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α,ω -Dithiol Oligo(phenylene vinylene)s for the Preparation of High-Quality π -Conjugated Self-Assembled Monolayers and Nanoparticle-Functionalized Electrodes

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Abstract

While thioacetate-terminated oligo(phenylene vinylene)s (OPVs) have been synthesized and employed in applications involving the formation of metal–molecule–metal junctions, the synthesis and application of potentially more versatile α,ω -dithiol OPVs have not previously been described. Here, a thiomethyl-precursor route to the synthesis of α,ω -dithiol OPVs is reported and their ability to form well-ordered self-assembled monolayers (SAMs) without the addition of exogenous deprotection reagents is described. α,ω -Dithiol OPV monolayers exhibit thicknesses consistent with molecular length and are nearly defect-free, as assayed by electrochemical measurements. To demonstrate the ease with which SAMs containing these bifunctional OPVs can, in contrast to thioacetate functionalized OPVs, be further functionalized with materials other than gold, we have modified them in a single step with a sub-monolayer of cadmium selenide nanocrystals (NCs). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) confirm that these NC-modified films are both smooth and uniform over the largest areas investigated ($> 10 \mu\text{m}^2$) and no evidence of NC aggregation is observed. To evaluate the electrochemical response of these metal–molecule–semiconductor assemblies we have fabricated NC-modified OPV SAMs with ferrocene-coated NCs. Variable-frequency alternating current voltammetry indicates that electron transfer in these assemblies is much more rapid than in analogous structures formed using simple alkane dithiols. It thus appears that α,ω -dithiol OPVs are well suited for the formation of high-quality conducting SAMs for the functionalization of gold and other surfaces.

1. Introduction

The physical and electronic attributes of oligo(phenylene vinylene)s (OPVs) render them useful as molecular conductors (“molecular wires”).^[1] Their rigid, planar structures and generally small energy highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) bandgaps provides some advantage relative to other conjugated structures.^[2] Consistent with these claims, thioacetate-terminated OPVs have been used in applications involving the formation and electrical testing of metal–molecule–metal junctions.^[3] In these cases the thioacetate functionality was used to attach the molecules between two gold surfaces. Similarly, thioacetate-containing OPVs can be used to molecularly link an array of gold nanowires.^[4]

Although thioacetate-containing OPVs have been of use in the formation of molecular links to gold, thiol chemistry would be of much more general utility. For example, thiols can be used for grafting molecules not only onto gold, but also onto

alloys such as stainless steel, semiconductor surfaces such as GaAs, semiconductor nanocrystals such as CdSe, ferromagnetic surfaces such as nickel, and noble metal surfaces such as silver, platinum, or palladium without the use of cumbersome deprotection steps.^[5] Bis-functional molecules containing two terminal thiol functionalities can thus be used as convenient molecular bridges for linking nanoparticles onto a variety of substrates,^[6] chemistries that have not been achieved using previously described thioacetate linking chemistry. Furthermore, in contrast to thioacetyl-terminated oligomers, free thiols do not require the addition of exogenous reagents for assembly, which can be problematic. Deprotection protocols for acetyl-protected aromatic thiols, such as treatment with excess NaOH, are often low yielding (approximately 50% even at elevated temperatures),^[7] take extended periods of time to transpire,^[8] produce mixtures of products that are difficult to isolate,^[9] and in many cases result in significant disulfide formation prior to the formation of the desired free-thiol targets.^[10] Deprotection of *S*-acetals in the presence of a gold sur-

