Experimental Section

All syntheses were routinely carried out under an argon atmosphere. Starting materials (POPAM dendrimer G2, 3,5-dihydroxybenzyl alcohol, 2-bromomethylnaphthalene, dansyl chloride) were purchased from Aldrich. 3,5-Bis(3′,5′-bis(2″-oxymethylnaphthyl)benzyloxy)benzyl bromide (obtained from precursor **3**) and **2** were synthesized according to literature procedures.[14,15]

1:Cesium carbonate (200 mg) was added to a solution of **2** (50.0 mg, 0.019 mmol) in DMF (10 mL) under argon. 3,5-bis(3′,5′-bis(2″-oxymethylnaphthyl)benzyloxy)benzyl bromide (193.0 mg, 0.19 mmol) in DMF (10 mL) was added to this solution, and the mixture was stirred for seven days, then filtered and the solvent evaporated. The residue was dissolved in CH_2Cl_2, washed with water, saturated $NaHCO_3$ solution, and again with water, then dried over Na_2SO_4 and evaporated. Purification by column chromatography on SiO_2 (63–100 μm) with chloroform/methanol (20:1) as eluent yielded a light-yellow solid in 48% yield, m.p. 103–108 °C, $R_f = 0.08$ (chloroform/methanol 20:1). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.59$ (brs, 24H, CH_2), 2.13 (brs, 32H, NCH_2), 2.47 (brs, 52H, $N(CH_3)_2$ and $N(CH_2)_2N$), 3.35 (s, 16H, SO_2NCH_2), 4.30 (s, 16H, SO_2NCH_2Ar), 4.44 (s, 32H, $ArOCH_2Ar$), 4.97 (s, 64H, $ArOCH_2Naph$), 6.23 (m, 16H, CH_{Ar}), 6.35 (m, 8H, CH_{Ar}), 6.54–6.74 (brm, 56H, 48 CH_{Ar} and 8 CH_{Dans}), 7.22–7.51 (brm, 104H, 96 CH_{Naph} and 8 CH_{Dans}), 7.59–7.87 (bm, 136H, 128 CH_{Naph} and 8 CH_{Dans}), 8.14 (m, 8H, CH_{Dans}), 8.29 ppm (m, 16H, CH_{Dans}); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): $\delta = 25.1$, 44.9, 45.1, 50.1, 50.5, 51.2, 101.6 (2C), 106.6 (2C), 114.9, 119.3, 123.1, 125.3, 125.9, 126.1, 126.2, 127.6, 127.9, 128.2, 129.3, 129.6, 129.9, 130.1, 130.2, 132.9, 133.1, 134.2, 135.0, 138.6, 139.1, 151.6, 159.8, 159.9 ppm; $C_{654}H_{580}N_{22}O_{64}S_8$; $M_w = 10028.24$.

In all experiments, the aqueous phase was buffered at pH 7.0 using a phosphate buffer. Spectroscopic equipment and techniques have been described elsewhere.[8b] The experiments were carried out in air-equilibrated solutions. Fluorescence quantum yields were standardized[16] using naphthalene ($\Phi = 0.23$ in deaerated cyclohexane)[17a] for dendron **3**, quinine sulfate ($\Phi = 0.55$ in 1 N $H_2SO_{4(aq)}$ solution)[17b] for dendrimers **1** and **2**, and fluorescein ($\Phi = 0.90$ in NaOH; 0.01 M)[17c] for eosin **4**.

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[11] Dynamic quenching can be ruled out because of the short lifetime of dansyl fluorescence and the very low concentration (less than 10^{-5} M) of extracted eosin.
[12] The curvature of the plot (Figure 1c, inset) at high eosin concentrations can be related to the fact that each dendrimer can host more than one eosin molecule, so that even at relatively high [eosin]:[**1**] ratios, there are still some "empty" dendrimers, which is in agreement with the unquenched fluorescence lifetime.
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Synthesis of Amphiphilic Conjugated Diblock Oligomers as Molecular Diodes[**]

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Nearly three decades ago Aviram and Ratner proposed that individual molecules of the type donor–spacer–acceptor (D-s-A) placed between two electrodes would act as molecular rectifiers under a suitable bias voltage.[1] Previous attempts to provide experimental proof of molecular rectifiers were complicated by difficulty in establishing reproducible electrical contacts between the metal and single molecules, the junction rectifying effect at the metal–molecule interface due

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to the Schottky barrier and/or salt formation, and the work function difference (however small) between anode and cathode in most configurations of metal/molecules/metal heterostructures. Still, there is uncertainty about the number of active molecules investigated in these microscopic systems.[2–6] More recently, as the drive towards miniaturizing electronic components intensifies, the development and realization of molecular-scale electronic devices based on assemblies of atoms and/or molecules has become an ultimate goal.[7] Various basic device components such as molecular wires, rectifying diodes, field-effect transistors, and single-electron transistors have been demonstrated in a host of materials, ranging from semiconductor and metal nanowires, carbon nanotubes, fullerenes, and small organic molecules to biomolecules.[2–13] However, there is no report on p-n junction molecules that are akin to those in semiconductors but with much more structural versatility. These functional molecular components are crucial to the development of molecular electronics.

