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Poly(*p*-phenylene ethynylene) Brushes

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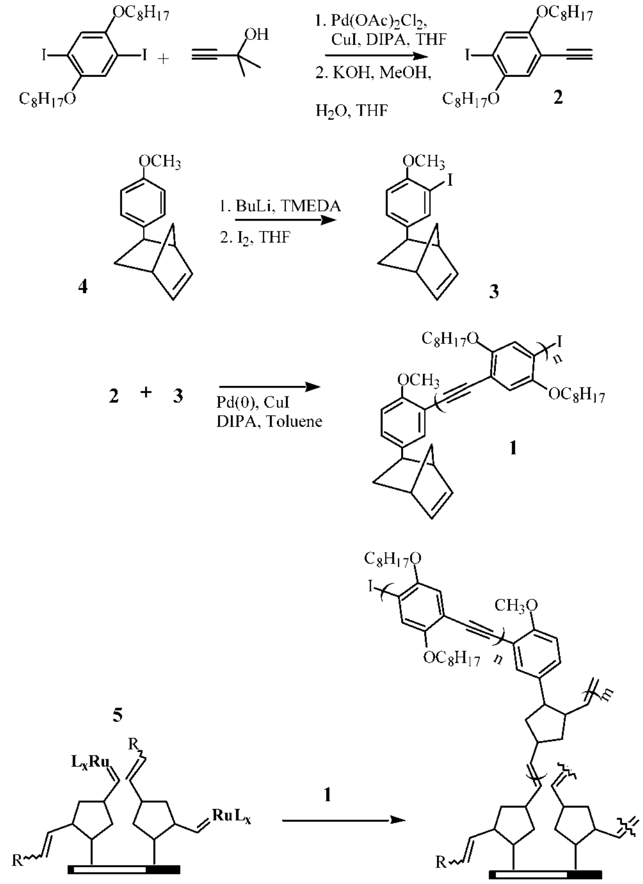
We have been developing poly(*p*-phenylene ethynylene) (PPE) derivatives as chemical sensory systems due to their ability to produce signal amplification resulting from efficient excited state (exciton) migration facilitated by their semiconductive nature.[1,2] In the quest for ever more sensitive polymers, we are in search of new ways to enhance both intrachain and interchain energy transfer.[3,4] This optimization requires a combination of modification of the electronic structure of the polymers as well as the arrangement of the polymers in thin films. In the former, we have recently established a relationship between the excited-state lifetimes and energy migration. PPE analogues with annulated aromatic ring systems in their backbone, such as triphenylene[3a] and dibenzo[*g,p*]chrysene,[3b] exhibit longer excited-state lifetimes and superior energy migration as compared to the poly(*p*-dialkoxyphenylene ethynylene)s. In efforts to further increase the sensory performance, we have produced polymer films by Langmuir−Blodgett deposition[4a,c] and layer-by-layer deposition techniques,[4b] respectively. These structures can include multiple PPEs with different band gaps organized in striated multilayers to produce efficient vectorial energy transfer to more effectively deliver the excitons proximate to the transduction event.[4a] Perhaps the most attractive means to assemble films of sensory polymers is to use covalent linkages between the polymers and substrates. These methods are easily adaptable to coat complex surfaces, and selective deposition is possible by patterning reactive anchors. Furthermore, sequential reactions between polymers and substrates can be used to create multilayer materials capable of functioning in our vectorial energy transport schemes. In this report, we detail an approach to the formation of high-density PPE brushes on oxidized silicon surfaces using ring opening metathesis polymerization (ROMP)[5] of a PPE macromonomer. This arrangement shows improved chemical stability and quantum efficiency relative to simple spin-cast films. We have synthesized PPE, **1**, end-capped with a norbornene group, which can then be grafted to a surface functionalized the Grubbs metathesis catalyst. The resulting PPE brush showed a higher quantum yield than a spin-cast film of the same material.

