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Sulfonation and Epoxidation of Substituted Polynorbornenes and Construction of Light-Emitting Devices

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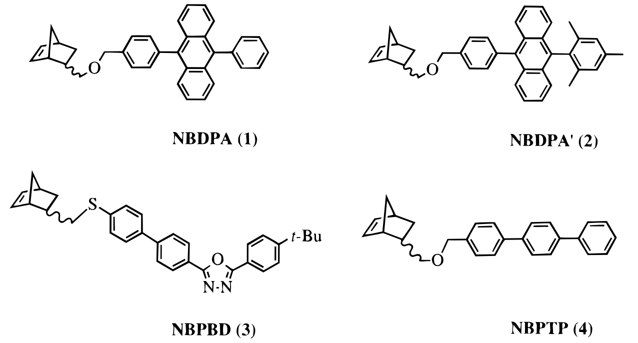
ABSTRACT: Efficient routes to sulfonation and epoxidation of the double bonds in a polynorbornene backbone have been found that do not interfere with side chain functional groups of interest for making light-emitting devices. Substituted norbornene monomers were prepared with ether or thioether linkages, which were stable to sulfonation. Oligomers (25mers or 50mers) of homo- and copolymers containing diphenylanthracene (for blue-light emission), oxadiazole (for electron transport), and *p*-triphenylene (for hole transport) side chains were prepared via ring-opening metathesis polymerization (ROMP) of the corresponding norbornene monomers. Sulfonation of the polynorbornene backbone yielded a polyanionic material that was suitable for creating films via sequential adsorption with the polycation, poly(allylamine HCl) (PAH). Devices with an indium tin oxide (ITO) anode and an aluminum cathode were constructed. A two-layer device comprised of a layer of diphenylanthracene/oxadiazole copolymer and a layer of *p*-triphenylene homopolymer showed better performance in terms of efficiency and light output than a single layer of diphenylanthracene/oxadiazole. However, a single layer of polymer containing 9-mesityl-10-phenylanthracene gave the best performance, up to 21 nW and 0.3 nW/mA efficiency.

Introduction

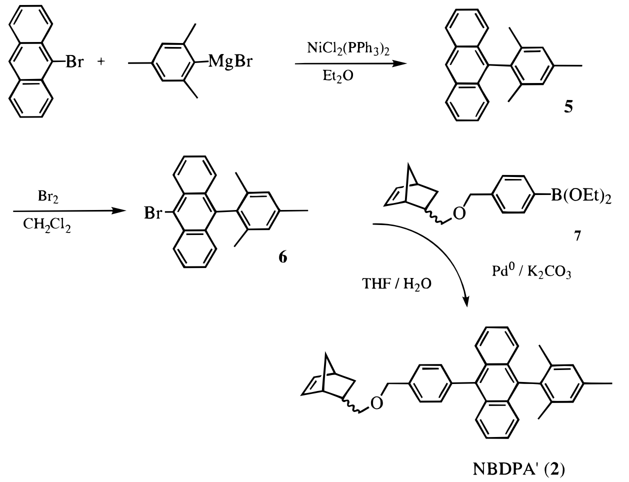
Although in recent years a variety of new blue-light emitters have been reported, the preparation of high-efficiency blue light in light-emitting devices (LEDs) remains a technical challenge.[1,2] In this paper we explore the synthesis and modification of a series of blue-light-emitting norbornene-based monomers and polymers prepared from them for LED application (Figure 1). For emission, we will focus on two monomers, **1** and **2**, that contain diphenylanthracene (DPA), a highly blue photoluminescent, yet electrochemically stable, species.[3−11] For electron transport, we employ the *tert*-butylphenyl-*p*-biphenyloxadiazole (PBD), since it is widely used as an electron carrier or hole blocker.[11−15] We have shown previously that PBD and DPA bound to polymerized norbornene are unable to separate and crystallize in spin-coated films, and so are useful for building devices, and that hole-transport (electron-blocking) monomers based on *N*,*N*-diethyl-2-methylaniline are effective in enhancing the performance of blue LEDs.[11] In this work we also describe the synthesis and polymerization of a new PBD-based monomer, **3**, as well as a new hole-transport monomer based on *p*-triphenylene (PTP), **4**.



NBDPA (1) **NBDPA' (2)** **NBPBD (3)** **NBPTP (4)**

Figure 1. Norbornene monomers for blue light emission (**1, 2**), electron transport (**3**), and hole transport (**4**).

Scheme 1



A main focus of this paper is an exploration of epoxidation and sulfonation techniques that are applicable to substituted polynorbornenes. These general methods should be suitable for *any* polynorbornene with relatively robust side groups, such as the monomers prepared for LED work. Chemical oxidation to form terminal epoxides is widely used to prepare graft copolymers or highly cross-linked materials and is frequently reported in the current polymer literature,[16−18] while polymers modified by sulfonation have been used for solid/liquid separation in water treatment,[19−21] ion-exchange resins,[17,22] reverse osmosis membranes,[20,23,24] and biomedical applications.[25−27] However, techniques for modifying polynorbornene formed by ring-opening metathesis polymerization (ROMP) have been limited to sulfonation,[28,29] hydrogenation,[30,31] and formation of carbonamide[32] derivatives. Of these, only hydrogenation has been reported for substituted norbornenes, despite the increasing interest in these materials in recent years

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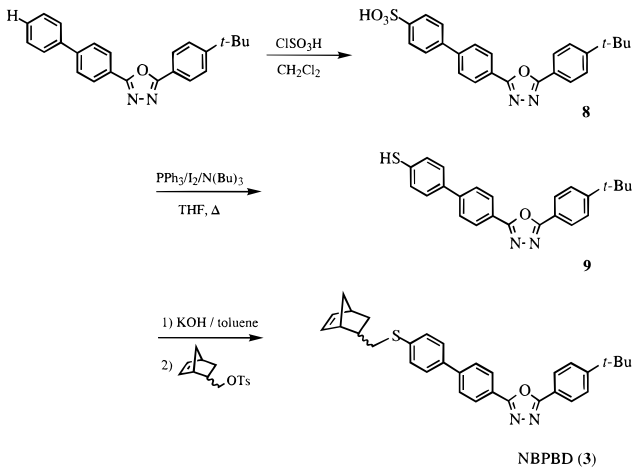
Scheme 2

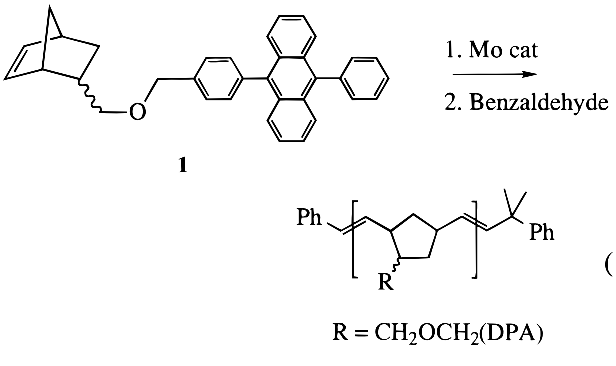


due to the availability of living ring-opening metathesis polymerization techniques[33,34] using well-defined molybdenum alkylidene catalysts.[35,36]

In a previous paper we showed that device performance improved significantly when a sequentially adsorbed film of poly(phenylenevinylene) (PPV) was employed in conjunction with spin-coated polynorbornene.[11] These improvements included an increase in output, a decrease in the threshold voltage, and more reliable device operation. Therefore, we became interested in the making of films and devices by sequential adsorption of sulfonated polynorbornenes, in particular the sequential adsorption technique that allows one to create complex film architectures containing layers that transport either holes or electrons.[37-40] These results are also reported herein.

Results and Discussion

Synthesis of Monomers and Polymers. The synthesis and polymerization of the blue-light-emitting monomer **1** (eq 1) have been described previously.[11] The absorption and emission properties of **1** were similar to those of 9,10-diphenylanthracene itself:[7] $\lambda_{\max,abs} = 398$ nm (DPA: $\lambda_{\max,abs} = 388$ nm); $\lambda_{\max,em} = 442$ nm $\{\lambda_{ex} = 360$ nm$\}$ (DPA: $\lambda_{\max,em} = 422$ nm $\{\lambda_{ex} = 265$ nm$\}$). Polymerization of 25 equiv of **1** with Mo(N-2,6-i-$Pr_2C_6H_3$)($CHMe_2Ph$)(O-t-Bu)$_2$ ([Mo]) in toluene,[41] followed by quenching with benzaldehyde, provided a high yield of homopolymer $\mathbf{1}_{25}$ (eq 1, Table 1). As expected, the polydispersity of $\mathbf{1}_{25}$ was low, consistent with the living nature of this ROMP reaction.[33,34] Unlike crystalline DPA, $\mathbf{1}_{25}$ formed transparent amorphous films when spin-coated from chlorobenzene. Polymers containing 25 or 50 equiv of monomer (on average) were chosen in this project since they can be precipitated readily in certain solvents, yet dissolve readily in others to give solutions that are suitable for preparing films.



(1)

Table 1. Substituted Polynorbornenes

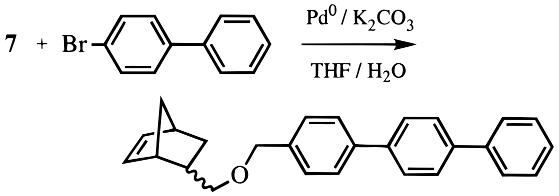
polymer[a]	yield (%)	mol wt (calcd)	M_n[b]	M_w/M_n
$\mathbf{1}_{25}$	95	12 800	19 400	1.04 ± 0.11
$\mathbf{2}_{25}$	94	12 900	8 000	1.07 ± 0.02
$\mathbf{3}_{25}$	99	12 400	8 700	1.19 ± 0.04
$\mathbf{4}_{50}$	99	18 600	21 600	1.81 ± 0.04

[a] Polymers consisted of 25 or 50 repeat units on average. [b] All molecular weights were determined by GPC in CH_2Cl_2 using a Wyatt miniDawn light scattering detector coupled to a differential refractometer.

