J. Am. Chem. Soc. **1998,** *120,* 13453−13460

Adsorption of Carboxyl-Terminated Dithiophene and Terthiophene Molecules on ITO Electrodes and Their Electrochemical Coupling to Polymer Layers. The Influence of Molecular Geometry

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Received July 13, 1998

Abstract: Carboxypentyl and carboxyhexyl bithiophenes and terthiophenes, in which the oligothiophene tail is either perpendicularly or linearly linked to the tethering carboxyalkyl chain, were adsorbed on ITO electrodes. The obtained stable monolayers are anodically oxidized in acetonitrile to produce polymer layers (storing a reversible charge of 15 μC cm^{-2}) in the case of perpendicular adsorbates whereas linear bithiophene and terthiophene are able to couple only with oligothiophenes in solution. Electrochemical and UV−vis spectroscopic analysis indicate that the polymer layers are in fact constituted by thiophene hexamers. The adsorbed linear terthiophene may be coupled with the terthiophene itself in solution to produce a one-end surface-grafted sexithiophene monolayer (reversible charge 40 μC cm^{-2}), whereas a two-end surface-grafted sexithiophene with the same coverage is produced by adsorption of the α-coupled terthiophene. The one-end and two-end grafted sexithiophene monolayers display different electrochemical and spectral patterns. Chronoamperometry and cyclic voltammetry show that the adsorbed linear bithiophene may be oxidatively coupled with 2,2′-bithiophene in solution to produce surface-anchored polythiophene chains.

1. Introduction

Organized mono- and multilayers of polyconjugated polymers or oligomers have recently attracted much attention for their possible use in many different fields. The conjugated π-electrons form a one-dimensional electron system with electrical and optical properties which are strongly influenced by interchain interactions. In particular oligothiophenes, and specifically sexithiophene,[1] have shown high ability in LEDs and FETs, and regularly alkylated oligothiophenes[2] display large 3rd order hyperpolarizabilities useful for NLO devices. Superlattice systems and multiple quantum wells structures are interesting in high-performance LED. Also they are attractive in the use for photovoltaic conversion due to the highly efficient charge separation expected from these segregated structures.

During the past five years self-assembly (SA), a most widely used method for the construction of organized supramolecular structures, has grown to an impressive level. In the field of conducting polymers an appreciable number of papers dealing with SA on electrode surfaces have recently appeared.[3−14] SA of alkanethiols bearing 1- and 3-substituted pyrroles has been reported.[3−5] Coupling of the pyrrole heads to a conducting layer was not possible with the 3-substituted pyrrole[4] but was produced with the *N*-substituted one.[3] More recently a disulfide bearing *N*-pyrroles via long linear alkyl spacers (bis(ω-*N*-(pyrrolyl)-*n*-undecyl) disulfide) and self-assembled over a gold electrode did not polymerize laterally to form polymer monolayers but coupled with pyrrole to a surface-bound polypyrrole network.[7] Similar improved pyrrole polymerization was obtained on cuprate supercondutors modified with a SA monolayer of *N*-(3-aminopropyl)pyrrole.[9] Considering aniline heads, a report on the polymerization of *o*-mercaptoaniline adsorbed on gold has appeared[6] though the electroactive layer formed by anodization of the adsorbed monomer monolayer is more likely constituted by dimers, as shown by the anodic oxidation of 4-aminothiophenol monolayers on gold.[8] Considering thiophene-based polymers, we recently produced adsorption of ferrocenylalkylbithiophenes and their anodic coupling to polythiophene layers over the electrode surface.[10] Previously reported is dithiophene sulfide on gold.[11] SA of thiol-terminated terthiophenes recently has been investigated with the terthiophene moiety sulfide linked to the surface either immediately[12] or via a short (hexyl[13]) or long (undecyl[12]) alkyl chain. In the case of the hexyl-terthiophene,[13] anodic coupling of the oligothiophene chains makes them dimerize laterally via β-linkages. Finally, tetrathiophene diphosphonate has been alternated with zirconium ions in regular multilayers[14] though their electroactivity was not tested.

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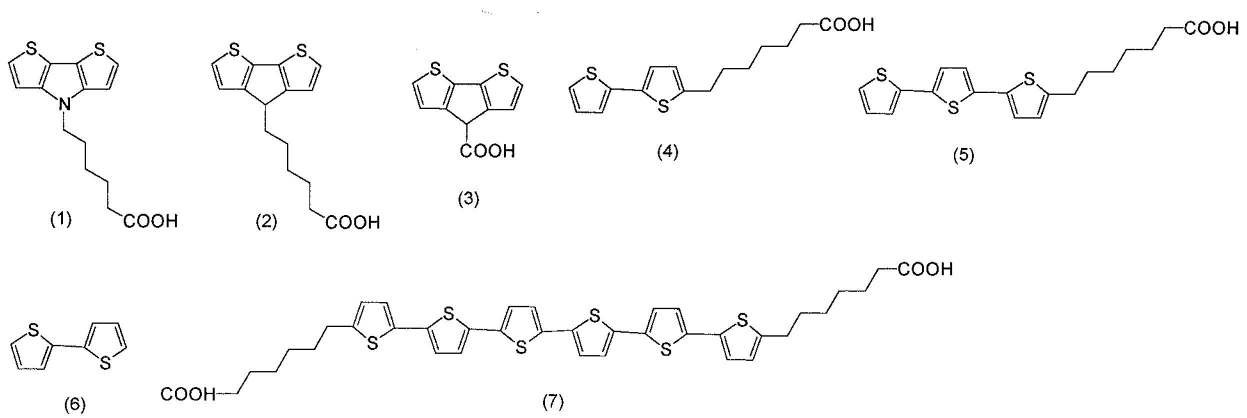
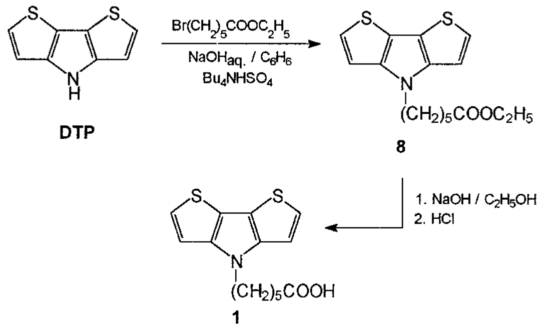
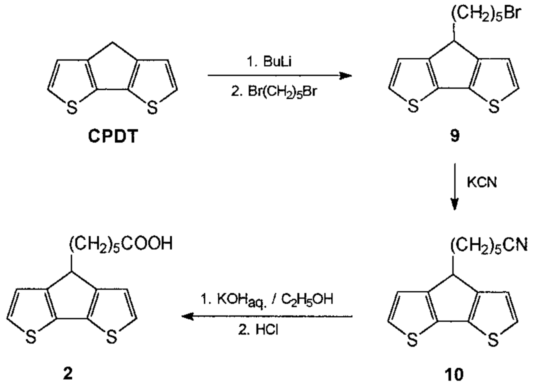
Chart 1. Formulas of Investigated Compounds