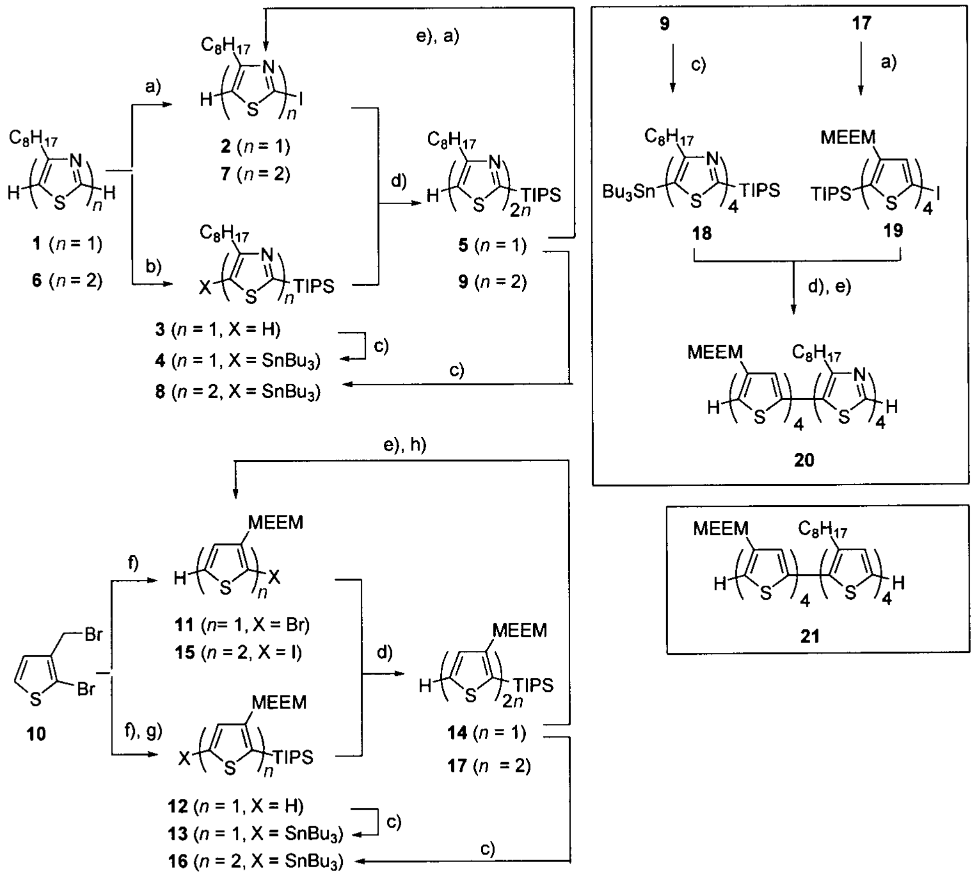
Just like semiconductor materials, the inspiration for p-n junction molecules can be found in semiconducting organic materials, conjugated polymers, and oligomers. These materials have been exploited as key electronic components in the development of a number of technologically important applications such as light-emitting diodes, plastic transistors, photovoltaic solar cells, sensory devices, and diode lasers.[14] These materials have tremendous structural versatility: p-type and n-type polymers with semiconducting properties have been synthesized. We introduce a new and useful concept in designing p-n junction molecules, a relatively simple diblock molecule incorporating two different conjugated blocks with opposite electronic demands. We show that this conjugated diblock molecule indeed exhibits a diodelike rectifying effect.

Polythiophenes (PT) and oligothiophenes (OT) are well-known p-type semiconducting materials, whereas polythiazoles are known to be electron-deficient compounds.[15] Our first target molecule was a regioregular, head-to-tail coupled diblock co-oligomer comprising an electron-rich oligo(3-alkylthiophene) as the donor block and an electron-poor oligo(4-alkylthiazole) as the acceptor block. Two different alkyl side groups with contrasting hydrophilicity/hydrophobicity were selectively incorporated in the two blocks. The surfactant-like amphiphilic conjugated diblock oligomer can be manipulated by the Langmuir–Blodgett (LB) technique at the air–water interface.

