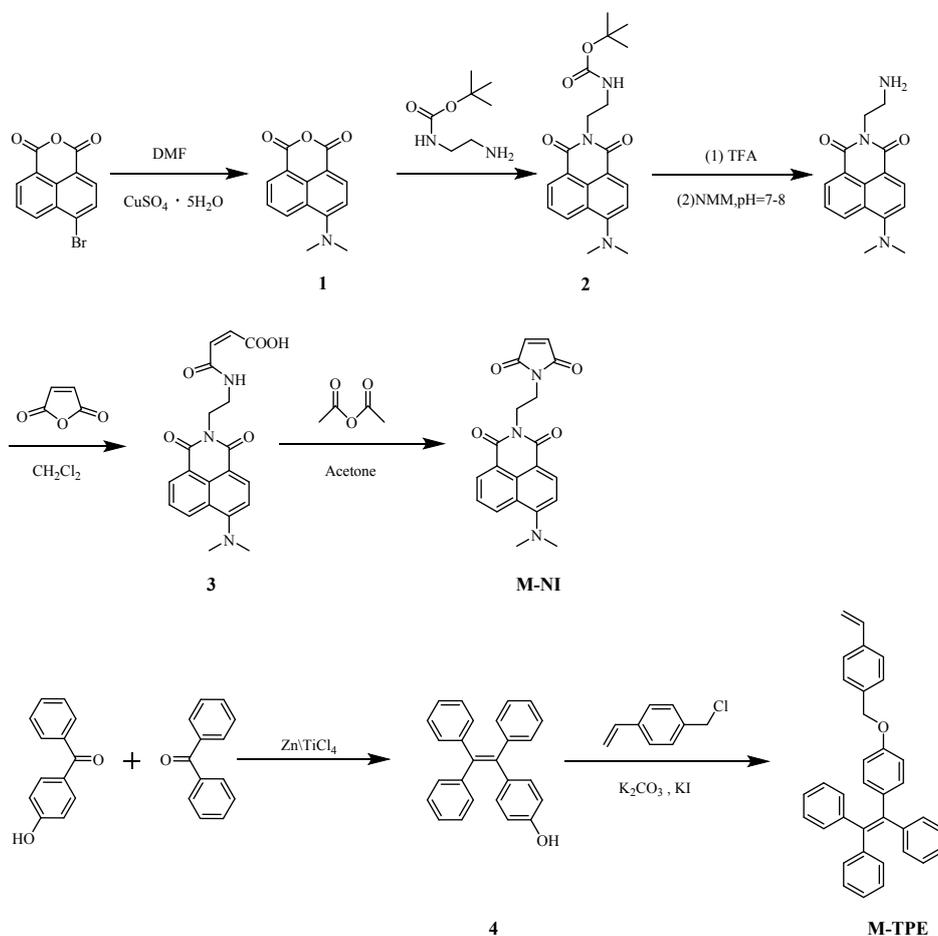


Novel side-chain alternative copolymer combined FRET and DRET with large pseudo-Stokes shift and polarity-sensitive fluorescent behavior

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Synthesis and characterization



Scheme S1. The chemical structures and synthetic procedures of the monomers.

Synthesis of 4-dimethylamino-1,8-naphthal anhydride (1)

The compound 1 was synthesized according to previous article.^[S1] A mixture of 4-bromine-1,8-naphthal anhydride (4.60 g, 16 mmol), copper (II) sulfate pentahydrate (0.40 g, 1 mmol) and N,N-dimethylformamide (80 ml) was heated under reflux for 4 h, the hot solution was poured into 400 ml of water. The resulting solution was adjusted to pH~5.5 by hydrochloric acid. The resulting precipitate was filtered, washed by water, dried and crystallized from the mixed solution of chlorobenzene and ethyl alcohol absolute (1:1) to give 2.95 g (I) in 76% yield. ¹H NMR (400 MHz, CDCl₃, ppm): δ = 8.60-8.56 (d, 1H), 8.53-8.48 (m, 2H), 7.73-7.69 (t, 1H), 7.16-7.13 (d, 1H), 3.20 (s, 6H).