Our interest in polymer brushes was prompted by our detailed studies of the rates of energy migration in thin PPE films.[4c] These mechanistic studies and more recent investigations[3a] suggest that energy is transported most rapidly intramolecularly along the polymer's backbone. Because of the long persistence length of PPE's,[6] there is a general tendency for the polymer chains to align parallel to the surface. Hence, in thicker films wherein optical excitations may be created deep in the material, energy transport to the film surface is limited by slower intermolecular energy transfer. Considering this factor, we believe that a polymer brush structure, wherein the polymer chains are directed normal to the film surface, may provide more rapid transport of the excitons to the film surface. This is particularly important for biosensor designs wherein it is absolutely necessary to deliver the excitons to the surface where the biomolecular recognition events occur.

Scheme 1



To ensure that polymer **1** has a single point of attachment to the surface and thereby forms well-defined polymer brushes, we synthesized the AB monomer **2** (Scheme 1). This material was produced by a literature procedure involving simple statistical cross-coupling of 2,5-dioctyloxy-1,4-diiodobenzene with 3-methyl-3-hydroxybutyne.[7a] The polar alcohol groups facilitate separation on silica gel and subsequent deprotection under strongly basic conditions gives **2**. The end-capping group, **3**, was synthesized by an ortho-lithiation of literature compound **4**[7c] followed by an iodine quench.[7b] Compound **3** was chosen to have a oxidative reactivity with palladium similar to that for monomer **2** to allow for a high capping efficiency. However, possibly due to steric congestion from the norbornene ring, **3** had a lower reactivity and larger ratios were needed to ensure high degrees of end-capping. Consequently, **1** was synthesized by palladium-catalyzed cross-coupling of a 3.4/1 mole ratio of **2**/**3**.[8] The presence of the norbornene end group was confirmed by the characteristic ^{1}H NMR peaks (6.24 and 6.18 ppm) of alkene group from norbornene unit. The gel permeation chromatography M_n of **1** relative to polystyrene standards was 12 100 (PDI = 1.8).

We used the method of Whitesides and Laibinis to form the catalyst-activated surface, **5**.[9] Placing **5** in a

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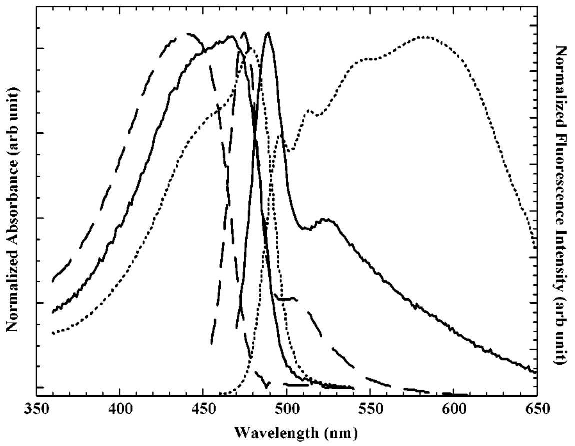

Figure 1. Normalized UV−vis and fluorescence spectra (λ_{ex} = 440 nm) of **1** in (a) chloroform (dashed line), (b) brush (solid line), and (c) spin-cast film (dotted line).

0.1 wt % solution of **1** produced a 73−110 Å thick PPE brush as measured by ellipsometry.[10] In general, the grafting of large macromolecules onto a surface generates a less dense layer than the polymerization of low molecular weight monomers from a surface.[11] This is the result of repulsive forces from first-grafted polymer chains that encumber additional approaching chains. Solution polymerization of macromonomer **1** with the Grubbs catalyst generated mixtures of PPE-*b*-poly(norbornene) comb polymers (47% conversion, M_n = 156 000, PDI = 1.2; DP≈17) and unreacted **1** (M_n = 12 900, PDI = 1.4).[12] The increased molecular weight of the remaining macromonomer represents a higher reactivity of the lower molecular weight components of **1** with the sterically encumbered growing polymer chain. Increased polymerization times did not increase the molecular weight of the resultant comb polymer, and hence, it appears that the macromonomer **1** exhibits self-limited growth. We expect the DP of the surface polymer to be even more limited due to the increased congestion associated with reactions at surfaces. As expected the norbornene ring system is critical to the polymerization and polymers lacking this end group were not polymerized by the Grubbs' catalyst and did not produce polymer brushes.

