

Supporting Information

Semiconducting Polymer Dots with Monofunctional Groups

*Fangmao Ye^a, Changfeng Wu^b, Wei Sun^a, Jiangbo Yu^a, Xuanjun Zhang^c, Yu Rong^a, Yue
Zhang^a, I-Che Wu^a, Yang-Hsiang Chan^d and Daniel T. Chiu^{a*}*

^a Department of Chemistry, University of Washington, Seattle, Washington 98195,
United States

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

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

^d Present address: Department of Chemistry, National Sun Yat-Sen University,
Kaohsiung, Taiwan

E-mail: chiu@chem.washington.edu

Synthesis of semiconducting conjugated polymers

Figure S1 shows the synthesis of alkyne-terminated linear poly(p-phenylenevinylene) derivative containing two pendent pentaphenylene (PPV-PPA). The synthesis of pentaphenylene dendrimer **7** was through a Diels-Alder reaction of 3,4-bis[4-(2-ethylhexyloxy)phenyl]-2,5-diphenylcyclopenta-2,4-dienone **6** with 1,4-diethynyl-2,5-dimethyl-benzene **3** in refluxing *o*-xylene ¹. **7** was then brominated with N-Bromosuccinimide (NBS) to obtain the corresponding 1,4-bis(bromomethyl) benzene **8**. The homopolymerization of **8** was then performed in THF and excess alkyne-OH was used to terminate molecules and form end groups to obtain PPV-PPA **9**. Overall yield: 6%. ¹H NMR (CDCl₃, 500 MHz): δ 7.03-6.60 (m, 42H), 3.61 (br, 8H), 1.57 (br, 4H), 1.25 (br, 32H), 0.85 (br, 24H). Number-average Degree of Polymerization (DP_n) is around 60 from GPC profiles. The proton signals from terminating ethynyl and alkyl groups are hard to observe, because of the very low molar ratios compared to the protons from the polymer backbone. For the same reason, the triple bond cannot be observed via FTIR (not shown). However, the triple bond was confirmed by the click reaction of Pdots, which was described in the main text.

Preparation of monovalent Pdot (*m*Pdot)

Briefly, 1 mL of 100 ppm multivalent Pdots prepared by nanoprecipitation with an alkyne surface moiety was added to 2 mL of 10 mg/mL SiO₂-N₃ in the presence of freshly prepared copper sulfate (0.5 mM, Sigma-Aldrich, > 99%) and L-sodium ascorbate (0.2 mM, Sigma, > 98%). The click reaction lasted for 2 hrs. Then the Pdot-silica particles were centrifuged down and rinsed three times with DI water, after which the solvent was changed to Tetrahydrofuran (THF, Sigma-Aldrich, dehydrate) and the Pdot-

silica was rinsed with THF solution under sonication (5 min). The solution was centrifuged (6000 rpm × 10 mins), and the THF rinsing process was repeated three times. 1 mL of the resulting Pdot-silica complex in THF solution was then injected into 2 mL of aqueous solution with sonication and the resulting solution was heated at 80 °C with N₂ stripping for 30 min to remove THF. The final solution (~2 mL) was filtered with 1- μ m membrane and the solvent was changed to aqueous solution containing 100 mM NaOH (Sigma) and 0.25% Triton 100 (Electron Microscopy Science) to cleave the Pdots from the silica surface. The solution was stirred overnight at room temperature and the Pdots collected from the supernatant by centrifuging the solution (6000 rpm × 10 mins). The pellet after centrifugation was not fluorescent indicating the complete cleavage of Pdots from the silica surface. The supernatant containing Pdots was further dialyzed with DI water to remove the NaOH and Triton 100. The final concentration of the Pdots was ~ 1ppm in 2 mL of DI water.

Preparation of regular multivalent Pdots

The preparation of Pdots has been described previously². Briefly, 2 mg of the semiconducting polymer, PPV-PPA, (Mn 86,000, polydispersity 3.1) was dissolved in 2-mL THF by stirring overnight in an inert atmosphere. The solution was then filtered through a 0.7- μ m glass fiber filter to remove any insoluble material. Multivalent Pdots were prepared by injecting 200 μ L of 1 mg/mL polymer (in THF) into 10 mL of MilliQ water under sonication. The THF was removed and the solution concentrated by continuous nitrogen stripping to 10 mL on a 90 °C hotplate. The solution was passed through a 0.2- μ m filter.

***m*Pdot coupling to form dumb-bell structures in the presence of Bis-azide**

PEG7-Bis-Azide (liquid, Jena Bioscience) with linker : *m*Pdot ratios of 10:1, 1:2, and 1:10 was added to 200 μ L of the as-prepared *m*Pdot solution (the concentration of the Pdot solution was calculated to be \sim 10 nM based on the size of the Pdot and its absorbance) or multivalent Pdot solution, which consisted of 20 mM HEPES buffer adjusted to pH 7.4 and contained freshly prepared copper sulfate (0.5 mM) and L-sodium ascorbate (0.2 mM) at room temperature. The mixture was stirred for two hours. The resulting solution was dialyzed for 2 days in DI water using a 10 kDa cut-off membrane. After dialysis, 20 μ L of the solution was used for AFM imaging.