In certain cases, polymers containing **1** formed self-quenching aggregates (discussed below). For this reason, a bulkier form of DPA became a synthetic target. The emission from DPA derivatives arises from the anthracene core; the phenyl groups block the reactive 9 and 10 sites on anthracene, as well as increase the photoluminescence quantum yield.[7,8] We hypothesized that addition of substituents above and below the anthracene plane to one or both of these phenyl rings should greatly decrease the ease of forming aggregates without modifying the emission properties. Aryl coupling between 9-bromoanthracene and mesitylmagnesium bromide successfully provided the desired intermediate, **5**, in 58% yield (see Scheme 1). Bromination of **5** with fresh Br_2 was carried out in 30 min at room temperature, yielding **6** virtually quantitatively. The norbornenylphenyl diethyl borate derivative, **7**, was prepared in situ and coupled to **6** in 58% yield to give **2**. The overall yield for the five steps was 32%. In **2** the anthracene is protected on one side by methyl groups above and below the ring plane. (The proton NMR spectra of **5**, **6**, and **2** show an upfield shift for these methyl group resonances as expected for their position relative to the anthracene ring current.) The homopolymer $\mathbf{2}_{25}$ was readily prepared using [Mo] in high yield and with low polydispersity (Table 1). The absorption and emission properties of **2** were similar to those of **1** and 9,10-diphenylanthracene itself: $\lambda_{\max,abs} = 399$ nm (**1**: $\lambda_{\max,abs} = 398$ nm); $\lambda_{\max,em} = 443$ nm $\{\lambda_{ex} = 360$ nm$\}$ (**1**: $\lambda_{\max,em} = 442$ nm $\{\lambda_{ex} = 360$ nm$\}$).

A norbornenyl monomer, NBPBD (**3**), was designed with the PBD structural unit attached via a thioether linkage, as shown in Scheme 2. The synthesis was accomplished in 20% overall yield in three steps on a gram scale. The first step involved the quantitative sulfonation of *tert*-butylphenyl-*p*-biphenyloxadiazole on a 10 g scale to give **8**. Reduction of **8** to **9** proceeded cleanly. Decomposition of **9** to a deep yellow material occurred within hours upon exposure to light. Since a significant loss of yield occurred if **9** was purified by column chromatography, the next step was carried out without purifying **9**. (The primary byproduct to form **9** was triphenylphospine oxide, the presence of which does not affect the nucleophilic substitution reaction in the final step.) The final product, NBPBD (**3**), was stable to light. Absorption and emission wavelengths for **3** were shifted somewhat from *tert*-butylphenyl-*p*-biphenyloxadiazole itself:[7] $\lambda_{\max,ab} = 339$ nm (PBD: $\lambda_{\max,ab} = 302$ nm); $\lambda_{\max,em} = 395$ nm $\{\lambda_{ex} = 360$ nm$\}$ (PBD: $\lambda_{\max,em} = 360$ nm $\{\lambda_{ex} = 313$ nm$\}$). Copolymers of **1** or **2** with **3** in various ratios were prepared to probe the extent of aggregate formation (described below).

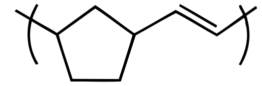
Synthesis of the hole-transport material, NBPTP (**4**), is shown in eq 2. NBPTP was prepared in three steps in 43% yield, following a procedure similar to that employed to prepare **2**.[11]



(2)

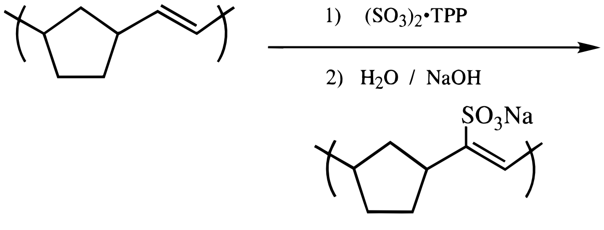
NBPTP (**4**)

Sulfonation of the Polynorbornene Backbone. Many sulfonation reagents can be employed to sulfonate ethers, esters, alcohols, and carbon−carbon double bonds or arenes.[42−45] These reagents vary in selectivity and reactivity. Many commercially available sulfonation reagents are sold as base adducts of SO_3, e.g., SO_3·pyridine or SO_3·*N*,*N*-dimethylacetamide. No reaction occurred upon treating a polynorbornene 100mer, $\mathbf{10_{100}}$, with SO_3·pyridine, the most reactive of the commercially available adducts. Apparently, the strength of the adduct makes it unsuitable for use as a sulfonation reagent for internal olefins.[42] At the other end of the reactivity spectrum are SO_3 and H_2SO_4. Although both are suitable for sulfonation of (e.g.) polystyrene, they readily react with most aromatic rings and therefore are unacceptable as a *general* technique for sulfonation of polynorbornene.



$\mathbf{10_{100}}$

In the only papers to our knowledge published on polynorbornene sulfonation, a reagent of intermediate reactivity, SO_3·triethyl phosphate (TPP), was employed.[28,29] This reaction conserved the double bond in the polymer (eq 3). However, we did not consider SO_3·TPP to be suitable because of its known tendency to react with aromatic rings and other sensitive groups, exactly the type of functionalities in monomers **1**−**4** that make them interesting for LED application. Sulfur trioxide·dioxane was found to be the most suitable reagent, as it has the reactivity necessary to effectively sulfonate the double bond but is generally inert toward aromatic rings and ethers. Unlike SO_3·TPP, SO_3·dioxane yields two products upon quenching of the reaction mixture (Scheme 3): one that contains a saturated C−C bond and the other in which the C−C double bond is regenerated.[43−45]



(3)

The SO_3·dioxane reagent was prepared by adding 10 equiv of SO_3 to 15 equiv of dioxane in dry CH_2Cl_2 at 0 °C. A polymer solution was then added over the course of 30 s, and the mixture was allowed to warm to room temperature. The reaction was stirred at room temperature for 3 h and quenched by addition of aqueous NaOH. All solvent was removed in vacuo, and the residue was extracted with DMSO overnight. The insoluble products (NaOH and the reaction byproduct, $NaSO_4$) were removed by centrifugation. The DMSO was removed from the supernatant in vacuo, leaving the sulfonated polymer.

Scheme 3

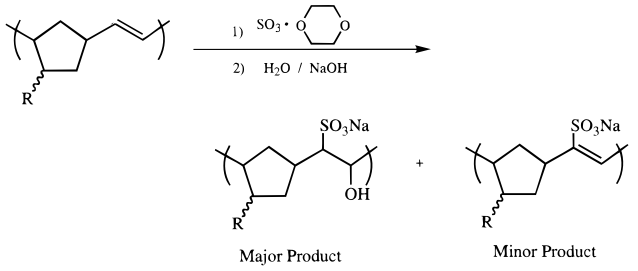


Table 2. Summary of Sulfonated Polynorbornenes

polymer	sulfonation (%)[a]	polymer	sulfonation (%)[a]
$\mathbf{sulf\text{-}10_{100}}$	79	$\mathbf{sulf\text{-}3_{25}}$	92
$\mathbf{sulf\text{-}1_{25}}$	85	$\mathbf{sulf\text{-}4_{50}}$	89
$\mathbf{sulf\text{-}2_{25}}$	90		

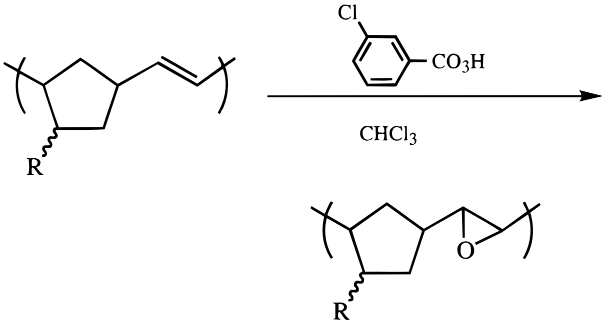
[a] Amount of sulfonation determined by integration in proton NMR of olefinic resonances, assuming that all olefin present is unreacted (this is a lower limit, see Scheme 3).

Sulfonation of $\mathbf{10_{100}}$ was carried out as a test case. The percent sulfonation of $\mathbf{sulf\text{-}10_{100}}$ was determined by proton NMR to be at least 79% by integrating the olefinic proton resonance at 5.3 ppm relative to the aliphatic proton resonances. Since a mixture of sulfonation products is expected (Scheme 3), some of the olefinic intensity can be ascribed to the sulfonated minor product. Therefore, sulfonation probably is greater than 79%. The IR spectrum of $\mathbf{sulf\text{-}10_{100}}$ shows characteristic peaks at 1199 and 1043 cm^{-1} ascribable to SO_2 stretching modes and no absorption ascribable to cis (740 cm^{-1}) or trans (966 cm^{-1}) bending vibrations.

Sulfonation of $\mathbf{1_{25}}$, $\mathbf{2_{25}}$, $\mathbf{3_{25}}$, and $\mathbf{4_{50}}$ by SO_3·dioxane proceeded smoothly. Since these polymers contain only ether and aromatic groups, they should be suitable for sulfonation by SO_3·dioxane. (A previously reported PBD-containing electron-transporting polymer was unsuitable because it linked the *tert*-butylphenyl-*p*-biphenyl-oxadiazole moiety to the norbornene via a reactive ester functionality.[11]) The results are listed in Table 2. The percent sulfonation was at least 85% in all cases. As explained above, this is a lower limit, since the minor products in Scheme 3 contain olefinic protons. Little change occurred in the aromatic region of the proton NMR spectra or in absorption spectra, indicating that the side chain electroluminescent groups were not harmed. For polymers containing **1** or **2**, the $\lambda_{max,abs}$ remained at 400 nm. However, the emission properties of these materials changed upon sulfonation. This phenomenon will be discussed below.