Synthesis of tert-Butyl 2-(4-dimethylamino-1,8-naphthalimide)ethylcarbamate (2)

4-dimethylamino-1,8-naphthal anhydride (1) (15.0 g, 62 mmol) was dissolved in 50 mL toluene, which was added to the solution of (2-aminoethyl) carbamic acid tert-butyl ester (6.60 g, 41 mmol) in toluene (200 mL). The mixture was refluxed for 12 h under nitrogen atmosphere. After removal of toluene, the solid was purified by silica gel column chromatography (SiO₂; dichloromethane/ethyl acetate 5:1) to give **2** as a yellow solid (15.2 g, 95%). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 8.62-8.60 (d, 1H), 8.52-8.46 (m, 2H), 7.71-7.67 (t, 1H), 7.16-7.13 (d, 1H), 5.08-5.07 (t, 1H), 4.40-4.37(t, 2H), 3.56-3.54 (t, 2H), 3.14 (s, 6H), 1.34 (s, 9H).

Synthesis of 4- dimethylamino-N-(2-maleimido)ethyl-1,8-naphthalimide (M-NI)

Trifluoroacetic acid (TFA, 4.30 mL) was added to a solution of **2** (3.10 g, 8.10 mmol) in CH₂Cl₂ (30 mL). The mixture was stirred at room temperature for 12 h. Then, the solvent was removed in vacuo at 40 °C. The residue was dissolved in acetone (30 mL) and the solution was neutralized with NMM to pH 7 - 8. Without isolation and purification, the neutralized solution was added dropwise to the solution of maleic anhydride (1.59 g, 16.2 mmol) in acetone (10 mL) and the mixture was stirred at room temperature for 6 h. The compound **3** was obtained as an intermediate in the mixture. Then anhydrous sodium acetate (0.10 g) and acetic anhydride (5 mL) were added to the mixture, which was refluxed for 2 h further. After removal of solvent, the residue was dissolved in 50 mL CH₂Cl₂, and washed by 1 M NaHCO₃ aqueous solution 20 mL three times, then dried by MgSO₄ and concentrated. The residues were purified by silica gel column chromatography (SiO₂; dichloromethane/ethyl acetate = 8:1) to give M-NI as an orange solid (1.48g, 50.4%). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 8.49-8.47 (d, 1H), 8.41-8.38 (m, 2H), 7.62-7.58 (t, 1H), 7.07-7.05 (d, 1H), 6.59 (s, 2H), 4.39-4.37 (t, 2H), 3.97-3.94 (t, 2H), 3.08 (s, 6H).

Synthesis of 4-(1,2,2-triphenylvinyl)phenol (4)

The compound **4** was synthesized according to previous article.^[S2] Under an nitrogen atmosphere, a three-necked flask equipped with a magnetic stirrer was charged with zinc powder (1.60 g, 24.0 mmol) and 40 mL dry THF. The mixture was cooled to -5 to 0°C, and TiCl₄ (1.30 mL, 12mmol) was slowly added by a syringe with the temperature kept under 10°C. The suspending mixture was warmed to room temperature and stirred for 0.5 h, then heated at reflux for 2.5 h. The mixture was again cooled to -5 to 0°C, charged with pyridine (0.50 mL, 6 mmol) and stirred for 10 min. The solution of diphenyl ketone and 4-hydroxy diphenyl ketone (in 1:1.2 mole ratio, 2.40 mmol) in 15 mL THF was added slowly. After addition, the reaction mixture was heated at reflux until the carbonyl compounds were consumed (monitored by TLC). The reaction was quenched with 10% K₂CO₃ aqueous solution and taken up with CH₂Cl₂. The organic layer was collected. After solvent evaporation, the crude product was purified on a silica gel column using ethyl acetate/petroleum ether (1:10 to 1:7, v/v) as eluent to give the desired product as a white powder in a yield of 76%. ¹H NMR (400 MHz, DMSO): δ = 9.37 (s, 1H), 7.16-6.95 (m, 15H), 6.75-6.73 (d, 2H), 6.51-6.50 (d, 2H).