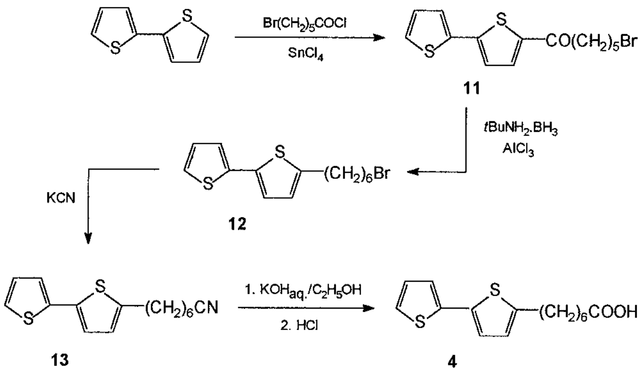
Scheme 1. Synthetic Access to Compound **1**



Scheme 2. Synthetic Access to Compound **2**



Scheme 3. Synthetic Access to Compound **4**



From this survey it appears that the molecular structural requirements for the formation of a surface-bound polyconjugated polymer network are still largely unclear. For this reason we have undertaken an investigation on the adsorption on ITO electrodes of a series of suitably designed bithiophene and terthiophene molecules terminated with the carboxylic moiety. The choice of ITO as the substrate and of carboxyl group as the anchoring head was made to overcome some problems arising with the most popular SA from alkanethiols on gold electrodes.[15] On one hand thiols are oxidatively unstable and often problematic[11] and on the other ITO electrodes may be interesting due to the combination of conductivity and transparency of the substrate. We have previously investigated the adsorption of variously substituted ferrocenes on ITO with the result that ferrocenylheptanoic acid is most able to SA on this kind of electrode substrate due to the SA driving ability of the linear alkyl chain.[16] Most important is the fact that the carboxyhexyl heads form on the ITO surface a layer packed loosely enough that redox processes at the tails are not prevented. As a matter of fact, recently it has been found that in azo-substituted alkane thiols[17] or in the previously mentioned undecylthiol-terthiophene,[12] a very close packing blocks the electroactivity of the tails.

The bithiophene and terthiophene moieties were preferred to thiophene to keep the oxidation potential low enough to prevent overoxidation, which is the most competitive pathway to coupling. Finally, the shape of the adsorbate was modulated to make the axis of the bithiophene moiety parallel or perpendicular to the substrate plane. This was produced (Chart 1) with the T-shaped molecules **1**−**3** for the parallel alignment whereas the linear molecules **4** and **5** were selected for the perpendicular alignment.

This paper reports on the adsorption of these molecules on ITO electrodes and their anodic oxidation to polymer layers.

2. Results and Discussion

2.1. Synthesis of the Monomers. The synthetic route we followed for the preparation of compound **1** is depicted in Scheme 1. DTP was reacted with ethyl 6-bromohexanoate under phase-transfer catalysis conditions in a mixture of benzene and 50% aqueous NaOH with Bu_4NHSO_4 as catalyst. Hydrolysis of the resulting ester **8** afforded compound **1**.

Compound **2** was prepared from CPDT (Scheme 2) through reaction with BuLi, followed by alkylation with 2,5-dibromopentane, nucleophilic substitution with KCN, and hydrolysis of the nitrile **10** under basic conditions.

Schemes 3 and 4 show the synthetic accesses to compounds **4** and **5**, respectively. Compound **6** was acylated with 6-bro-

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Scheme 4. Synthetic Access to Compound **5**

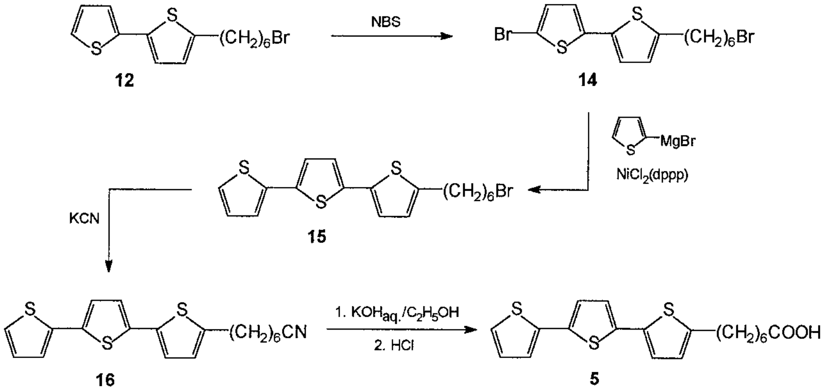

Table 1. Electrochemical and UV−Vis Absorption Data for the Investigated Compounds (Oxidation Peak Potential E_p and Maximum Absorption λ_m) and Their Coupling Products (Redox Potential $E°$ and Maximum Absorption λ_p)

monomer	E_p/V	$E°$/V	$\lambda_m{}^a$/nm	λ_p/nm
1	0.56	−0.2/0.2	295	505
2	0.67	0.0/0.3	311	580
3	0.80	0.4	307	490
4	0.80	0.7	310	340
5	0.65	0.65	360	430

[a] In acetonitrile solution.

mohexanoyl chloride under Friedel-Craft conditions, and the resulting ketone was reduced with $BuNH_2{\cdot}BH_3$ in the presence of $AlCl_3$. Nucleophilic substitution with KCN of compound **12**, followed by hydrolysis of the resulting nitrile **13**, afforded compound **4**.

