Supporting information for

Noncovalent functionalization of SWNTs with azobenzene containing polymers: Solubility, stability and enhancement of photoresponsive properties

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Synthesis and Characterization

1. Synthesis of azobenzene derivatives (1a-b). 1a-b was synthesized according to a previous report.\textsuperscript{S1} 4-Cyanoaniline (2.54g, 21.5 mmol, 1.0 equiv.) or aniline (2.00g, 21.5 mmol, 1.0 equiv.) was made into a suspension in water (20 mL) by stirring. Addition of conc. HCl (4.2 mL) to the suspension yielded clear solution. The reaction mixture was placed in an ice bath to reduce the temperature below 5 ºC. An ice cold solution of NaNO\textsubscript{2} (1.63g, 23.65 mmol, 1.1 equiv.) in water (8 mL) was added drop wise to the reaction mixture and continued stirring for another 15 minutes. The resultant mixture was added to an ice cold solution of ethylanilinoethanol (3.55g, 21.5 mmol, 1.0 equiv.) in glacial acetic acid (8.5 mL) and water (20 mL). The mixture was stirred for 5 min in the ice bath and aq. Na\textsubscript{2}CO\textsubscript{3} solution was added to adjust pH to 6. The solid was filtered, air-dried and recrystallized from 3:2 ethanol-water mixture.

1a: Yield 72%; \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): \(\delta\) [ppm] 1.27 (t,3H), 1.64 (s,1H), 3.56 (q, 2H), 3.62 (t,2H), 3.89 (t,3H), 6.81 (d, 2H), 7.74 (d,2H), 7.87 (dd,4H); HRMS: m/z = 294.1502 (calc. = 294.1481).

1b: Yield 70%; \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): \(\delta\) [ppm] 1.22 (t,3H), 1.77 (s,1H), 3.52 (q,2H), 3.57 (t,2H), 3.85 (t,2H), 6.78 (d,2H), 7.38 (t,1H) 7.48 (t,2H), 7.84 (m,4H); HRMS: m/z = 269.1514 (calc. = 269.1528).

2. Synthesis of monomers (2a-b, 3).\textsuperscript{S2} Under argon atmosphere, 1a (2.21g, 7.5 mmol, 1 equiv.) or 1b (2.02g, 7.5 mmol, 1 equiv.) or 1-pyrenemethanol (1.74g, 7.5 mmol, 1 equiv.) was dissolved in anhydrous THF (30 mL) followed by the addition of triethylamine (3.79g, 37.5 mmol, 5 equiv.). The solution was cooled to 0 ºC using an ice bath and distilled methacryloyl chloride (3.79g, 30.0 mmol, 4 equiv.) was added drop wise to the solution over 1h. The reaction mixture was stirred for 8h at room temperature, poured into water and extracted with chloroform. The organic layer was then treated with 1 M aq. NaOH solution and extracted again with chloroform. The combined extracts were dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, CH\textsubscript{2}Cl\textsubscript{2}).

2a: Yield 75%; \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): \(\delta\) [ppm] 1.26 (t,3H), 1.94 (s,3H), 3.55 (q,2H), 3.73 (t,2H),
4.37 (t,2H), 5.60 (s,1H), 6.11 (s,1H), 6.82 (d,2H), 7.75 (d,2H), 7.88 (dd,4H); HRMS: m/z = 362.1732 (calc. = 362.1743).

2b: Yield 76%; ^1H NMR (600 MHz, CDCl$_3$): $\delta$ [ppm] 1.24(t,3H), 1.95(s,3H), 3.58(q2H), 3.72(t,2H), 4.35(t,2H), 5.60(s,1H), 6.12(s,1H), 6.81(d,2H), 7.38 (t,1H) 7.49(t,2H), 7.86(m,4H); HRMS: m/z = 337.1802 (calc. = 337.1790).

3: Yield 73%; ^1H NMR (600 MHz, CDCl$_3$): $\delta$ [ppm] 1.97 (s, 3H), 5.57 (s, 1H), 5.91 (s, 2 H), 6.15 (s, 1H), 8.01-8.31 (m, 9H); HRMS: m/z = 300.1147 (calc. = 300.1150).

3. General method for the synthesis of polymers (P1-3). Required amounts of monomers and catalytic amounts of AIBN was taken in a Schlenk flask and dissolved in anhydrous THF by stirring under argon atmosphere. The solution was degassed by freeze-pump-thaw cycles for three times. The mixture was heated at 60 ºC and the reaction conversion was followed by thin layer chromatography. The reaction was stopped after complete conversion and solvent was evaporated under reduced pressure. The residue was then dissolved in THF and the polymer was precipitated by adding hexane followed by filtration. The precipitation process was repeated several times to yield pure polymer with low polydispersity. The NMR spectrum was very broad and hence the relative amounts of pyrene and azobenzene monomers in the polymer chain was determined by comparing the molar extinction coefficients of each chromophore in the polymer absorption spectrum with that of the corresponding monomers.
**Figure S1.** TGA plots of polymer P1-3. Dotted blue line represents the $T_5$ values (260.7 °C for P1, 263.8 °C for P2, 242.6 °C for P3).

**Figure S2.** DSC plots of polymer P1-3.
**Figure S3.** TGA plots of P1-3/SWNT composites containing 20 wt% of SWNT. Dotted blue line represents the $T_5$ values (319.8 °C for P1/SWNT, 314.2 °C for P2/SWNT, 291.7 °C for P3/SWNT).

**Figure S4.** Comparison of the emission spectrum of P3 before (blue) and after (red) addition of SWNT with that of 3 (green) in THF ($c = 10 \mu g/mL$, $l = 1 \text{ cm}$, $\lambda_{ex} = 345 \text{ nm}$).
References