As shown in Figure 1, the absorption and emission maxima of both the brush and a spin-cast film of **1** are red shifted compared to the solution spectra. These differences are due to the packing of PPE, which leads to increased planarization (conjugation), and in the case of the spin-cast films, strong interchain $\pi-\pi$ interactions. On the basis of recent studies that have clarified the effects of intra- and inter−polymer electronic interactions in PPEs,[13] we conclude that **1**'s absorption and broad emission bear the signature of disordered but strong intermolecular electronic interactions. This type of interaction generally results in low luminescent quantum yields in conjugated polymers and reduces their effectiveness in fluorescent sensory applications. In stark contrast brushes of **1** display a spectrum that suggests that the chains are planarized yet electronically isolated. Solid-state fluorescence quantum yields are difficult to determine with accuracy and the results here are relative to film of similar optical density of 9,10-diphenylanthracene in PMMA (Φ_F = 0.83). The situation is more complex in the case of polymer brushes where we expect an anisotropic emission. However in simple front face fluorescence measurements and we find that the polymer brushes of **1** displayed 3−5 times brighter fluorescence than the spin-cast films. The measured absolute quantum yield of the polymer brush was determined to be 4.5% relative to a PMMA film of 9,10-diphenylanthracene. Even with significant errors originating from the anisotropic brush structure this value is smaller than would be normally expected from a film with electronically isolated polymers. A likely explanation for this low quantum yield is the low molecular weight of **1**, which results in iodine end groups (vide infra), and residual ruthenium compounds both of which promote intersystem crossing.

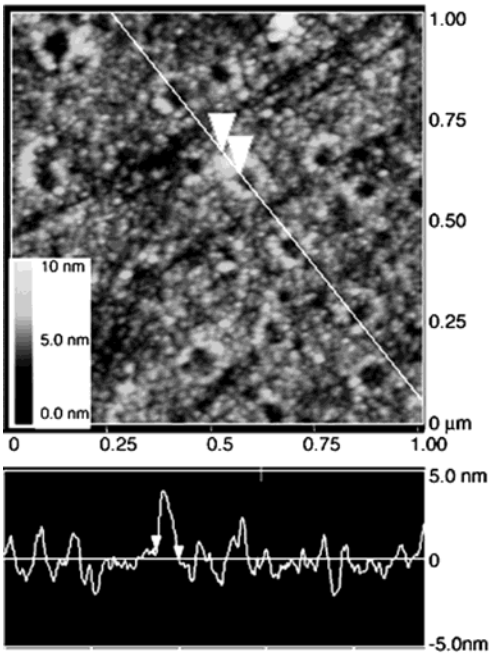

Figure 2. Atomic force microscopic (AFM) image of the PPE brush. For more details on the AFM image, see the Supporting Information.

AFM analysis of surfaces prepared similarly (Figure 2) confirmed the brush formation, but revealed a heterogeneous coverage of PPEs. The section analysis of a selected area clearly showed periodicity in thickness reflecting formation of the islands (more details, see supporting materials). The horizontal distance of a tall island in Figure 2 (marked as solid gray triangles) was measured as 66.4 nm. The reason for the heterogeneous nature of the surface is unclear, but it could be due to spatial variations in the catalyst coverage/activity or due to the selective agglomeration of polymer chains at nucleation sites.