Compound **5** was analogously synthesized starting from the bromoderivative **15**, which in its turn was obtained by reaction of **14** with 2-thienylmagnesium bromide in the presence of $NiCl_2$(dppp).

2.2. Anodic Coupling of Compounds. Before considering the formation of adsorbed monolayers and their anodic coupling, we report the anodic coupling process of the monomers in solution and the characterization of the products.

2.2.1. Anodic Coupling of 1−3. Oxidation of dithienopyrrole **1** and cyclopentadithiophenes **2** and **3** occurs at peak potentials E_p given in Table 1. Oxidation couples the monomers to polymers displaying electrochemical, optical, and conduction characteristics of polythiophenes.[18−20] Cyclic voltammetry CV on these carboxyl-functionalized homologues has confirmed the expected polymerization pattern. The electrochemical and optical characteristics of the polymers are given in Table 1. Poly(**1**) behaves like poly(dithienopyrrole) in both the CV and the electronic spectrum;[18] poly(**2**) is similar to poly(cyclopentadithiophene) with a hexyl chain in position 4;[19] poly(**3**) behaves like unsubstituted poly(cyclopentadithiophene)[20] but for the 0.3 V higher redox potential, due to the electron-withdrawing carboxyl group directly linked to position 4.

2.2.2. Anodic Coupling of 4 and 5. In these cases, in which the oligomer is one-end capped, oxidation is expected to result in α-coupling to dimer. It will be shown that this is indeed the case of compound **5** but not of compound **4**.

Compound **4** is oxidized at $E_p = 0.8$ V with a number of apparently exchanged electrons $n_{app} = 2.7$ e. This value is higher than the value of 2 expected for coupling to dimer and oxidation of the latter to the dication. Furthermore, the backward CV scan shows a low reductive current at ca. 0.6 V in which only 5% of the oxidative charge is recovered (vs the theoretical value of 50%).

CV cycling produces a deposit on the electrode that unexpectedly is insoluble in any solvent. Moreover, the material displays a conjugation lower than that of a thiophene tetramer, since it is reversibly oxidized at a potential ($E° = 0.7$ V) higher than that (0.5 V) found for the methyl end-capped thiophene tetramer Me_2T_4.[21] For the same reason its UV−visible spectrum displays a maximum absorption at 340 nm vs 390 and 400 nm for the thiophene tetramers T_4[22] and Me_2T_4,[21] respectively. Finally, the IR spectrum shows that the out-of-plane CH bending bands of the thiophene rings[23] are too weak and displays a new strong band at 1100 cm^{-1}, attributable to C−O−C stretching. These changes, which involve the β-positions of the thiophene rings, suggest degradation and cross-coupling, which latter may account for the insolubility of the material.

The conclusion of all the collected results is that, although α-dimerization of compound **4** may occur, the dimer is severely degraded in reactions following its oxidation.

At difference with bithiophene **4**, oxidation of terthiophene **5** results in an efficient α-dimerization. Repetitive CV of a solution of **5** up to the oxidation peak at 0.65 V ($n_{app} = 2$) displays the progressive deposition of the product of coupling. The charge recovered in the backward scan is ca. 30% of the charge passed in the forward scan, which is much higher than for **4** and closer to the theoretical ratio of 50%.

The film is oxidized in compound-free solution showing the hysteretic CV typical of sexithiophene (Figure 1) with a two-electron oxidation at 0.75 V and two one-electron reduction peaks at 0.66 and 0.34 V. The latter values are comparable with the two subsequent one-electron reduction processes of the dication form of methyl end-capped sexithiophene Me_2T_6.[24]

The identification of the product as the α-dimerized **5**, bis(carboxyhexyl)sexithiophene **7** (see Chart 1), has been confirmed by the UV−vis spectrum (maximum absorption at 430 nm, the same as T_6[22]) and the MALDI mass spectrum (*m*/*z* 751, $[M + H]^+$ ion). In perfect agreement with the suggested formulation, the IR spectrum is practically identical with that of the monomer but for the disappearance of the band at 690 cm^{-1}, due to the

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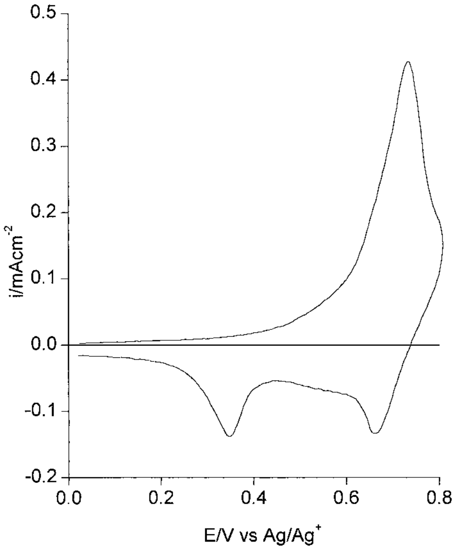


Figure 1. CV of **7** deposited in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.1 V s^{-1}. Reversible charge: 0.5 mC cm^{-2}.

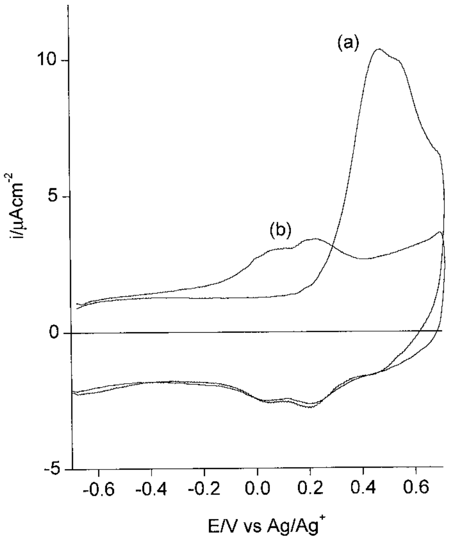


Figure 2. CV of **1** monolayer on ITO in acetonitrile + 0.1 M Bu_4NClO_4: (a) first scan; (b) last scan. Scan rate: 0.1 V s^{-1}.

out-of-plane bending modes of the hydrogen atoms at the terminal thiophene rings, and the presence of a single strong band at 790 cm^{-1}, due to the corresponding mode of the inner thiophene rings.[23]

Compound **7** is insoluble in the usual organic solvents but slightly soluble (ca. 2×10^{-6} M) in boiling chlorobenzene and appreciably in pyridine ($>10^{-5}$ M).

