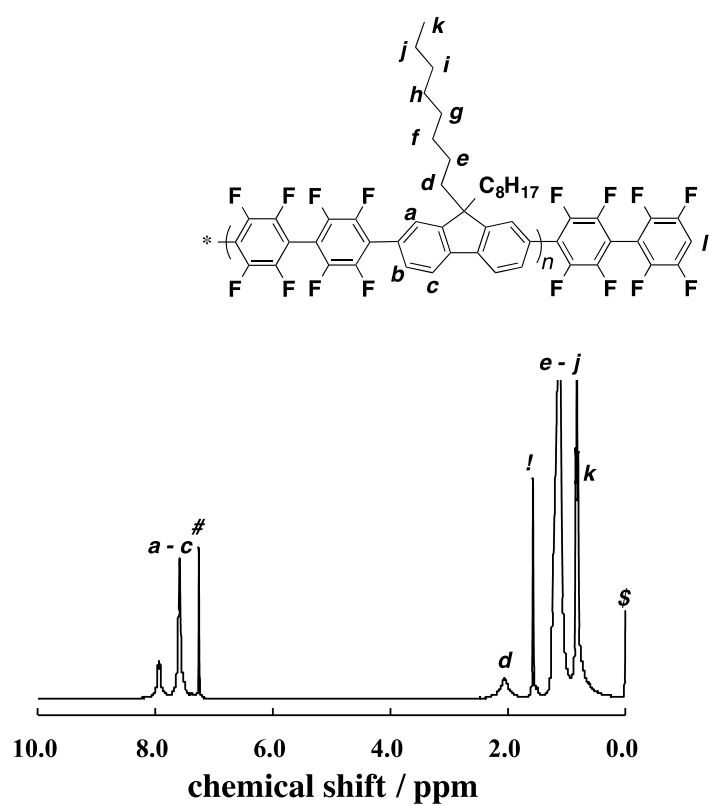


Figure S4. ^1H NMR spectrum of **PpOPPF8**. #: CHCl_3 . !: H_2O . \$: TMS.

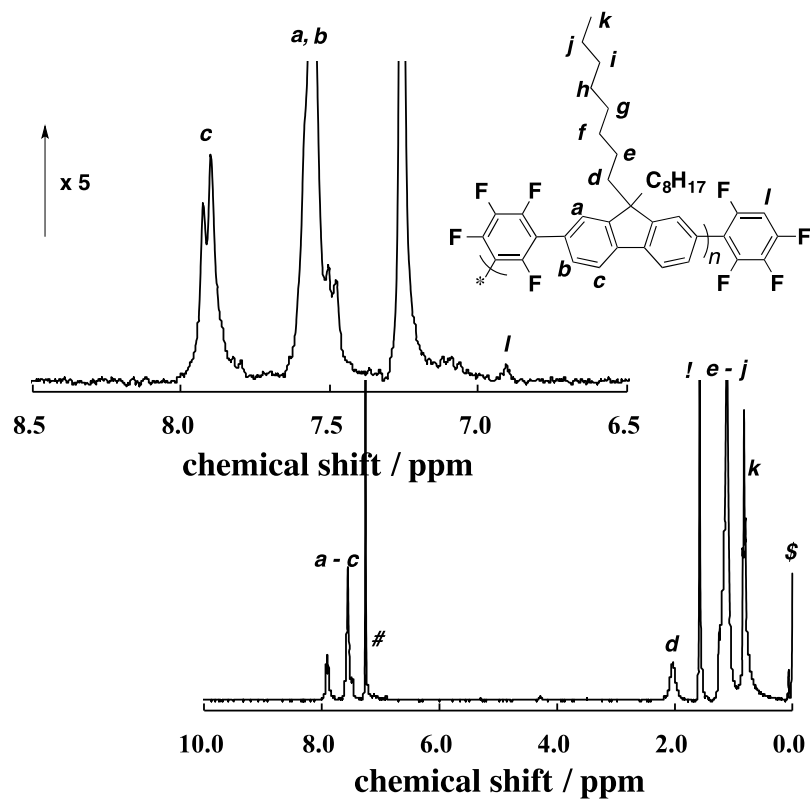


Figure S5. ^1H NMR spectrum of **PmTPF8**. #: CHCl_3 . !: H_2O . \$: TMS.

