Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information (ESI)

Strong Main-Chain Length-Dependence for the β-Phase Formation of Oligofluorenes

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Materials

Triisopropyl borate, 2-bromofluorene, iodine, anhydrous THF, *n*-butyl lithium, and tetrabutylammonium bromide were purchased from Wako Pure Chemical Industry. $(PPh_3)_4Pd^0$, 1-bromooctane and bromine were bought from Tokyo Chemical Industry. $Ni(COD)_2$, COD, 2,2'-dibromo-9,9-dioctylfluorene and 2,2′-bipyridine were purchased from Sigma Aldrich Co. PFO (Mw ~58200, PDI ~3.68) was purchased from Sigma-Aldrich. All reagents were used without further purification.

Instruments and procedure

AV300M (BRUKER BIOSPIN, 300 MHz) was used to measure ^1H and ^{13}C NMR spectra. UV-visible (UV/vis) absorption and fluorescence (Flu) spectra were measured using a spectrophotometer (JASCO, type V-670) and a spectrofluorometer (Horiba-Jobin Yvon, SPEX Fluorolog-3-NIR) equipped with a liquid-nitrogen-cooled InGaAs near-IR detector. Synthesized oligomers were separated using recycling gel permeation chromatography (GPC) (JAI, LC-908W-C60 equipped with preparative columns: JAIGEL-2.5H-40 and JAIGEL-2H-40). The computational calculation based on the density function theory (DFT) was carried out using Materials Science Suite (SCHRÖDINGER, Release 2014-2, Jaguar package) with no solvation. The initial structures were input maintaining C_{2v} symmetry in all the **FOn**. The distribution of the orbitals are visualized with the isovalue of 0.02.