2.3. Adsorption and Oxidation of Compounds. As recently observed for $Fc(CH_2)_6COOH$[16] and $Fc(CH_2)_{11}COOH$[25] on ITO, the adsorption process is favored by a nonpolar solvent (isooctane) with a low content (5%) of a polar solvent (ethanol) to allow solubility. The adsorbed layers of compounds **1**−**4** were produced by dipping the ITO electrode in a 10^{-3} M solution of the suitable compound in ethanol:hexane 5:95 and subsequent washing with acetonitrile and drying. Due to its low solubility in either ethanol or hexane, **5** was similarly adsorbed from acetonitrile solution.

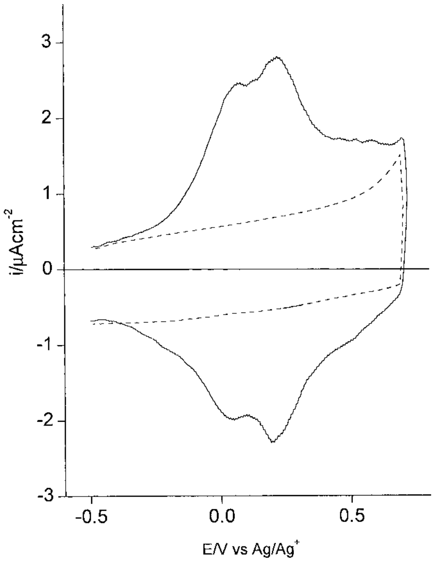
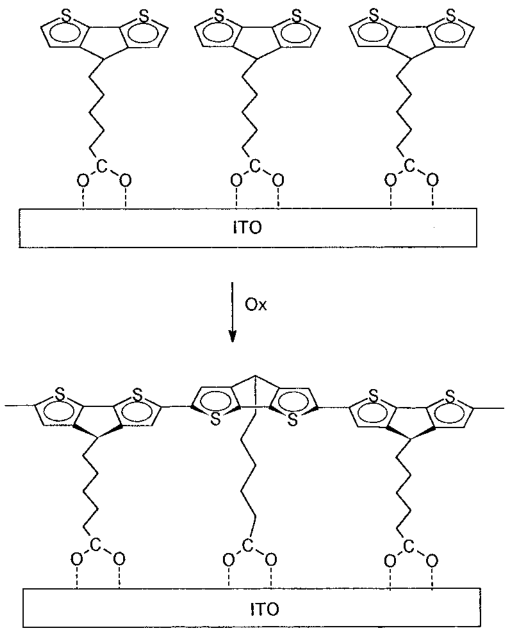


Figure 3. CV of poly(**1**) monolayer on ITO in acetonitrile + 0.1 M Bu_4NClO_4 (dashed line: bare electrode). Scan rate: 0.1 V s^{-1}. Reversible charge: 15 μC cm^{-2}.

Scheme 5. Oxidation of **2** Monolayer on ITO



Oxidative CV in compound-free acetonitrile solution shows the response of the adsorbed layer, as reported below for the individual adsorbates. On the basis of previous results from carboxyl-substituted ferrocenes,[16] a saturative coverage of 1×10^{-10} mol cm^{-2} is obtained up from 1 min of dipping. The adsorbed layers are sufficiently stable in acetonitrile since they do not give any sign of dissolution after 5 min of dipping with stirring.

The adsorbed layers of **1** and **2** show a CV irreversible peak (a in Figure 2) at E_p = 0.5 and 0.65 V, respectively, which involves an oxidation charge of 30 μC cm^{-2}. Further CV shows the response of the polymer (b in Figure 2) which is fully developed after a single CV cycle at 0.1 V s^{-1}. The redox process is twin (Figure 3) and occurs at $E°$ = 0.04 and 0.20 V for **1** and $E°$ = 0.15 and 0.30 V for **2** with the involvement of a reversible charge of 15 μC cm^{-2} for both. Thus in these cases coupling to polymer occurs, as depicted in Scheme 5. The poly(**1**) and poly(**2**) layers are insoluble in both $CHCl_3$ and water;

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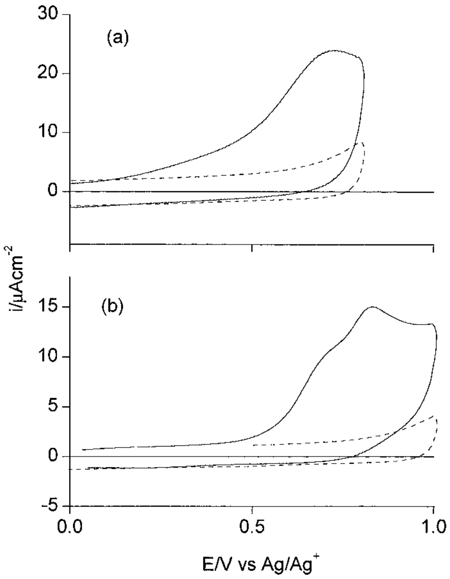

Figure 4. CV of (a) **3** and (b) **4** monolayers on ITO in acetonitrile + 0.1 M Bu_4NClO_4. Scan rate: 0.1 V s^{-1}.

they may be instantaneously removed by immersion in acetonitrile + 1.0 M ammonia.

Also the adsorbed layer of **3** shows a CV irreversible peak (Figure 4a) at $E_p = 0.7$ V, which involves a charge of ca. 40 μC cm^{-2}, but at difference from **1** and **2**, further CV does not show any sign of polymer formation.

The adsorbed layers of **4** and **5** show a CV irreversible peak (Figure 4b) at $E_p = 0.8$ and 0.65 V, respectively. Further CV does not show the response of the α-coupled dimer, which in this case is not surprising given the expected parallel alignment of the oligothiophene moieties in the layer. Irreversible multielectron overoxidation processes may explain the higher charge involved (ca. 60 μC cm^{-2}, ca. twice the charge used for **1** and **2**).

