

Supporting Information for

Controllable Biocompatible Post-Polymerization Functionalization of Poly(*p*-Phenylene Ethynylene)s and Highly Sensitive Detection of Streptavidin

Brett VanVeller and Timothy M. Swager*

*Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139
Email: tswager@mit.edu*

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Materials: Silica gel (40 μm) was purchased from SiliCycle. All solvents used for photophysical experiments were spectral grade. $\text{Pd}(\text{PPh}_3)_4$ was purchased from Strem Chemicals, Inc. All other reagent grade materials were purchased from Aldrich, TCI America, and Alfa Aesar, and used without further purification.

Experimental:

NMR Spectroscopy: ^1H and ^{13}C NMR spectra for all compounds were acquired in CDCl_3 , D_2O and DMF-d_7 on a Bruker Avance Spectrometer operating at 400 and 100 MHz, respectively. The chemical shift data are reported in units of δ (ppm) relative to residual solvent.

Gel Permeation Chromatography (GPC): Polymer molecular weights were determined using a triple detection method for calibration with poly(acrylic acid) standards on a Viscotek TDA 305-040 instrument equipped with two Viscotek A-MBHMW-3078 columns and analyzed with light scattering and refractive index detectors. Samples were dissolved in 5% NH_4OH .

Absorption and Emission Spectroscopy: Fluorescence spectra were measured on a SPEX Fluorolog- τ 3 fluorometer (model FL-321, 450 W Xenon lamp) using right-angle detection. Ultraviolet-visible absorption spectra were measured with an Agilent 8453 diode array spectrophotometer and corrected for background signal with a solvent filled cuvette. Fluorescence quantum yields of **3a** in both water and 1X PBS were determined relative to perylene and are corrected for solvent refractive index and absorption differences at the excitation wavelength.

Synthetic Procedures

Biotin functionalization, synthesis of 3a: Polymer **1** (11.8 mg, 14.6 μmol based on

repeat unit) was dissolved in 4 mL of H₂O and NaIO₄ (2.92 μmol in 0.2 mL) was added dropwise under vigorous stirring. After 30 min, **a** (Biotin-PEG₃-NH₂, 3 mg, 7 μmol in 1 mL of 0.2M Na₂HPO₄) was added and the reaction was stirred for 20 min. A solution of NaCNBH₃ (15 mg, 239 μmol in 1 mL of 40 mM Na₂HPO₄) was added and the reaction stirred for 3 hours. The reaction was dialyzed against water with 5 changes of water and lyophilized to yield **3a**. GPC gave M_n = 38,474, PDI = 3.4. ¹H NMR (600 MHz, D₂O): δ 7.44 (s, 2H), 4.64 (broad, 4H), 4.37 (broad, 4H), 4.05 (broad, 4H), 3.89 (broad, 4H), 3.80-3.30 (biotin, PEG), 3.18 (broad, 4H) 2.35 (broad, 4H), 1.30-0.90 (biotin).

Piv-Lysine functionalization, synthesis of 3b: Prepared using identical conditions as above for **3a** except that **b** (Piv-Lys-NH₂) was used in place of **a**. GPC gave M_n = 49,073, PDI = 4.9. ¹H NMR (600 MHz, D₂O): δ 7.42 (s, 2H), 4.61 (broad, 4H), 4.35 (broad, 4H), 4.03 (broad, 4H), 3.88 (broad, 4H), 3.16 (broad, 4H), 2.33 (broad, 4H), 1.05 (broad, tBu, 1.6–1.8*).

*Based on three experiments and corresponds to 18–20%.

Synthesis of tetraaldehyde 5: A solution NaIO₄ (0.200 g, 0.935 mmol) in 10 mL of water was added to a solution of **4** (0.200 g, 0.248 mmol) in 10 mL of THF. Solid TBAIO₄ (54 mg, 0.124 mmol) was added directly and the solution was refluxed for 30 min. After cooling, the reaction was partitioned between EtOAc and brine and the organic phase collected. The aqueous layer was washed with fresh EtOAc and the combined organic layers were dried over Na₂SO₄ and concentrated *in vacuo*. The residue was eluted through a silica gel plug using EtOAc to give **5** (95%). ¹H NMR (400 MHz, CDCl₃): δ 9.65 (d, *J*=2, 4H), 4.98 (nfo, actual ddd, *J*=6.6, 2.8, 2, 4H), 4.89 (dd, *J*=6.6, 2.8, 4H), 1.48 (s, 6H), 1.46 (s, 6H), 1.12 (s, 42H). ¹³C NMR (125 MHz, CDCl₃) δ 197.6, 134.1, 125.9, 110.7, 105.7, 101.2, 73.9, 54.5, 25.9, 24.2, 18.8, 11.4. HRMS (EI) calcd. for C₄₆H₆₆O₈Si₂ [M+H] 803.4369, found 803.4344.

