

Supporting information for:

Aggregation Enhanced Pure Violet Emission of a Spiral *Meta*-Polyfluorene by Supramolecular control of Excimer Formation

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1.Synthesis and characterization of PsF36

PsF36 was prepared via a typical Suzuki-Miyaura reaction.¹ Under an argon atmosphere, 3,6-dibromo-2'-(3,7-dimethyloctyloxy)-9,9'-spirobifluorene (0.1575 g, 0.25 mmol), 2,7-Bis(4,4,5,5-tetramethyl[1.3.2]dioxaborolan-2-yl)-2'-(3,7-dimethyloctyloxy)-9,9'-spirobifluorene (0.181 g, 0.25 mmol), tetrabutylammonium hydroxide (25% aqueous solution, 1.1 mL, 1.8 mmol), Pd(OAc)₂ (0.5 mg, 0.0022 mmol) and tri(o-tolyl)phosphine (3.25 mg, 0.0106 mmol) were dissolved in a mixture of toluene (0.25 mL) and dioxane (0.05 mL) and heated to 110 °C. After 24 hr, the sticky solution was diluted with 0.5 mL of toluene and 0.1 mL of dioxane. Another two portions of toluene/dioxane (0.5 mL/0.1 mL) were added after 48 hr and 72 hr successively. Pd(OAc)₂ (0.5 mg, 0.0022 mmol) and tri(o-tolyl)phosphine (3.25 mg, 0.0106 mmol) together with 4-methylphenyl boronic acid (30 mg, 0.22 mmol) was added and the mixture was heated for another 12 hr. Finally, 4-bromotoluene (0.2 mL) was added and heated overnight. After cooling down, the mixture was poured into the mixture of toluene (5 mL) and HCl aqueous solution (10 wt%, 5 mL) and vigorously stirred for 4 hr. The organic phase was washed with deionized water several times, concentrated to 3 mL and poured into 30 mL of methanol. The precipitate was filtered and purified by column chromatography (silica gel, toluene as an eluent). The solvent was removed under reduced pressure, and the crude polymer was dissolved in 3 mL of toluene and reprecipitated twice from 30 mL of methanol to afford 99 mg of PsF36 as a white powder. (yield 42.5 %). ¹H NMR (300MHz, CDCl₃, ppm): 8.53(s), 8.13(d), 7.75(s, 2H), 7.41(d, 2H), 7.33(d, 1H), 7.00(s, 1H), 6.90(d, 1H), 6.81(s, 2H), 6.72(d, 1H), 6.32(dd, 1H), 3.79(s, 2H), 1.60(d, 2H), 1.42(d, 2H), 1.22(d, 3H), 1.04(s, 3H), 0.79(dt, 9H). GPC: M_n 14,000, M_w 26,500, PDI 1.9.

2. ^1H NMR spectrum of PsF36

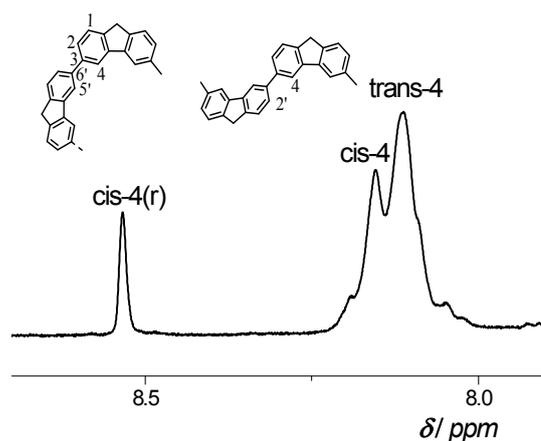


Fig S1 ^1H NMR spectrum of PsF36.

The weak signal around 8.53 ppm should be assigned to 4-proton in low polymerized macrocyclic PsF36 with all *cis*-conformation. The two main peaks at 8.15 and 8.11 ppm should be corresponding to the *cis*- and *trans*- conformation in linear polymer chain or high polymerized macrocycles, even though it is difficult to determine which is which experimentally. We tend to assign the one at 8.15 ppm to *cis*-conformation and that at 8.11 ppm to *trans*-conformation, because the torsion angle of *cis*-conformation is 2 degree smaller than that of *trans*-, which would induce a little stronger interaction between 4, 5' protons in *cis*-conformation than the interaction between 4, 2' protons in *trans*-conformation. Based on this hypothesis, the ratio of *cis*- and *trans*-conformation would be 33% and 67% by integral area accounts.