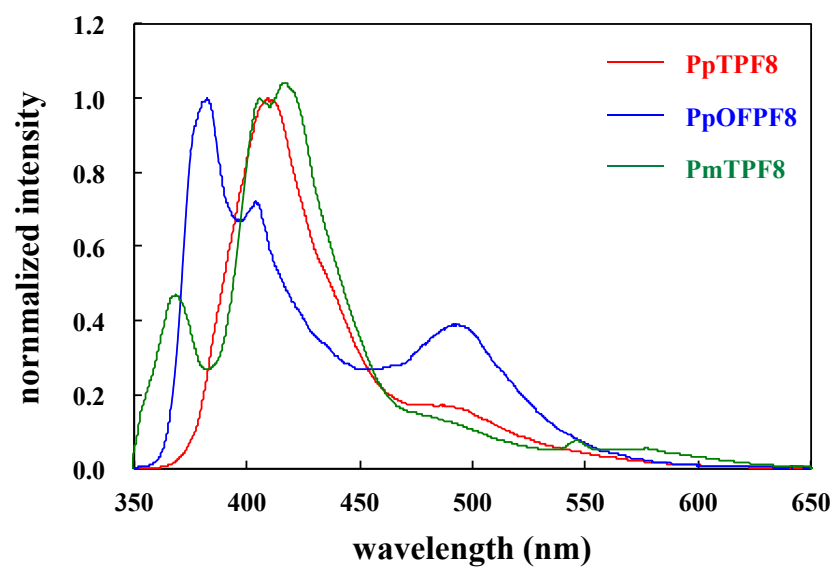


Figure S6. Fluorescence spectra of the polymers (**PpTPF8**, **PpOPF8**, **PmTPF8**) in chloroform.

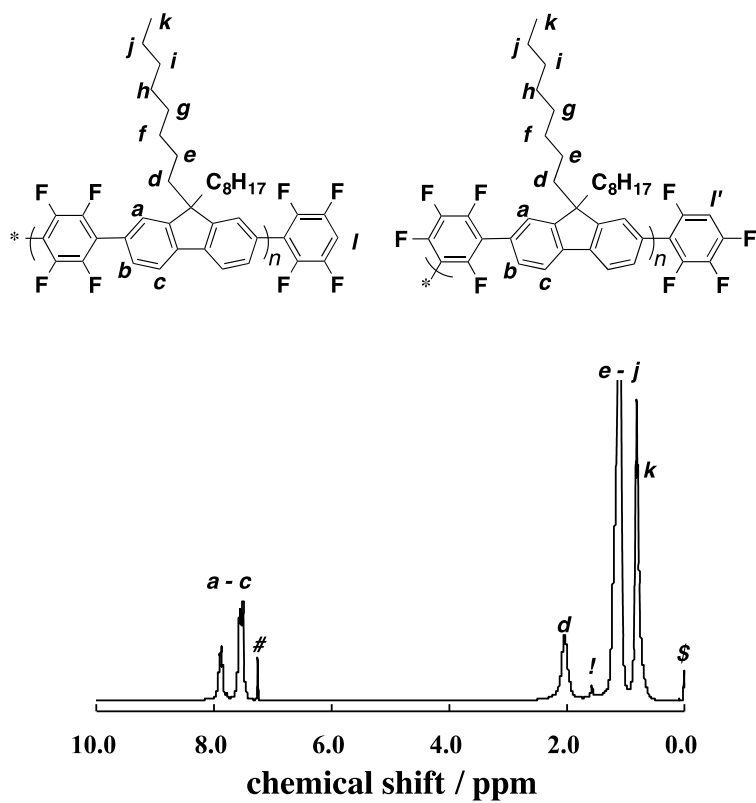


Figure S7. ¹H NMR spectrum of **RC2**. #: CHCl₃. !: H₂O. \$: TMS.

