

Supporting information for

Stabilizing Bicontinuous Nano-Phase Segregation in π CP-C₆₀ Donor-Acceptor Blends

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Synthesis and characterization of vinyl triazole monomer (5) and its NMRP

1-(p-Anisoyl) 2-(4'-bromo)benzoyl hydrazide (1). A solution of 4-bromobenzoyl hydrazine (25.0 g, 116 mmol) and sodium carbonate (12.3 g, 116 mmol) in dioxane (300 mL) was stirred and heated to 40 °C under nitrogen. A solution of p-anisoyl chloride (19.8 g, 116 mmol) in dioxane (50 mL) was added dropwise and the mixture allowed to react at ambient temperature for 24 h. After the reaction was completed, 300 mL of 3 M aqueous HCl was added to precipitate the crude product. The precipitate was collected by filtration, washed with deionized water and dried under vacuum overnight. The yield was 76.2 % (30 g). ¹ H NMR (DMSO-d₆), δ (ppm): 10.58 (1H, s), 10.43 (1H, s), 7.94 (2H, d), 7.89 (2H, d), 7.75 (2H, d), 7.06 (2H, d), 3.83 (3H, s).

3-(4'-Anisyl)-4-(4'-n-butylphenyl)-5-(4'-bromophenyl)-1,2,4-triazole (2). A solution of 4-*n*-butylaniline (60 mL, 0.38 mol) in *o*-dichlorobenzene (80 mL) was stirred under nitrogen, and a solution of phosphorous chloride (13.9 g, 0.10 mol) in *o*-dichlorobenzene (40 mL) added dropwise. The mixture was allowed to heat at 100 °C for 1 h. A suspension of (1) (30 g, 85.9 mmol) in *o*-dichlorobenzene (80 mL) was added to the solution and the mixture refluxed at 180 °C for 3 h. Residual solvent was removed by azeotropic distillation with added water. The solid was filtered and dried. Recrystallization from ethyl acetate gave 32.5 g of a white solid (yield 82.1 %). ¹H NMR (CD₂Cl₂), δ (ppm): 7.44 (2 H, d), 7.35 (2 H, d), 7.30 (2 H, d), 7.26 (2 H, d), 7.07 (2 H, d), 6.82 (2 H, d), 3.78 (3 H, s), 2.68 (2 H, t), 1.63 (2 H, quintet), 1.36 (2 H, sextet), 0.94 (3 H, t).

3-(4'-Phenoyl)-4-(4'-n-butylphenyl)-5-(4'-bromophenyl)-1,2,4-triazole (3). Boron tribromide (3.5 mL, 37 mmol) in 10 ml dichloromethane was added dropwise to a suspension of (2) (8.6 g, 19 mmol) in dichloromethane (50 ml) at -78 °C under nitrogen. The mixture was allowed to warm to room temperature and subsequently stirred overnight. The clear solution was poured into water and the precipitate filtered, and dried over vacuum to yield 7.5 g of product (yield 90%). ¹H NMR (500 MHz, DMSO-d₆), δ(ppm): 9.96 (1 H, s), 7.53 (2 H, d), 7.26 (2 H, d), 7.15 (2 H, d), 6.66 (2 H, d), 2.58 (2 H, t), 1.51 (2 H, quintet), 1.21 (2 H, sextet), 0.84 (3 H, t).

3-(4'-(2''-ethylhexyloxy)phenyl)-4-(4'-n-butylphenyl)-5-(4'-bromophenyl)-1,2,4-triazole (4). A mixture of (3) (8.40 g, 18.9 mmol), 2-ethylhexylbromide (4.40 g, 22.7 mmol) and potassium carbonate (14.9 g, 75.6 mmol) in 150 mL DMSO and 30 mL toluene was stirred at 120 °C overnight, equipped with a Dean-Stark trap. After cooling, the mixture was poured into water. The precipitate was filtered and recrystallized from ethyl acetate:hexane to provide 9.09 g (yield 85.8%) of a white solid. ¹H NMR (500 MHz, CD₂Cl₂), δ(ppm): 7.45 (d, 2 H), 7.26-7.36 (6 H, 6 peaks), 7.07 (2 H, d), 6.82 (2 H, d), 3.84 (2 H, d), 2.69 (2 H, t), 1.32-1.74 (13 H, m), 0.89-0.97 (9 H, m).