The synthetic approach to the diblock co-oligomer is shown in Scheme 1. The diblock co-oligomer **20** was synthesized by a Stille coupling between **18** and **19**, which were both obtained almost quantitatively from the corresponding precursors **9** and **17**, respectively. It is noteworthy that electrophilic iodination of **17** proceeded with complete chemo- and regioselectivity at the unsubstituted *α* position. After the Stille reaction was completed, in situ desilylation by addition of excess TBAF afforded the amphiphilic head-to-tail coupled oligothiophene-oligothiazole diblock system **20**.

For the purpose of comparison with the p-n junction molecules, a reference compound, amphiphilic octathiophene **21** with the same alkyl side chains, was also synthesized (Scheme 1). This reference compound is almost an exact replica of the diblock molecule except for the replacement of the nitrogen atoms on the electronegative thiazole ring by methine groups.

The amphiphilic conjugated diblock molecule was oriented at the air–water interface by the Langmuir–Blodgett technique, with the donor part adjacent to the water subphase and the acceptor block away from it. A typical pressure–area (*P*–*A*) isotherm of the diblock molecules is shown in



Scheme 1. Synthetic approach to diblock co-oligomer **20** and reference compound **21**. Reagents and conditions: a) LDA, THF, −78 °C, then I_2; b) LDA, THF, −78 °C, then TIPSOTf) ; c) *n*BuLi, TMEDA, THF, −78 °C, then Bu_3SnCl; d) 2.5 mol% $[Pd_2(dba)_3]$, 20 mol% PPh_3, 50 mol% Cu_2O, DMF, 115 °C; e) TBAF, THF, RT. f) NaH, diethyleneglycol monomethyl ether, THF, 0 °C; g) *n*BuLi, Et_2O, −78 °C, then TIPSOTf; h) NIS, $CHCl_3$/HOAc. LDA = lithium diisopropylamide, TIPSOTf = triisopropylsilyl trifluoromethanesulfonate, TMEDA = tetramethylethylenediamine, dba = dibenzylidene acetone, TBAF = tetrabutylammonium fluoride, NIS = *N*-iodosuccinimide; MEEM = methoxyethoxyethoxymethyl.

Figure 1a. As the molecular monolayer is compressed, the surface pressure increases slowly in the region between 230 and 130 Å^{2}mol^{-1}, followed by a kink at $P\sim14$ mN m^{-1} ($A\sim130$ Å^{2}mol^{-1}), which is tentatively assigned as a phase transition from the initially flat-lying conformation of the monolayer to an increasingly more perpendicular orientation. This is followed by a monotonic increase in surface pressure with a characteristically steeper slope (solid-state region). Close packing of the molecules continues until collapse of the monolayer was observed at approximately 80 Å^{2}mol^{-1}. Extrapolation of the linear portion of the solid-state region of the isotherm to zero surface pressure gives an estimate of the area ideally occupied by an isolated molecule (112 Å^2) at infinite dilution. This value is in fairly good agreement with that determined (115 Å^2) from the space-filling model of the AM1-optimized geometry in the gas phase (Figure 1b). The Langmuir monolayer was subsequently transferred onto glass, silicon wafer, or hydrophilic gold substrates with a transfer ratio of 1.0 ± 0.05. The LB monolayer was fully characterized by optical ellipsometry and UV/Vis spectroscopy. After careful drying of the sample, the electrical properties of the monolayer were investigated by using scanning tunneling microscope (STM) and scanning tunneling spectroscopy (STS).

