Supporting Information

Single-Chain Semiconducting Polymer Dots

Fangmao Ye¹§, Wei Sun¹§, Yue Zhang¹, Changfeng Wu², Xuanjun Zhang³, Jiangbo Yu¹, Yu Rong¹, Miqin Zhang⁴ and Daniel T. Chiu¹*

¹Department of Chemistry, University of Washington, Seattle, Washington 98195, United States

² Present address: State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun, Jilin 130012, China

³ Present address: Division of Molecular Surface Physics & Nanoscience, Department of Physics, Chemistry, and Biology, Linköping University, Linköping 58183, Sweden

⁴Department of Material Science and Engineering, University of Washington, Seattle, Washington 98195, United States

E-mail: chiu@chem.washington.edu
Synthesis of semiconducting polymers

**Figure S1** shows the synthesis of alkyne-functionalized PFBTA (poly[(9,9-dioctylfluoren-2,7-diyl)-co-(1,4-benzo-2,10,3-thiadazole)]). In a PFBT-C14 solution in THF (56 mg in 3 mL) \(^1\), we added 2-propynylamine (0.04 mmol, 2.2 mg, 2.56 µL) and N,N'-Dicyclohexylcarbodiimide (DCC, 0.04 mmol, 8.25 mg). The mixture was stirred at room temperature overnight. After being filtered through a 0.2-µm membrane, the polymer was precipitated in 30-mL methanol, filtered and washed thoroughly with methanol and ethanol, and then dried in vacuum. Yield: 42 mg (72.4%). \(^1\)HNMR (500 MHz, CDCl\(_3\)): δ = 7.75-8.10 (m, 9H), 6.6-6.0 (broad, 0.6H), 3.90-3.56 (broad, 1H), 3.50-3.35 (s, 0.6H), 2.76-2.56 (broad, 2H), 2.30-2.00 (broad, 4H), 1.26-1.05 (m, 20H), 1.02-0.90 (broad, 4H), 0.82-0.79 (t, d = 6 Hz, 6H).

**Figure S2** shows the synthesis of alkyne-functionalized PFOA (poly[(9,9-dioctylfluoren-2,7-diyl)-co-(9,9-dipropylcarboxylfluoren-2,7-diyl)]). We added 2-propynylamine (0.01 mmol, 0.5 mg, 0.6 µL) and DCC (0.01 mmol, 2.0 mg) to a PFO-C5 \(^1\) solution in THF (10 mg in 1 mL). The mixture was stirred at room temperature overnight. After being filtered through a 0.2-µm membrane, the polymer was precipitated in 15-mL methanol, filtered, washed thoroughly with methanol and ethanol, and dried in vacuum. Yield: 7.5 mg (74.3%). \(^1\)HNMR (500 MHz, CDCl\(_3\)): δ = 7.86-7.50 (m, 6H), 6.50-6.00 (broad, 0.1H), 3.84-3.56 (broad, 0.2H), 3.50-3.35 (s, 0.1H), 2.78-2.58 (broad, 0.4H), 2.28-2.06 (broad, 4H), 1.26-1.15 (m, 19H), 1.00-0.90 (broad, 4H), 0.82-0.79 (t, d = 6 Hz, 6H).

**Preparation of azide-modified silica particles**

Silica particles with diameters of ~ 200 nm were prepared by the Stöber method\(^2\). 1.8 mL of DI water was added to a flask containing 90-mL ethanol, after which 5.94-mL
tetraethoxysilane (TEOS) was added to the mixture under stirring. Finally, 2.88-mL saturated ammonium hydroxide was added to the mixture. The mixture was stirred for three days. The milky solution was then centrifuged at 6000 rpm for 10 min. The silica pellet was rinsed with water 3 times by sonication and centrifugation, then re-suspended in water to get ~20 mg/mL concentration of silica particle suspension. 20 µL (3-chloropropyl) trimethoxysilane and 20 µL of 1M acetic acid were added to 1 mL of the above silica suspension to introduce chloride groups onto the silica surface and the mixture was stirred overnight. The silica particles were centrifuged down and rinsed three times with DI water and then was dried overnight at 70 ºC in the oven. 50 mg of completely dry silica particles was dissolved in 5-mL sodium azide saturated DMF solution under sonication. The mixture was stirred for 3 hours at 80 ºC. The silica with azide surface moiety (SiO$_2$-N$_3$) was then centrifuged down and rinsed with water three times, and finally was re-suspended in water with a concentration of ~10 mg/mL.

**Control Experiments**

Several control experiments were performed to validate the click reaction between SiO$_2$-N$_3$ and the Pdots with the alkyne surface moiety:

1. 1 mL of 100 ppm multi-chain PFBTA Pdots was added to 2-mL 10 mg/mL SiO$_2$-Cl in the presence of freshly prepared copper sulfate (0.5 mM) and L-sodium ascorbate (0.2 mM). The reaction lasted for 2 hours then the silica was centrifuged down. No fluorescence was observed in the silica pellet, indicating nonspecific binding between SiO$_2$-Cl and PFBTA Pdot with alkyne surface moiety did not occur (**Fig. S4a**);