A dramatic change was observed in solubility of the polynorbornenes before and after sulfonation. The original polynorbornenes were readily soluble in nonpolar solvents such as toluene, chloroform, and chlorobenzene. After sulfonation, the polymers were no longer soluble in these solvents but were quite soluble in DMSO or *N*,*N*-dimethylacetamide (DMA). None was readily soluble in water. However, after dissolving the polymer in 1 mL of DMSO or DMA, the solution was easily diluted with water without any polymer precipitation, even at very high water concentrations (>98% water). The series of copolymers containing monomers **1**−**3** was also sulfonated using this technique. The physical properties were similar to those of the sulfonated homopolymers.

Epoxidation of the Polynorbornene Backbone. *m*-Chloroperoxybenzoic acid is a widely used and commercially available reagent for generating organic epoxides. It was found to be an excellent choice for converting the polynorbornene double bond into the corresponding epoxide (eq 4). This process (also known as the Prilezhaev reaction) is efficient but also tolerant of functionalities such as aromatic rings, ethers, or esters.[46] Epoxidation of $\mathbf{10}_{100}$ rapidly proceeded to completion to yield **epox-**$\mathbf{10}_{100}$. Monitoring the reaction by proton NMR revealed that the olefinic resonances at 5.3 ppm disappeared completely after 5 min. A new broad peak was observed at 2.81 ppm, consistent with protons on an epoxide ring, while a resonance at 62.19 ppm in the carbon-13 NMR spectrum appeared that can be assigned to the epoxide ring carbons. The IR spectrum displayed the characteristic 8μ, 11μ, and 12μ epoxide ring stretches at 1258, 889, and 730 cm^{-1} respectively.[47,48] The IR spectrum also showed a trace of the overoxidized product, a C=O stretch at 1725 cm^{-1}. However, no evidence of overoxidation was found in the carbonyl region of the carbon-13 NMR spectrum.



(4)

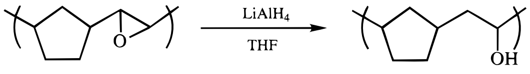
Attempts to react the epoxidized polynorbornene with a variety of nucleophiles such as NaOH, NaOMe, or $KOCH_2CH_2NMe_2$ at room temperature to 100 °C left the starting material unchanged. This was not especially surprising because the reactivity of internal epoxides is known to be limited, especially when large groups are close to the double bond, as in this case.[46] The reactivity of **epox-**$\mathbf{10}_{100}$ was further hampered by the insolubility of the material in polar solvents such as CH_3CN or DMSO, which would be expected to increase the rate of a nucleophilic substitution reaction. The reaction between **epox-**$\mathbf{10}_{100}$ and aqueous HCl also failed. Since **epox-**$\mathbf{10}_{100}$ was very insoluble in water (the polymer precipitated even in 5% water/95% THF), reactions requiring water were bound to be sluggish. Combining **epox-**$\mathbf{10}_{100}$ with 2 equiv of 1 M HCl in ether, followed by addition of water, led to a dark intractable material. The proton NMR spectrum taken of a dilute sample showed mostly starting material resonances.

One reaction that proceeded relatively cleanly with **epox-**$\mathbf{10}_{100}$ was the reaction with $LiAlH_4$ (eq 5). Addition of 2 equiv of $LiAlH_4$ in THF to **epox-**$\mathbf{10}_{100}$ led to complete conversion of the epoxide to the alcohol. The resonances assigned to the epoxide ring were replaced by a resonance at 4.14 ppm, typical of −C*H*(OH)−. Also, the carbon-13 NMR spectrum showed a new resonance at 72.70 ppm (−*C*(OH)−) and the IR spectrum a strong, broad OH stretch at 3448 cm^{-1}. Characteristic epoxide μ stretches were no longer apparent.

Table 3. Deposition of Sulfonated Polynorbornenes[a]

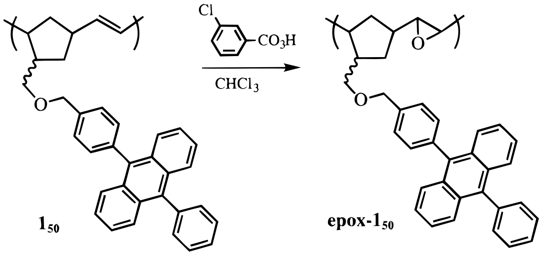
polymer	thickness/bilayer (Å)[b]
no salt	
sulf-$\mathbf{1}_{25}$	10
sulf-$\mathbf{2}_{25}$	8
sulf-$\mathbf{4}_{25}$	13
$(\mathbf{1}_{50\%}\mathbf{3}_{50\%})_{50}$	8
$(\mathbf{1}_{10\%}\mathbf{3}_{90\%})_{50}$	10
$(\mathbf{1}_{2\%}\mathbf{3}_{98\%})_{50}$	13
$(\mathbf{2}_{50\%}\mathbf{3}_{50\%})_{50}$	11
with salt[c]	
sulf-$\mathbf{4}_{50}$	23

[a] Deposition of polymer alternating with PAH, onto a silicon wafer prepared with five bilayers of PAH/PMA. [b] Determined by ellipsometry. [c] Both dipping solutions contain 0.1 M NaCl.



(5)

To test the generality of the epoxidation reaction, $\mathbf{1}_{50}$ was treated under the reaction conditions described above (eq 6); **epox-**$\mathbf{1}_{50}$ formed quickly and completely. As expected, the DPA group was not harmed by the process. However, since the utility of epoxidized polymers was judged to be limited, no further reactions were explored.



(6)

Layer-by-Layer Deposition of Ultrathin Films by Sequential Adsorption. The layer-by-layer deposition of the sulfonated polynorbornenes was accomplished using techniques that have been reported elsewhere.[37,38,49,50] We found that **sulf-**$\mathbf{1}_{25}$ did not immediately deposit onto a cleaned glass slide or silicon wafer when adsorbed sequentially with poly(allylamine HCl) (PAH). However, after first sequentially adsorbing five bilayers of PAH with poly(methylacrylic acid) (PMA), it was possible to sequentially adsorb polymers containing **1**−**4**. Table 3 lists the thickness of each PAH/polynorbornene bilayer. Figure 2 shows the linear deposition of **sulf-**$\mathbf{1}_{25}$ with PAH, measured by ellipsometry. Films prepared by this method appeared to be uniform, both visually and as measured by profilometry and ellipsometry. As expected for highly charged sulfonates, each bilayer (with PAH) was relatively thin (8−13 Å[37]). No deposition of **sulf-**$\mathbf{4}_{50}$ occurred unless 0.1 M NaCl was added to both dipping solutions. Films of sulfonated copolymers were also prepared in this manner. The deposition characteristics listed in Table 3 show that these materials were very similar to the homopolymers. In both the copolymers and homopolymers, a transition region existed in the film where the thickness of the PAH/PMA prep layer influenced the PAH/polynorbornene layer (see Figure 2). Generally, after the first five bilayers of polynorbornene were

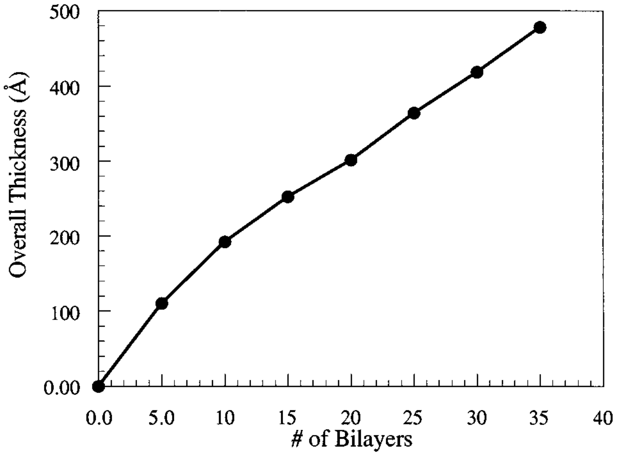


Figure 2. Ellipsometry measurements on a coating prepared by sequential adsorption of **sulf-1**$_{25}$ and PAH onto a silicon wafer primed with five bilayers of PAH/PMA.

deposited on the prep layer, the thickness per bilayer assumed a more constant value. By sequentially building layers containing different homopolymers and copolymers, it was possible to create a variety of film structures. The properties of these films will be discussed in the sections below.

Aggregate Formation with DPA-Containing Polymers. The photoluminescent emission of 1 × 10^{-3} M solution of **sulf-1**$_{25}$ in DMSO or DMA was the same as that observed for **1**$_{25}$ in nonpolar solvents, intense blue light at 450 nm (λ_{ex} = 360 nm).[7,11] However, the photoluminescence of **sulf-1**$_{25}$ at a similar concentration in predominantly water (95% or greater) was broader, red-shifted to 600 nm, and had a much lower intensity. This effect was unexpected, since the nonpolar form did not exhibit this behavior. However, considerable precedent exists for anthracene-like molecular structures, including diphenylanthracene, to form aggregates,[51−58] which frequently have much lower quantum yield of emission. It has also been shown that aggregate (namely excimer) formation is facilitated by π stacking within a distance of several angstroms. Apparently, in water the nonpolar DPA units interact at close range. Therefore, aggregate formation and emission are favored over monochromophore emission.