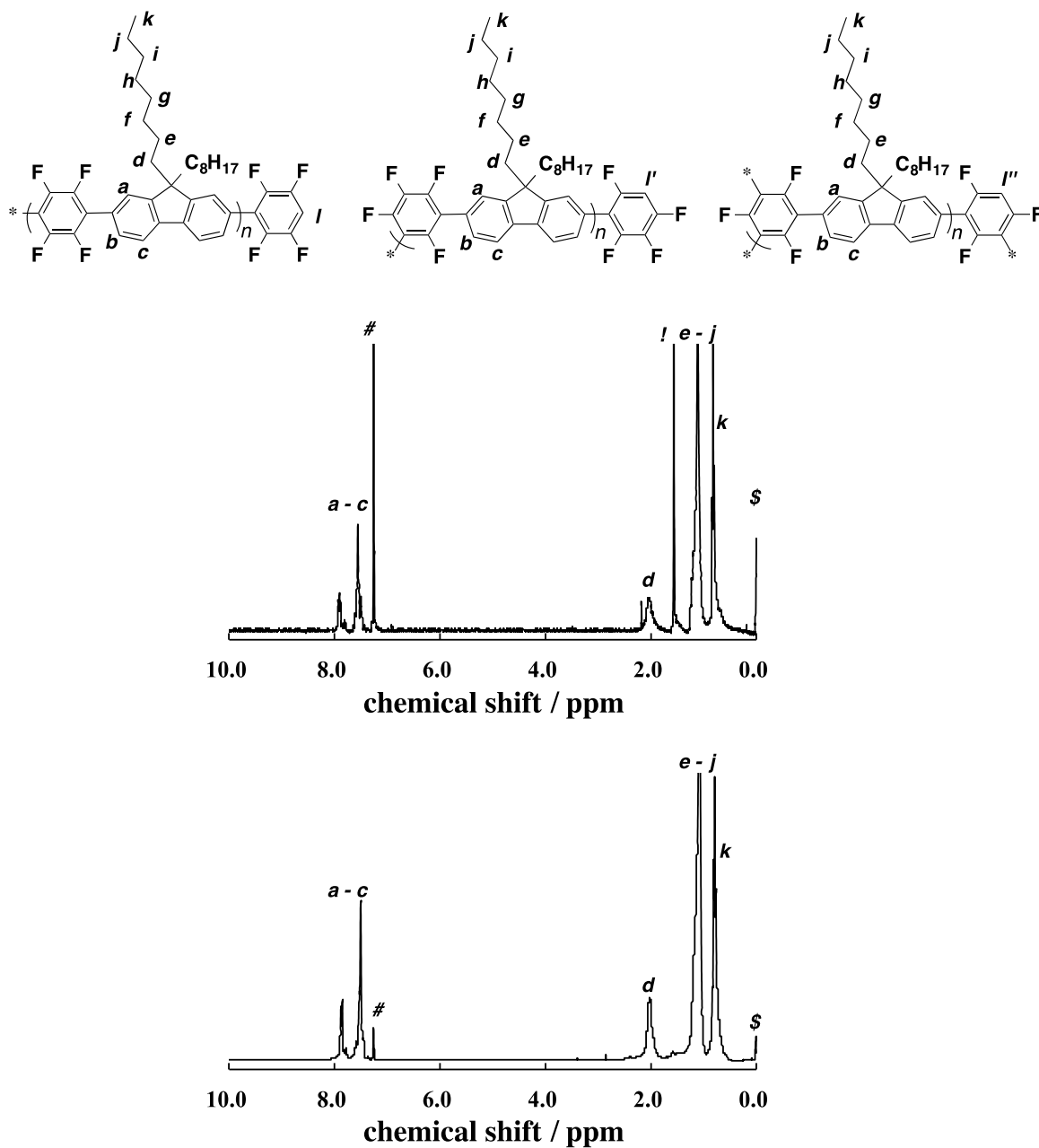


Figure S8. ^1H NMR spectra of **BRCA2** (top) and **BRCB2** (bottom). #: CHCl_3 . !: H_2O . §: TMS.