All monomer (and eventually polymer) layers are open to electrolyte permeation, as shown by the capacitive currents in the CVs (Figures 3 and 4), which are unchanged from those of the bare ITO electrode (dashed curves).

2.4. Characterization of Poly(1) and Poly(2) Layers. The polymerized layers of **1** and **2** display their CV at potentials ca. 0.1 V higher than those of the corresponding bulk polymers. This result is the first indication that the layers are oligomeric in nature. As further support the separation of the two redox potentials $\Delta E°$ (ca. 0.15 V) is comparable with that of sexithiophenes in solution.[26] It must also be observed that $\Delta E°$ is lower than in the bulk polymers (0.3−0.4 V), in which π-dimerization is operating.[27] The absence of π-dimerization between one-electron oxidized oligothiophenes is obvious in monolayers of flat noninteracting adsorbates.

The UV−visible spectra of both poly(**1**) and poly(**2**) layers display a maximum absorption at $\lambda_{max} = 460$ nm. A comparison with the bulk polymers, which display their maxima at 500−600 nm (Table 1), confirms the oligomeric nature of the layers. More precisely, from λ_{max} of a long-chain poly(**2**) (600 nm)[19] and of the monomer (316 nm), using the linear relationship between the inverse of λ_{max} and the inverse of the degree of polymerization n[28] we interpolate for the layers a value of $n = 3$ (six thiophene rings). It must be remarked that a low degree of polymerization is commonly found when polymer growth is kinetically restricted[29] or limited by the distance the tethered monomeric ends can move.[30]

The reversible oxidation charge associated with the polymer layers (15 μC cm^{-2}) is comparable with that (10 μC cm^{-2}) recorded with $Fc(CH_2)_6COOH$ adsorbed on ITO.[16] Given that on one hand the steric requirements of the bithiophene moiety are higher than those of ferrocene and that on the other sexithiophene is reversibly oxidized in two one-electron processes,[31] the experimental value for the polymer layers indicates that the yield of the coupling process is considerably high.

Coupling could in principle produce syn- or anti-coupled monomeric units in the polymers. In practice the syn structure is only speculative[32] whereas a large body of evidence favors the anti structure.[33] We believe that this is also true in our case so that it is required that the bithiophenes bend around the flexible alkyl chains to allow this conformation. Within this frame the absence of polymerization from adsorbed **3** may be attributed to the rigid connection to the surface (the long and flexible alkyl chain in **1** and **2** is absent), which prevents a correct alignment of the bithiophene moieties.

2.5. Coupling of Dissolved 5 on ITO-Adsorbed 5. The absence of α-coupling of adsorbed **4** and **5** is the result of the reciprocally parallel disposition of the oligothiophene tails which does not allow α-coupling with neighbor chains. As a consequence the tail undergoes oxidative demolition instead. In fact a recent paper by Garnier[13] reports that SA layers on platinum of the **5**-homologue thiol-terminated molecule do in fact produce surface-bound dimers via reciprocal β-coupling. We believe that the difference between our results and those obtained by Garnier is due to the fact that the layers formed by carboxyl-terminated molecules on ITO are not as compact as those formed by alkyl sulfides on platinum, so that in our case the tail undergoes oxidative demolition rather than cross-coupling.

It is in any case expected that coupling of adsorbed **4** and **5** with thiophenes coming from the solution is favored (Scheme 6). This has been checked with the use of the same oligothiophenes so that coupling is limited to the first coupling (dimerization) step.

4-modified ITO did not give significant results with dissolved **4**, which is attributable to the instability to overoxidation of the produced tetrathiophene.[21] Due to the stability of the oxidized forms of the dimer of **5** (compound **7**), the adsorbed **5** layer is on the contrary suitable for a complete reaction with itself from the solution to yield a monolayer. We found that a suitable concentration of **5** is 2×10^{-5} M. Under this condition a single sweep at 0.1 V s^{-1} does not produce a significant amount of **7** on bare ITO but the formation of a substantial layer of **7** on **5**-modified ITO. Concentrations lower than 2×10^{-5} M produce layers with lower coverages; concentrations higher but between ca. 2×10^{-5} and 4×10^{-5} M yield the same layers, whereas even higher concentrations start to produce precipitation of the bulk material.

The coupling process gives the expected spectral changes (Figure 5a) from the band at 360 nm of **5** to that of **7** intensity enhanced at 430 nm. The CV (Figure 6a) shows an oxidation