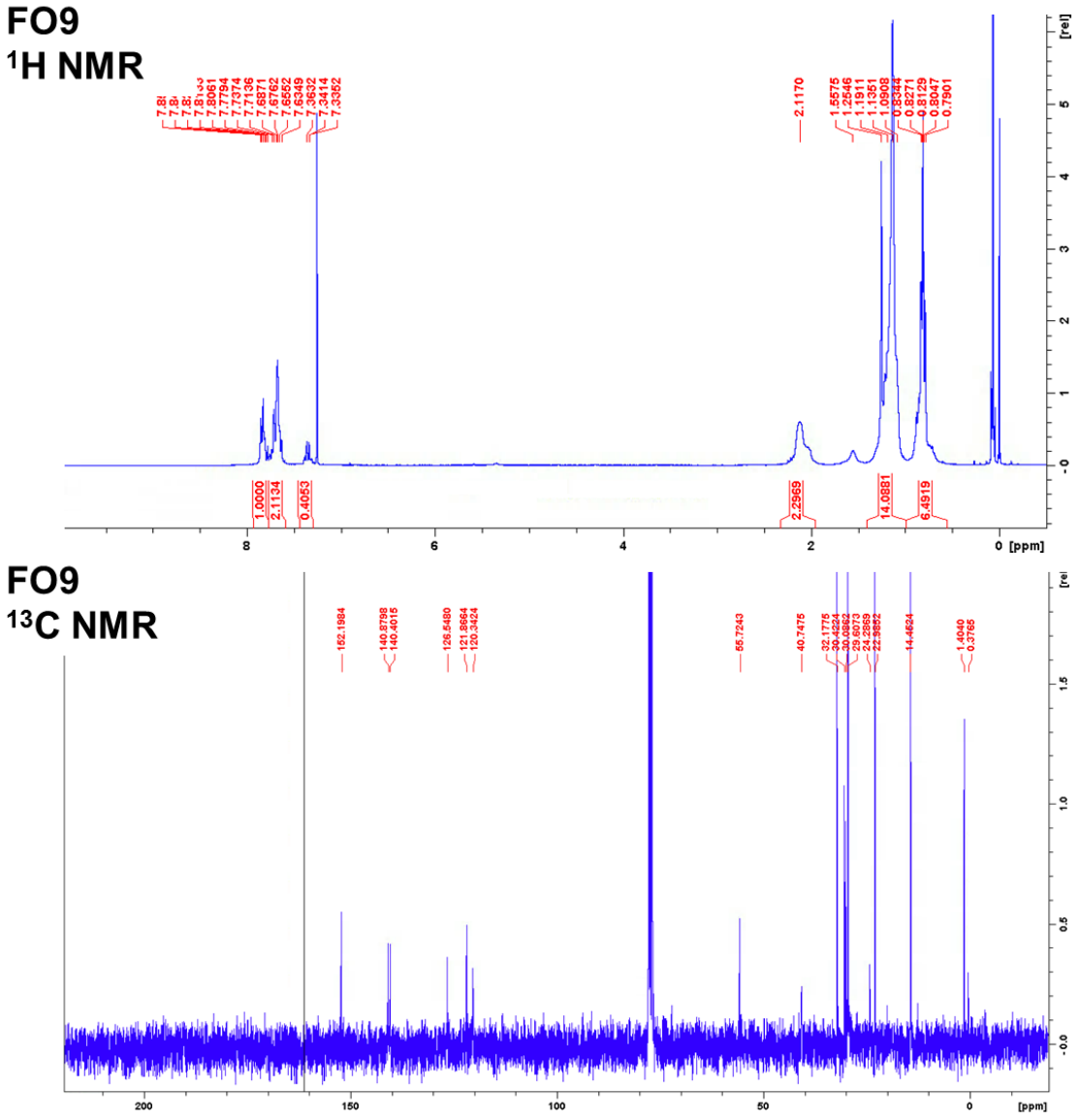

Fig. S1 ^{1}H and ^{13}C NMR spectra of **FO9**; $CDCl_3$, r.t.