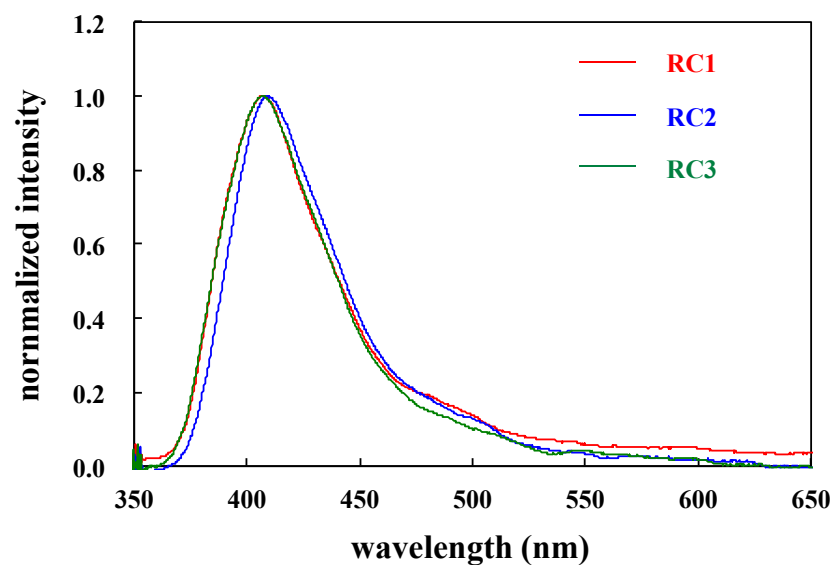


Figure S9. Fluorescence spectra of **RCs** in chloroform.