3. Fluorescence spectra of PsF27 in mixture solvent

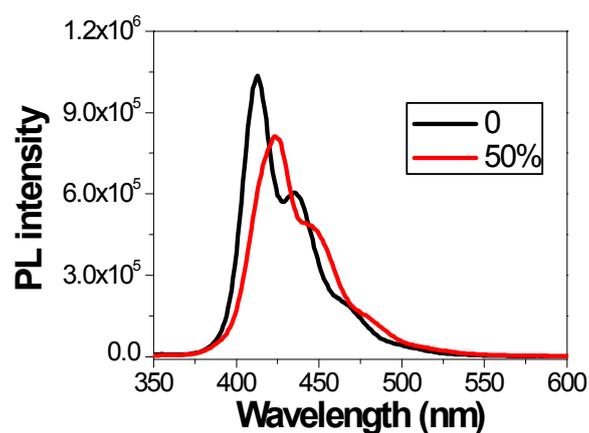


Fig S2 Fluorescence spectra of PsF27 in THF:H₂O (1.5×10^{-5} M) as a function of H₂O ratio.

The emission spectrum of PsF27 in THF/H₂O mixture solvent has a 10 nm redshift compared with that in dilute good solvent. That is because of an extended chain conjugation length as in the β -phase of *para*-linked polyfluorenes.

4. Fluorescence spectra of PsF36 in mixture solvent

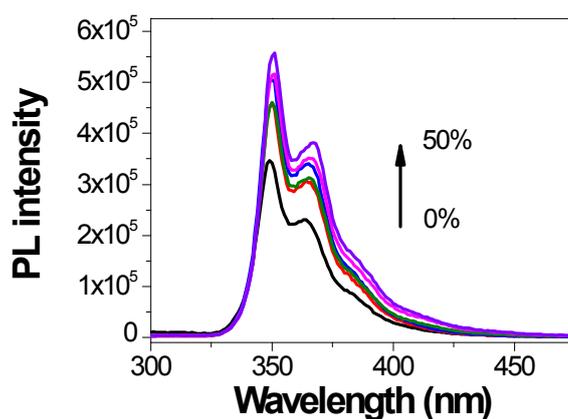


Fig S3 Fluorescence spectra of PsF36 in THF:H₂O (1.5×10^{-5} M) as a function of H₂O ratio.

When the H₂O ratio is 50%, the mixture solvent is transparent enough to obtain credible fluorescence spectra. But at this concentration of 7.5×10^{-5} M, PsF36 aggregate becomes opaque when the H₂O ratio is higher than 25%, which indicates the formation of big aggregates and the credible PL intensity cannot be recorded. Also, the concentration of 7.5×10^{-5} M is too high to obtain absorption spectra.

5. The absorbance at 270 nm and unaggregated fraction

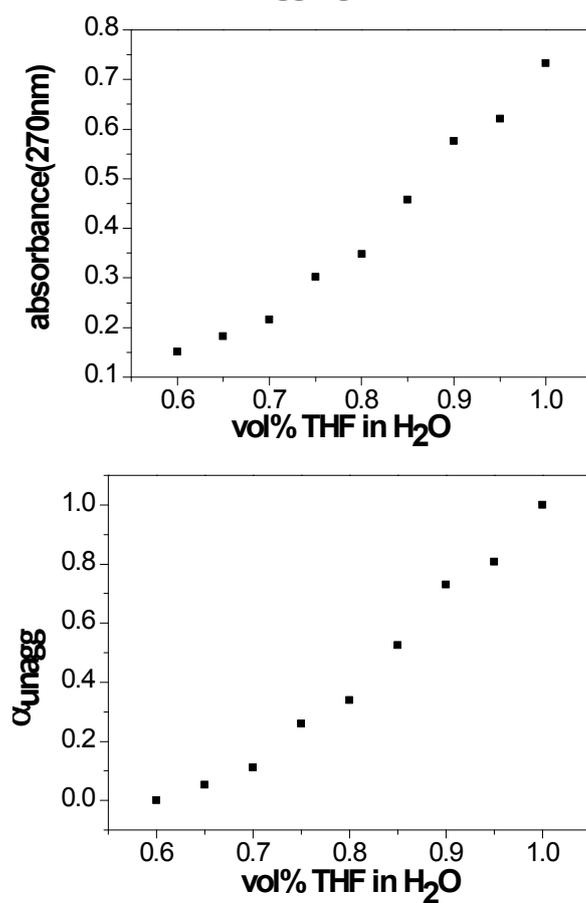


Fig S4. The absorbance at 270 nm, unaggregated fraction (α_{unagg}) respectively as a function of THF ratio.

Reference

- (1) Brookins, R. N.; Schanze, K. S.; Reynolds, J. R. Base-Free Suzuki Polymerization for the Synthesis of Polyfluorenes Functionalized with Carboxylic Acids *Macromolecules*, **2007**, *40*, 3524-3526.