Figure 3 shows the effect of dilution on emission from **sulf-1**$_{25}$ in water. Decreased concentration led to a gradual shift to the higher energy and more intense monochromophore emission spectrum. However, sequentially adsorbed films prepared from solutions with different concentrations of **sulf-1**$_{25}$ did not show any variation in emission. Even when the solution of **sulf-1**$_{25}$ used was at high dilution (1 × 10^{-4} M or less), the photoluminescent emission from the films was quite weak and red-shifted. The lack of dependence upon solution concentration is a consequence of the polymer concentration at the substrate surface always being high. To control emission, the composition of the polymer itself therefore must be controlled. Previous work with the perylene chromophore in Langmuir−Blodgett films provides a precedent for this approach.[52]

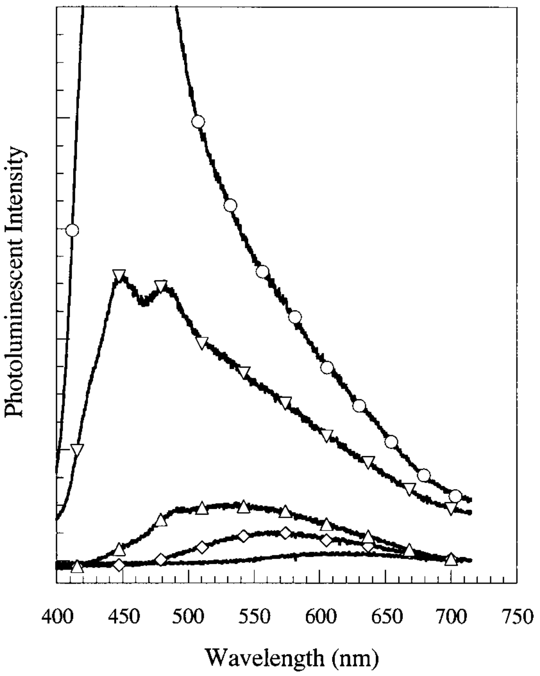


Figure 3. Solution photoluminescence of **sulf-1**$_{25}$ in water: no symbols, 7 × 10^{-3} M; ◇, 2 × 10^{-3} M; △, 9 × 10^{-4} M; ▽, 5 × 10^{-4} M; ○, 2 × 10^{-4} M. As the concentration of **sulf-1**$_{25}$ decreases, the emission increases.

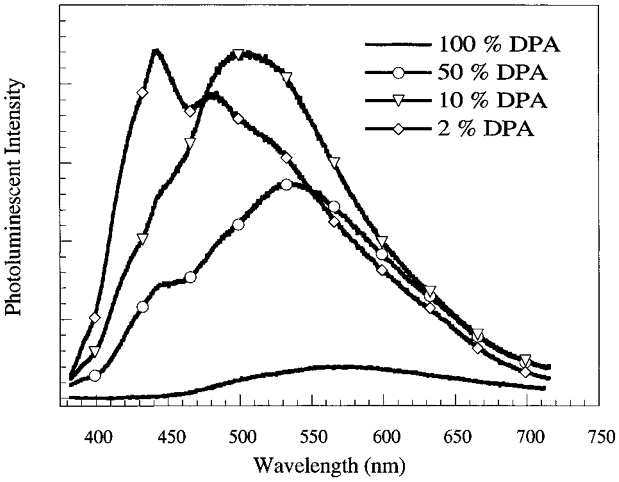


Figure 4. Photoluminescence of films of **sulf-(1**$_{x\%}$**3**$_{100-x\%}$**)**$_{50}$ showing increased emission with decreasing percent of NBDPA (**1**) in the copolymer. All films were 600 Å thick.

When *chemically* diluted DPA-containing copolymers, **sulf-(1**$_{x\%}$**3**$_{100-x\%}$**)**$_{50}$ (where the diluant was the PBD-containing monomer, **3**), were sequentially adsorbed in equal thicknesses onto a prepared substrate, the emission shifted back to that expected from the monochromophore (Figure 4). As the percent **1** in the copolymer decreased from 100% to 2%, the intensity of emission also increased by a factor of 30. This effect is similar to that reported in the literature for chemical dilution and provides further evidence for the existence of aggregates. The solution emission at 1 × 10^{-3} M of this series mirrored this trend. As mentioned above, at high dilution, solutions of all of the polymers were brightly luminescent at 450 nm. This behavior contrasted starkly with that observed for the spin-coated films of similar polymers. Spin-coated films were highly blue luminescent for both the DPA homopolymer and the 50% copolymer. Additionally, the intensity of emission for the spin-coated film was over 15 times greater than that of the sequentially adsorbed film.

Another method of potentially controlling aggregate formation is by sterically protecting the anthracene structural unit from π stacking interactions[53,59] by

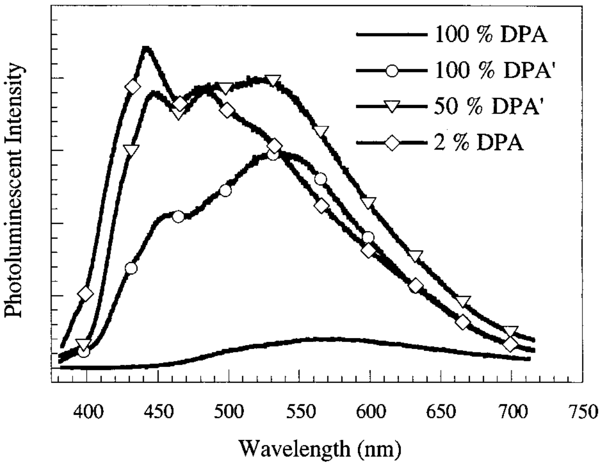


Figure 5. Photoluminescence of films of **sulf-$(1_{x\%}3_{100-x\%})_{50}$** and **sulf-$(2_{x\%}3_{100-x\%})_{50}$**. All films were 600 Å thick.

blocking access above and below the anthracene plane. The synthesis of a suitable monomer (**2**, Scheme 1) in which methyl groups project above and below the anthracene ring was described above. This approach was successful; the modified DPA polymers, **sulf-2_{25}** and **sulf-$(2_{50\%}3_{50\%})_{50}$**, were highly luminescent in aqueous solution. The new **sulf-2_{25}** was more luminescent at 1×10^{-3} M than any of the previously prepared copolymers containing **1** and **3**. However, the copolymer, **sulf-$(2_{50\%}3_{50\%})_{50}$**, was even more luminescent than **sulf-2_{25}**, indicating that some degree of self-quenching behavior remains at this concentration.

Films were formed readily by sequential adsorption of **sulf-2_{25}** and **sulf-$(2_{50\%}3_{50\%})_{50}$** with PAH on glass or silicon prepared with five bilayers of PAH/PMA. The films appeared uniform and emitted uniformly under UV lamp excitation. The photoluminescent intensity of **sulf-2_{25}** films was much greater than that of **sulf-1_{25}** (see Figure 5). However, the spectrum was still red-shifted from 450 nm, indicating that aggregates were still present. The film with **sulf-$(2_{50\%}3_{50\%})_{50}$** was more intensely photoluminescent overall and showed a more intense 450 nm emission band than the **sulf-2_{25}** film. Visually, under UV lamp excitation, the films with **sulf-2_{25}** appeared green-white, while films made from **sulf-$(2_{50\%}3_{50\%})_{50}$** appeared blue-white.

Construction of Light-Emitting Devices. Single-layer devices were constructed by depositing films of **sulf-$(1_{x\%}3_{100-x\%})_{50}$** or **sulf-$(2_{x\%}3_{100-x\%})_{50}$** onto an indium tin oxide (ITO) anode and then placing a 2000 Å thick aluminum cathode on top via thermal evaporation (Figure 6a). The device behavior is summarized in Table 4. Interestingly, even with its low-intensity photoluminescent emission (see Figure 4), the single-layer device made with sequentially adsorbed films of **sulf-1_{25}** showed greater output and efficiency than the previously reported device made by spin-coating **1_{25}**.[11] In the spin-coated device, a maximum of 0.5 nW light was obtained with an efficiency of 0.03 nW/mA, but the film itself was brightly blue photoluminescent. For **sulf-1_{25}**, even though the film was only weakly luminescent, the output and efficiency were *greater* (6 nW and 0.1 nW/mA). In this case improvement in film quality more than made up for the vast difference in luminescence. Figure 7 shows the I−V and L−V curves for this device. The percentage of operating pixels and the overall stability of these new devices were better than the spin-coated devices. The threshold voltage also was considerably lower than in the spin-coated device, which may help to explain some of the added device stability.

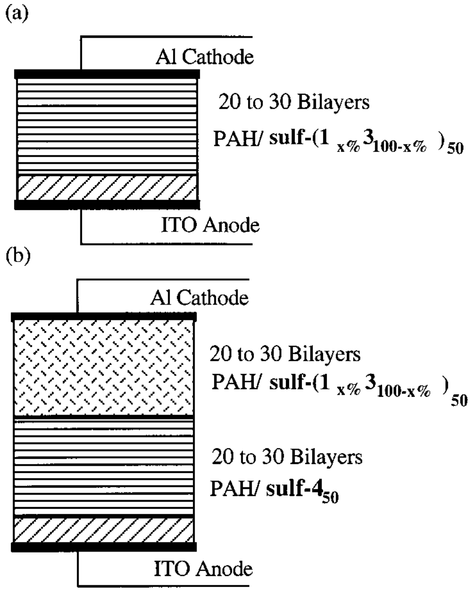


Figure 6. Configuration of polymer EL devices: (a) single layer, ITO/PAH−PMA (5 bilayers)/PAH-**sulf-$(1_{x\%}3_{100-x\%})_{50}$** (20−30 bilayers)/Al; (b) dual layer, ITO/PAH−PMA (5 bilayers)/PAH-**sulf-4_{50}**/PAH-**sulf-$(1_{x\%}3_{100-x\%})_{50}$** (20−30 bilayers)/Al.