Preparation of *m*Pdot-COOH and coupling with copper (II) ion

2 μ L of 100 nM carboxylic-PEG-azide in DI water was added to 200 μ L of the as-prepared *m*Pdot in 20 mM HEPES buffer (pH = 7.4). Freshly prepared copper sulfate (0.5 mM) and L-sodium ascorbate (0.2 mM) were added to the above *m*Pdot solution. The mixture was stirred for 2 hrs and then dialyzed in DI water for two days using a 10 kDa cut-off membrane. Then different concentrations of copper (II) ions were introduced to the *m*Pdot solution.

Characterization of Pdots

TEM experiments were performed on a FEI Tecnai F20 transmission electron microscope. 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 nanoparticle dispersion was placed on a freshly APTEOS-coated mica substrate. 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.

Figure S1

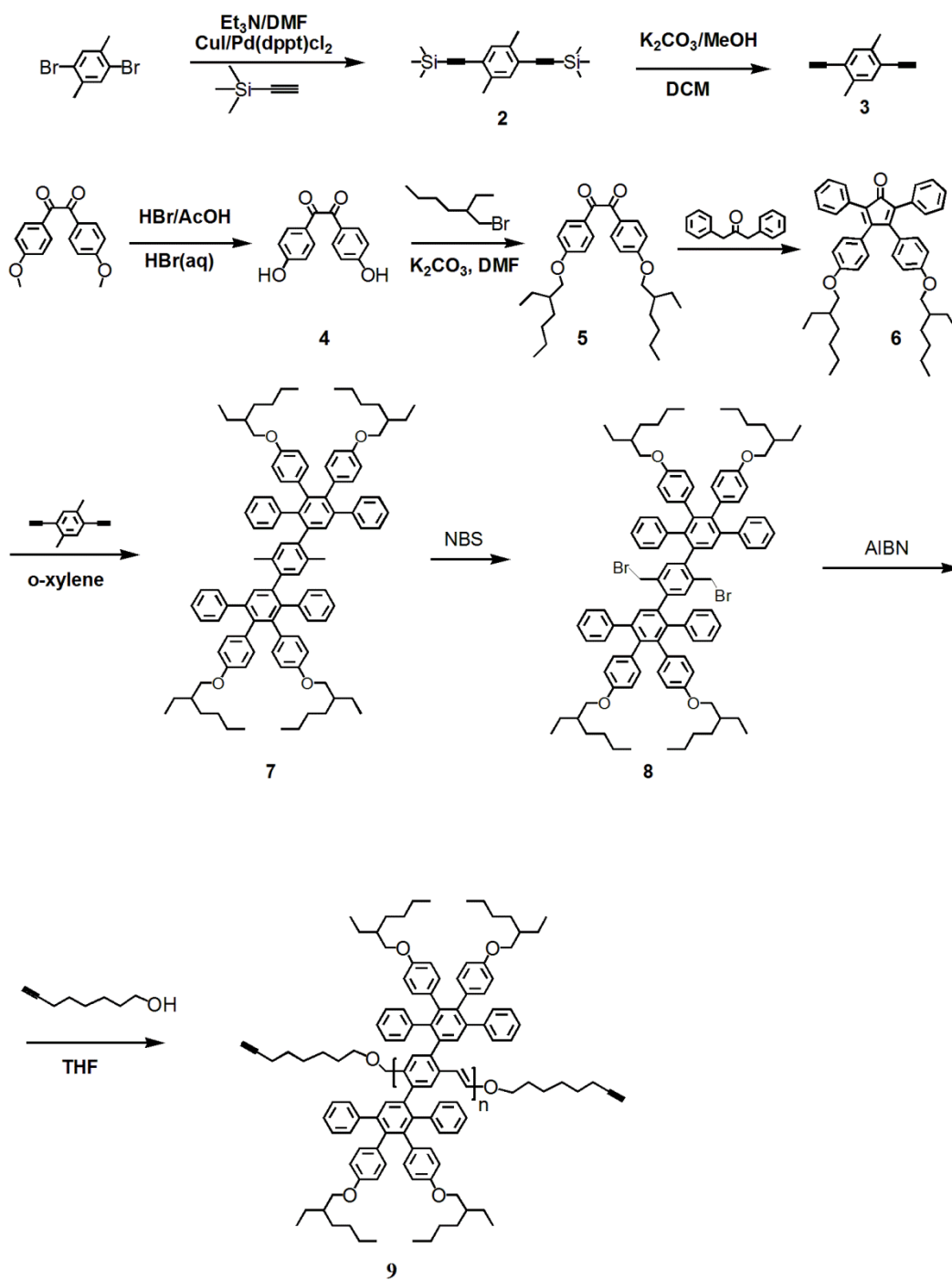


Figure S1, Synthesis of PPV-PPA

Figure S2

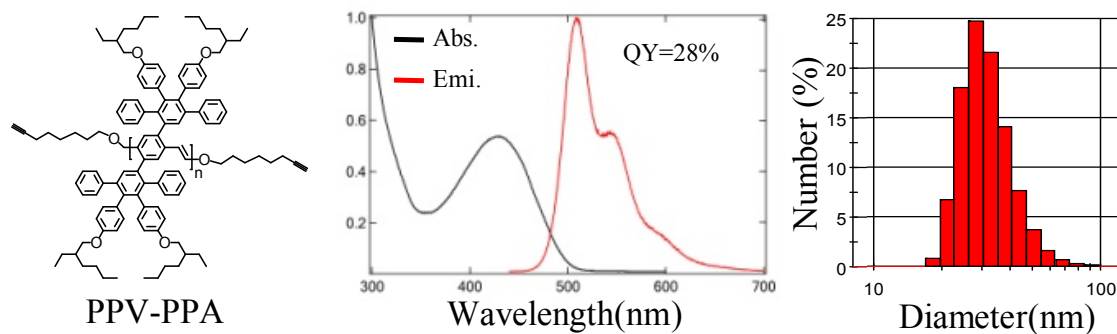