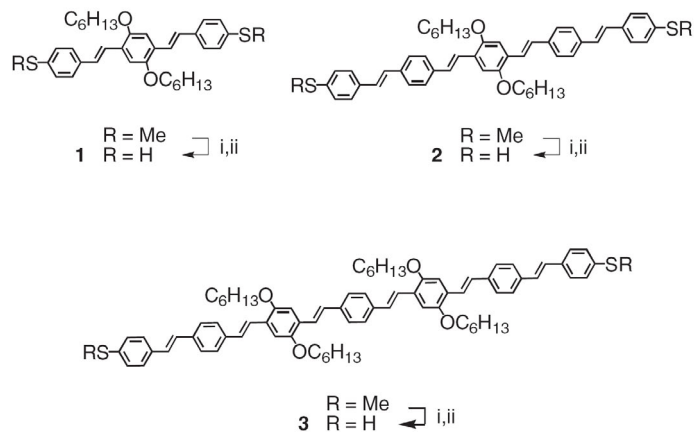
face has been used to circumvent these problems by forming the surface active functionality in situ.^[11] However, many investigators have found that in situ *S*-acetyl deprotection is difficult to control, which can lead to either poor-quality monolayers that contain both thiol and thioacetate adsorbates,^[12] or multilayers that contain over-deposited material.^[11,13] In situ deprotection is also problematic when the molecules contain functionalities that are reactive under the required deprotection conditions,^[14] or similarly when assembling on surfaces that are reactive towards the deprotection reagents (for example NH_4OH , a popular deprotecting reagent,^[11] is known to chemically etch semiconductor surfaces such as GaAs^[15]). These problems would likely be avoided via the use of unprotected thiols.

Although the synthesis of α,ω -dithioacetate-terminated OPVs has been reported,^[16] dithiol-terminated OPV molecular wires have not been reported to date despite their potential advantages. In general, dithiol molecular wires remain more elusive targets than their thioacetate counterparts, with investigators reporting that these structures are unstable and difficult to isolate.^[11,17] In this contribution, however, we report the preparation and isolation of conjugated α,ω -dithiol OPVs with up to seven aromatic units and their spontaneous formation of self-assembled monolayers (SAMs) on gold surfaces. To demonstrate their utility in fabricating heterojunctions involving gold and nonaurous substrates, we also report the synthesis and characterization of semiconductor nanocrystal (NC)-modified electrode surfaces using these SAMs as molecular interconnects.

2. Results

2.1. Synthesis

Synthetic entry into the target dithiol-terminated OPVs begins with the *S*-methyl protected precursors, rather than the *S*-acetyls traditionally employed, and subsequently uses a convenient dealkylation protocol.^[18] This method was found to provide a simple and high-yield route for the synthesis of *free* α,ω -dithiol-terminated OPVs (Scheme 1). For example: 1,4-dihexyloxy-2,5-bis[4'-(methylthio)styryl]benzene was converted to 1,4-dihexyloxy-2,5-bis[4'-thiolstyryl]benzene (**1**) in 90% yield. Under these conditions, the free dithiol precipitates from the reaction mixture upon addition of aqueous acid and can be isolated in high purity. The compound was sufficiently stable under air for characterization by NMR spectroscopy and mass spectrometry. Long-term storage is possible under an inert atmosphere. Two additional α,ω -dithiol OPVs are reported here, 1,4-dihexyloxy-2,5-bis[4'-(4''-thiolstyryl)styryl]benzene (**2**) and 1,4-bis[2',5'-dihexyloxy-4'-(4'''-thiolstyryl)styryl]benzene (**3**), and were isolated in 97% and 92% yield, starting from 1,4-dihexyloxy-2,5-bis[4'-(4''-(methylthio)styryl)styryl]benzene and 1,4-bis[2',5'-dihexyloxy-4'-(4'''-(methylthio)styryl)styryl]benzene, respectively. The hexyloxy side chains in these structures are necessary for solubility in common organic solvents.



Scheme 1. Synthetic entry to 3, 5, and 7-ring oligomers of fully conjugated OPV dithiols. Reagents and conditions for the dealkylation step for OPVs **1–3**: i) NaSMe, dimethylformamide (DMF), 140 °C, 24 h. ii) aqueous H_2SO_4 (4 M), 0 °C.

NMR spectroscopy studies on **1** in C_6D_6 in the presence of an internal standard reveal a characteristic S–H singlet at $\delta = 3.1$ ppm (Figure 1). Although approximately 16% of the NMR signal was lost during the course of one-month's storage in the sealed NMR tube (presumably due to adsorption onto the borosilicate glass sidewalls), no degradation of OPV was observed for several days, which is well beyond the timescale required for the preparation of OPV-modified surfaces, and provides evidence of the stability of these compounds.