3-(4'-(2''-ethylhexyloxy)phenyl)-4-4'-n-butylphenyl)-5-(4'-vinylphenyl)-1,2,4-triazole (5). A mixture of 3-(4'-(2''-ethylhexyloxy)phenyl)-4-4'-n-butylphenyl)-5-(4'-bromophenyl)-1,2,4-triazole. (11) (1.00 g, 1.78 mmol), vinyltributyltin (0.71 g, 2.24 mmol) and Pd(PPh₃)₄ (21 mg) in 30 mL toluene was heated at 110 °C under nitrogen for 24 h. After cooling, the mixture was diluted with toluene, washed with brine, and dried over MgSO₄. Purification by column gave 0.66 g of a white product (yield 72.8%). ¹H NMR (500 MHz, CD₂Cl₂), δ (ppm): 7.30~7.40 (6 H, m), 7.249 (2 H, d), 7.075 (2 H, d),

6.808 (2 H, d), 6.692 (1 H, q), 5.780 (1 H, d), 5.293 (1 H, d), 3.830 (2 H, d), 2.676 (2 H, t), 1.59~1.71 (1 H, m), 1.21~1.39 (8 H, m), 0.88~0.96 (6 H, m). Analysis: Calcd $C_{34}H_{41}N_3O$: C, 80.43, H, 8.14, N, 8.28. Found C, 80.07, H, 8.11, N, 8.40.

PVTAZ (6). The nitroxide-mediated radical polymerization (NMRP) technique^{1,2} was used for the polymerization of **5**. Solution polymerization was carried out in argon using p-xylene as the solvent. TEMPO initiator (**7**) (20 mg, 0.008 mmol), acetic anhydride 0.3 mL, and (**5**) (0.20 g, 0.40 mmol) in 1.5 mL p-xylene were heated to 125°C. Samples were extracted every 90 minutes for analyses of molecular weight. After the reaction, the solvent was dried under vacuum and dissolved in chloroform, followed by precipitation in methanol.

1-Phenyl-1-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)-ethane (7). Using a similar method described in the literature,³ ethylbenzene (50 mL), di-tert-butylperoxide (2.5 g, 16.5 mmol) and TEMPO (5.25 g, 33.0 mmol) were refluxed under nitrogen overnight and evaporated the excessive ethylbenzene to get dry crude product. The crude product was purified by flash chromatography using hexane, with gradual addition of ethyl acetate. The colorless oil was recrystallized from cold ethanol (-78 °C) to give a white solid (2.1 g, 24% yield). ¹H NMR (500 MHz, CD₂Cl₂), δ(ppm): 0.66, 1.03, 1.17, 1.38 (each br s, 12H), 1.23-1.58 (m, 6H), 1.47 (d, 3H), 4.79 (q, 1H), 7.25-7.35 (m, 5H).

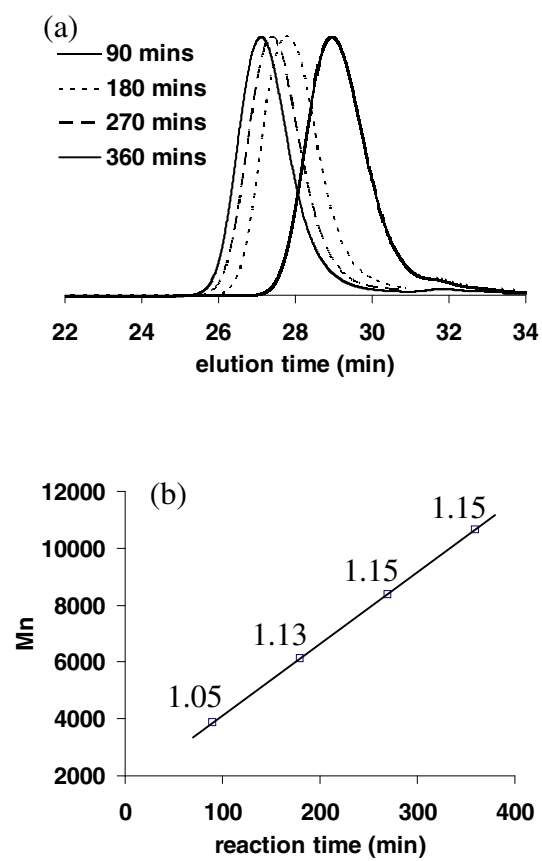


Figure S1 (a) Evolution of GPC peaks of **6** with reaction time. (b) Polymer chain growth vs. reaction time for **6**. Polydispersity indices are shown above data points.