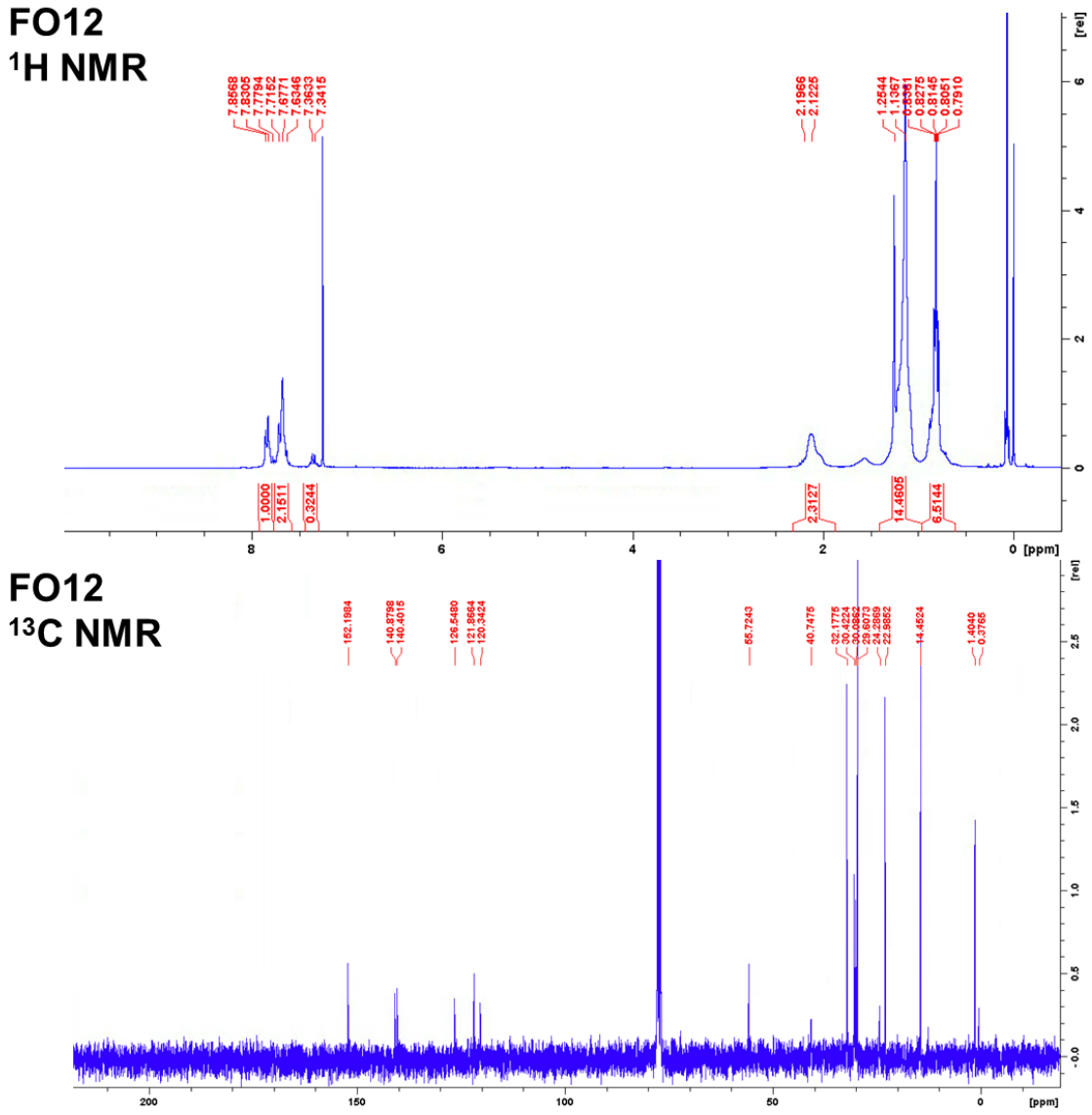

Fig. S2 ^{1}H and ^{13}C NMR spectra of **FO12**; $CDCl_3$, r.t.