Synthesis of amine 6: To a solution of **5** (0.150 g, 0.186 mmol) in 10 mL of MeOH was added butyl amine (82 mg, 1.12 mmol). After stirring for 10 min at room temperature, NaCNBH₃ (0.250 g, 3.98 mmol) was added and the mixture was refluxed for 3 hours. Once cool, 1 mL of sat. NaHCO₃ was added and the solvent was removed *in vacuo*. The residue was partitioned between DCM and sat. NaHCO₃. The organic layer was dried over Na₂SO₄ and evaporated to dryness. Silica gel chromatography (EtOAc:Hex, 8:2) provided **6** (65%) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 4.33 (dd, *J*=4.0, 2.4, 4H), 4.00 (m, 4H), 2.84 (d, *J*=12, 4H), 2.58 (dd, *J*=11.8, 7.5, 4H), 2.29 (br t, 4H), 1.64 (s, 6H), 1.40 (s, 6H), 1.28 (m, 4H), 1.12 (br s, 42H), 1.06 (m, 4H), 0.74 (t, *J*=7.4, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 139.5, 119.8, 110.8, 103.2, 98.3, 76.5, 57.4, 48.7, 41.5, 28.7, 25.9, 24.7, 20.7, 19.0, 14.1, 11.6. HRMS (EI) calcd. for C₅₄H₈₈N₂O₄Si₂ [M+H] 885.6355, found 885.6357.