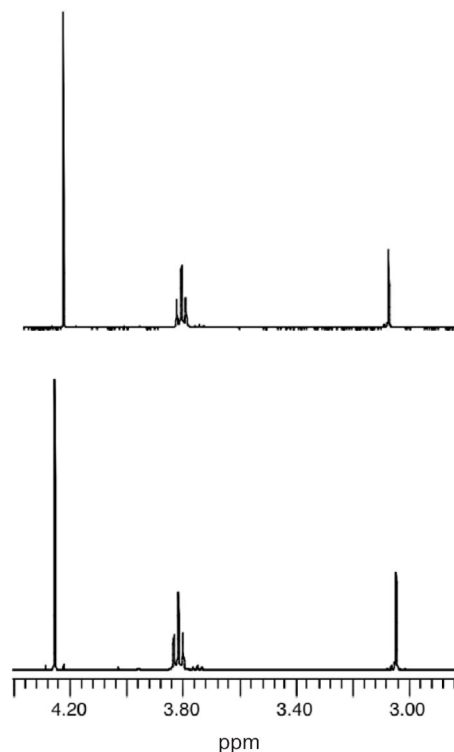


Figure 1. ^1H NMR spectra (C_6D_6). The $-\text{OCH}_2-$ (3.8 ppm) and $-\text{SH}$ peaks (3.1 ppm) in **1** integrate properly (2:1) in the isolated product (bottom) and after 32 days (top). Comparison against an internal standard reveals a 16% reduction of the resonance signal intensities after 32 days.

2.2. SAM Formation and Characterization

SAMs were prepared on gold surfaces by immersing a clean substrate into a 0.2–0.4 mM solution of OPV dithiol in toluene for 14 h. Ellipsometry measurements indicated that the thickness of the SAM formed from compound **1** was 57% of the thickness of the SAM formed from compound **2**. When taken with the observation that compound **1** has 60 % of the length of compound **2**, this suggests that both molecules adopt a similar tilt angle when closely packed on the gold surface. If we assume an index of refraction of 1.55,^[11,19,20] the observed thicknesses (17 ± 1 and 30 ± 1 Å, respectively) are very close to the estimated lengths of the extended molecules (19.8 and 33.1 Å for **1** and **2**, respectively), suggesting that the tilt angle is quite small. We should note, however, that other investigators have suggested that the index of refraction of a related oligo(phenylene ethynylene) (OPE) compound is 2.32.^[21] If we adopt this value, the estimated tilt angle is somewhat greater. The former value, however, allows us to compare our work more directly with prior measurements. Doing so, we find that the 10 to 16 % discrepancies between the dimensions of these OPVs and the thickness of SAMs fabricated from them suggest similar geometries to those previously reported for biphenylthiols,^[19] oligo(phenylene)s (OPs),^[20] and OPEs.^[14] In contrast to the less than 20 % discrepancy between molecular length and SAM thickness observed in **1** and **2**, the longest OPV structure we have characterized, **3**, forms an 18 ± 2 Å film, which is less than half of its 46.4 Å molecular length. This suggests that monolayers fabricated from this compound are much less dense, and/or the molecular orientation relative to the surface is much more tilted than those produced by the shorter OPVs. Because of this discrepancy, compound **3** was not included in subsequent studies. No indication of multilayer formation was observed in any of the films prepared from these free dithiol OPVs. This observation, taken with the stability observed by NMR spectroscopy on the prepared free thiol **1**, suggests that the multilayer formation that has been noted in previous reports^[11,13] likely results from side reactions that take place during the deprotection procedure rather than being a consequence of the spontaneous disulfide formation that is inherent to the structures.