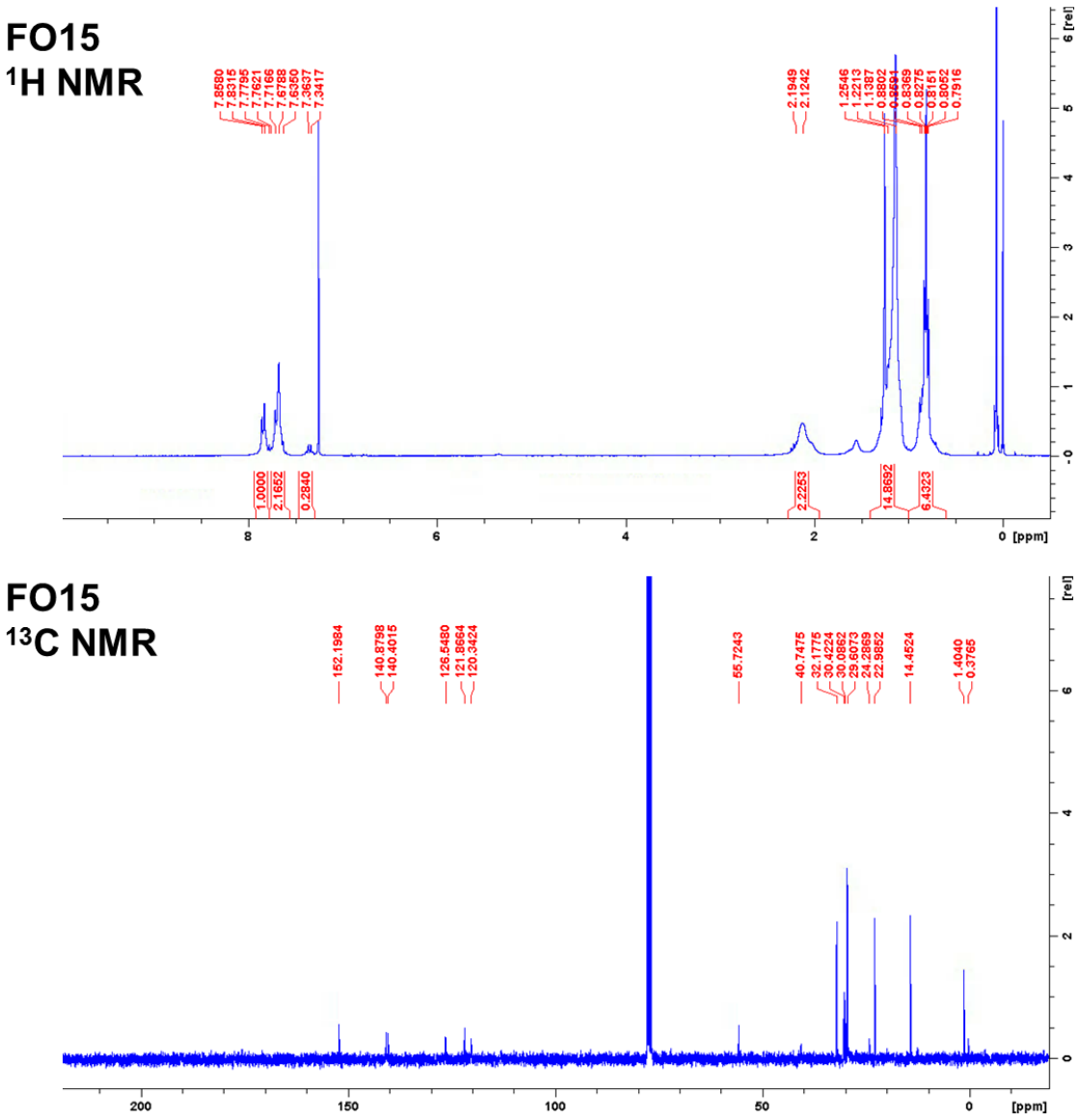

Fig. S3 ^{1}H and ^{13}C NMR spectra of **FO15**; $CDCl_3$, r.t.