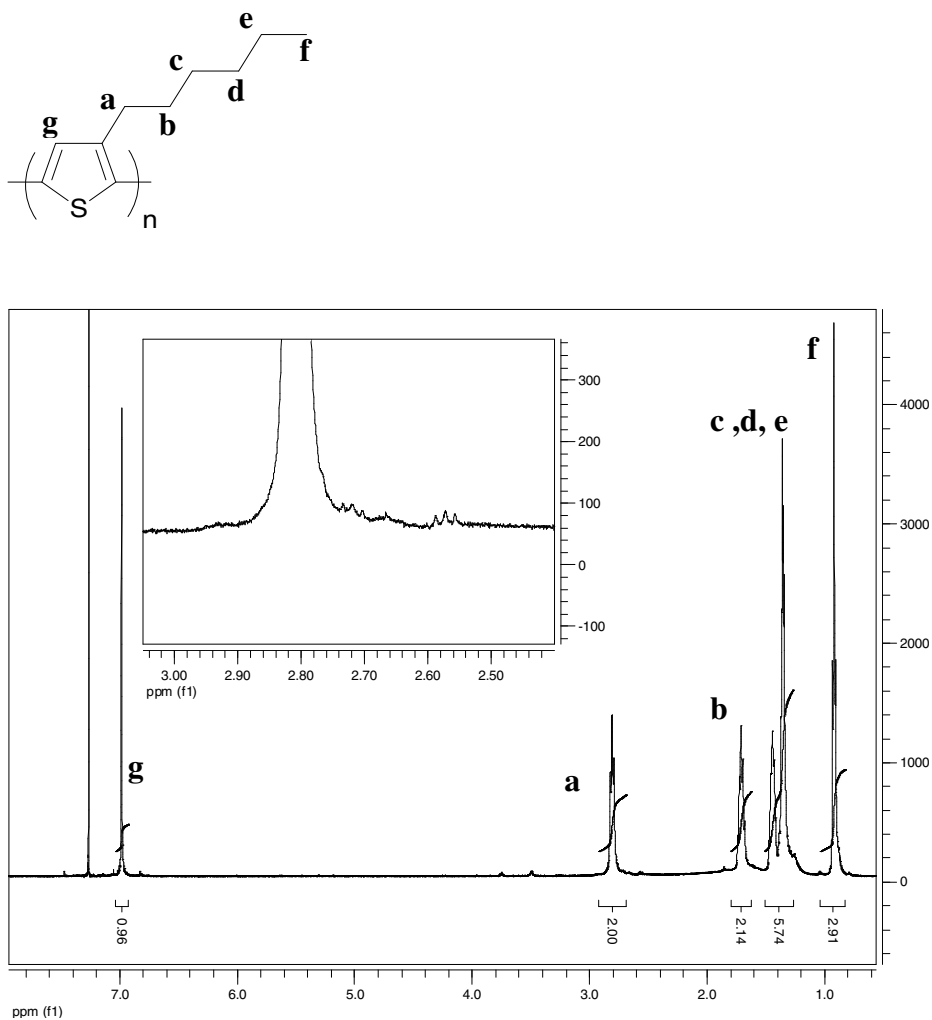


Figure S2. NMR spectrum of regioregular P3HT in CDCl₃.