In order to further assess the quality of these adsorbed monolayers we conducted electrochemical blocking experiments in the presence of 1 mM ferricyanide ($\text{Fe}(\text{CN})_6^{3-}$).^[22] These experiments indicate that monolayers fabricated from OPVs **1** and **2** block redox processes more effectively than other rigid-rod conjugated molecules such as OPs^[20] and OPEs^[14] (Figure 2); the absence of a current peak and the sigmoidal shape of the wave indicate only minor pinhole defects, and that the SAMs are relatively defect free.^[23]

2.3. Cadmium Selenide Nanocrystal Attachment

To demonstrate the ability of OPV dithiols to bind to semiconductor nanoparticle surfaces, OPV SAMs were functionalized with cadmium selenide NCs, presumably by reaction with the pendant (unreacted) thiols. Immersing an OPV-modified substrate into a 10^{-7} M toluene solution of CdSe NCs for

24 h, followed by copious toluene rinsing, resulted in the formation of a NC layer. To characterize the formation of the NC film, the substrates were examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The CdSe NC overlayer and the underlying gold substrate are clearly visible in the SEM images (Figure 3, A & B). The coverage of NCs appears to be a uniform sub-monolayer. Analysis of the number of visible particles was used to estimate the surface coverage of NC in the two films. The calculated density was $3.7 \pm 0.3 \times 10^{11}$ and $5.9 \pm 0.3 \times 10^{11}$ NCs/cm² for assemblies formed with **1** and **2**, respectively. These values indicate sub-monolayer coverage when compared to the estimate of a perfect hexagonal-close-packed monolayer (2.6×10^{12} NCs/cm²). Although the longer linker yields about a 50 % higher NC density, perhaps because of its improved ability to penetrate through the ca. 11 Å tri-*n*-octyl phosphine oxide (TOPO) surfactant layer on the NC, both compounds provide an efficient and stable NC–electrode link.

AFM studies reveal a change in film morphology after NC treatment. The original ca. 100 nm grains on the polycrystalline gold (Figure 3,C) are now covered with new and smaller overlying features (Figure 3, D & E), although the underlying gold structure can still be identified. The root-mean-square (RMS) roughness increases minimally from 1.9 nm to 2.4 nm after the procedure, indicating a smooth NC coating. The topography measured from the AFM images appears to match the SEM images very closely. From the sectional analysis, the heights of the new features compared to bare spots match the average NC diameter (6.6 nm). It is noteworthy that the films appear dense and uniform in both the SEM and AFM images; this indicates that aggregation or stacking on the surface is not problematic and that the NCs adsorb as ≤ 1 layer.

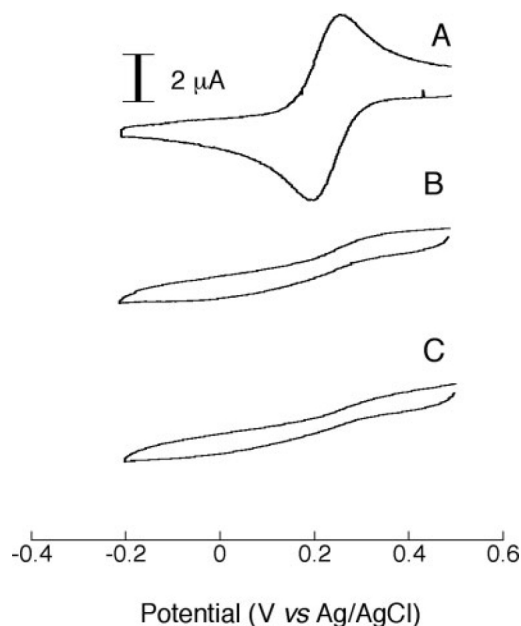


Figure 2. Cyclic voltammetry (potential versus Ag/AgCl) for A) Au, B) Au/**1**, and C) Au/**2** electrodes in a 1 mM $\text{Fe}(\text{CN})_6^{3-}$ /1 M KCl (aq) solution.