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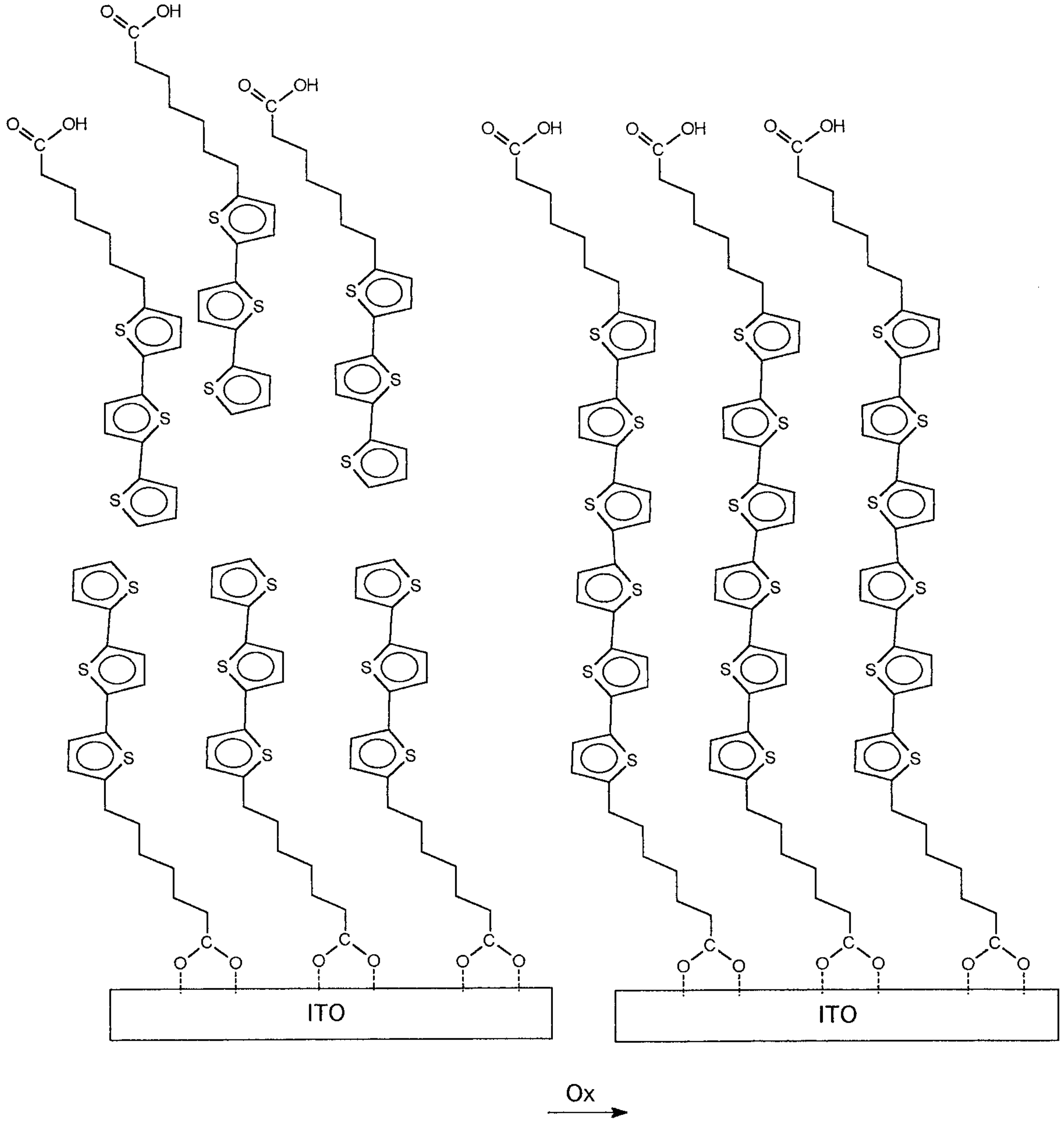
Scheme 6. Oxidation of **5** Monolayer on ITO with **5** in Solution



peak at 0.77 V and a reduction peak at 0.31 V in the reverse scan, i.e., with a high separation indicative of strong hysteretic behavior.

Since we evaluated for **5** a diffusion coefficient of ca. 2 × 10^{-5} cm^2 s^{-1}, in the time window of the CV (ca. 1 s at 0.1 V s^{-1}) the diffusion path is 0.5 × 10^{-2} cm (50 μm), which matches exactly the thickness of the solution, close to the electrode, containing an amount of **5** equal to that adsorbed on the surface (1 × 10^{-10} mol cm^{-2}). This calculation shows that coupling of adsorbed **5** with dissolved **5** is controlled by diffusion of **5**: at a scan rate of 0.1 V s^{-1} concentrations lower than 2 × 10^{-5} M produce less surface dimer than the maximum possible whereas higher concentrations produce a dimer excess in the solution close to the surface.

The reversible charge of the sexithiophene monolayer is 40 μC cm^{-2}, 20 μC cm^{-2} for a one-electron process. The two-electron value, comparable with the one-electron value of 45 μC cm^{-2} for ferrocene and the two-electron value of 34 μC cm^{-2} for β-dimerized terthiophene layers,[13] indicates a high yield of coupling.

2.6. End-On and Flat ITO-Adsorbed 7. A monolayer of sexithiophene **7**, besides coupling from **5** on **5**-modified ITO (**7A**), may also be produced from direct adsorption of **7** (**7B**). After 1−2 min of dipping in a hot chlorobenzene solution of **7** (prepared from bulk anodic coupling of **5**, see before), followed by washing in hot chlorobenzene, the ITO displays the CV of adsorbed **7** as a couple of reversible processes at 0.45 and 0.75 V (Figure 6b) with a reversible charge of ca. 40 μC cm^{-2}. The film is stable to dissolution even in boiling chlorobenzene. Though the reversible charge of **7B** is the same as that of **7A**, the CV does not display hysteresis. Furthermore, the UV−vis spectrum of **7B** (Figure 5b) is markedly different from that of **7A** since the adsorption is hypsochromically shifted from 430 to 390 nm with an intensity ca. 4 times enhanced.

These differences may be accounted for by a perpendicular arrangement of the molecules end-on adsorbed on the ITO surface in **7A** and by their flat planar disposition with anchoring of both carboxyl ends in **7B**. The hysteresis in the CV of **7A** indicates a strong interaction between the linear chains, which is obviously absent in **7B**. In **7B** the nonzero angle formed by

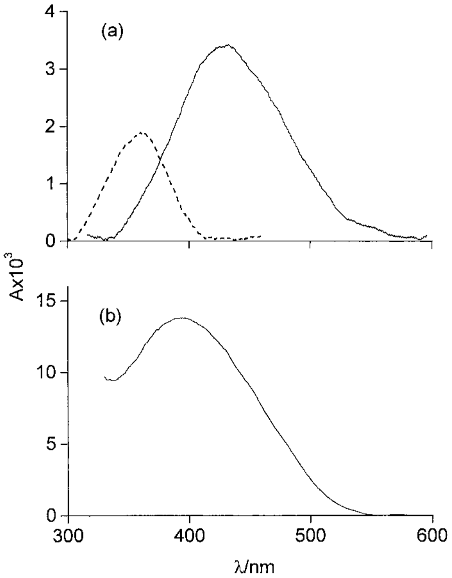


Figure 5. UV−vis spectra of (a) **5** monolayer on ITO (- - -) before and (—) after coupling with **5** in solution (**7A** monolayer); (b) **7** monolayer on ITO from chlorobenzene solution of **7** (**7B** monolayer).