2. 1 mL of 100 ppm multi-chain PFBTA Pdots was added to 2 mL of 10 mg/mL SiO$_2$-N$_3$ in the presence of freshly prepared L-sodium ascorbate (0.2 mM) but without
copper sulfate. The reaction lasted for 2 hours then the silica was centrifuged down. Again no fluorescence was observed in the silica pellet, indicating there was not any nonspecific binding between SiO$_2$-N$_3$ and Pdots with the alkyne surface moiety (Fig. S4b);

(3) 1 mL of 100 ppm multi-chain PFBTA Pdots with the alkyne surface moiety was added to 2 mL of 10 mg/mL SiO$_2$-N$_3$ in the presence of freshly prepared copper sulfate (0.5 mM) and L-sodium ascorbate (0.2 mM). The click reaction lasted for 2 hours then the Pdot-silica was centrifuged down. The pellet this time was fluorescent, indicating the click reaction between Pdots and silica was successful. The pellet was rinsed three times with DI water (Fig. S4c). The solvent of the resulting solution was changed to water containing 100 mM NaOH and 0.25% Triton 100 to cleave the Pdots from the silica surface. The solution was stirred overnight at room temperature and the Pdots were obtained in the supernatant by centrifuging the solution (6000 rpm × 10 mins). The pellet after centrifugation was not fluorescent indicating the complete cleavage of the Pdots from the silica surface (Fig. S4d). Moreover, the PFBTA Pdots obtained after this entire procedure retained the same size (before: 14 nm; after: 14 nm) and optical properties (quantum yield: before 23%; after: 23%), indicating there was not any damage or change of the Pdots during the click reaction and cleavage procedure.

**Characterization of Pdots**

DLS experiments were conducted using a Malvern Zetasizer NanoZS. UV-Vis absorption spectra were recorded with a DU 720 spectrophotometer. Fluorescence spectra were collected with a Fluorolog-3 fluorometer.
In the AFM measurement, one drop of the Pdot solution was placed on a fresh APTEOS-coated mica substrate, where the negatively charged Pdots could be bound effectively by the positively charged amine (APTEOS) surface. Using APTEOS-coated mica or coverslip to adhere Pdots has proven to be an efficient method for preparing Pdots for AFM measurements; we did not observe noticeable aggregation as long as an appropriate concentration of Pdots was used. After evaporation of the water solution, the surface topography was imaged with a Dimension 3100 multimode AFM in tapping mode. The AFM was done with FESP silicon probe from Veeco Probes. A resonant frequency of 273.3 kHz was used and height and phase images were collected at a scan rate of 1 Hz and a resolution of 256 x 256 pixels.
| Pdots | Average molecular weight | Concentration in THF (wt%) | Hydrodynamic diameter (nm) |
|-------|--------------------------|---------------------------|---------------------------|
| PFBT  | 150,000                  | 0.0005                    | 15                        |
| PFPV  | 220,000                  | 0.0005                    | 14                        |
| PFO   | 80,000                   | 0.0005                    | 15                        |

**Table S1.** Size of Pdots generated from the reprecipitation method using an ultra-diluted polymer solution
Figure S1, Synthesis of PFBTA
Figure S2, Synthesis of PFOA
Figure S3. Top panel: Absorbance of the physically mixed multi-chain PFOA/PFBTA Pdots with different ratios of PFOA : PFBTA, ranging from 1:0 (100%), 1:2 (50%), 1:5 (20%), 1:10 (10%), and 1:20 (5%). Bottom panel: Plot showing the dependence of RA ($\frac{\text{Abs}(370\text{nm})}{\text{Abs}(450\text{nm})}$) as a function of the ratios of PFOA:PFBTA.
Figure S4. Control experiments. (a) After sonication and centrifugation of the solution containing Pdots and Cu⁺, the resulting pellet, which should comprise SiO₂-Cl, was not fluorescent in the presence of Cu⁺, indicating there was not any nonspecific binding between SiO₂-Cl and Pdot with the alkyne surface moiety. Photo on the left shows the sample before adding Pdots under UV light (after centrifugation). Photo on the right shows the sample after adding Pdot and Cu⁺ (after centrifugation). (b) After sonication and centrifugation of the solution containing Pdots, the pellet of SiO₂-N₃ was also not fluorescent in the absence of Cu⁺, again indicating there was not any nonspecific binding between SiO₂-N₃ and Pdots with the alkyne surface moiety. Photo on the left shows sample before adding Pdot under UV light (after centrifugation). Photo on the right shows the sample after adding Pdots (after centrifugation). (c) After sonication and centrifugation of the solution containing Pdots and Cu⁺, the pellet of SiO₂-N₃ was
fluorescent in the presence of Cu\(^{+}\), indicating the reaction between SiO\(_2\)-N\(_3\) and Pdot with alkyne surface moiety was successful. (d) In the presence of 100 mM NaOH and 0.25 \% Triton 100, the Pdots were cleaved from the silica surface, after which the pellet was not fluorescent any more, indicating the cleavage reaction was successful.
**Figure S5.** Profile of the Xenon lamp (450 W) output as a function of wavelength for the Fluorolog-3 setup (Horiba).
References

(1) Zhang, X.; Yu, J.; Wu, C.; Jin, Y.; Rong, Y.; Ye, F.; Chiu, D. T. ACS Nano 2012, 6, 5429.

(2) Stober, W.; Fink, A.; Bohn, E. Journal of Colloid and Interface Science 1968, 26, 62.