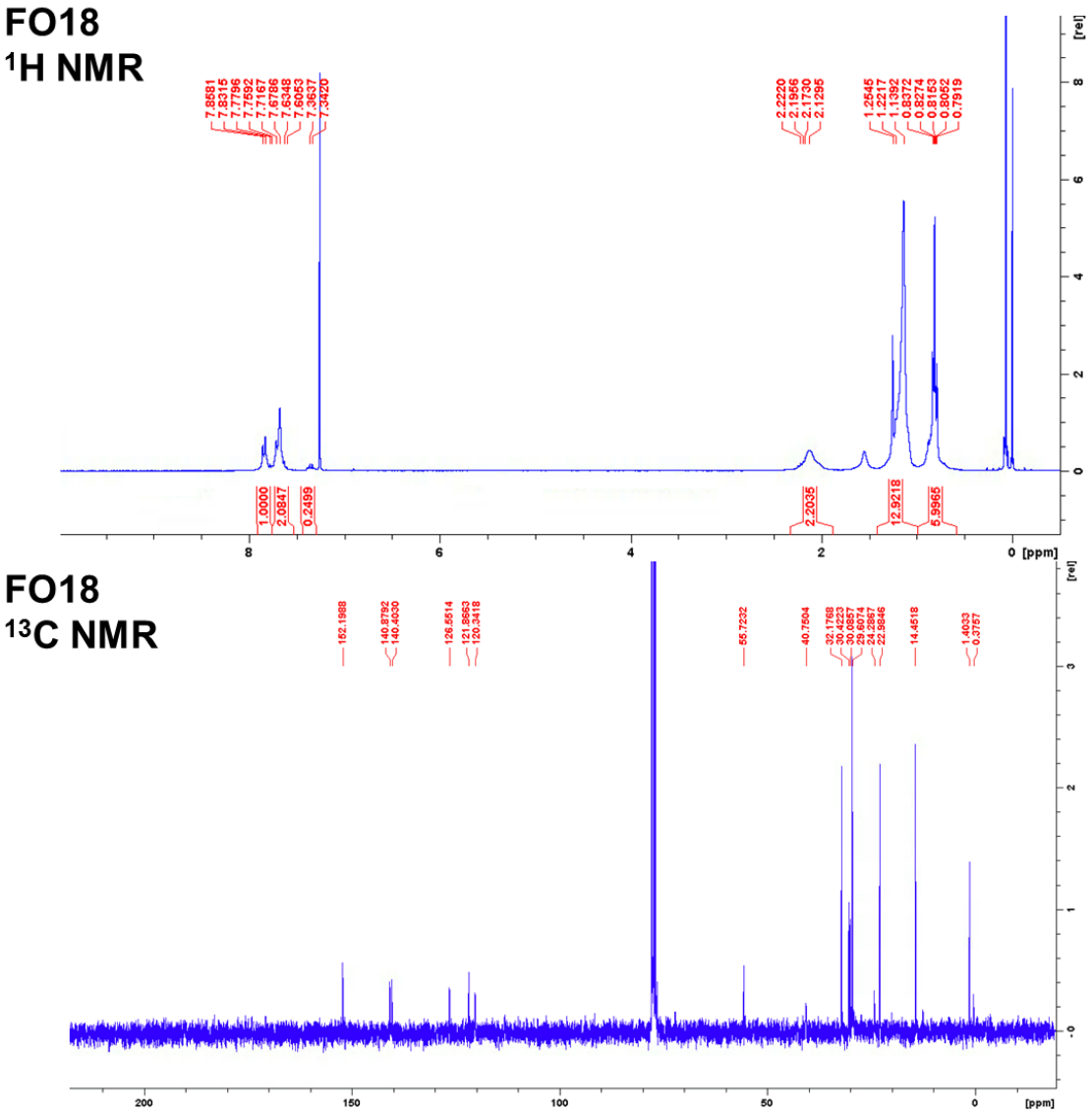

Fig. S4 ^{1}H and ^{13}C NMR spectra of **FO18**; $CDCl_3$, r.t.