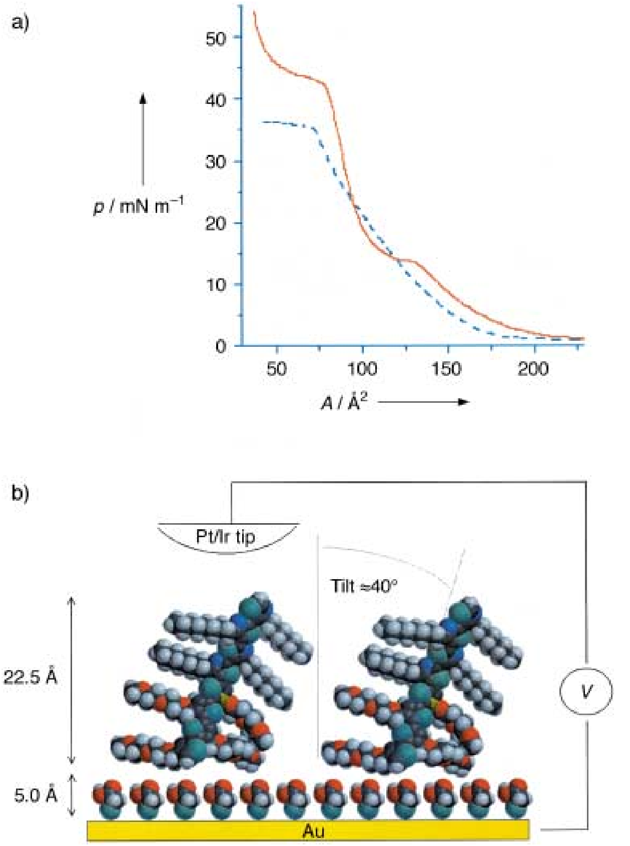


Figure 1. a) Surface pressure–area isotherms of conjugated diblock oligomer **20** (red solid line) and the reference model oligomer **21** (blue dashed line). Monolayers of **20** and **21** were transferred to a hydrophilic gold substrate at 35 mN m^{-1} and 28 mN m^{-1}, respectively, 5 mN m^{-1} below collapse pressure. b) Plausible orientation of a LB monolayer of diblock molecules on a hydrophilic gold surface modified with a thioglycolic acid monolayer.

After a stable STM scan was obtained, the feedback loop for the STM control was briefly interrupted. The Pt/Ir STM tip (grounded to zero potential) was then held at a constant position above the film; the tip–sample separation was determined by the impedance used, which typically ranged from 60 to 300 GΩ in our experiments. High impedance was used throughout the STM experiment to avoid large fluctuations in tip movement and prevent mechanical damage to the sample surface. The voltage was then ramped from positive to negative bias while the current tunneling through both the air gap and the molecule was recorded. These current–voltage (I–V) measurements were performed at various setpoint tunnel currents in order to minimize artifacts resulting from strong tip–sample interactions. As can be seen from Figure 2a, pronounced asymmetric I–V behavior was consistently observed at various setpoint tunneling currents, indicative of intrinsic molecular p-n junction character in the diblock molecule. In the STM convention, the direction of easy electron flow corresponds to electron tunneling from the STM

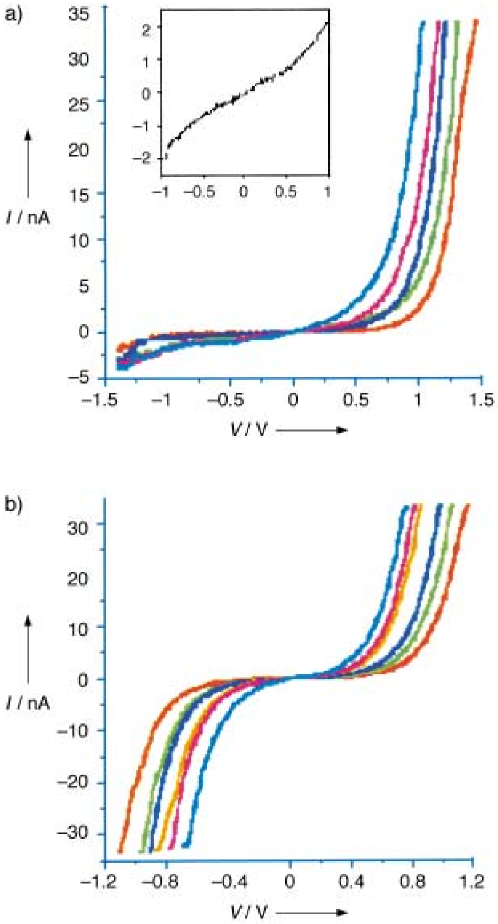


Figure 2. a) Current–voltage plots for a LB monolayer of diblock oligomer **20** measured with the tunneling current setpoint at different values ($I_{set}=2$ (red), 4 (green), 6 (blue), 8 (purple), 10 pA (light blue)) and a bias voltage of +600 mV. The inset shows the I–V characteristics of a gold surface modified with a thioglycolic acid monolayer. b) I–V curves for a LB monolayer of the reference oligomer **21** measured with the tunneling current setpoints at different values ($I_{set}=1$ (red), 2 (green), 4 (blue), 6 (orange), 8 (purple), 10 pA (light blue)) and a bias voltage of +600 mV.