Figure S2. Polymer structure of PPV-PPA (left panel), the absorption and emission of PPV-PPA Pdot (central panel), and the hydrodynamic diameter of multivalent PPV-PPA Pdot (right panel; average diameter = 32 nm).

Figure S3

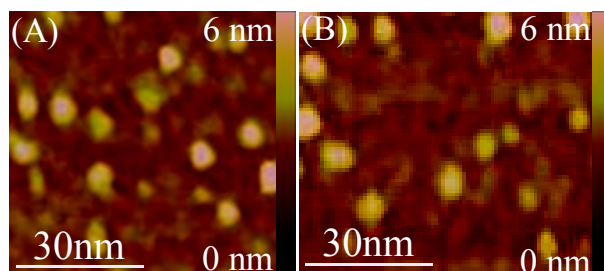


Figure S3. Representative AFM images of *mPdots* with both PEG7-Bis-Azide and copper sulfate and L- sodium ascorbate at a linker : Pdot ratio of (A) 10:1 and (B) 1:10. No dumb-bell features were observed.

Figure S4

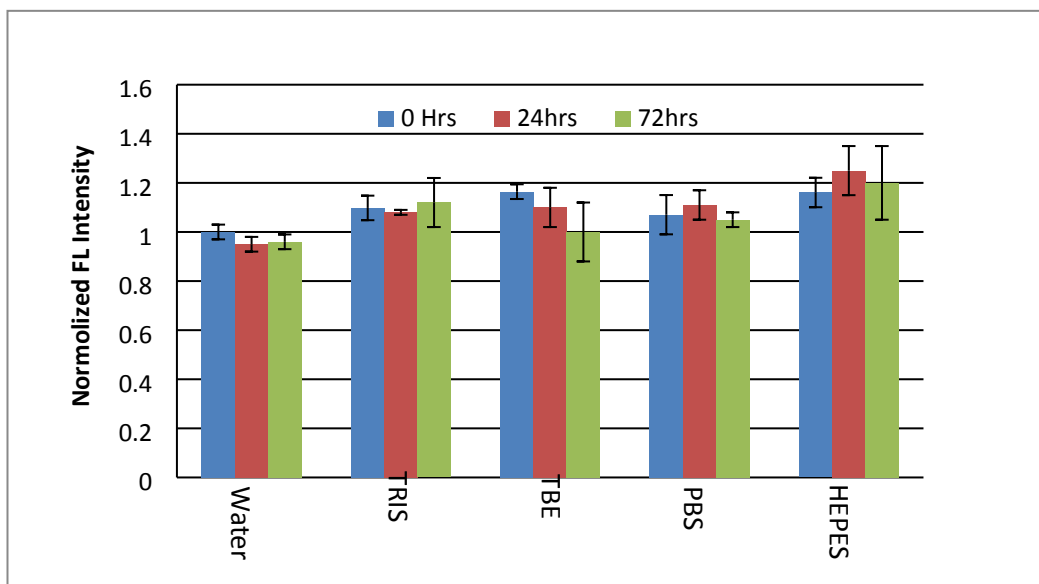


Figure S4. Stability of *mPdots* in different buffers. *mPdots* (~5nM) was stored in water, 1× TRIS (pH=8.0), 0.5 × TBE (pH=8.1), 1× PBS (pH=7.0), and 20mM HEPES (pH=7.3) for up to 3 days at room temperature, respectively. The y-axis shows the normalized fluorescence (FL) intensity of *mPdots* in buffers; any aggregation of *Pdots* will result in self quenching and a decrease in fluorescence³. No *mPdots* aggregation was observed during the experimental period.

References

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- (3) Jin, Y.; Ye, F.; Wu, C.; Chan, Y.; Chiu, D. T. *Chem. Comm.* **2012**, *48*, 3161