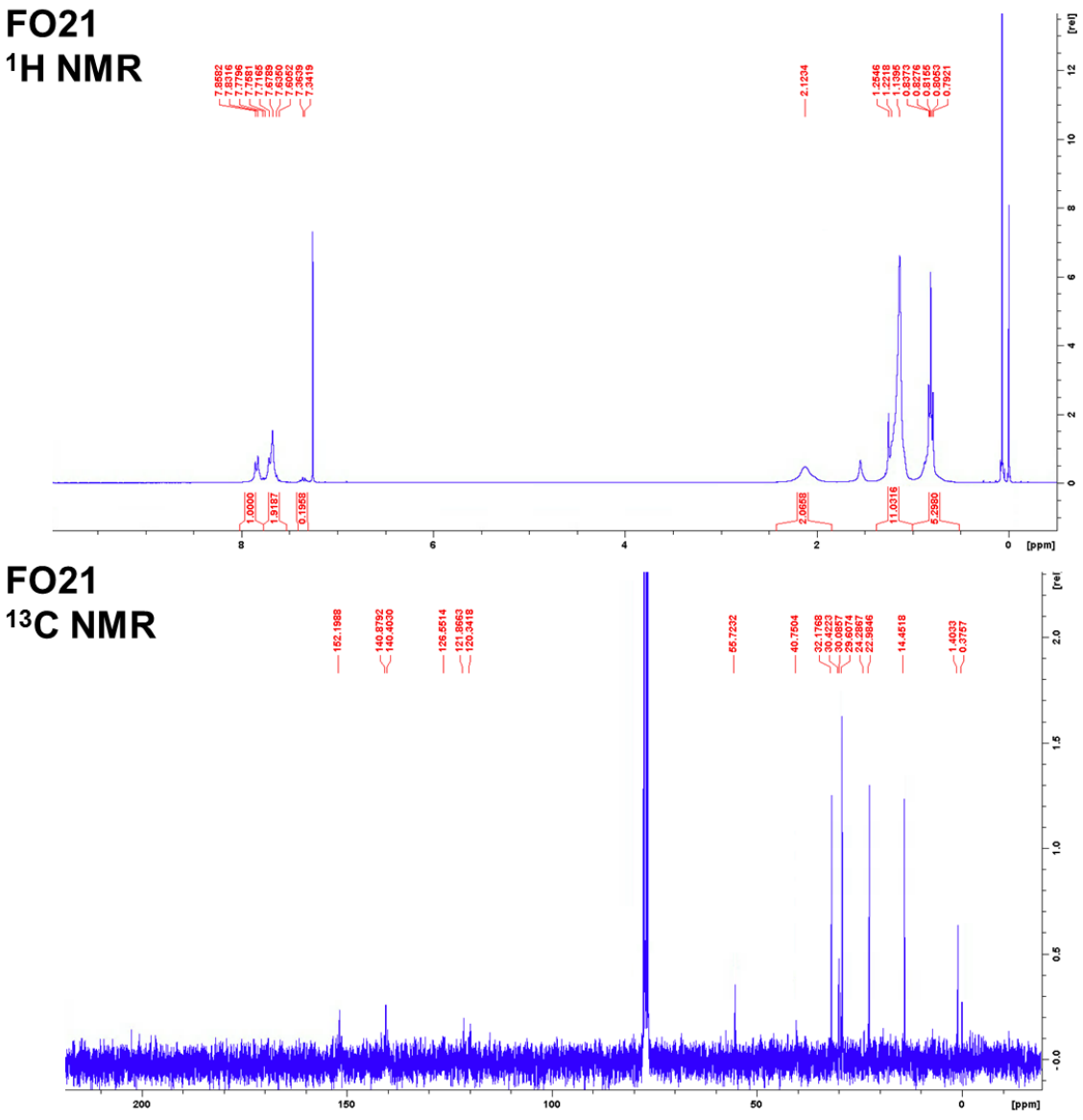

Fig. S5 ^{1}H and ^{13}C NMR spectra of **FO21**; $CDCl_3$, r.t.

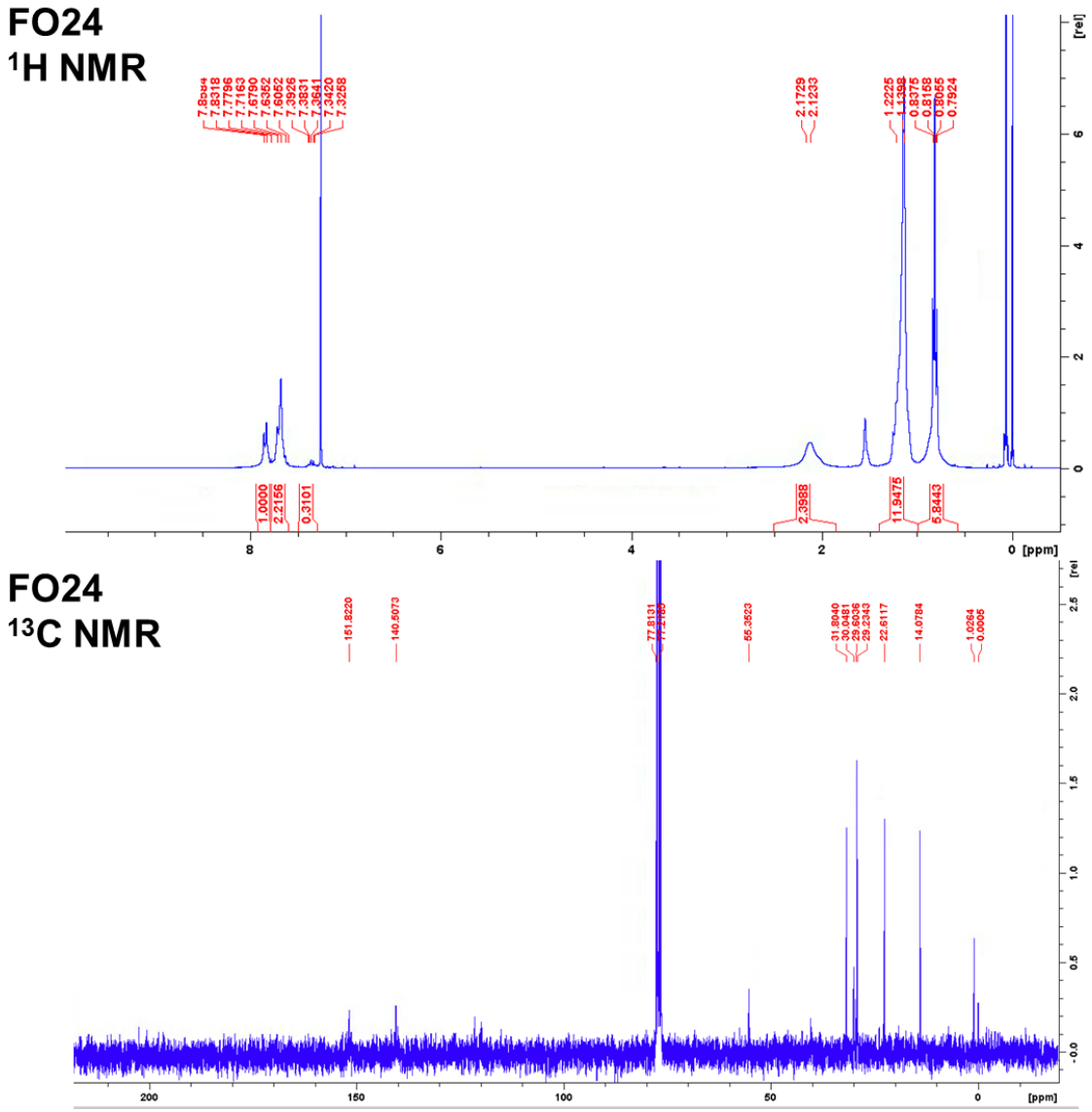

Fig. S6 ^{1}H and ^{13}C NMR spectra of **FO24**; $CDCl_3$, r.t.