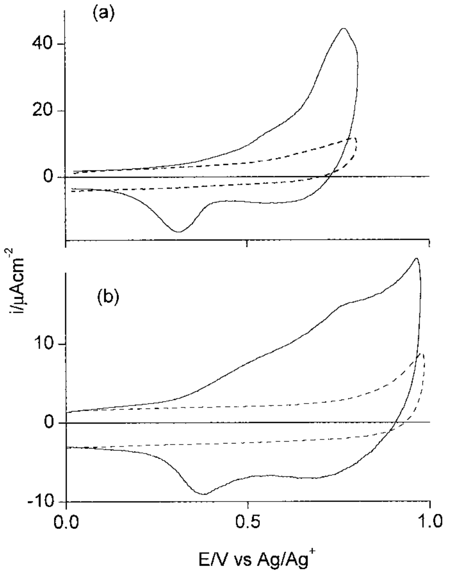


Figure 6. CV in acetonitrile + 0.1 M Bu_4NClO_4 of **7** monolayer (a) produced from coupling on **5**-modified ITO (**7A** monolayer) and (b) adsorbed on ITO from a chlorobenzene solution of **7** (**7B** monolayer). Scan rate: 0.1 V s^{-1}. Reversible charge: 40 μC cm^{-2}.

the carboxyl ends and the surface[34] and the short alkyl chains do not allow a fully coplanar disposition of the thiophene rings, which causes the observed hypsochromic shift of the maximum absorption. The enhancement of absorption from **7A** to **7B** is also in line with a perpendicular (**7A**) and parallel (**7B**) disposition of the molecules with respect to the ITO surface. X-ray analysis[35] has confirmed the suggested order in these monolayers. It must be recalled that a similar optical behavior has been previously observed for oriented *p*-sexiphenylene thin films.[36]

The presence of two carboxyl ends was expected to make the adsorbed molecules in **7B** more strongly bound and the layer less spatially extended in comparison with **7A**. This recently has been shown[37] for the adsorption of benzoic and terephthalic acid on TiO_2, with a 100 higher adsorption constant (2×10^5 M^{-1}) and ca. twice lower coverage (6×10^{-11} mol cm^{-2}) for the latter vs 2×10^2 M^{-1} and 1.4×10^{-10} mol cm^{-2} for the former. In fact, **7B** adsorbs more strongly than **7A** but the resulting coverage is the same. This result is explained by the fact that the coverage of ITO by monofunctionalized adsorbates is 1/3 of the available area,[16] which leaves room enough for a flat disposition of the difunctionalized adsorbate to a similar extent of coverage.

2.7. Polythiophene Electrodeposition on ITO-Adsorbed 4. As reported above, the tail of adsorbed **5** reacts with **5** coming from the solution. This suggested that adsorbed **4** and **5** molecules could act as anchoring sites for the production of organized or at least oriented polythiophene chains over the electrode surface.

To this end we ruled out thiophene as monomer since it is oxidized at a potential so high that the adsorbed layer cannot stand it. Given the characteristics of **4** and **5**, we could choose between 2,2′-bithiophene (**6**) and 2,2′:5′,2″-terthiophene, but since the latter produces on coupling short oligomers rather than polymer, compound **6** was preferred. Compound **6** is oxidized at a potential (1.0 V vs Ag/Ag^{+} [38]) close (ca. 0.2 V higher) to that of **4**. The fact that the oxidation potential of **4** is lower, which is attributable to the electron donor properties of the alkyl chain, allows the polymerization on the modified electrode without (or with a limited extent) bulk polymerization. In a 5×10^{-3} M solution of **6** the CV up to 0.8 V on the bare ITO electrode shows only a low oxidation current at the anodic limit without polymer formation on the electrode surface. On the contrary the **4**-modified electrode, which in monomer-free solution is irreversibly oxidized with deactivation, in the solution of **6** undergoes increased oxidation with the consumption of ca. twice the charge and with polymer deposition. Subsequent CV in monomer-free solution shows redox processes attributable to oligomeric polythiophene with an appreciable reversible charge (5 μC cm^{-2}).

If the oxidation potential is extended more anodically to produce higher concentrations of radical cations of **6**, coupling is expected to proceed further. This has been in fact clearly evidenced in transient chronoamperometric (CA) experiments. Typically the CA of the **4**-modified surface in a 10^{-3} M solution of **6** at an applied potential of 0.8 V (Figure 7) shows a faster attainment of the steady oxidation current compared with the bare electrode, which requires several seconds for the nucleation-and-growth transient.[39]

CV and CA responses similar to those of adsorbed **4** are not shown by adsorbed **5**. In this latter case the CV is the same in both the absence and the presence of **6** in solution while the CA transient in the presence of **6** is almost unchanged from that on the bare ITO. The reason may be found in the much lower reactivity of the terthiophene radical cation to coupling so that simple intercoupling of **6** and oxidative demolition of adsorbed **5** proceed in a parallel fashion.

3. Conclusions

Stable monolayers on ITO electrodes have been produced from carboxyalkyl-functionalized bithiophenes and terthiophenes

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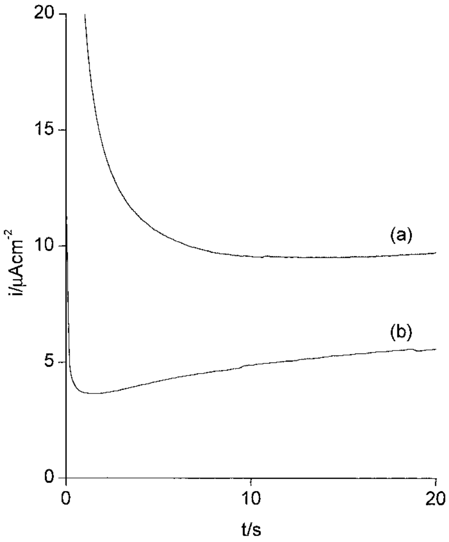

Figure 7. Chronoamperometric transients for (a) **4**-modified ITO and (b) bare ITO in 1 × 10^{-3} M **6** in acetonitrile + 0.1 M Bu_4NClO_4. Applied potential: 0.8 V.

bearing the oligothiophene tail either perpendicularly or linearly linked to the electrode bound carboxyl-terminated alkyl chain. Electrochemical oxidation of the layers of perpendicular adsorbates has produced polymer monolayers essentially constituted by thiophene hexamers. The linear bithiophene may be oxidatively coupled with 2,2′-bithiophene in solution to polythiophene chains. The linear terthiophene may be coupled with itself in solution to produce a one-end surface-grafted sexithiophene monolayer whereas a two-end surface-grafted sexithiophene with the same coverage is produced by direct adsorption of the dicarboxyl-functionalized sexithiophene.