2.4. Electron-Transfer Kinetics of Redox Modified Nanocrystals

Having established the quality of CdSe NC layers on a gold surface covered with SAMs of **1** or **2**, we now compare the electron-transfer kinetics in OPV assemblies relative to those constructed with saturated alkane dithiol linkers. Because nanoparticle (NP)-functionalized electrodes are useful electrochemical platforms for addressing redox reactions, especially in buried interfaces,^[24] a set of experiments was designed to probe how the OPV layer influences an electrochemical reaction rate between a redox site bound to the NC surface and the electrode surface. A convergent assembly protocol was adopted. First, NCs were functionalized with the electrochemically reversible ferrocene (Fc) moiety, then a SAM of OPV was deposited onto a gold electrode, and finally this SAM was used to bind the redox active NCs onto the electrode (Figure 4). An analogous control assembly was built using 1,10-dodecanedithiol, and used for comparison with the OPVs. Ellipsometry suggests that the 1,10-dodecanedithiol forms a 10 Å thick film. Because previous electrochemical experiments indicated that OPVs (and also 1,10-dodecanedithiol) are relatively effective at blocking electrodes, we employed alternating current voltammetry (ACV), which is a more sensitive electrochemical technique.^[25] In all cases, we observed fully reversible Faradaic currents at 0.1 V versus Ag/AgCl that were not present in control samples formed with TOPO-coated CdSe and these are assigned to the electrochemically reversible $\text{Fc}^{0/+}$ couple.

Variable-frequency ACV^[26] was used to probe the electron-transfer rate in the films (Figure 5). Although the net current differs between the different assemblies, the ACV ramping technique uses a current-ratio analysis and can accurately measure electron-transfer rates irrespective of the current associated with the redox process.^[26] We found that films prepared with the conjugated linkers showed excellent response at even the highest frequencies (10 000 Hz). In fact, the electron-transfer rates of assemblies prepared with **1** and **2** are too rapid to measure ($> 1 \times 10^5 \text{ s}^{-1}$) with our instrumentation. The ACV response in films prepared with 1,10-dodecanedithiol begins to diminish at frequencies greater than 700 Hz, and does not produce any current response above 5,000 Hz, indicating that the electron-transfer rate is significantly slower in these assemblies. From these data the rate of electron transfer in the 1,10-dodecanedithiol assembly can be estimated to be $5 \times 10^3 \text{ s}^{-1}$ which is in excellent agreement with the work of Sumner et al. for Fc connected to an electrode by an 11 carbon alkane bridge.^[27] Because the electrochemical blocking experiments indicate

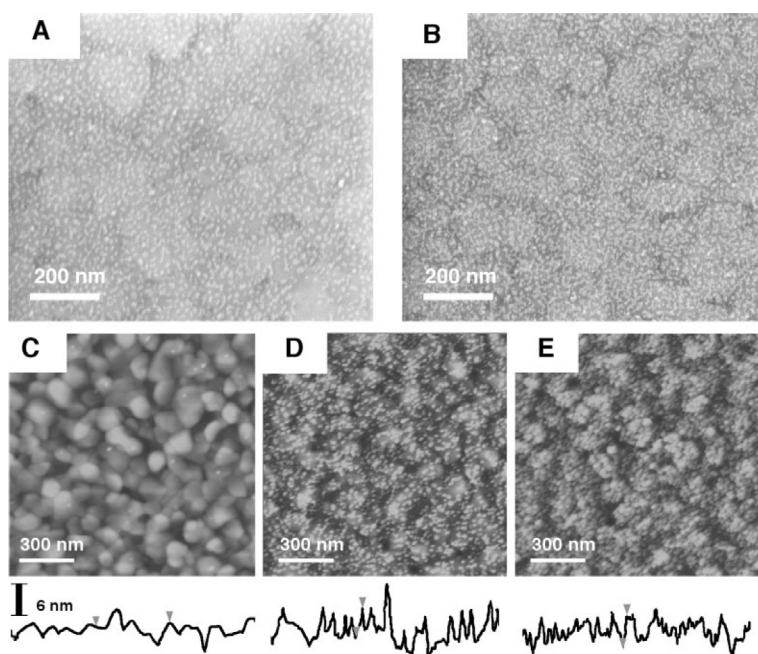


Figure 3. Scanning electron microscopy images of the NC layers formed with molecules A) **1** and B) **2**. C) Atomic force microscopy (tapping mode) images of unmodified gold surfaces compared to gold surfaces functionalized with NC layers formed with molecules D) **1** and E) **2** and the respective section analysis (below).

covered electrode surfaces, we presume that the increased rate of electron transfer observed in OPV assemblies arises because of molecular-wire-like transport through OPV SAMs, as opposed to the more insulating alkane chains.^[28] Although the exact mechanism of electron transfer in the assemblies cannot be elucidated from this simple, relative comparison, the overall set of observations suggests that OPVs are more useful than alkanes for creating modified electrodes if a fast electrochemical response is desired.