The performance of devices prepared with other copolymers in the **sulf-$(1_{x\%}3_{100-x\%})_{50}$** series is summarized in Table 4. Even though the photoluminescent emission of the film was greatest for **sulf-$(1_{2\%}3_{98\%})_{50}$** (see Figure 4), it actually displayed the worst device performance, 0.5 nW of light and 0.01 nW/mA. As the percent of monomer **1** in the copolymer decreased, the devices exhibited a loss of output and efficiency. This decrease indicated a charge balance problem caused by the increased dilution with the electron carrier (or hole blocker), **3**. As the percent **1** decreased (and percent **3** increased), the electron flow increasingly dominated recombination with holes to form the emissive DPA species. This explanation was supported by the high current density that was displayed in all devices (typically 400−800 mA/cm^2), including those with very little output. For all devices the threshold was 10 V or lower, which was lower than any single-layer device made with spin-coated polymers containing the monomer **1**.

Devices made by assembling the bulkier DPA monomer, **2**, performed better than any of those containing **1**. The best result for single-layer devices was 21 nW and 0.3 nW/mA, obtained for **sulf-2_{25}**, which was comparable to the best spin-coated single-layer devices with similar polymers.[11] The two devices with **2** had higher threshold voltages than those with **1**, especially the device containing **sulf-$(2_{50\%}4_{50\%})_{50}$**. Also, devices with this copolymer performed far worse than those with the homopolymer. This is unusual, since devices made with 50% copolymers of **1** and an electron-transporting monomer performed better than those with the homopolymer. It is possible that the bulkiness of **2** does prevent aggregate formation but also makes transfer of charge more difficult. This would also explain the higher threshold voltages that are required in order to inject charge and produce light.

To address the charge balance problem, dual-layer structures were assembled that contained a hole-transporting (electron-blocking) layer of **sulf-4_{50}**. Figure 6b shows the composition of these devices, constructed

Table 4. Performance of Single-Layer Devices with NBDPA (1) and NBDPA′ (2)

polymer[a]	thickness (Å)	output (nW)	current (mA/cm^2)	efficiency (nW/mA)	threshold[b] (V)
devices with **1**					
sulf-1$_{25}$	250	5	830	0.1	6
sulf-(1$_{50\%}$3$_{50\%}$)$_{50}$	400	5	420	0.2	10
sulf-(1$_{10\%}$3$_{90\%}$)$_{50}$	400	1	830	0.02	9
sulf-(1$_{2\%}$3$_{98\%}$)$_{50}$	400	0.5	830	0.01	9
devices with **2**					
sulf-2$_{25}$	400	21	920	0.3	13
sulf-(2$_{50\%}$3$_{50\%}$)$_{50}$	400	0.8	130	0.1	16

[a] All films were made by sequential adsorption of polymer (1×10^{-4} M) with PAH (1×10^{-2} M) onto a prepared ITO substrate (prepared with five bilayers of PAH/PMA). Additional thickness of prepared layer: 100 Å. [b] The voltage at which light output rises above 0.5 nW (well above baseline noise).

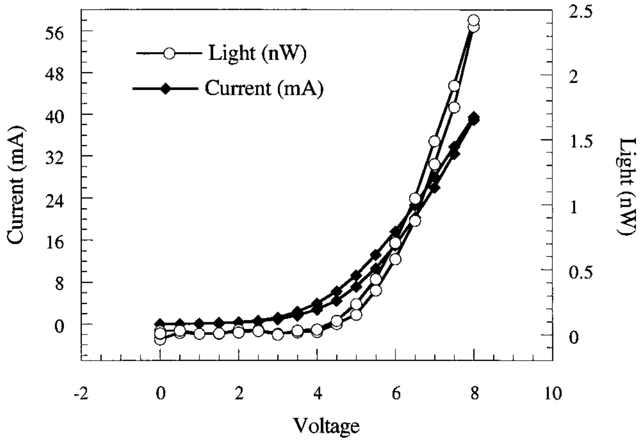


Figure 7. Performance of device ITO/PAH−PMA(5 bilayers)/PAH-**sulf-1$_{25}$** (35 bilayers)/Al: current−voltage (diamonds) and light−voltage (open circles) curves.

Table 5. Performance of Dual-Layer Devices with NBDPA (1) and NBDPA′ (2)

polymer[a]	thickness (Å)	output (nW)	current (mA/cm^2)	efficiency (nW/mA)	thresh[b] (V)
sulf-4$_{50}$	350				
sulf-(1$_{2\%}$3$_{98\%}$)$_{50}$	400	7	380	0.3	7.5
sulf-4$_{50}$	250				
sulf-2$_{25}$	400	3.2	330	0.5	18

[a] All films for devices were made by sequential adsorption of polymer (1×10^{-4} M) with PAH (1×10^{-2} M) onto a prepared ITO substrate (prepared with five bilayers of PAH/PMA). Additional thickness of prepared layer: 100 Å. [b] The voltage at which light output rises above 0.5 nW (well above baseline noise).

in a similar fashion as the single-layer devices, with 250−350 Å of **sulf-4$_{50}$** with PAH onto which 400 Å of **sulf-(1$_{2\%}$3$_{98\%}$)$_{50}$** or **sulf-2$_{50}$** with PAH was deposited. The total film thickness was about 800 Å (including the PAH/PMA prep layer). Table 5 summarizes the behavior of these devices. For the films containing **sulf-(1$_{2\%}$3$_{98\%}$)$_{50}$**, a layer of **sulf-4$_{50}$** improved the performance compared to the single-layer **sulf-(1$_{2\%}$3$_{98\%}$)$_{50}$** device (7 vs 0.5 nW and 0.3 vs 0.01 nW/mA). The threshold voltage was similar to that seen for the single-layer device, even though the film was almost twice as thick. This indicated that the barrier to hole injection was lowered by the PTP layer. This greater than 10-fold improvement in performance was similar to that obtained by employing the PPV multilayer heterostructure as a hole-transporting/electron-blocking layer with a spin-coated film of polynorbornene emitter. Dual-layer devices made with the homopolymer of **2** showed little increase in output and efficiency compared to the single-layer device, and the threshold voltage was very high, making device operation difficult. Although the dual-layer device with **sulf-2$_{25}$** had a somewhat better efficiency than the single-layer device, the higher threshold voltages made it more difficult to get greater light output without burning out the device. Therefore, the single layer of sequentially adsorbed **sulf-2$_{25}$** remained the all-norbornene device with the greatest output and efficiency (21 nW of light and 0.3 nW/mA).

Conclusions

We have shown that a variety of monomers that contain both emission and charge transport functional units can be synthesized readily. Homopolymers and copolymers were polymerized with the molybdenum catalyst, demonstrating once again its utility in making well-defined materials. Sulfonation with SO_3·dioxane allows one to readily convert these substituted polynorbornenes from a nonpolar form to a polyionic form. It is straightforward to prepare polynorbornenes with functional groups that are both potentially useful for applications, such as light-emitting devices, and also robust enough to withstand the sulfonation conditions. Since the SO_3·dioxane reagent is tolerant of aromatic rings, including heterocycles, it is possible to functionalize a wide variety of polymers in this manner. The epoxidation reaction, although high yielding and rapid, is disappointing from a synthetic point of view. However, if the synthetic target is only to remove the double bonds, this procedure may provide an alternative to hydrogenation. The limited reactivity in this case would be advantageous, not interfering in subsequent application or reaction. The primary advantages over hydrogenation would be (1) the solubility characteristics are more favorable than the relatively insoluble hydrogenated polymer[30] and (2) the reaction is quick and complete.

Sulfonation of the polynorbornene backbone should be possible for a wide variety of polymers that have potential in light-emitting devices. Incorporation of hole and electron-transporting monomers provided a means both to control charge flow and to prevent aggregate formation by DPA structural units. Aggregate formation was also controlled by increasing the bulkiness of the groups flanking the anthracene core. Dual-layer devices with separate hole and electron transport layers increased the output from polymers containing **1** by a factor of 10. The greatest electroluminescent emission was from a single-layer film of the “bulky DPA” polymer, **2$_{25}$**: 21 nW of blue-white light with an efficiency (photons/electron) of 3.3×10^{-6}%.

Experimental Section

General. HPLC grade CH_2Cl_2 was used in gel permeation chromatography (GPC) runs and was distilled over CaH_2 prior to use. GPC was carried out using a Waters Ultrastyragel 10573: Shodex KF-802.5, 803, 804, 805, and 800P columns; a Visotek differential refractometer/viscometer H-500; and a Spectroflow 757 absorbance detector on samples 0.1−0.3% (w/v) in CH_2Cl_2. Samples were first filtered through a Millex-SR 0.5 μm filter in order to remove particulates. GPC columns were calibrated versus polystyrene standards (Polymer Laboratories Ltd.) which ranged from MW = 1260 to 2.75×10^6. Elemental analyses were performed by H. Kolbe Laboratories, Mülhiem an der Ruhr, Germany. NMR data were obtained at 300 or 500 MHz and listed in parts per million downfield from tetramethylsilane. IR spectra were taken with a Perkin-Elmer FT-IR of either a cast polymer film on a NaCl plate or of powdered polymer in a KBr pellet. Absorbance spectra were taken with an Oriel Instaspec spectrophotometer. Photoluminescence spectra were taken using a spectrograph coupled to a Peltier-cooled CCD array (Oriel Instaspec IV). The system response was calibrated using a tungsten lamp. Excitation for the photoluminescence was from the multiline UV mode of an argon ion laser. Spectra were obtained at 25 °C unless otherwise noted. Film thicknesses were measured with a Gartner ellipsometer and a Sloan Dektak 8000 profilometer. Measurements of current and luminescence as a function of applied field were made under forward bias. A silicon photodiode (Newport Instruments, model 1830-C) was used to measure device light output, which is measured in nanowatts.