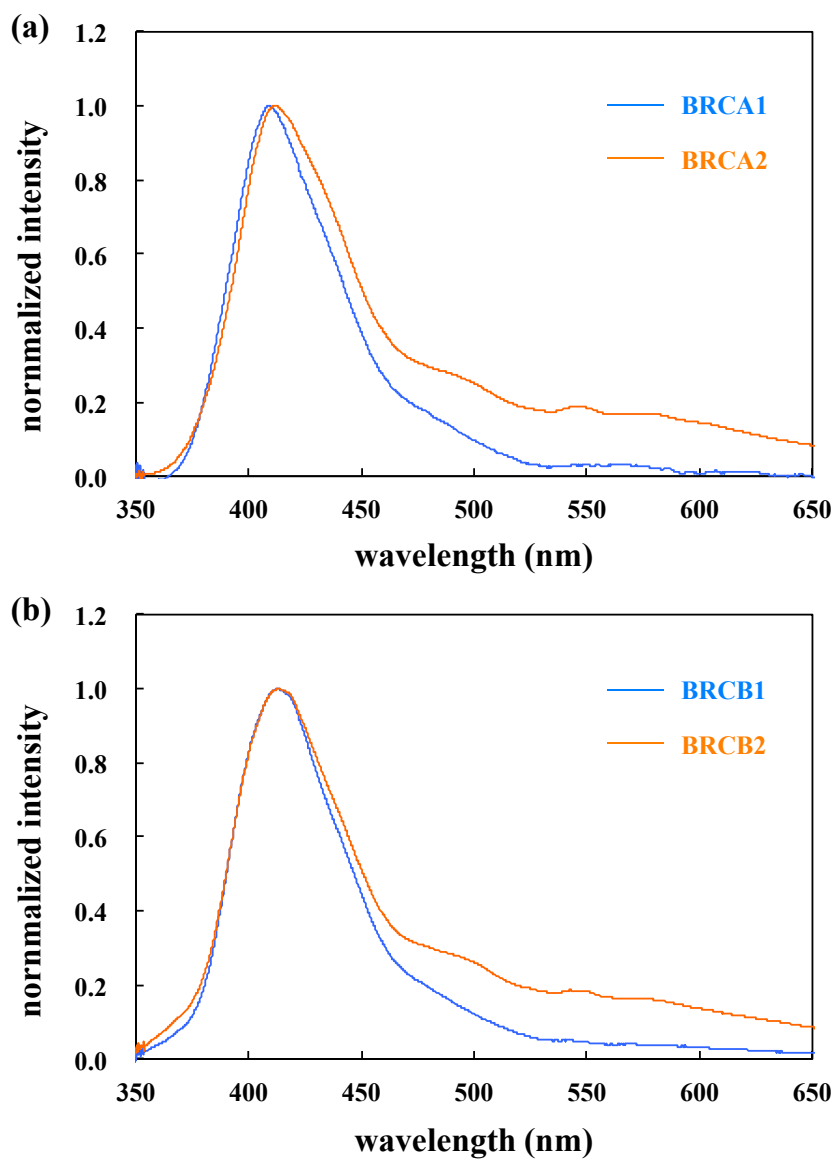


Figure S10. Fluorescence spectra of **BRCA**s (a) and **BRCB**s (b) in chloroform. #: CHCl₃. !: H₂O. §: TMS.