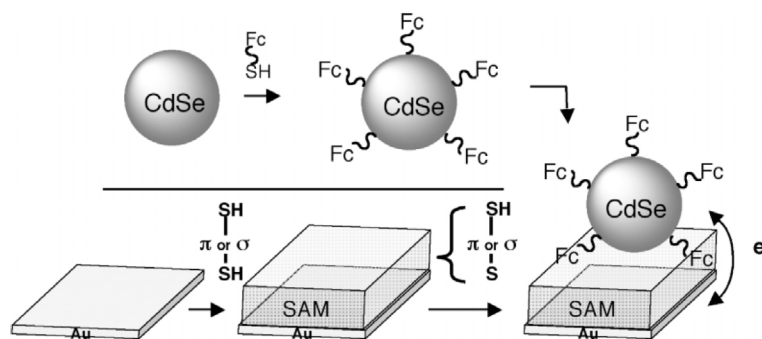


Figure 4. Preparation of the films used in electron-transfer kinetics measurements. Ferrocene (Fc) was tethered to the CdSe NC surfaces and attached to the gold electrode surface using a preformed SAM of π -conjugated OPV or 1,10-dodecanedithiol.

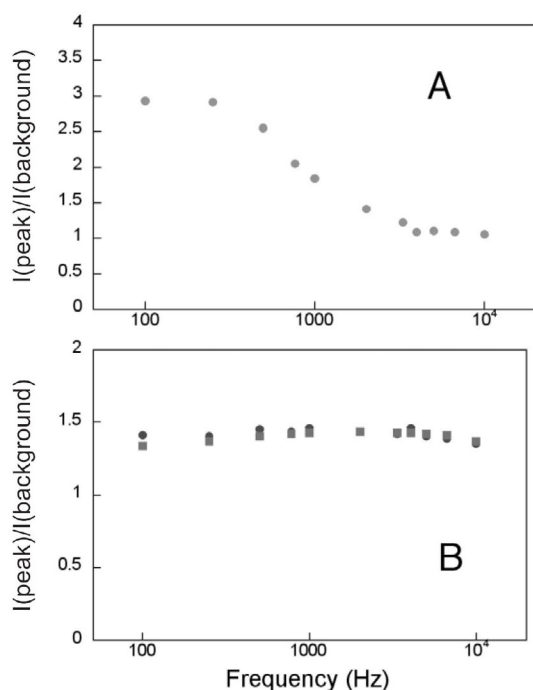


Figure 5. Electrochemical kinetics. Plot of peak current/background current versus frequency (logarithmic scale) for electroactive NCs assembled with A) 1,10-dodecanedithiol, B) **1** (●) and **2** (■). The diminished current in 1,10-dodecanedithiol at the higher frequencies indicates a slowed electron-transfer rate relative to OPVs **1** and **2**.

3. Discussion and Conclusions

The prepared α,ω -dithiol OPVs are notably stable materials. These compounds form well-structured, nearly defect-free SAMs on gold via a simple, single-step deposition process that eliminates potentially problematic deprotection conditions, and does not appear to lead to the formation of multilayers. These OPV SAMs are readily modified, for example, with semiconductor materials, by functionalizing their thiol-containing external face. The film morphology of semiconductor-NC-modified electrodes is smooth over areas greater than $10\ \mu\text{m}^2$, and exhibit electron-transfer rates that significantly exceed those observed in the equivalent alkane-thiol assemblies. When taken with the synthetically facile thiomethyl precursor route to their synthesis, these observations suggest that α,ω -dithiol OPVs may be of greater utility for fabricating functionalizable interfaces for electronic applications as compared to their thioacetate-terminated counterparts.

