Support Information

Fluorescent and stimuli-responsive performance of polymer composites filled with tetraphenylethene derivatives

Fang-Hong Yang, ^{a, b} Bin Hao, ^{a, b} Xiu Yue^{*a, b} and Peng-Cheng Ma^{* a, b}
^a Laboratory of Environmental Science and Technology, The Xinjiang Technical Institute of Physics and Chemistry, Key Laboratory of Functional Materials and Devices for Special Environments, Chinese Academy of Sciences, Urumqi 830011, China.
^b Center of Material Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.

* Corresponding authors: E-mail: yuexiu@ms.xjb.ac.cn (X. Yue), mapc@ms.xjb.ac.cn (P.-C. Ma)

Synthesis of 2-bis(4-(but-3-en-1-yloxy)phenyl)-1,2-diphenylethene (TPE-2BO)

TPE-2OH (182.8 mg, 0.50 mmol) and potassium carbonate (276.0 mg, 2.00 mmol) were added in acetonitrile (15 mL)and stirred for 2.5 h at room temperature. Then, 4-bromine-1-butene (0.40 mL, 2.00 mmol) was injected and the mixture was refluxed at ~85 ° C for 20 h. After the solvent was evaporated off, the residue was dissolved in dichloromethane (10 mL) and extracted with water three times. The organic layer was dried on anhydrous sodium sulfate. After the evaporation of dichloromethane, the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=25/1 (v/v)) to obtain TPE-BO as a yellow powder (124 mg 0.26 mmol, 53%). ¹H NMR (400 MHz, DMSO-d6) 7.20-6.99 (m, 6H), 6.97-6.87 (m, 4H), 6.87-6.74 (m, 4H), 6.73-6.59 (m, 4H), 5.90-5.75 (m, 2H), 5.20-5.00 (m, 4H), 4.00-3.85 (m, 4H), 2.45-2.30 (m, 4H).

Synthesis of Tetra (4-(1-butenyl) oxyphenyl) ethene (TPE-4BO)

TPE-4OH (395.0 mg, 1.0 mmol) and sodium hydroxide (168.0 mg, 4.2 mmol) were added in 1, 4-dioxane and water (v:v=4:1) mixed solvent (20 mL)and stirred for 2.5 h at room temperature. Then the solvent was evaporated off and 1, 4-dioxane 20 mL was added in, after 4-bromine-1-butene (2.0 mL, 10 mmol) was injected and the mixture was reacted at ~85 $^{\circ}$ C for 20 h. After the solvent was evaporated off, the residue was dissolved in dichloromethane (10 mL) and extracted with water three times. The organic layer was dried on anhydrous sodium sulfate. After the evaporation of dichloromethane, the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=30/1 (v/v)) to obtain TPE-4BO as a yellow powder (206 mg, 0.34 mmol 34%). ¹H NMR (400 MHz, DMSO-d6) 6.90-6.80 (m, 8H),6.70-6.56 (m, 8H), 5.90-5.79 (ddt, 4H), 5.20-5.00 (m, 8H), 3.95-3.90 (t, 8H), 2.48-2.38 (m, 8H).



Scheme S1 Synthetic routes of TPE derivatives (A: TPE-BO, B: TPE-2BO, C:TPE-4BO).



Fig. S1 ¹H NMR of TPE and its derivatives.



Fig. S2 Photographs of TPE derivatives in THF and THF/water mixture under UV illumination (A:TPE, B: TPE-BO, C: TPE-2BO, D:TPE-4BO).



Fig. S3 The FT-IR spectra of PDMS before curing, TPE-2BO@PDMS before and after curing.



Fig. S4 Fluorescent microscopy images of composite films with different malor concentrations (A/C: before curing, B/D: after cured).

Fig. S4 shows the fluorescent microscopy images of composite films with different malor concentrations, the microcrystalline particles were formed in PDMS mixture when the concentration of TPE was 0.0020 mmol/g. Compared with TPE@PDMS mixture, other mixtures exhibited blue fluorescence emission and no obvious particles were found at the same concentration. After being cured, the surface of TPE-0.0020@PDMS composites emerged many microcrystalline particles, other composites showed homogeneous blue FL emission. Otherwise, the fluorescence intensity increased with the number of substitutes and the concentration of AIE molecules.



Fig. S5 The temperature-dependent fluorescence spectra of AIE@PDMS composites (A: TPE@PDMS, B: TPE-BO@PDMS, C: TPE-2BO@PDMS, D: TPE-4BO@PDMS).



Fig. S6 Cycle experiment of the fluorescent properties with different temperatures. (A: TPE@PDMS, B: TPE-BO@PDMS, C: TPE-2BO@PDMS, D: TPE-4BO@PDMS).



Fig. S7 Fluorescence images of AIE@PDMS under different tensile strains (A: TPE@PDMS, B: TPE-BO@PDMS, C: TPE-2BO@PDMS).