Supporting Information

Bulky 4, 6-disubstituted tetraphenylethene-naphthalimide

dyad: synthesis, copolymerization, stimuli-responsive

fluorescence and cellular imaging

Qiong-Xin Hua, Bo Xin, Jun-Xia Liu, Ling-Xi Zhao, Zu-Jing Xiong, Tao Chen, Ze-Qiang Chen, Chong Li, Wen-Liang Gong^{*}, Zhen-Li Huang^{*} and Ming-Qiang Zhu^{*}

Wuhan National Lab for Optoelectronic, College of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China;
E-mail: mqzhu@hust.edu.cn; leo@mail.hust.edu.cn; wlgong@hust.edu.cn.

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Figure S1. A comparison of the molar absorptivity spectra of NI-1TPE (black line) and NI-2TPE (red line) in THF. The concentration of the solution are prepared to be 2×10^{-5} mol/L. Inset show the photos of NI-1TPE and NI-2TPE in daylight (left) and under illumination of 365 nm (right) in THF (10⁻⁴ mol/L).



FigureS2. TD-DFT calculation of NI-2TPE



Figure S3. Kinetic spectra of FL intensity @580 nm of P (NIPAM-co-NI-2TPE) in water from boiling temperature to room temperature



Figure S4. (a) UV-vis spectra of P (NIPAM-co-NI-2TPE) in water from boiling temperature to room temperature, (b) the absorption spectrum of P (NIPAM-co-NI-2TPE) in water at room temperature.



Figure S5. The fluorescence intensity @580 nm with T (from 30-40°C)



Figure S6. GPC traces recorded for P (NIPAM-co-NI-2TPE) in THF

6. Synthesis

Synthetic procedure of 1, 8-Dibromoacenaphthene

5, 6-Dibromoacenaphthene: Following the reported procedure from *J. Org. Chem*, 2011, 76, 6383-6388

5, 6-Dibromoacenaphthene: Acenaphthene (77.1 g, 0.50 mol) and N-bromosuccinimide (222.5 g, 1.25 mol) were combined in DMF (500 mL) and stirred overnight at $30-32^{\circ}$ C. The reaction was then cooled to room temperature, filtered to obtain the crude product, and purified via recrystallization from hexanes (25-30% yield). ¹H NMR: δ 7.78 (d, J = 7.6 Hz, 2 H), 7.07(d, J = 7.6 Hz, 2 H), 3.30 (s, 4 H).

Synthetic procedure of 5, 6-Dibromo-1, 2-acenaphthenequinone

5, 6-Dibromo-1, 2-acenaphthenequinone: Following the reported procedure from *Eur. J. Inorg. Chem.* 2001, 1183-1188

1, 8-Dibromoacenaphthenedione: 1, 8-Dibromoace-naphthene (8.51 g, 27.3 mmol) was dissolved in acetic anhydride (1 L) at 110 °C. CrO3 (21.1 g, 211 mmol) was added carefully to the stirred solution over a period of 2 h. The resulting green suspension was stirred at 160 °C for 30 min., and then poured while hot onto crushed ice (1 kg). Conc. HCl (20 mL) was added and the mixture was filtered. The brownish precipitate was washed with water, dried in vacuo and recrystallized from acetic anhydride (2 L). 1, 8-Dibromoacenaphthenedione (6.23 g, 67%) was obtained as a light brown solid. ¹H NMR: δ 8.25 (d, J = 7.5 Hz, 2 H), 7.92 (d, J = 7.5 Hz 2 H).¹H NMR data agrees well with previously reported values.

Synthetic procedure of 1, 8-Dibromonaphthoic Anhydride

1, 8-Dibromonaphthoic Anhydride: Following the reported procedure from *Org. Lett.* 2010, 12, 4690-4693

1, 8-Dibromonaphthoic Anhydride: 1, 8-Dibromoacenaphthenedione (2) (2.00 g, 5.92 mmol) was suspended in methanol (150 mL) and oxone (2.50 g, 16.4 mmol) was added. The mixture was stirred at reflux for 72 h. After cooling, the mixture was poured into water and the orange precipitate was washed with water and then methanol and dried to afford an orange solid 4 (1.88g) in yield 90%. This compound is very insoluble in mormal organic solvents like CHCl₃, CH₂Cl₂ or DMSO and the ¹H NMR and ¹³C NMR spectra were not easy to record. We just use it for next step directly without further purification.

7. NMR spectra



Figure S7. ¹H NMR spectrum of 1, 8-Dibromoacenaphthene in CDCl₃



Figure S8. ¹H NMR spectrum of 5, 6-Dibromo-1, 2-acenaphthenequinone in CDCl₃



Figure S9. ¹H NMR spectrum of 2-propene-4, 6-Dibromo-1, 8-naphthalimide in CDCl₃



Figure S10. ¹H NMR spectrum of 2-propene-4, 6-Di(tetraphenylethene)-1, 8-naphthalimide in CDCl₃



Figure S11. ¹H NMR spectrum of P (NIPAM-co-NI-2TPE) in CDCl₃



Figure S12. ¹³C NMR spectrum of P (NIPAM-co-NI-2TPE) in CDCl₃



Figure S13. ¹H NMR spectrum of P (HEA-co-NI-2TPE-co-[6-(acryloyloxy) hexyl] triphenylphosphonium bromide) in D₂O



Figure S14. ¹³C NMR spectrum of P (HEA-co-NI-2TPE-co-[6-(acryloyloxy) hexyl] triphenylphosphonium bromide) in D₂O

8. MS and IR spectra



Figure S15. MALDI-TOF spectrum of NI-2TPE



Figure S16. IR spectrum of NI-2TPE



Figure S17. IR spectrum of P (NIPAM-co-NI-2TPE)