The quality and electronic properties of the OPV SAMs match or exceed those of other commonly employed π -conjugated SAMs. For example, the coverage and thickness of OPV-based SAMs match those of OPs^[20] and OPEs,^[14] which are generally thought to form high-quality SAMs.^[29] Specifically, compounds **1** and **2** form films with nearly complete monolayer thicknesses and low defect densities, as determined by electrochemistry, relative to other rigid-rod conjugated molecules. More importantly, the electronic delocalization in OPVs exceeds that of OPs and OPEs,^[2,3] suggesting that OPV SAMs will have better charge-transport properties.

Indirect support of this claim is provided by the rapid electron transfer kinetics we have observed through these SAMs.

The described OPVs appear to offer significant advantages over alkane dithiols, perhaps particularly for applications involving nanoparticle-functionalized electrode surfaces such as vapor sensing,^[30] metal-ion detection,^[31] and biological detection assays.^[24] First, because alkane dithiols are flexible (leading to head-and-tail attachments to the gold substrate), the SAMs they form are less well ordered than those comprising the equivalent monothiol alkanes.^[32] The rigidity of the OPVs suggests that they are less likely to exhibit looping or double binding^[33] and should also provide a more mechanically robust link between the NC and the electrode surface. A second advantage is that the bandgap of OPV is energetically similar to a number of NC semiconductors of interest for optoelectronic applications, and significantly lower than that of saturated alkanes and even other conjugated molecules.^[2] Thus, OPVs will provide better coupling of the electronic features of semiconductors with surfaces. Finally, because tethering nanoparticles to an electrode has been used to extend the electrode surface to access redox reactions in buried biological interfaces,^[24] and also to build functional electronic structures,^[30,31] the OPV-linked NC platform is interesting because it combines the rich surface chemistry and interfacial properties of colloidal nanocrystals with the proven ability of OPV to mediate electron transfer.

4. Experimental

TOPO-passivated cadmium selenide nanocrystals were purchased from Evident Technologies. 11-ferrocenylundecanethiol was purchased from Dojindo Molecular Technologies. 1-decanethiol and 1,10-decanedithiol were purchased from Aldrich and Lancaster, respectively. All reagents were of the highest purity available and stored in an inert atmosphere glove-box. For ellipsometry and AFM, gold substrates (1000 Å Au/50 Å Ti evaporated on a silicon wafer) were purchased from Platyplus Technologies and cleaned with a UVO cleaner (10 min) followed by rinsing with Milli-Q deionized water and absolute ethanol [34]. For electrochemistry, gold electrodes (2.0 mm² area) were purchased from Bioanalytical Systems Inc. and cleaned by repetitive oxidative cycling in 0.1 M H₂SO₄, polished with a 0.1 μm alumina slurry, sonicated in Milli-Q water, and repetitively scanned until there was no change in the Au oxide formation/removal peak.

1,4-Dihexyloxy-2,5-bis[4'-thiolstyryl]benzene (1): 1,4-Dihexyloxy-2,5-bis[4'-(methylthio)styryl]benzene (58 mg, 0.10 mmol) was dissolved in dimethylformamide (DMF, 1 mL). Sodium thiomethoxide (26 mg, 0.37 mmol) was added and the solution was heated to 140 °C for 24 h. Upon cooling to 0 °C, H₂SO₄ (aq) (4 M, 0.5 mL) was added to form a green precipitate, and the product (49 mg, 90 %) was isolated by filtration. ¹H NMR (CDCl₃) δ 7.438 (d, ³J_{trans} = 16.47 Hz, 2H), 7.407 (d, ³J = 8.37 Hz, 4H), 7.266 (d, 4H), 7.108 (s, 2H), 7.079 (d, 2H), 4.050 (t, 4H), 3.499 (s, 2H), 1.876 (m, 4H), 1.559 (m, 4H), 1.404 (m, 8H), 0.946 (t, 6H) ppm. ¹³C NMR (CDCl₃) δ 151.3, 135.8, 129.84, 129.80, 128.1, 127.4, 127.0, 123.4, 110.7, 69.7, 31.8, 29.7, 26.2, 22.9, 14.3 ppm. High-resolution electron ionization mass spectrometry (HREI-MS) 546.2647 Δ = 3.7 ppm.