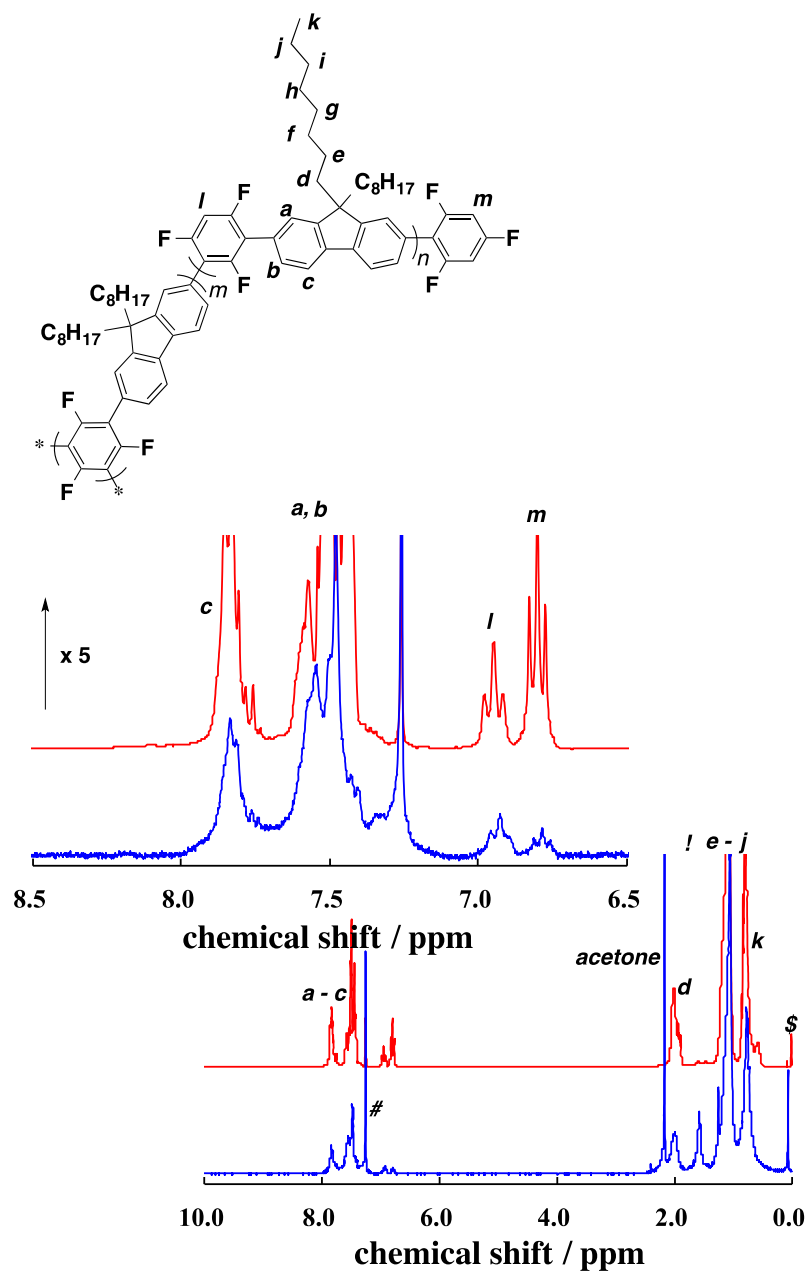


Figure S11. ¹H NMR spectra of **BP1** (red line) and **BP5** (blue line). #: CHCl₃. !: H₂O. \$: TMS.