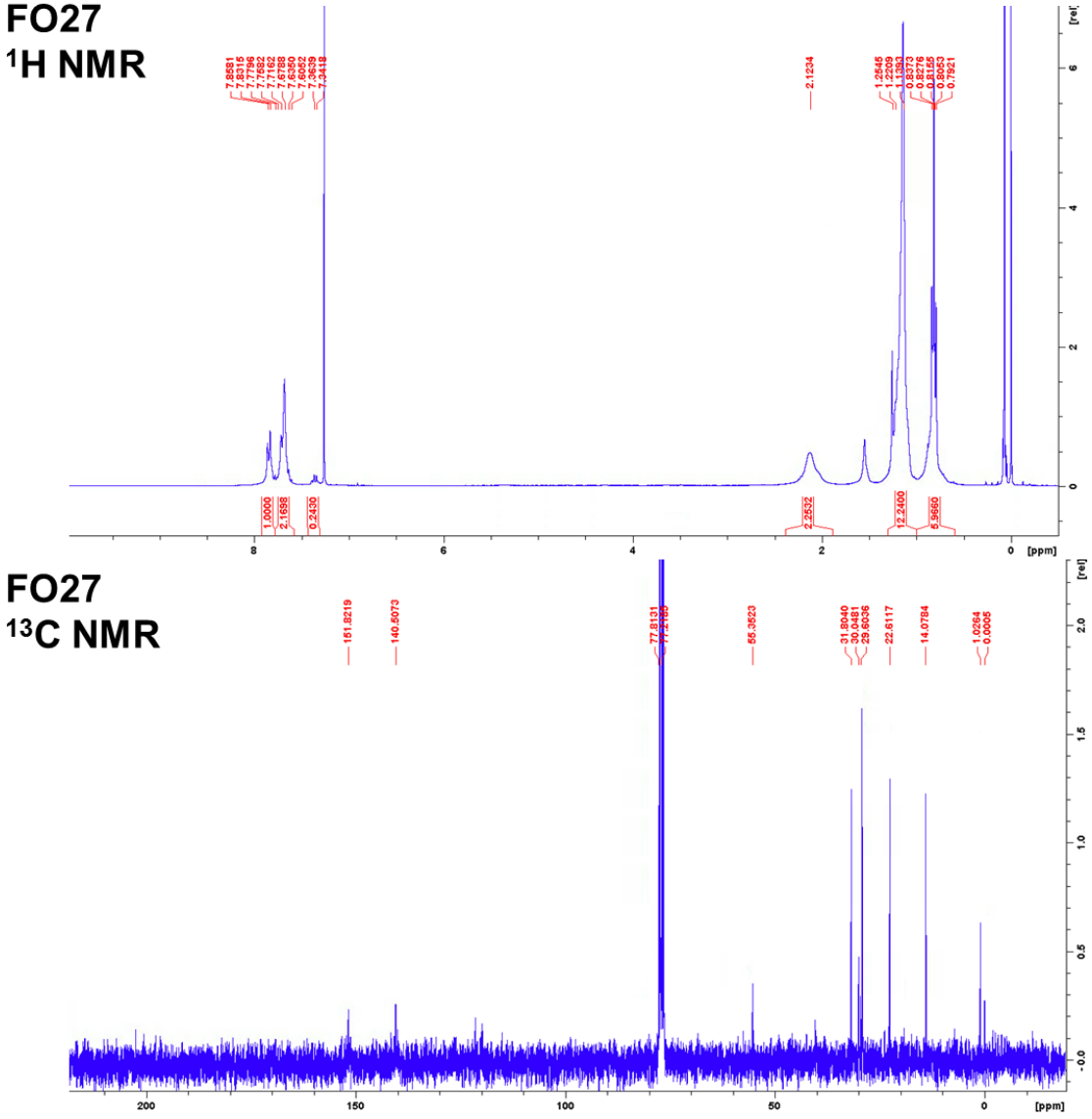

Fig. S7 ^{1}H- and ^{13}C NMR spectra of **FO27**; $CDCl_3$, r.t.