The one-end and two-end grafted sexithiophene monolayers display electrochemical and spectral patterns characteristic of the different types of grafting. X-ray characterization of these monolayers and the high-vacuum deposition onto them of ordered sexithiophene multilayers will be the object of a forthcoming paper.[35]

4. Experimental Section

4.1. Chemicals and Reagents. All melting points are uncorrected. All reactions of air- and water-sensitive materials were performed under nitrogen. Air- and water-sensitive solutions were transferred with double-ended needles. The solvents used in the reactions were dried by conventional methods and freshly distilled under nitrogen.

Acetonitrile was reagent grade (Uvasol, Merck) with a water content <0.01%. The supporting electrolyte tetrabutylammonium perchlorate (Bu_4NClO_4) was previously dried under vacuum at 70 °C. All other chemicals were reagent grade and used as received.

^{1}H NMR spectra were recorded on a Bruker AC 300 (300 MHz for ^{1}H); chemical shift values are given in ppm and are referred to tetramethylsilane. Electron-impact mass spectra (EI-MS) were taken on a VG 7070 EQ-HF spectrometer.

The following compounds were prepared according to literature prescriptions: 4*H*-dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP),[40] 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (CPDT),[41] (4*H*-cyclopenta[2,1-*b*:3,4-*b*′]-dithiophene)-4-carboxylic acid (**3**),[41] 2,2′-bithiophene (**6**),[42] and nickel(II) [1,3-bis(diphenylphosphino)propane] chloride ($NiCl_2$(dppp)).[43] Compounds **1**, **2**, **4**, and **5** were prepared following the synthetic routes depicted in Schemes 1−4. The relevant analytical data are reported as follows.

6-(4*H*-Dithieno[3,2-*b*:2,3′-*d*]pyrrol-4-yl)hexanoic acid (1): mp 105 °C. Anal. Calcd for $C_{14}H_{15}NO_2S_2$: C, 57.34; H, 5.12; N, 4.77. Found: C, 57.51; H, 5.23; N, 4.61. ^{1}H NMR ($CDCl_3$) δ 1.35 (m, 2H), 1.62 (m, 2H), 1.87 (m, 2H), 2.25 (t, 2H), 4.20 (t, 2H), 7.00−7.10 (AB system, J = 5.2 Hz, 4H).

6-(4*H*-Cyclopenta[2,1-*b*:3,4-*b*′]dithien-4-yl)hexanoic acid (2): mp 80 °C. Anal. Calcd for $C_{15}H_{16}O_2S_2$: C, 61.64; H, 5.47. Found: C, 61.52; H, 5.63. ^{1}H NMR ($CDCl_3$) δ 1.50 (m, 8H), 2.30 (t, 2H), 3.51 (t, 1H), 7.05−7.15 (AB system, J = 5.2 Hz, 4H).

7-(2,2′-Bithien-5-yl)heptanoic acid (4): mp 102 °C. Anal. Calcd for $C_{15}H_{18}O_2S_2$: C, 61.22; H, 6.11. Found: C, 60.97, H, 5.97. ^{1}H NMR ($CDCl_3$) δ 1.39−1.72 (m, 8H), 2.36 (t, 2H), 2.79 (t, 2H), 6.67 (d, J = 3.6 Hz, 1H), 6.97 (d, J = 3.6 Hz, 1H), 6.98 (dd, J = 4.7 Hz, J = 3.6 Hz, 1H), 7.09 (d, J = 3.6 Hz, 1H), 7.17 (d, J = 4.7 Hz, 1H). MS, *m*/*e* 294 ($M^{\bullet+}$).

7-(2,2′:5′,2″-Terthien-5-yl)heptanoic acid (5): mp 125 °C. Anal. Calcd for $C_{19}H_{20}O_2S_3$: C, 60.63; H, 5.31. Found: C, 60.52, H, 5.23. ^{1}H NMR ($CDCl_3$) δ 1.35−1.78 (m, 8H), 2.36 (t, 2H), 2.79 (t, 2H), 6.68 (d, J = 3.6 Hz, 1H), 6.97 (d, J = 3.6 Hz, 1H), 6.99 (d, J = 3.7 Hz, 1H), 7.02 (dd, J = 3.7 Hz, J = 5.1 Hz, 1H), 7.05 (d, J = 3.7 Hz, 1H), 7.15 (d, J = 3.6 Hz, 1H), 7.19 (d, J = 5.1 Hz, 1H). MS, *m*/*e* 376 ($M^{\bullet+}$).

4.2. Electrochemical Apparatus and Procedure. Experiments were performed at 25 °C under nitrogen in three electrode cells in acetonitrile + 0.1 M Bu_4NClO_4. The reference electrode was a silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE) separated from the test solution by a acetonitrile + 0.1 M Bu_4NClO_4 bridge to avoid silver contamination of the ITO surface. The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator.

The working electrodes were 1 × 2 cm indium−tin-oxide (ITO) sheets (20 ohm/sq, Balzers, Liechtenstein) with 1 cm^2 active area. The ITO microstructure consists of grains ca. 100 nm long with an amorphous phase along the grain boundaries. The ITO electrodes were cleaned with acetone and dried prior to use.

Electronic spectra were taken with a Perkin-Elmer Lambda 15 spectrometer; IR spectra were taken on a Perkin-Elmer 2000 FTIR spectrometer. Matrix-assisted laser desorption ionization (MALDI) mass spectra were taken on a Reflex TOF spectrometer (Bruker) with 2,5-dihydroxybenzoic acid as matrix.

Acknowledgment. The authors would like to thank R. Salmaso and S. Sitran of CNR for technical assistance.

Supporting Information Available: Experimental procedures and characterization data for **1**, **2**, **4**, **5**, and **8−16** (5 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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