Synthesis of (2-(4-((4-vinylbenzyl)oxy)phenyl)ethene-1,1,2-triyl)tribenzene (M-TPE)

1-(chloromethyl)-4-vinylbenzene (0.88 g, 5.74 mmol), compound **4** (1.00 g, 2.87 mmol), potassium carbonate (1.98 g, 14.4 mmol) and catalytic amount of potassium iodide was dissolved in 50 mL acetone, and 1 drop of nitrobenzene was added in the solution. The mixture was stirred and refluxed for 8 h. After filtered, the filtrate was concentrated by rotary evaporation and then purified using silica gel column chromatography (SiO₂; dichloromethane/petroleum ether, 1 : 2) to give M-TPE as a white solid. ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.42-7.34 (d, 2H), 7.10-6.99(m, 19H), 6.94-6.92 (t, 1H), 6.73-6.69 (d, 2H), 5.78 -5.74 (d,1H), 5.27-5.24 (d, 1H), 4.96 (s, 2H).

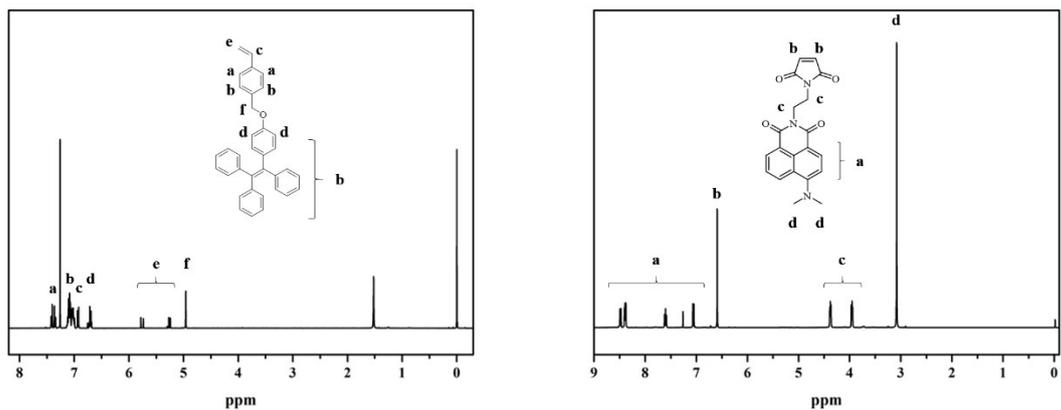


Figure S1. The ¹H NMR spectra of monomers M-TPE and M-NI in CDCl₃.