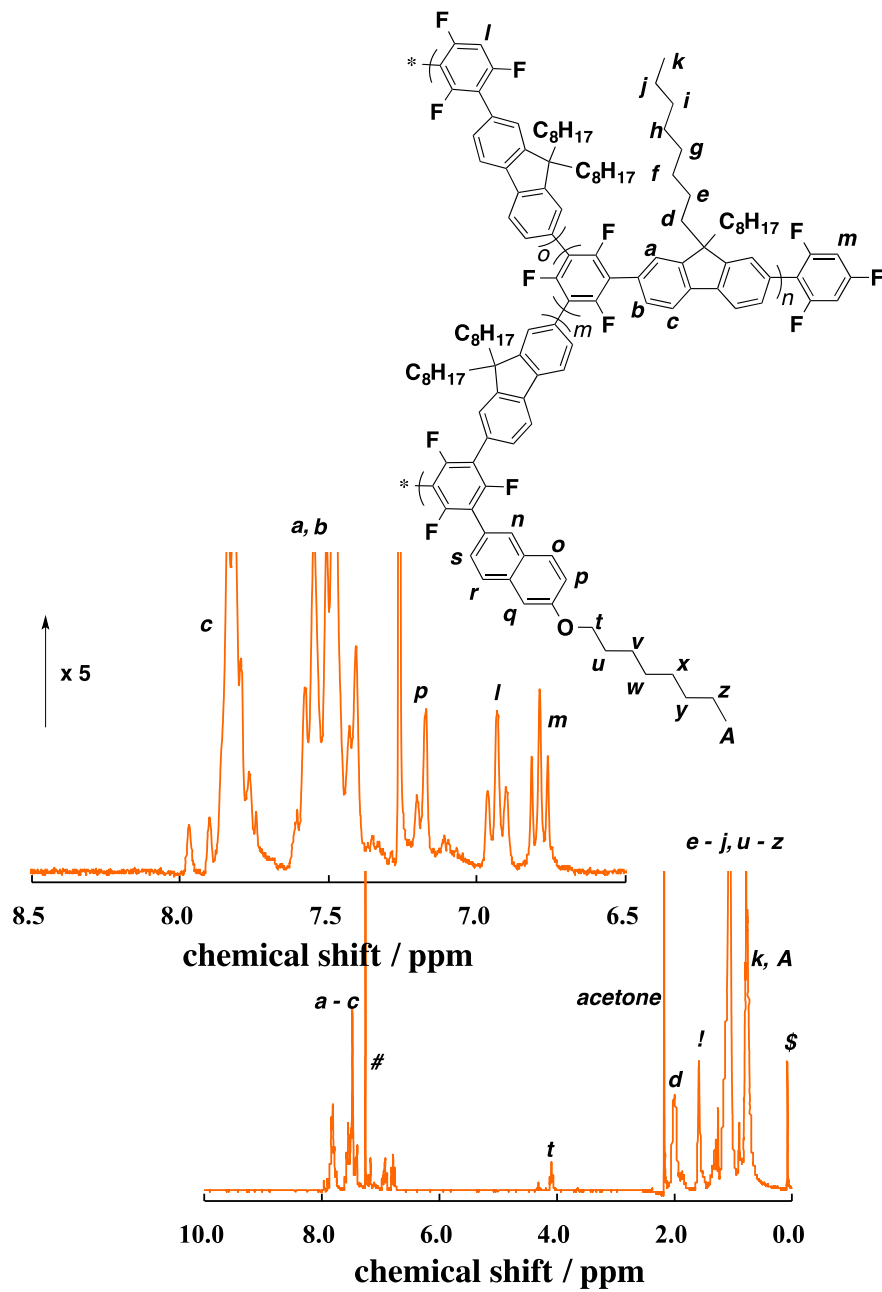


Figure S12. ¹H NMR spectrum of **BPNap**. #: CHCl₃. !: H₂O. \$: TMS.

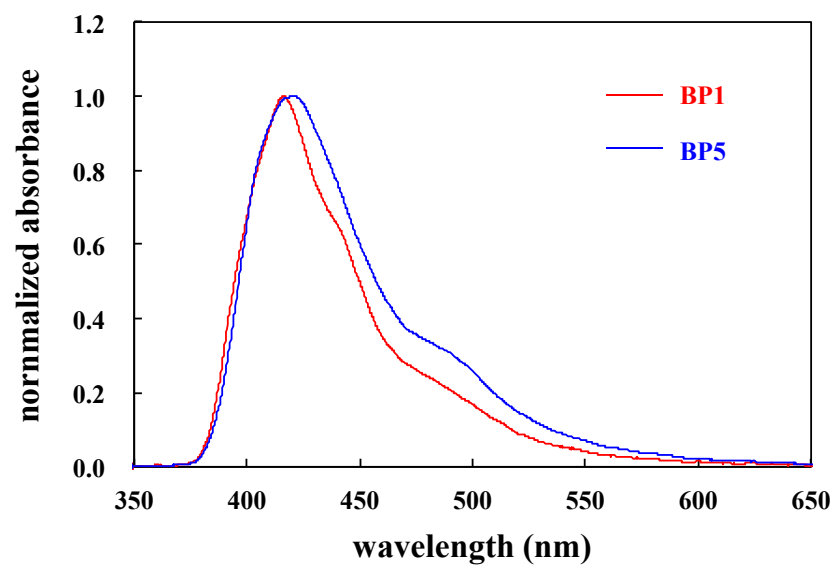


Figure S13. Fluorescence spectra of **BPs** in chloroform.

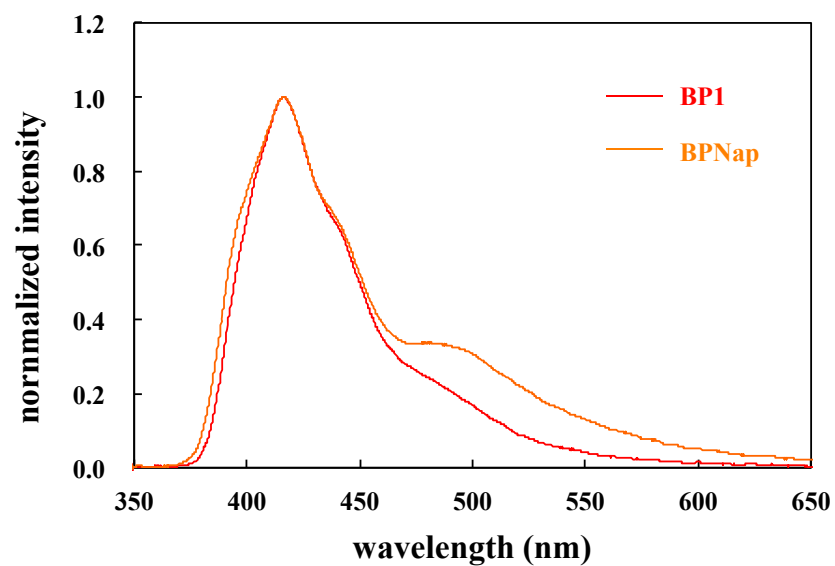


Figure S14. Fluorescence spectra of **BP1** and **BPNap** in chloroform.