tip to the acceptor part (oligothiazole) of the sample. The average turn-on voltage in the positive sample bias region is about 0.65–0.75 eV, whereas only small current signals were recorded in the reverse bias. The rectification ratio remains small in the low-bias regimes but increases gradually to about 18 at a bipolar bias of 1.0 V. The slight differences in turn-on voltages at various current setpoints result mainly from the difference in tunneling gap resistances between the tip and molecules, as was previously observed.[16] The differential conductance (dI/dV) was obtained from the data in Figure 2a, which is roughly proportional to the local density of states (LDOS) of the sample. It is a good measure of the rectifying behavior of the diblock molecules. Large asymmetry is observed in the corresponding conductance versus voltage spectra with threshold voltages at a bipolar bias of about 0.7 V (Figure 3a). It is clear that the direction of easy electron flow is from the tip to the thiazole block and then to the thiophene block. This is consistent with the fact that the thiophene block is electron donating and the thiazole block is electron accepting. In the excited state the thiazole block would bear negative charge, the thiophene block positive charge, and the electrons would flow from the thiazole to the thiophene block.

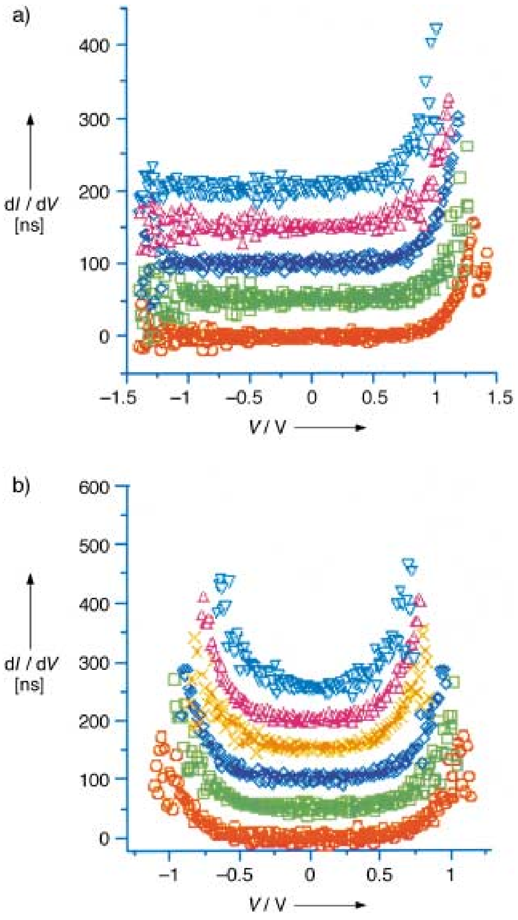


Figure 3. a) Differential conductance (dI/dV) of a LB monolayer of diblock oligomer **20** obtained from the data shown in Figure 2a ($I_{set} = 2$ (red), 4 (green), 6 (blue), 8 (purple), 10 pA (light blue)). Each curve has been offset in the vertical direction for clarity. b) Differential conductance (dI/dV) of a LB monolayer of reference oligomer **21** obtained from the data shown in Figure 2b ($I_{set} = 1$ (red), 2 (green), 4 (blue), 6 (orange), 8 (purple), 10 pA (light blue)). Each curve has been offset in the vertical direction for clarity.

Many rectifying diodes based on molecular systems have been reported previously, but few are truly of molecular origin.[2–6] In order to exclude contributions to the observed I–V asymmetry from other effects such as molecule interfacial effect between the LB monolayer and the underlying thioglycolic acid monolayer, the difference in the work functions of the electrodes (Au substrate and Pt/Ir tip), or other poorly controlled experimental parameters, control LB films of the reference molecule were prepared and subjected to STS studies under the same experimental conditions as described above. The spectroscopic measurements revealed only symmetric I–V behavior at various setpoint currents (Figure 2b). The corresponding tunneling differential conductance clearly shows the molecular wire behavior, again with threshold turn-on voltages depending upon the preset tunneling gap resistance (Figure 3b). The electron-transfer mechanism (tunneling or through-bond transfer) for the rectifying effect observed in our diblock system is not completely clear at this stage; further theoretical treatment to clarify this point is in progress.

In summary, an amphiphilic conjugated diblock oligomer exhibiting a molecular p-n junction has been synthesized and its rectification effect demonstrated. The synthetic approach developed is rather general for coupling heterocycles and should lead to the synthesis of other p-n junction molecules. The clear distinction between the I–V behaviors for the diblock and the reference molecules in the present study constitutes concrete evidence for the molecular origin of the observed rectifying effect.[17] The rectifying conjugated molecule described in this report provides an easy entry to molecular-scale electronic components for the design of logic circuits. Many variations in structure and electronic properties of this diblock system can be envisaged, and optimizations of these features are the subject of ongoing efforts.

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