Preparation of Monomers. Unless otherwise stated, all experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenck techniques. All chemicals were reagent grade and were purified by standard methods. $Pd(PPh_3)_4$ and $NiCl_2(PPh_3)_4$ were purchased from Strem Chemicals. All other chemicals were purchased from Aldrich Chemical Co. and used as received.

9-Mesitylanthracene (5). 9-Bromoanthracene (0.998 g, 3.88 mmol) and $NiCl_2(PPh_3)_2$ (127 mg, 0.194 mmol) were combined in 100 mL of diethyl ether, and the mixture was cooled to −35 °C. Mesitylmagnesium bromide (1.5 equiv, 5.3 mL, 1.10 M in ether) was added, and the reaction was stirred at room temperature. Over the course of several hours the solution darkened. Another 2 mL of Grignard was added after 2 h, and the solution was refluxed under N_2 overnight. The reaction was quenched with HCl(aq), and the layers were separated. The organic layer was washed with water and dried over $MgSO_4$, and the solvent was removed in vacuo, yielding a yellow-brown residue (1.40 g). Purification by column chromatography (silica gel, hexanes with 1% MeOH) gave 619 mg of a white powder (58% yield). ^{1}H NMR ($CDCl_3$): δ 8.51 (s, 1, Ar), 8.17 (d, 2, Ar), 7.48 (t, 2, Ar), 7.46 (d, 2, Ar), 7.37 (t, 2, Ar), 7.12 (s, 2, Ar), 2.49 (s, 3, ArCH_3), 1.74 (s, 6, ArCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 137.69, 137.23, 135.89, 134.61, 131.75, 129.89, 128.77, 128.40, 126.13, 125.72, 125.50, 125.33, 21.61, 20.34.

9-Bromo-10-mesitylanthracene (6). 9-Mesitylanthracene (610 mg, 2.06 mmol) was dissolved in 100 mL of dry CH_2Cl_2. Bromine (0.115 mL, 2.23 mmol) was added, and the solution was stirred for 35 min. (The reaction is much cleaner if Br_2 is used fresh from an ampule.) The mixture was quenched with 50 mL of saturated $NaSO_3$(aq) solution. After another hour, additional ether was added and the phases were separated. The organic phase was washed with water and dried over $MgSO_4$, and the solvent was removed in vacuo to yield 764 mg of a yellow powder (99%) that was pure by ^{1}H and ^{13}C NMR and used in the next step without further purification. ^{1}H NMR ($CDCl_3$): δ 8.61 (d, 2, Ar), 7.59 (t, 2, Ar), 7.49 (d, 2, Ar), 7.34 (t, 2, Ar), 7.08 (s, 2, Ar), 2.47 (s, 3, ArCH_3), 1.71 (s, 6, ArCH_3). ^{13}C NMR {^{1}H} ($CDCl_3$): δ 137.58, 137.53, 136.68, 134.19, 130.69, 130.64, 128.47, 128.20, 127.18, 126.50, 126.00, 122.38, 21.56, 20.30.

***p*-(Diethylborate)benzyl (5-Norbornenyl)methyl Ether (7).** In a nitrogen-filled drybox *n*-butyllithium (1 mL, 2.5 M in hexanes) was added to *p*-bromobenzyl (5-norbornenyl)methyl ether (422 mg, 1.44 mmol) in 25 mL of ether. An additional 1 mL portion of *n*-butyllithium (total of 5 mmol) was added after 20 min. The flask was cooled to −35 °C after 20 min, and $B(OEt)_3$ (1.75 mL, 10.3 mmol) was added. It was necessary at this point to add THF to the mixture in order to dissolve the products. (If THF is used instead of ether during the lithiation step, the yield decreases dramatically.) This solution was stirred for 1.5 h and used directly to prepare either **2** or **4**.

***p*-(10-Mesitylanthracyl)benzyl (5-Norbornenyl)methyl)] Ether [NBDPA′] (2).** A solution of **7** (4.741 mmol) was prepared as described above. To that mixture, **6** (1.609 g, 4.287 mmol) was added, and the reaction flask was removed from the drybox. An aqueous solution of K_2CO_3 (100 mL, 1.0 M, sparged 25 min with N_2) was then added. The mixture was brought to reflux under N_2, and $Pd(PPh_3)_4$ (97 mg, 0.084 mmol) in 1.5 mL of THF (prepared in the drybox) was added via syringe. The flask was covered with Al foil, and the mixture refluxed under N_2 for 16 h. An aliquot showed mostly starting material by proton NMR, so 100 mg more Pd^0 was added to the reaction. After 3 days, ether was added and the phases separated. The organic layer was washed with water and dried over $MgSO_4$, and the solvent was removed in vacuo, yielding a dark yellow solid (3.176 g). Purification by column chromatography (silica gel, 1:3 CH_2Cl_2:hexanes with 1% MeOH) gave 1.253 g of white powder (57.5% for both steps). ^{1}H NMR ($CDCl_3$, endo): δ 7.73 (m, 2, Ar), 7.50 (m, 6, Ar), 7.29 (m, 4, Ar), 7.11 (s, 2, Ar), 6.18 (m, 1, olefin), 5.98 (m, 1, olefin), 4.62 (q, 2, ArCH_2O), 3.47 (q, 1, nor-CH_2−O), 3.23 (t, 1, nor-CH_2−O), 3.04 (broad s, 1), 2.84 (broad s, 1), 2.51 (m, 1), 2.49 (s, 3, ArCH_3), 1.88 (m, 1), 1.79 (s, 6, ArCH_3), 1.48 (m, 1), 1.24 (m, 1), 0.59 (m, 1); (exo) δ 7.73 (m, 2, Ar), 7.50 (m, 6, Ar), 7.29 (m, 4, Ar), 7.11 (s, 2, Ar), 6.18 (m, 1, olefin), 6.11 (m, 1, olefin), 4.62 (q, 2, ArCH_2O), 3.71 (q, 1, nor-CH_2−O), 3.66 (t, 1, nor-CH_2−O), 3.04 (broad s, 1), 2.84 (broad s, 1), 2.51 (m, 1), 2.49 (s, 3, ArCH_3), 1.88 (m, 1), 1.79 (s, 6, ArCH_3), 1.48 (m, 1), 1.24 (m, 1), 0.89 (m, 1). ^{13}C NMR {^{1}H} ($CDCl_3$): δ 138.18, 137.91, 137.42, 137.36, 136.75, 136.02, 135.00, 132.76, 131.74, 130.37, 129.67, 128.53, 127.92, 127.54, 126.29, 125.47, 125.21, 74.63, 73.29, 49.72, 44.42, 42.62, 39.20, 29.58, 21.66, 20.41. Anal. Calcd for $C_{38}H_{36}O$: C, 89.72; H, 7.13. Found: C, 89.67; H, 7.18.

4-(5-(4-*tert*-Butylphenyl)-1,3,4-oxadiazole-2-yl)-biphenyl-4′-yl Sulfonic Acid (8). $ClSO_3H$ (32 mL) was added dropwise to a solution of *t*-Bu-PBD (10.13 g, 28.58 mmol) in 50 mL of CH_2Cl_2 at 0 °C. After addition was complete, the mixture was brought to reflux. After 4 h 100 mL of ice and water was slowly added, and the solution was concentrated in vacuo to remove the CH_2Cl_2. The resulting white sludge was collected by filtration. Excess water was removed by adding benzene and removing the azeotrope and excess benzene in vacuo. This yielded 12.31 g of pure white powder (99%). No further purification was necessary. ^{1}H NMR ($CDCl_3$): δ 8.27 (d, 2, Ar), 8.14 (d, 2, Ar), 8.08 (d, 2, Ar), 7.87 (d, 2, Ar), 7.78 (d, 2, Ar), 7.56 (d, 2, Ar), 1.37 (CMe_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.0, 165.8, 155.6, 146.8, 143.6, 141.5, 128.3, 128.1, 127.7, 127.6, 126.8, 126.1, 125.5, 124.6, 120.9, 35.1 (CMe$_3$), 31.1 (CMe_3).

4-(5-(4-*tert*-Butylphenyl)-1,3,4-oxadiazole-2-yl)-biphenyl-4′-thiol (9). Anhydrous **8** (11.608 g, 26.72 mmol) was dissolved in 250 mL of dry THF. A solution of PPh_3 (28.40 g, 108.3 mmol) and I_2 (3.411 mg, 13.43 mmol) in 50 mL of THF was added dropwise. Triethylamine (2 mL, 19.76 mmol) was added, and the solution was brought to reflux. The dark solution gradually changed into a mustard yellow-orange suspension. 1,4-Dioxane (60 mL) in water (30 mL) was added after 1 h. The solution immediately became colorless and the solid dissolved. The mixture was refluxed for an additional hour, and then ether was added. The organic layer was washed with water and dried over $MgSO_4$, and the solvent was removed in vacuo. Although conversion of **8** to **9** was complete, a significant quantity of triphenylphosphine oxide remained, which was difficult to remove without using column chromatography. However, since **9** is quite light sensitive, higher overall yields were obtained by proceeding to the next step without further purification. ^{1}H NMR ($CDCl_3$): δ 8.16 (d, 2, Ar), 8.05 (d 2, Ar), 7.68 (d, 2, Ar), 7.54 (d, 2, Ar), 7.50 (d, 2, Ar), 7.34 (d, 2, Ar), 3.52 (s, SH), 1.35 (s, CMe_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.8, 164.3, 155.4, 143.4, 137.1, 131.5, 129.8, 127.7, 127.5, 127.3, 126.9, 126.1, 122.9, 121.2, 35.2 (CMe$_3$), 31.2 (CMe_3).