NMR Spectra

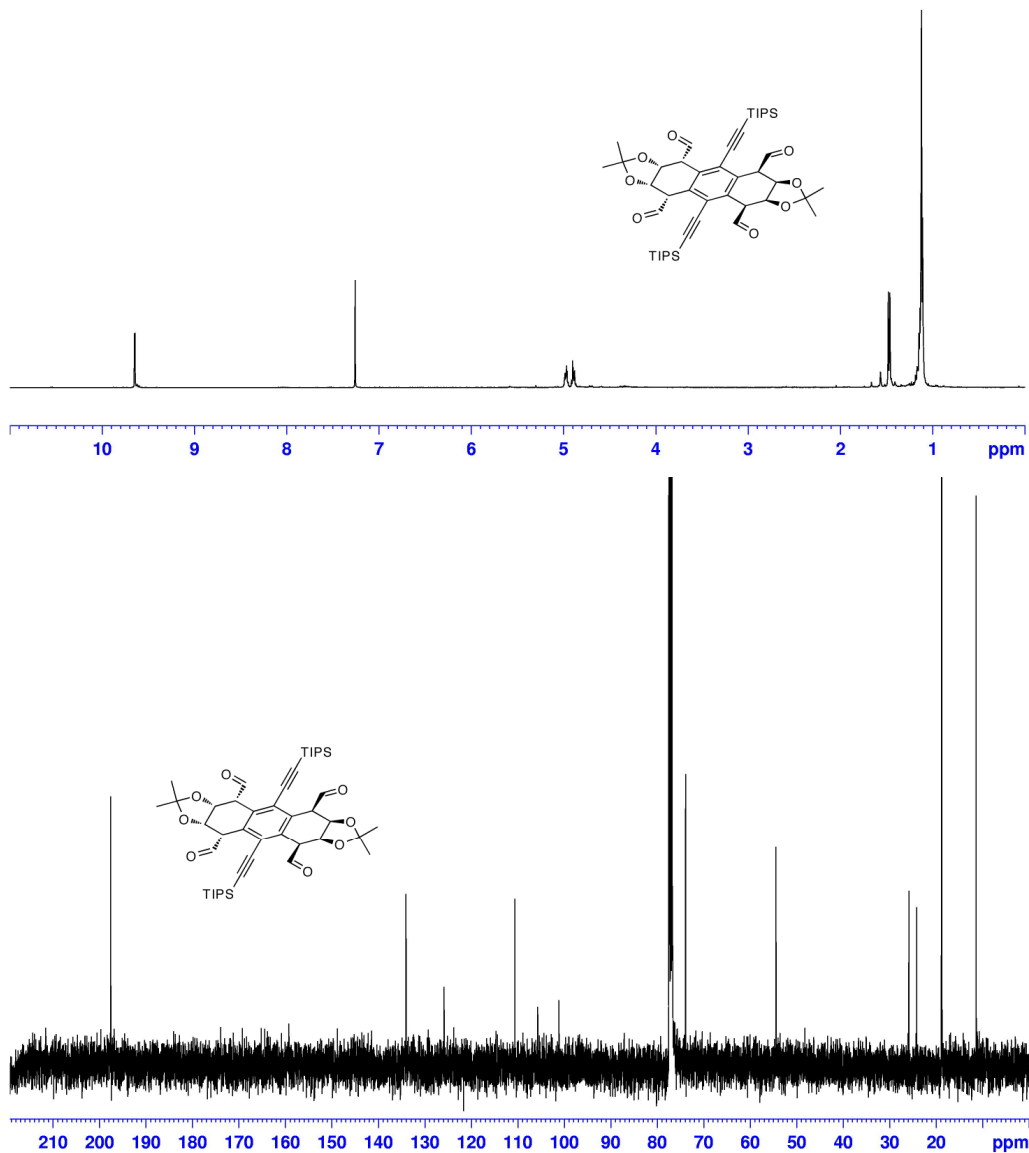


Figure S1: ^1H and ^{13}C NMR spectra of compound **5**

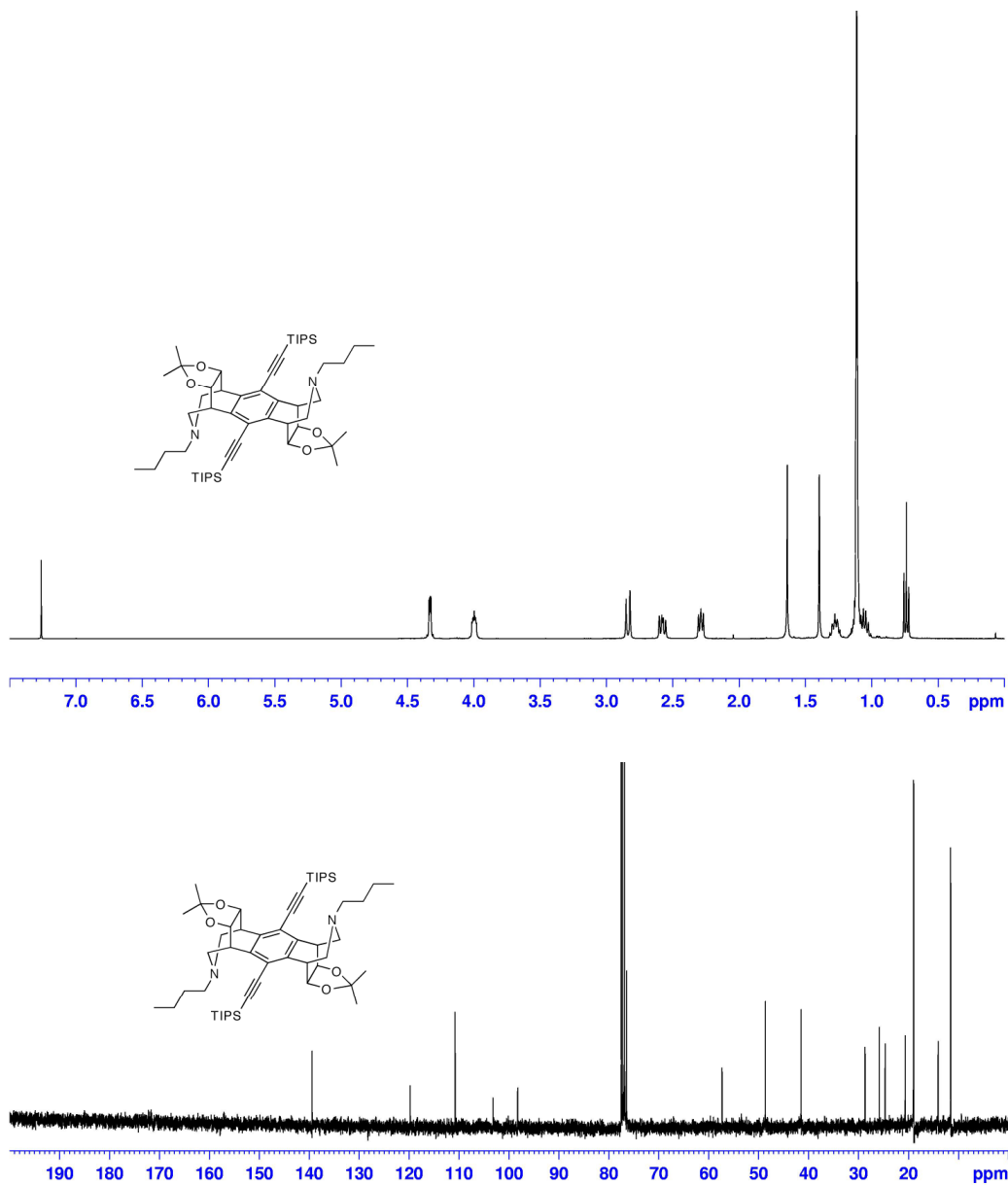


Figure S2: ^1H and ^{13}C NMR spectra of compound 6

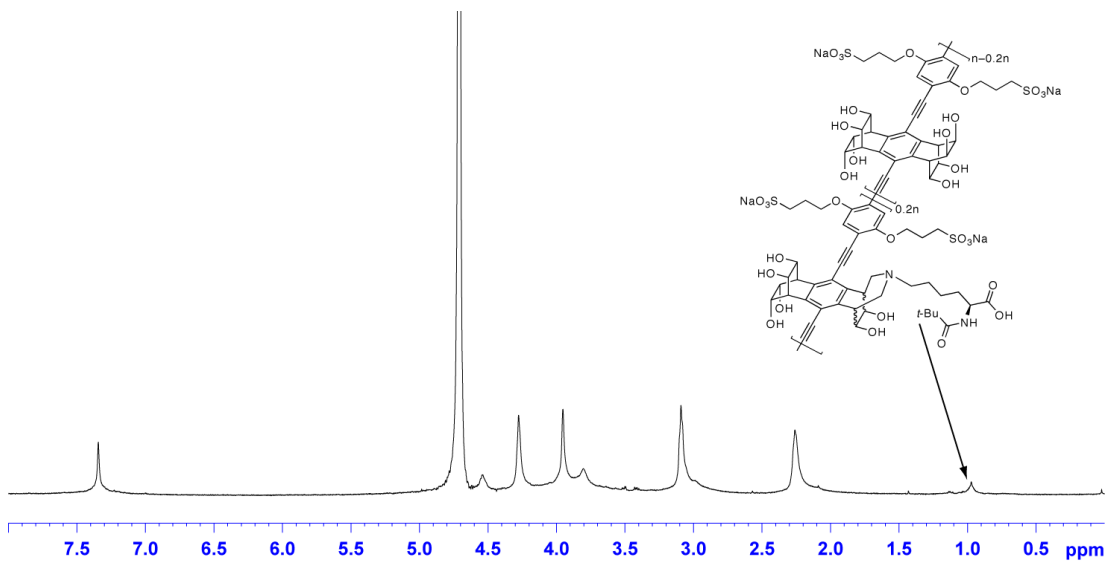


Figure S3: ¹H spectrum of compound **3b**

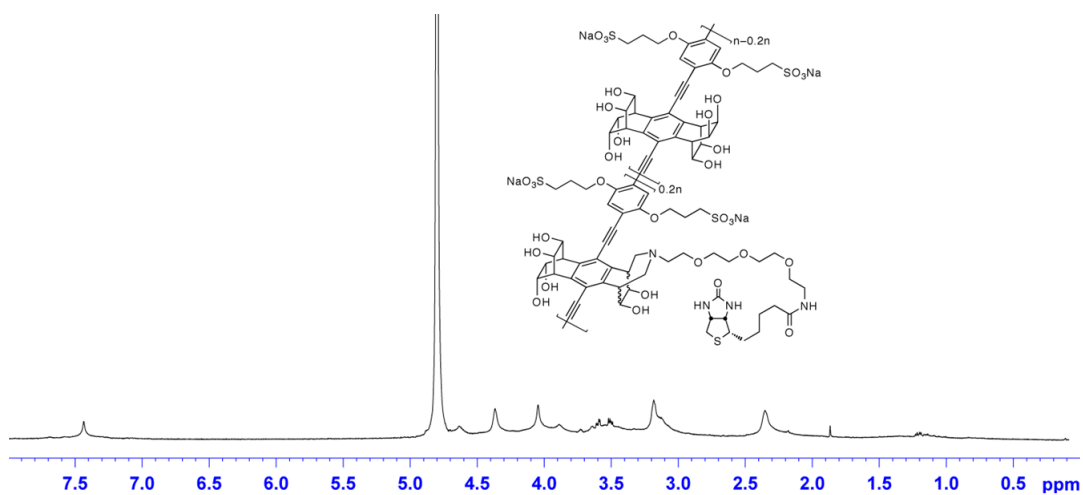


Figure S4: ¹H spectrum of compound **3a**

UV-vis and Fluorescence data