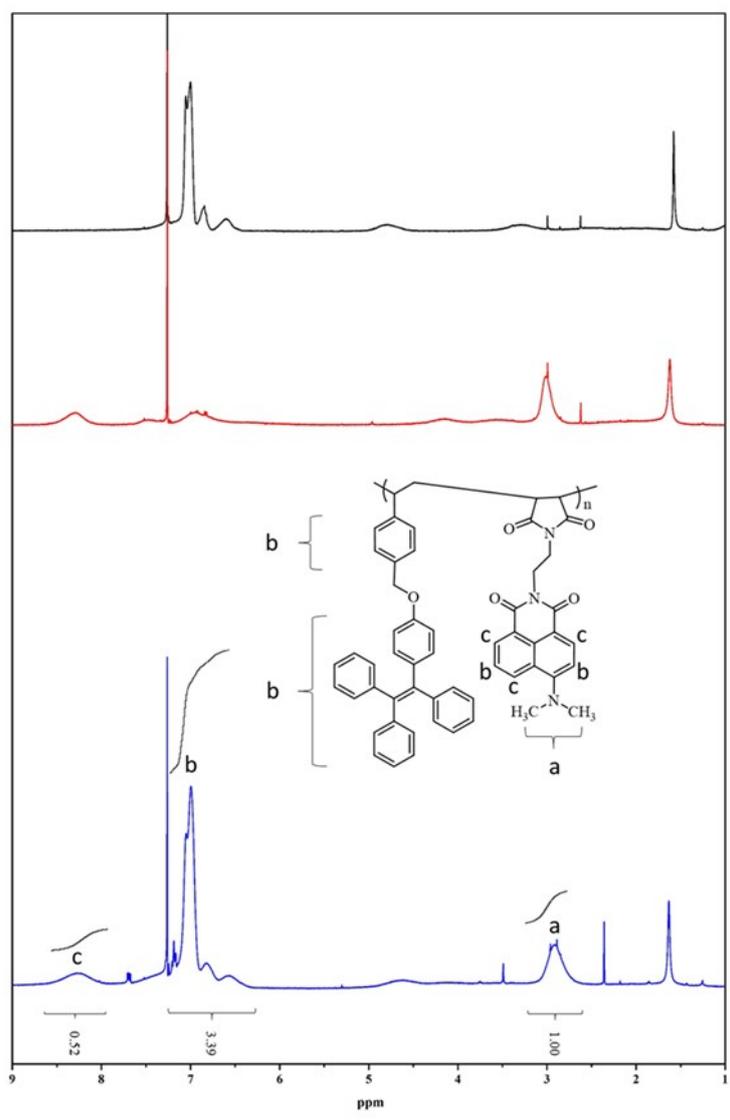


Figure S2. The ¹H NMR spectra of copolymers P-TPE (black line), P-NI (red line) and P(TPE-alt-NI) (blue line) in CDCl₃.

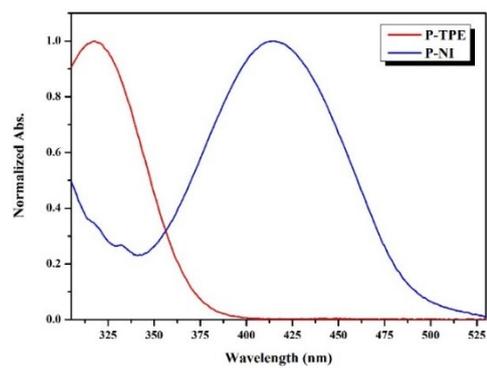


Figure S3. UV-Vis absorption spectra of P-TPE and P-NI in THF solution (1×10^{-5} M)

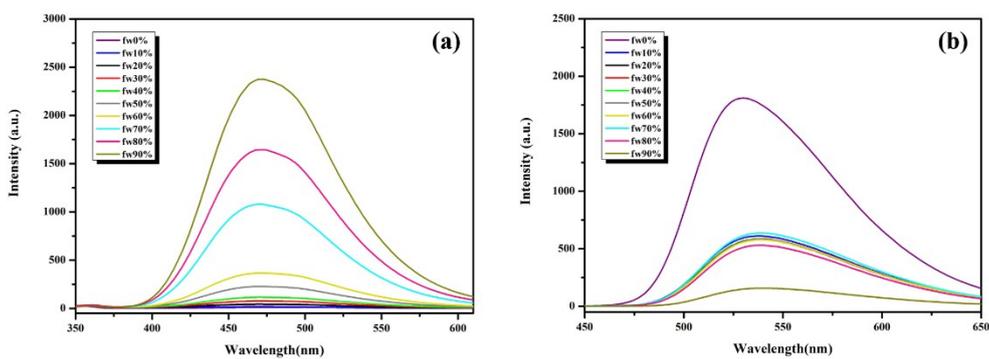


Figure S4. Emission spectra of P-TPE (a) and P-NI (b) in different ratio water/THF (1×10^{-5} M)

