Supplementary Information

Rewritable ternary data storage device based on polymethacrylate containing pendent azobenzene-naphthalene with combined effects of conformation change and charge traps

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Synthesis of compound 1

1-aminonaphthalene (2.86 g, 0.02 mol), water (8 mL) and concentrated hydrochloric acid (8 g, 0.08 mol) were mixed in 100 mL flask with stirring, and heated to 80 °C for 30 minutes. Then put the flask into an ice-salt bath and stirred rapidly to precipitate the hydrochloride salt as fine crystals. Keeping the temperature at 0~5 °C and the solution of sodium nitrite (0.024 mol) in 10 mL water was added dropwise into the mixture with stirring. After 30 minutes, urea (5 mg) was added to consume the residual sodium nitrite and confirmed by the starch-iodide paper. Then filtered and the diazonium salt solution was obtained. Phenol (1.96 g, 0.02 mol) and NaOH (2 g, 0.05 mol) were dissolved in 200 mL water and the solution was kept at 0~5 °C. The solution of the diazonium salt was slowly added and reacted for 30 minutes, after adjusting pH to 7-8 and continue reaction for 4 hours, the obtained mixture was recrystallized from ethanol to give yellow powder (yield 61%). ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.3 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.94 (dd, *J* = 13.0, 8.2 Hz, 2H), 7.79 (d, *J* = 7.4 Hz, 1H), 7.70 – 7.48 (m, 3H), 6.99 (d, *J* = 8.5 Hz, 2H), 5.29 (s, 1H).

Synthesis of compound 2

Compound 1 (1.24 g, 5 mmol) and potassium carbonate anhydrous (0.83 g, 6 mmol) dissolved in 50 mL DMF, and stirred for 2 hour at 80 °C. Then the solution of 2-chloroethanol (6 mmol, 0.48 g) in 10 mL DMF was added dropwise with stirring. The mixture was heated to 125 °C and reacted for 4 hous. The solvent was removed through vacuum evaporation and the obtained mixture was purified by chromatographed on a silica gel column (ethylacetate:petroleum ether = 4:1) to give yellow powder (yield 90%). ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 8.1 Hz, 1H), 8.11 (d, J = 8.6 Hz, 2H), 7.97 (dd, J = 17.5, 7.9 Hz, 2H), 7.83 (d, J = 7.4 Hz, 1H), 7.62 (m, 3H), 7.34 (d, J = 8.6 Hz, 2H), 6.42 (s, 1H), 5.82 (s, 1H), 2.11 (s, 3H).

Synthesis of compound 3

Compound 1 (1.24 g, 5 mmol) dissolved in dry THF (40 mL) and triethylamine (1 mL), then it was added to a 150 mL flask and the mixture was cooled in the ice bath. Methacryloyl chloride (0.6 g, 6.6 mmol) was diluted in THF (5 mL) and then was added dropwise to the above cooled solution. The resultant mixture was vigorously stirred in the ice bath for 2 hours and then kept at 25 °C overnight. The solution was filtered and the filtrate was concentrated. The obtained product was recrystallized from ethanol to give orange powder(compound 3, yield 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.92 (d, *J* = 8.1 Hz, 1H), 8.11 (d, *J* = 8.6 Hz, 2H), 7.97 (dd, *J* = 17.5, 7.9 Hz, 2H), 7.83 (d, *J* = 7.4 Hz, 1H), 7.62 (m, 3H), 7.34 (d, *J* = 8.6 Hz, 2H), 6.42 (s, 1H), 5.82 (s, 1H), 2.11 (s, 3H).

Synthesis of compound 4

The synthesis of compound 4 is similar to compound 3, compound 4 (orange powder, yield 76%), ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.91 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 2H), 7.94 (t, *J* = 8.9 Hz, 2H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.70 – 7.48 (m, 3H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.17 (s, 1H), 5.61 (s, 1H), 4.55 (s, 2H), 4.33 (s, 2H), 1.97 (s, 3H).

Instruments

^{1}HNMR spectra were obtained on an Inova 400 MHz FT-NMR spectrometer. UV-Vis absorption spectra were recorded by a Perkin-Elmer Lambda-17 spectrophotometer at room temperature. SEM images were taken on a Hitachi S-4700 scanning electron microscope. Molecular weights (Mn) and polydispersity (Mw/Mn) were determined on a Waters 1515 gel permeation chromatography (GPC) using DMF as a mobile phase and with column temperature of 30 ^{o}C. Thermo gravimetric analysis (TGA) was conducted on a TA instrument Dynamic TGA 2950 with a heating rate of 10 ^{o}C/min under nitrogen flow rate of 50 mL/min. The X-ray diffraction (XRD) analysis was performed on film using a Shimadzu XRD-6000 spectrometer with a Cu KR monochromatic radiation source at 40 kV and 30 mA. The 2θ angle was scanned from 5 to 30^{o}.