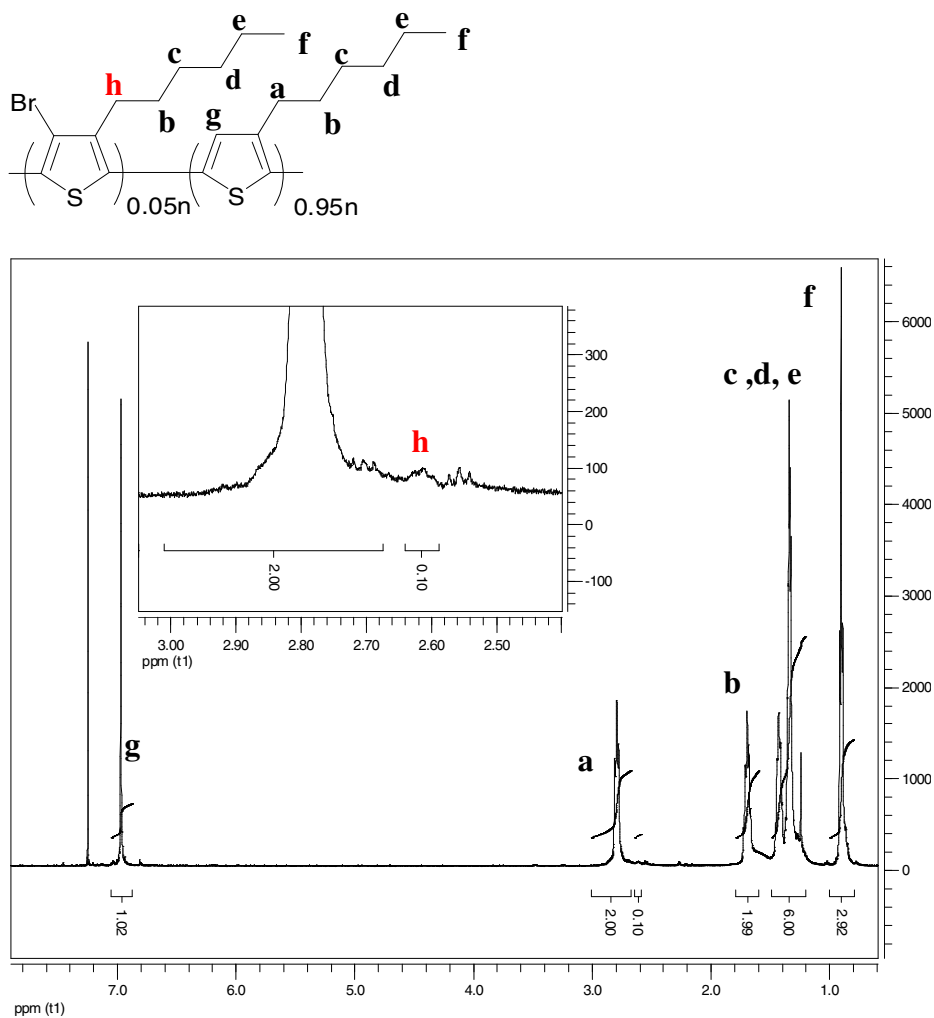


Figure S3. NMR spectrum of brominated P3HT (**9**) in CDCl_3 .

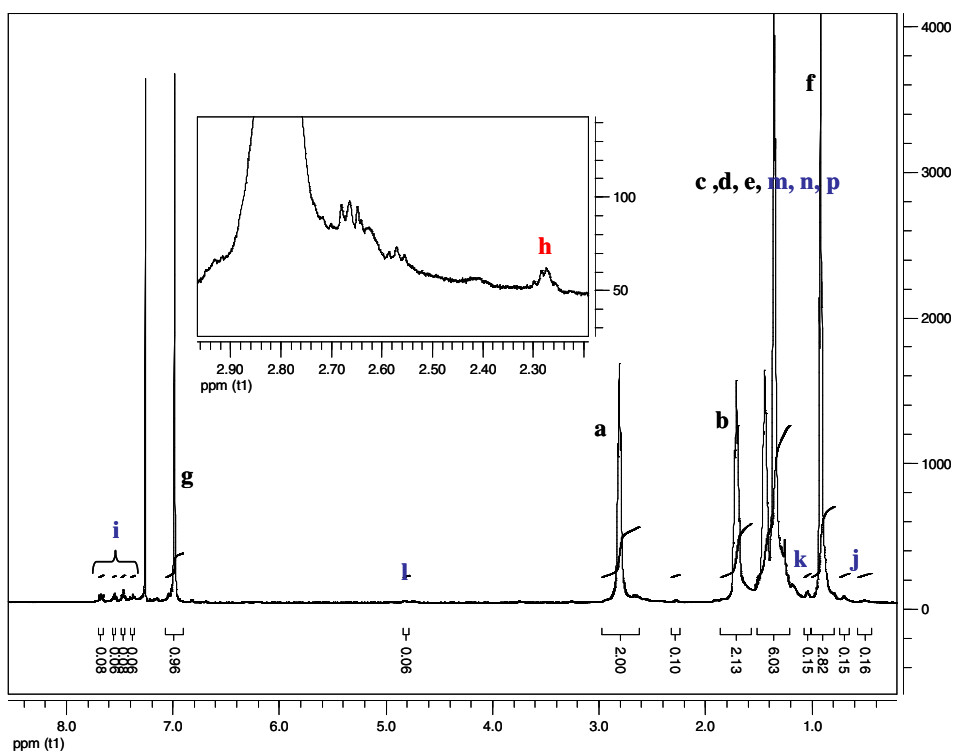
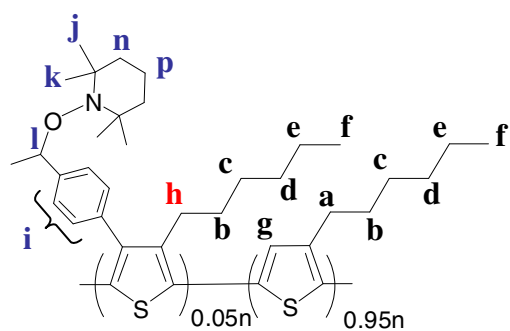