Table S1: Summary of photophysical data of **3a**

	Abs λ_{\max} (nm)	Em λ_{\max} (nm)	log ϵ	\sqrt{F}
3a , water	436	451	4.52	8%
3a , 1X PBS	450	461	4.58	7%

General protocol for energy transfer assays in PBS:

50 μL of a stock polymer solution (0.056 mg/mL in PBS) was diluted with PBS to a total volume of 3 mL in a fluorescence cuvette. To this was added aliquots of Texas Red-XTM labeled streptavidin (0.5 μL of a 1 mg/mL solution) and fluorescence emission was taken at each addition. Excitation wavelength was 426 nm.

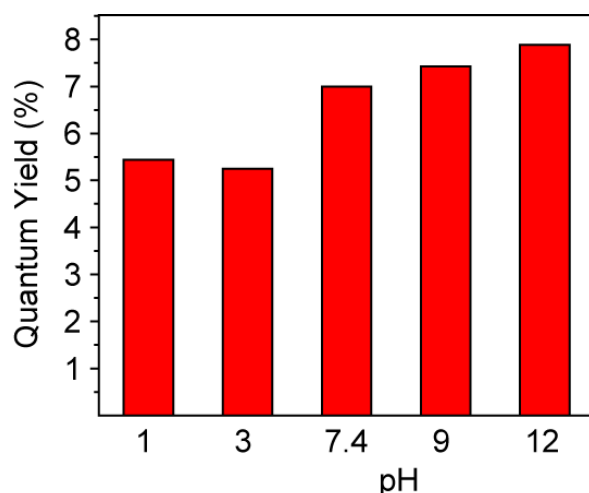


Figure S5: Effect of quantum yield of **3a** at different pH. Measurements performed in PBS where pH was adjusted with HCl or NaOH.

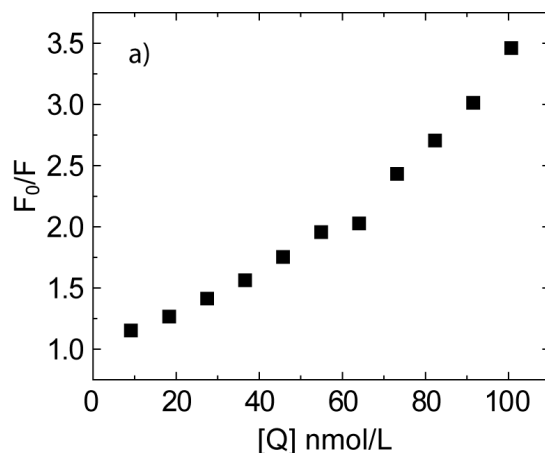


Figure S6: Stern–Volmer quenching analysis of Figure 1d in main text.