(5-Norbornenyl)methyl-(2-(Biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole)-4′-yl Thioether [NBPBD] (3). Crude **9** (10.32 g, 26.72 mmol of product) was dissolved in 200 mL of toluene. KOH powder (6.80 g, 121 mmol) and 8 drops of Aliquat 336 were added to form the potassium salt. After stirring the mixture for 45 min at 22 °C, (5-norbornenyl)methyl tosylate (6.636 g, 23.85 mmol) was added to the bright orange mixture, and the reaction was heated to reflux. After 48 h the reaction was cooled to room temperature, and ether was added. The organic layer was washed with water and dried over $MgSO_4$, and the solvents were removed in vacuo. The crude was purified by column chromatography (silica gel, 6:1 hexane: EtOAc with 1% MeOH) to yield 2.515 g (20%) of a white powder. ^1H NMR ($CDCl_3$): δ 8.15 (d, 2, Ar), 8.05 (d, 2), 7.70 (d, 2, Ar), 7.52 (m, 4, Ar), 7.39 (d, 2, Ar), 6.10 (m, 2, olefin), 3.02 (m, 2), 2.74 (m, 3), 2.32 (m, 1), 1.97 (m, 1), 1.36 (s, 9H, *t*-Bu), 1.28 (m, 2), 0.69 (m, 1). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 164.85, 164.43, 155.53, 143.80, 138.23, 138.14, 137.05, 132.21, 129.09, 129.02, 127.58, 127.48, 126.98, 126.25, 122.89, 121.31, 49.88, 45.66, 42.96, 38.63, 38.34, 35.28, 32.95, 31.32. Anal. Calcd for $C_{32}H_{32}N_2OS$: C, 78.01; H, 6.55; N, 5.69. Found: C, 77.94; H, 6.51; N, 5.62.

(*p*-Triphenyl)methyl (5-Norbornenylmethyl) Ether [NBPTP] (4). A solution of **7** (1.44 mmol) was prepared as described above. To that mixture, 4-bromobiphenyl (480 mg, 1.44 mmol) was added, and the reaction flask was removed from the drybox. An aqueous solution of K_2CO_3 (50 mL, 1.0 M, sparged 25 min with N_2) was then added. The mixture was brought to reflux under N_2, and $Pd(PPh_3)_4$ (30 mg, 0.026 mmol) in 2 mL of THF (prepared in the drybox) was added via a syringe. The flask was covered in Al foil and refluxed under N_2 overnight. This mixture was cooled to 22 °C, and *n*-hexane (200 mL) was added. The organic layer was washed with water and dried over $MgSO_4$, and the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel, 3:1 hexanes:CH_2Cl_2 with 1% MeOH) to give 330 mg (49%) of a white powder. ^1H NMR ($CDCl_3$): (endo) δ 7.75−7.58 (m, 8, Ar), 7.50−7.32 (m, 5, Ar), 6.10 (m, 1, olefin), 5.90 (m, 1, olefin), 4.53 (dd, 2, O−CH_2−Ar), 3.25 (q, 1, nor-CH_2−O), 3.10 (t, 1, nor-CH_2−O), 2.98 (broad s, 1), 2.80 (broad s, 1), 2.50−2.35 (m, 1), 1.84 (m, 1), 1.43 (broad d, 1), 1.26 (broad d, 1), 0.57 (m, 1); (exo) δ 7.75−7.58 (m, 8, Ar), 7.50−7.32 (m, 5, Ar), 6.10 (m, 1, olefin), 6.07 (m, 1, olefin), 4.53 (dd, 2, O−CH_2−Ar), 3.57 (q, 1, nor-CH_2−O), 3.42 (t, 1, nor-CH_2−O), 2.98 (broad s, 1), 2.80 (broad s, 1), 2.50−2.35 (m, 1), 1.84 (m, 1), 1.43 (broad d, 1, J = 8.0 Hz), 1.26 (broad d, 1), 1.14 (m, 1). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.96, 140.36, 140.12, 138.24, 137.47, 132.73, 129.08, 128.38, 127.77, 127.70, 127.61, 127.31, 127.25, 74.21, 73.02, 49.95, 44.18, 42.46, 39.67, 29.55. Anal. Calcd for $C_{27}H_{26}O$: C, 88.48; H, 7.15. Found: C, 88.26; H, 7.30.

Preparation of Polymers. All handling of catalyst and polymerization were done in a nitrogen-filled drybox. Dichloromethane employed as a polymerization solvent was dried by distillation over CaH_2. Toluene was distilled from sodium benzophenone. THF was dried by passing it through two large columns of activated alumina.[60] All solvents were stored over 4 Å molecular sieves prior to use in the drybox.[61] Mo(NAr)-($CHCMe_2Ph$)(O-*t*-Bu)$_2$ was prepared as described in the literature.[62]

General Polymerization Procedure: Homopolymers. To a rapidly stirred solution of monomer (0.50 mmol) in 10 mL of toluene, the catalyst Mo(NAr)($CHCMe_2Ph$)(O-*t*-Bu)$_2$ (11 mg, 0.020 mmol) in 2 mL of toluene was added all at once. The reaction mixture was stirred for 1 h, quenched with 4 drops benzaldehyde, and further stirred for 15 min. Precipitation into 75 mL of MeOH afforded high yield (92−99%) of polymer. M_n and M_w/M_n are provided in the tables. NMR and IR data are given below.

(NBDPA)$_{25}$ (1$_{25}$). ^1H NMR ($CDCl_3$): δ 7.70−7.10 (broad, 17, Ar), 5.50−5.30 (broad, 2, olefin), 4.65−4.40 (broad, 2), 3.65−3.25 (broad, 2), 2.80−1.10 (broad, 7). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.28, 138.21, 137.30, 134.77, 133.45, 131.47, 130.05, 123.68, 128.57, 127.77, 127.70, 127.62, 127.17, 127.14, 125.17, 73.05, 46.86, 44.28, 43.02, 40.12, 37.57. IR: ν(CH_2 bend) 1437 cm^{-1}, ν(olefinic CH bend, trans) 939 cm^{-1}, ν(olefinic CH bend, cis) 766 cm^{-1}.

(NBDPA′)$_{25}$ (2$_{25}$). ^1H NMR ($CDCl_3$): δ 7.73 (broad, 2, Ar), 7.50 (broad, 6, Ar), 7.29 (broad, 4, Ar), 7.11 (broad, 2, Ar), 5.51 (broad, 2, olefin), 4.47 (broad, 2, ArCH_2O), 3.43 (broad, 1), 3.38 (broad, 1), 2.36 (broad s, 3, ArCH_3), 1.95 (broad, 1), 1.55 (broad s, 6, ArCH_3), 1.41 (broad, 1), 1.13 (broad, 2), 0.81 (broad, 1).

(NBPBD)$_{25}$ (3$_{25}$). ^1H NMR ($CDCl_3$): δ 8.10−7.95 (broad, 4, Ar), 7.71−7.26 (broad, 8), 5.50−5.25 (broad, 2, olefin), 3.10−2.45 (broad, 4), 2.40−1.65 (broad, 5), 1.16 (CMe_3, 9). IR: ν-(CH_2 bend) 1479 cm^{-1}, ν(olefinic CH bend, trans) 962 cm^{-1}, ν(olefinic CH bend, cis) 738 cm^{-1}.

(NBPTP)$_{50}$ (4$_{50}$). ^1H NMR ($CDCl_3$): δ 7.70−7.30 (broad, 13, Ar), 5.45−5.25 (broad, 2, olefin), 4.65−4.35 (broad, 2), 3.50−3.20 (broad, 2), 2.70−1.10 (broad, 7). IR: ν(CH_2 bend) 1446 cm^{-1}, ν(olefinic CH bend, trans) 968 cm^{-1}, ν(olefinic CH bend, cis) 759 cm^{-1}.

(NB)$_{100}$ (10$_{50}$). ^1H NMR ($CDCl_3$): δ 5.35−5.17 (broad, 2, olefin), 2.78 (broad, 1), 2.43 (broad, 1), 1.85−1.72 (broad, 2), 1.33 (broad, 4), 1.04 (broad 1). ^{13}C NMR $\{^1H\}$ ($CDCl_3$): δ 134.24 (olefin), 133.20 (olefin), 43.67, 43.37, 41.82, 38.80, 38.66, 33.34, 33.10, 32.61, 32.46. IR: ν(CH_2 bend) 1447 cm^{-1}, ν(olefinic CH bend, trans) 966 cm^{-1}, ν(olefinic CH bend, cis) 740 cm^{-1}. GPC: $M_n = 7200 \pm 300$, $M_w/M_n = 1.02 \pm 0.05$.

General Polymerization Procedure: Copolymers. A well-mixed solution of two monomers (0.50 mmol total) in 5 mL of toluene was added over the course of 1 h to a solution of the catalyst, Mo(NAr)($CHCMe_2Ph$)(O-*t*-Bu)$_2$ (11 mg, 0.020 mmol), in 10 mL of toluene. The reaction mixture was stirred for 1 h, quenched with 4 drops benzaldehyde, and further stirred for 15 min. Precipitation into 75 mL of MeOH afforded a high yield (88−99%) of polymer. ^1H NMR data are given below.

[(NBDPA)$_{50\%}$(NBPBD)$_{50\%}$]$_{50}$ [(1$_{50\%}$3$_{50\%}$)]$_{50}$. ^1H NMR ($CDCl_3$): δ 8.10−7.95 (broad, 4, Ar), 7.70−7.10 (broad, 25, Ar), 5.50−5.25 (broad, 4, olefin), 4.65−4.40 (broad, 2), 3.65−3.25 (broad, 2), 3.10−2.45 (broad, 6), 2.40−1.20 (broad, 10), 1.16 (CMe_3, 9).

[(NBDPA)$_{10\%}$(NBPBD)$_{90\%}$]$_{50}$ [(1$_{10\%}$3$_{90\%}$)]$_{50}$. ^1H NMR ($CDCl_3$): δ Identical peaks as above, except ratio of resonances from **1** to **3** is 1:10 instead of 1:1.