Figure S4. NMR spectrum of macroinitiator (**10**) in CDCl_3 .

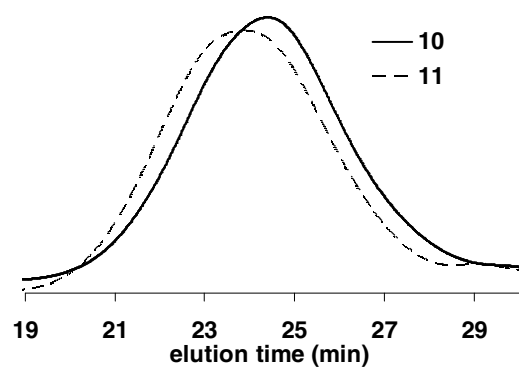


Figure S5. GPC trace of TEMPO-P3HT macroinitiator (**10**) (solid line), the graft copolymer P3HT-g-PVTAZ (**11**) (dashed line).

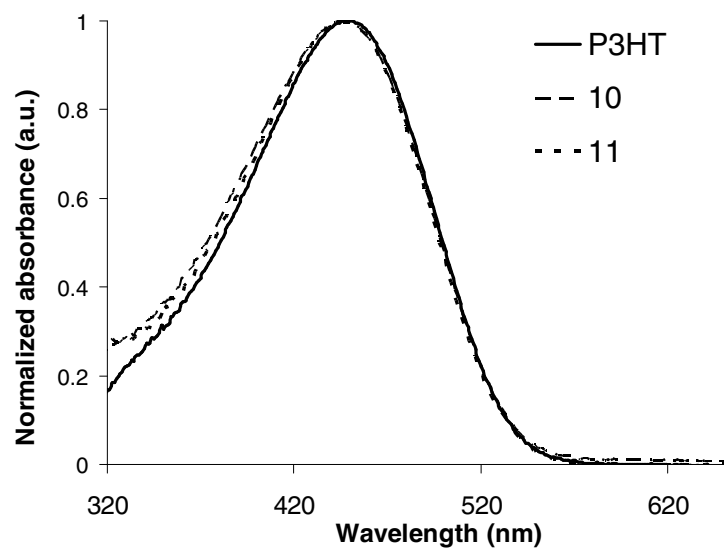


Figure S6. UV-vis absorption spectra of P3HT, 10, 11 in THF solution.

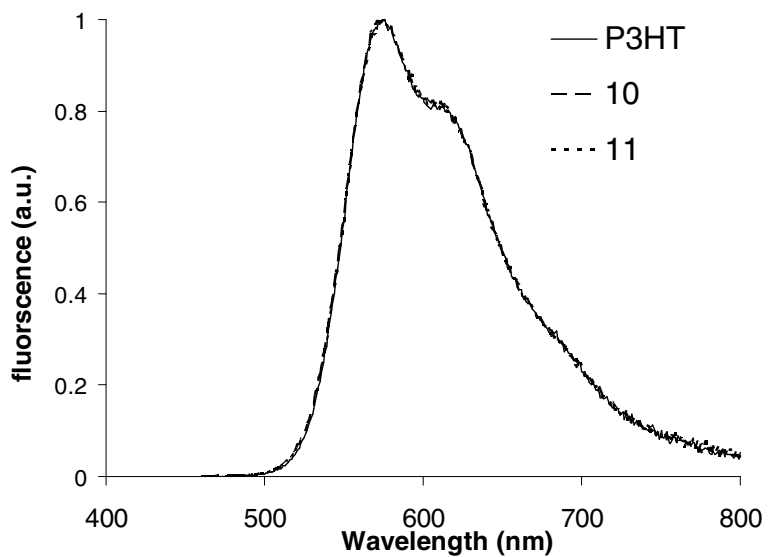


Figure S7. photoluminescence spectra of P3HT, 10, 11 in THF solution.