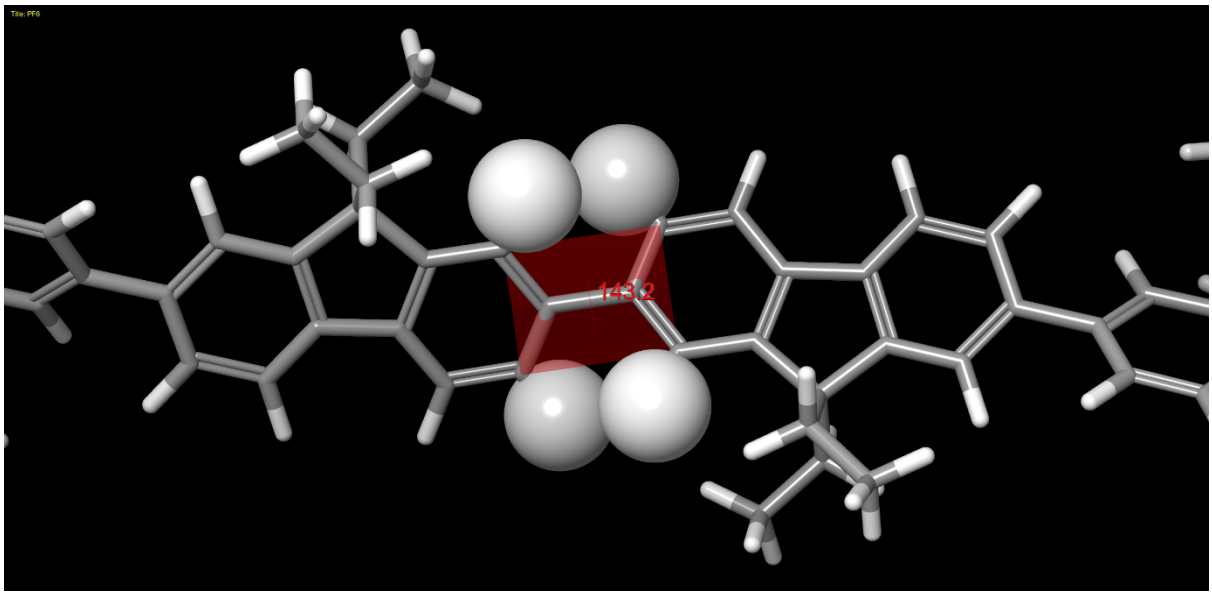

Fig. S8 A magnified illustration of the fused fluorene moiety and its dihedral angel (red). The hydrogen atoms around the fluorene-fluorene bond are represented in CPK model to clarify the steric repulsions.

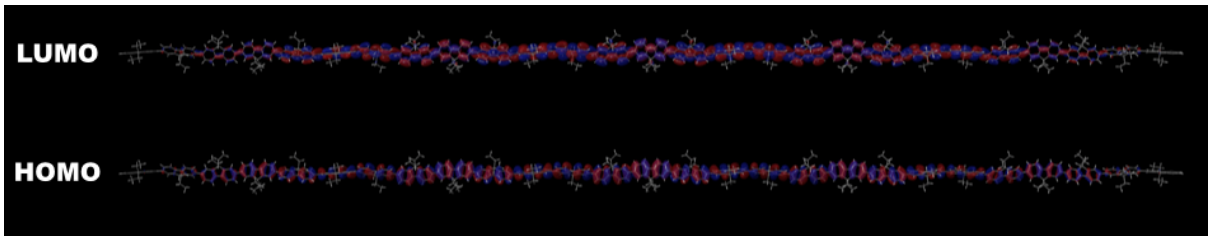

Fig. S9 Energy minimized structures of **FO27** obtained through a density functional theory (DFT) calculation based on the B3LYP 6-31G* level. Visualized frontier orbitals (HOMO and LUMO) are overlaid in each image with the isovalue of 0.005.