The high persistence length of PPEs and a dense polymer brush structure leads to a directional orientation of the polymers with the polynorbornene at the surface and the iodide end groups at the air interface. This structure was confirmed by X-ray photoelectron spectroscopy by analyzing peaks from the I_{3d} at 620 and 631 eV. The relative atomic concentration of I_{3d} over C_{1s} was 0.08% at normal incidence and this ratio increased to 0.17% at grazing incidence (70°). Grazing incidence is most sensitive to the surface and hence the iodine end groups are clearly concentrated at the surface as expected.[14]

We were also interested in investigating if we could use ROMP to produce multilayer films of polymer

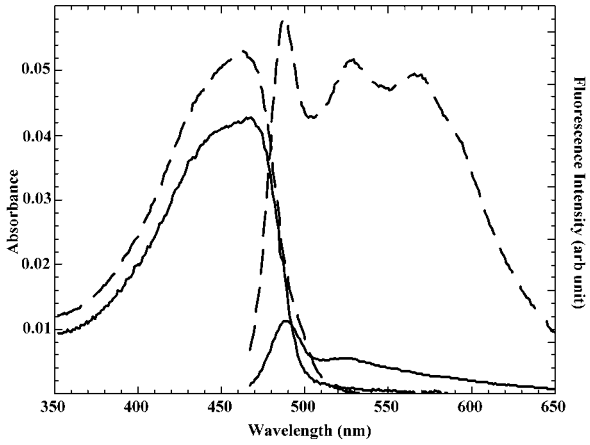

Figure 3. Absorption and emission spectra of (a) a PPE brush (solid line), and (b) a PPE brush reacted with 5-(bicycloheptenyl)triethoxysilane and **1**, consecutively (dashed line).

brushes. As the brushes almost certainly undergo self-limiting growth, we considered that a low molar mass monomer should be added to allow the active chain end to emerge from within the sterically congested regions proximate to the substrate. After initial exposure to **1**, the catalysts may be attached to an active polymer of **1** or may have been laying dormant since the initial surface treatment with the Grubbs catalyst. As a result, we investigated a procedure whereby a polymer brush of **1** was consecutively exposed to 5-(bicycloheptenyl)-triethoxysilane and **1** for 1 and 30 min, respectively. Ellipsometry showed the polymer film's thickness to grow from ~100 to 166−204 Å. As shown in Figure 3, the polymer's absorbance maximum at 464 nm was increased only by 25%, suggesting a lower efficiency of the second polymerization of **1**. We did however observe a dramatic (>400%) increase in the emission intensity of the composite layer. This is all the more interesting when we consider that the composite layer shows an additional prominent aggregation band at 566 nm, which is associated with the presence of less emissive strongly electronically interacting polymer chains. The presence of the aggregation spectroscopic features in the composite film demonstrates that the initial brush structure constrains the polymer and prevents favorable interactions between the PPEs. Once a flexible tether is inserted between the polymer and the surface, the polymers are free to aggregate. The increased quantum yield supports the possibility that the remaining catalyst proximate to the polymer causes quenching. Insertion of a tether between the catalyst and the PPE reduces this quenching. Further attempts to produce another layer of **1** failed due to apparent lack of active catalyst sites. Neither absorbance nor emission intensity were increased after repeated treatment with the same monomers.

In summary, we have demonstrated a novel approach to the fabrication of PPE brushes using ROMP. Chemically bound 71−110 Å thick PPE brushes were constrained from forming aggregates and gave higher emission quantum yields than spin-cast films.