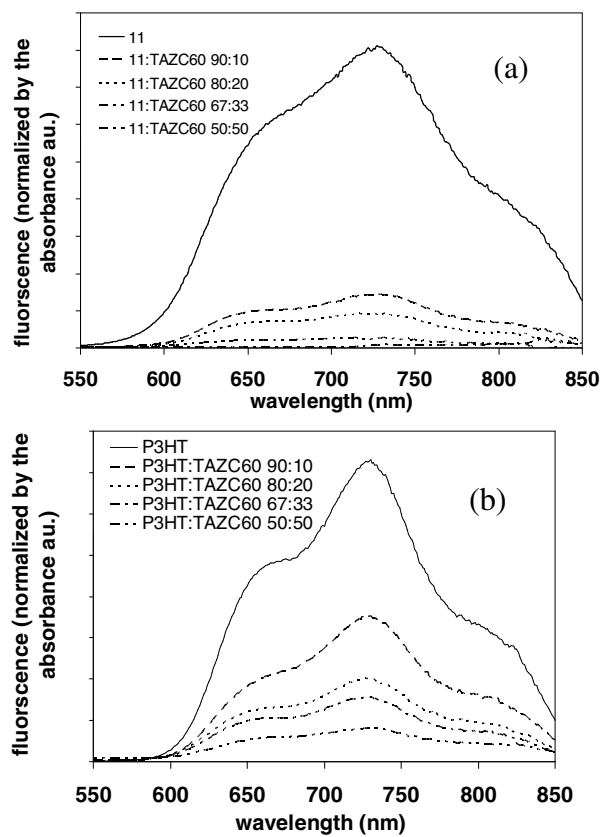


Figure S8. Photoluminescence spectra of films: (a) 11, (b) P3HT, containing various weight ratios of TAZC₆₀. Spectra normalized to absorbance at 480 nm.

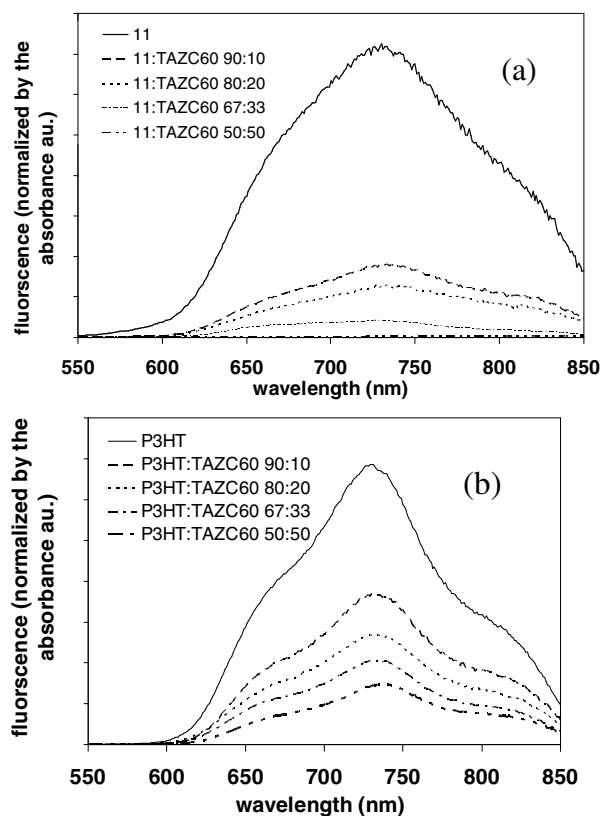


Figure S9. Photoluminescence spectra of films after annealing at 140 °C for 1 hour: (a) **11**, (b) **P3HT**, containing various weight ratios of **TAZC₆₀**. Spectra normalized to absorbance at 480 nm.

Reference List

- (1) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem.Rev.* **2001**, *101*, 3661-3688.
- (2) Malmstrom, E.; Miller, R. D.; Hawker, C. J. *Tetrahedron* **1997**, *53*, 15225-15236.
- (3) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J.Am.Chem.Soc.* **1999**, *121*, 3904-3920.