[(NBDPA)$_{2\%}$(NBPBD)$_{98\%}$]$_{50}$ [(1$_{2\%}$3$_{98\%}$)]$_{50}$. ^1H NMR ($CDCl_3$): δ 8.10−7.95 (broad, 4, Ar), 7.71−7.26 (broad, 8), 5.50−5.25 (broad, 2, olefin), 3.10−2.45 (broad, 4), 2.40−1.65 (broad, 5), 1.16 (CMe_3, 9). (Essentially identical to the spectrum of **3$_{25}$**.)

[(NBDPA′)$_{50\%}$(NBPBD)$_{50\%}$]$_{50}$ [(2$_{50\%}$3$_{50\%}$)$_{50}$]. ^1H NMR ($CDCl_3$): δ 8.05 (broad, 4), 7.73 (broad, 2, Ar), 7.50 (broad, 10, Ar), 7.29 (broad, 8, Ar), 7.11 (broad, 4, Ar), 5.51 (broad, 2, olefin), 4.47 (broad, 2, ArCH_2O), 3.43 (broad, 1), 3.38 (broad, 1), 3.02 (broad, 1), 2.65 (broad, 4), 2.38 (broad s, 3, ArCH_3), 2.22 (broad, 1), 1.95 (broad, 5), 1.55 (broad s, 6, ArCH_3), 1.41 (broad, 1), 1.31 (broad s, 9, CCH_3), 1.13 (broad, 2), 0.81 (broad, 2). GPC: $M_n = 13\,100 \pm 200$, $M_w/M_n = 1.10 \pm 0.02$.

General Sulfonation Procedure. (NBDPA)$_{25}$ (1 equiv) was dissolved in several milliliters of dry CH_2Cl_2. In a separate flask, dioxane (15 equiv) was dissolved in 30 mL of CH_2Cl_2. The dioxane solution was removed from the drybox and chilled to ice bath temperature. Under a flow of N_2, melted SO_3 (10 equiv) was added via gastight syringe (CAUTION: VERY CORROSIVE MATERIAL), and the solution was stirred for 0.5 h. Still at ice bath temperature, the polymer was added slowly under N_2 flow, and the solution was stirred for 4 h. Aqueous NaOH was added to quench the reaction (added until just basic by pH paper), and then all solvents were removed in vacuo. Extraction by DMSO (to remove insoluble Na_2SO_4 and NaOH), centrifugation, collection of the supernatant, and distillation of DMSO yielded 85−99% product as a light tan powder. Proton NMR was similar to spectra detailed above, except that the olefinic region was depleted. IR data of sulfonated homopolymers are provided below.

Sulfonated (NB)$_{100}$ (sulf-10$_{100}$). Sulfonation was 79% by ^1H NMR olefin integration (versus aliphatic region). IR: ν-(CH_2 bend) 1454 cm^{-1}, ν(SO_2 stretch) 1199, 1043 cm^{-1}.

Sulfonated (NBDPA)$_{25}$ (sulf-1$_{25}$). Sulfonation was 85% by ^{1}H NMR olefin integration (versus aromatic region). IR: ν(CH$_2$ bend) 1450 cm^{-1}, ν(SO$_2$ stretch) 1222, 1112 cm^{-1}.

Sulfonated (NBDPA′)$_{25}$ (sulf-2$_{25}$). Sulfonation was 90% by ^{1}H NMR olefin integration (versus aromatic region). IR: ν(CH$_2$ bend) 1430 cm^{-1}, ν(SO$_2$ stretch) 1221, 1041 cm^{-1}.

Sulfonated (NBPBD)$_{25}$ (sulf-3$_{25}$). Sulfonation was 92% by ^{1}H NMR olefin integration (versus aromatic region and *tert*-butyl peak). IR: ν(CH$_2$ bend) 1483 cm^{-1}, ν(SO$_2$ stretch) 1189, 1041 cm^{-1}.

Sulfonated (NBPTP)$_{50}$ (sulf-4$_{50}$). Sulfonation was 89% by ^{1}H NMR olefin integration (versus aromatic region). IR: ν(CH$_2$ bend) 1425 cm^{-1}, ν(SO$_2$ stretch) 1137, 1055 cm^{-1}.

General Epoxidation Procedure. (NB)$_{100}$ (134 mg, 1.4 mmol by monomer) was dissolved in 10 mL of CHCl$_3$. A 2 equiv sample of m-ClC$_6$H$_4$CO$_3$H (0.86 g of 57%) was added, and the solution was stirred for 10 min. Precipitation from MeOH yielded 159 mg of a white powder (100%). NMR and IR data of the epoxidized polymers are provided below.

Epoxidized (NB)$_{100}$ (epox-10$_{100}$). ^{1}H NMR (CDCl$_3$): δ 2.81 (broad, 1), 2.67 (broad, 1), 2.12 (broad, 1), 1.95 (broad, 3), 1.79 (broad, 2), 1.51 (broad, 1), 1.20 (broad, 1). ^{13}C NMR {^{1}H} (CDCl$_3$): δ 62.19 (epoxide), 61.53 (epoxide), 41.70, 38.88, 35.16, 32.66, 30.74, 28.69. IR: ν(epoxide CH rocking) 1258 cm^{-1}, 8μ; 889 cm^{-1},11 μ; 730 cm^{-1}, 12 μ. GPC: $M_n = 6300 \pm 400$, $M_w/M_n = 1.03 \pm 0.08$.

Epoxidized (NBDPA)$_{50}$ (epox-1$_{50}$). ^{1}H NMR (CDCl$_3$): δ 7.62−7.01 (broad, 17, Ar), 4.51 (broad, 2), 3.42 (broad, 2), 2.58 (broad, 2), 2.36 (broad, 1), 1.73 (broad, 4), 1.19 (broad, 1), 0.81 (broad, 1). ^{13}C NMR {^{1}H} (CDCl$_3$): δ 133.50, 131.56, 129.98, 128.52, 127.84, 127.67, 127.14, 125.22, 123.64, 73.26, 62.01 (broad, epoxide), 42.05 (broad), 33.26 (broad). IR: ν(epoxide CH rocking) 1249 cm^{-1}, 8μ; 902 cm^{-1},11 μ; 732 cm^{-1}, 12 μ.

(NB(OH))$_{100}$. A solution of **epox-10$_{100}$** (127 mg, 1.15 mmol) in 3 mL of THF was cooled to −35 °C and added to a −35 °C solution of LiAlH$_4$ (2.3 mmol, 2 equiv) in THF. The mixture was allowed to come to RT and stirred overnight. After quenching with 10 mL of 1 M NH$_4$Cl(aq) adjusted to pH 5, all solvent was removed in vacuo. The residue was washed with water and MeOH to remove salts. ^{1}H NMR (DMSO): δ 4.14 (broad, 1, C*H*OH), 3.18 (broad, 2, CHOHC*H*$_2$), 1.95 (broad, 2), 1.73 (broad, 2), 1.71−1.12 (broad, 4). ^{13}C NMR {^{1}H} (DMSO): δ 72.70 (*C*HOH), 46.45, 42.998, 39.20, 36.47, 32.04, 26.57. IR: ν (OH stretch) 3448 cm^{-1}; ν (C−O stretch) 1090, 1037 cm^{-1}.

Formation of Thin Films, Layer-by-Layer Adsorption. Silicon slides were cleaned by etching in a chromic acid bath overnight and rinsing with Milli-Q water immediately prior to dipping. Glass slides were cleaned as described in the literature and sonicated prior to use.[38] Both glass and silicon substrates were prepared by depositing five bilayers (100 Å) of poly(allylamine HCl)/poly(methylacrylic acid) using 1×10^{-2} M aqueous solutions at pH 3.5 of each polymer. It was then possible to begin deposition of single- or dual-layer films. Solutions of sulfonated polynorbornene were prepared by first dissolving an appropriate quantity of material into 1 mL of dimethylacetamide. This solution was then diluted to the desired concentration for dipping, typically 1×10^{-4} M. All solutions were adjusted to pH 3.5 with dilute HCl and then filtered through a 0.5 μ syringe filter. No salt was added for homo- and copolymers of **1** and **2**. It was necessary to add 0.1 M NaCl to the polymer solutions containing **4**. A HMS series programmable slide stainer from Carl Zeiss, Inc., was used to automatically dip the substrates in the appropriate solution. Thicknesses were measured by ellipsometry and verified by profilometry. See Table 3 for bilayer thickness data.

Light-Emitting Device Fabrication. Commercially patterned indium tin oxide (ITO) (two 3 mm wide strips, spaced 4 mm apart) on a 1 in. × 1 in. piece of glass was prepared by a previously reported cleaning/sonication procedure.[38] The ITO was prepared with five bilayers (100 Å) of poly(allylamine HCl)/poly(methylacrylic acid) using 1×10^{-2} M aqueous solutions of each polymer. Films of sulfonated polynorbornenes were deposited from 1×10^{-4} M aqueous solutions alternating with 1×10^{-2} M poly(allylamine HCl). All solutions were adjusted to pH 3.5 with dilute HCl before dipping. In a single-layer device, 400 Å of additional material was sequentially adsorbed. For dual-layer devices, 300 Å of one polynorbornene and 400 Å of a second polynorbornene were adsorbed. No salt was added for homo- and copolymers of **1** and **2**. It was necessary to add 0.1 M NaCl to the polymer solutions containing **4**. Four 2000 Å thick aluminum strips, 2 mm wide and spaced 2 mm apart, were laid perpendicular to the ITO by thermal evaporation at 1×10^{-6} Torr. Connection to the electrodes was made with gold wire, generating eight individually addressed "pixels" where the electrodes crossed.

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