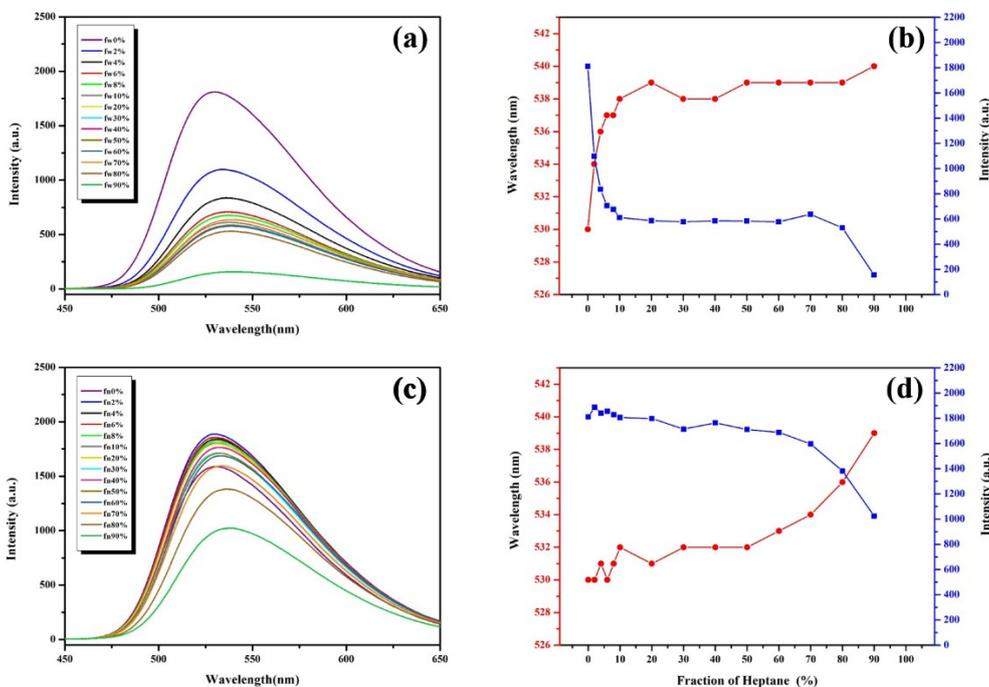
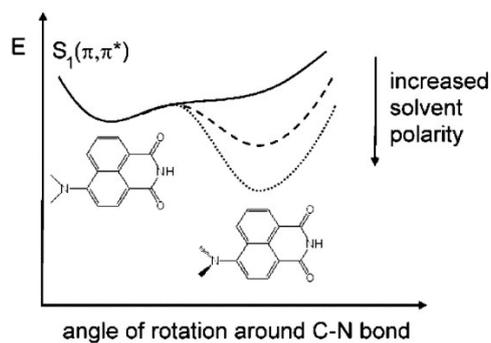


Figure S5. Emission spectra of 1×10^{-5} M P-NI in different ratio water/THF (a) and n-heptane/THF (c) excited at 430 nm. Variation of PL intensity and wavelength maximum of 1×10^{-5} M P-NI in different ratio water/THF. (b) and n-heptane/THF (d) excited at 430 nm.



Scheme S2. Schematic Representation of the Effect of Solvent Polarity on the Energy of S_1 State in $\text{Me}_2\text{N-NI}$. Reprinted with permission from Ref. 39 □ © 2009 American Chemical Society.

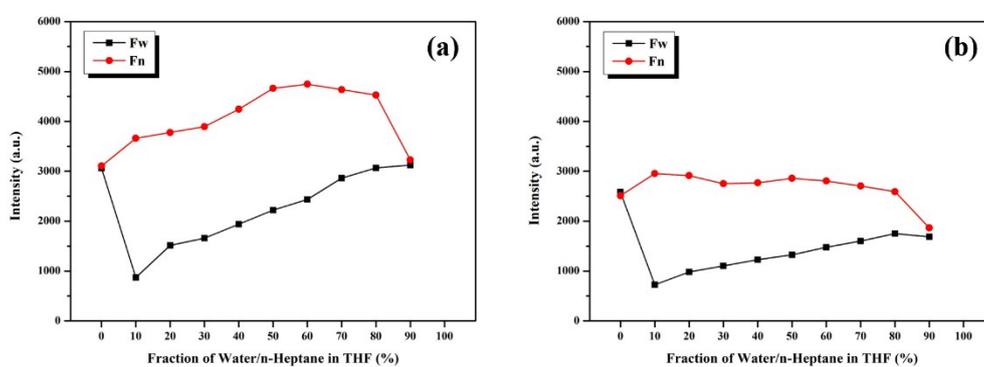


Figure S6. Variation of PL intensity of 1×10^{-5} M P(TPE-alt-NI) in different ratio n-heptane/THF or water/THF excited at 320 nm (a) and 430 nm (b).

References

- [S1] C. Li, X. Pan, C. Hua, J. Su, H. Tian, *Eur. Polym. J.* **2003**, *39*, 1091-1097.
 [S2] L. Zhang, W. Hu, L. Yu, Y. Wang, *Chem. Commun.* **2015**, *51*, 4298-4301.