1,4-Dihexyloxy-2,5-bis[4'-(4''-thiolstyryl)styryl]benzene (2): 46 mg (97 % yield) of the title compound was isolated by filtration following the same protocol as described above. ¹H NMR (CDCl₃) δ 7.516 (d, ³J_{trans} = 16.47 Hz, 2H), 7.518 (m, 8H), 7.408 (d, ³J_{trans} = 8.37, 4H), 7.274 (d, 4H), 7.147 (d, 2H), 7.144 (s, 2H), 7.075 (s, 4H), 4.078 (t, 4H), 3.503 (s, 2H), 1.898 (m, 4H), 1.576 (m, 4H), 1.413 (m, 8H), 0.948 (t, 6H) ppm.

Low solubility precluded obtaining a ^{13}C NMR spectra. Fast atom bombardment (FAB)-MS calcd. 750, found 750.

1,4-Bis[2',5'-dihexyloxy-4'-(4''-(4'''-thiolstyryl)styryl)styryl]benzene (3): 13.4 mg (92 % yield) of the title compound was isolated by filtration following the same protocol as described above. ^1H NMR (CDCl_3) δ 7.48–7.58 (m, 16H), 7.411 (d, $^3J = 8.37$ Hz, 4H), 7.265 (d, 4H), 7.151 (m, 8H), 7.077 (s, 4H), 4.084 (t, 8H), 3.504 (s, 2H), 1.903 (m, 8H), 1.581 (m, 8H), 1.418 (m, 16H), 0.951 (t, 12H) ppm. Low solubility precluded obtaining a ^{13}C NMR spectra. FAB-MS calcd. 1155, found 1155.

SAM Formation: Working in an inert atmosphere glove-box, 1.0 mg of the compound was dissolved in 5 mL of anhydrous toluene. A clean substrate/electrode was immersed into the solution overnight (ca. 14 h). The substrate was removed, and rinsed with toluene and ethanol and dried with a stream of argon.

11-Ferrocenylundecanethiol-Capped CdSe NCs: Working in an inert atmosphere glove-box, a 500 μL solution of trioctylphosphine oxide capped cadmium selenide NCs (CdSe/TOPO) in toluene (10^{-5} M) was added to a 1 mL toluene solution containing 1 mg 11-ferrocenylundecanethiol. The reaction was stirred in a glove-box overnight (~ 14 h) at room temperature. The ferrocene-passivated NCs (CdSe/Fc) were precipitated into methanol (1 \times), 50:50 methanol/ethanol (2 \times), and ethanol (2 \times), and dried on a vacuum line.

Nanoparticle Binding: A dithiol SAM-modified gold substrate/electrode was immersed in a 5×10^{-7} M solution of CdSe NCs in an inert atmosphere glove-box for 24 h. The substrate was rinsed in dichloromethane (DCM), ethanol, and Milli-Q water.

Ellipsometry: Layer thickness measurements were performed on a Rudolf Auto EL instrument with a 632.8 nm light source at a 70° angle of incidence. Measurement of the analyzer and polarizer angles of the substrate were made immediately before and after deposition in the thiol containing solutions. The change in sample thickness was calculated assuming values of 1.55 and 0 for the n and k optical constants for the organic layer respectively.

Atomic Force Microscopy: Images of the gold substrates were obtained using a Digital Instruments Dimension 3000 microscope operating in tapping mode. Images were plane-fit, and flattened.

Electrochemical Measurements: Cyclic voltammetry was performed at room temperature with a CHI 730B workstation (CH Instruments, Austin, TX) and using a standard three-electrode cell with a polycrystalline gold disk working electrode (2.0 mm^2 area), a platinum counter electrode, and a silver quasi-reference electrode. Kinetics measurements were carried out in 1.0 M HClO_4 solution. The potential was calibrated with ferricyanide $^3^-$ /ferrocyanide $^2^-$ redox couple after the experiment and the potential is reported with respect to a Ag/AgCl reference electrode.

Acknowledgments

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