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Supporting Information Available: AFM images and XPS spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) (a) 1-Ethynyl-4-iodo-2,5-dioctyloxybenzene (**2**) was synthesized as in the following report: Kukula, H.; Veit, S.; Godt, A. *Eur. J. Org. Chem.* **1999**, *277*, 7. Yield: 34% (two steps). ^{1}H NMR ($CDCl_3$): 7.29 (s, 1H), 6.87 (s, 1H), 3.95 (m, 4H), 3.30 (s, 1H), 1.80 (m, 4H), 1.48 (m, 4H), 1.33 (m, 16H), 0.94 (t, 6H). ^{13}C NMR ($CDCl_3$): 155.22, 152.07, 124.15, 117.09, 112.60, 88.72, 82.17, 80.08, 70.48, 70.27, 32.20, 29.66, 29.63, 29.53, 29.51, 26.45, 26.27, 23.07, 14.54. Exact mass ([M + H]): calcd for $C_{24}H_{37}IO_2$, 485.1911; found, 485.1909. (b) 5-(1-iodo-2-methoxyphenyl)bicyclo[2.2.1]hept-2-ene (**3**): To a solution of 14.98 mmol of **5** and 18.1 mmol of TMEDA in THF (60 mL) was added 17.98 mmol of *n*-butyllithium (1.6 M in hexane) at −78 °C under Ar. The mixture was warmed to room temp. After 4 h stirring at room temp., the solution was cooled again to −78 °C, and then quenched by adding of a solution of I_2 in THF (43.3 mmol in 40 mL). The resulting solution was warmed to room temp. and stirred for overnight. The mixture was extracted with ethylacetate (EA), and the organic layer was washed with $Na_2S_2O_3$ and brine and dried over $MgSO_4$. The crude product was purified by flash chromatography (hexane/EA, 100/1) to yield a colorless oil (2.69 g, yield 54%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.71 (dd, 1H), 7.23 (ddd, 1H), 6.78 (d, 1H), 6.26 (dd, 1H), 6.18 (dd, 1H), 3.89 (s, 3H), 2.98 (s, 1H), 2.87 (s, 1H), 2.64 (dd, 1H), 1.74−1.53 (m, 3H), 1.45 (m, 1H). ^{13}C NMR ($CDCl_3$): 156.47, 140.89, 139.00, 137.83, 137.54128.82, 111.08, 86.38, 56.82, 48.79, 46.08, 42.96, 42.67, 34.10. Exact mass ([M + H]): calcd for $C_{14}H_{15}IO$, 349.0060; found, 349.0058. (c) **4** was synthesized according to the literature: Arcadi, A.; Marinelli, F.; Bernocchi, E.; Cacchi, S.; Ortar, G. *J. Organomet. Chem.* **1989**, *368*, 249.

(8) A 3.1 mmol sample of **2**, 0.9 mmol of **3**, 0.1 mmol of $(PPh_3)_4$-Pd, and 0.1 mmol of CuI were combined in a degassed solution of 4 mL of diisopropylamine and 9 mL of toluene under Ar. The mixture was heated at 60 °C overnight. The polymer mixture was washed with NH_4Cl and water, respectively, and then dried over $MgSO_4$. The orange-yellow polymer was collected after precipitation in acetone and methanol, respectively, in 67% yield. The molecular weight (M_n) was determined as 12 100 relative to polystyrene standards in THF by GPC (PDI = 1.8). ^{1}H NMR (400 MHz, $CDCl_3$): 7.04 (s, 0.96H), 6.24 (m), 6.18 (m), 4.06 (t, 2.0H), 1.88 (m, 2.2H), 1.54 (m, 2.5H), 1.30 (br, 9.0H), 0.89 (t, 3.4H). ^{13}C NMR ($CDCl_3$): 153.89, 70.06, 32.29, 29.85, 29.77, 26.43, 23.10, 14.53.

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(10) The norbornenylsilane-modified substrates were placed in a Grubbs' catalyst, $RuCl_2(CHC_6H_5)[P(C_6H_{11})_3]_2$, solution (40 mg in 40 mL of CH_2Cl_2) at room temperature for 30 min in a glovebox. After rinsing with CH_2Cl_2, the substrates were transferred into a **1** (32 mg) in CH_2Cl_2 (20 mL) for 3h. The resulting PPE layers were quenched by ethylvinyl ether and washed with MC, chloroform, and toluene, respectively.

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(12) A 2 mg sample of $RuCl_2[C_{21}H_{26}N_2][CHC_6H_5]P(C_6H_{11})_3$ was dissolved in a mixed solvent of 1,2-dichlorobenzene (1 mL) and CH_2Cl_2 (1 mL), which was used for catalyst solution. To the catalyst solution was transferred a 0.217 g of **1** in CH_2Cl_2 all at once. The solution was stirred for overnight. A small portion of the solution was precipitated in methanol, and the resulting polymer was characterized with GPC.

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