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Electroactive and luminescent polymers: new fluorene–heterocycle-based hybrids

Barbara Tsuie,[a] Jerry L. Reddinger,[a] Gregory A. Sotzing,[a] Jadwiga Soloducho,[b,c] Alan R. Katritzky[b] and John R. Reynolds*[a]

[a]*Center for Macromolecular Science and Engineering, Department of Chemistry, University of Florida, Gainesville, FL 32611, USA*
[b]*Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, FL 32611, USA*
[c]*Institute for Organic Chemistry, Biochemistry, and Biotechnology, Wroclaw University of Technology, Wroclaw, Poland*

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The synthesis, characterization, and electrochromic properties of copolymers derived from 9,9-dialkyl-2,7-dibromofluorene (**18a**, alkyl = $C_{10}H_{21}$; **24**, alkyl = Et) and pyrrole, thiophene, 3,4-ethylenedioxythiophene, and furan are described. Two synthetic routes to 9,9-diethyl-2,7-bis(pyrrol-2-yl)fluorene (**30**) afford product in 30% and 20% yields, respectively. Monomer **30** undergoes electropolymerization to yield electroactive polymer films. The lowest monomer oxidation potential ($E_{p,m} = 0.4$ V *vs.* Ag/Ag$^+$) is found in tetraethylammonium tosylate (TEATOS)–CH_3CN, but film formation is slow. Spectroelectrochemical analysis of poly(**30**) reveals a band gap at 2.4 eV and upon polymer oxidation, two low energy absorptions peaking at 1.2 and 2.2 eV appear. This phenomenon is attributed to formation of bipolaron bands between the valence and conduction bands. Soluble fluorene–heterocycle polymers **34a-d** have been synthesized by the Stille coupling reaction of **18a** and 2,5-bis(trimethylstannyl)thiophene (**21a**), 5,5′-bis(trimethylstannyl)-2,2′-bithiophene (**21b**), 2,5-bis(trimethylstannyl)-3,4-ethylenedioxythiophene (**21c**), and 2,5-bis(trimethylstannyl)furan (**22**), respectively, in high yields. The NMR spectra are consistent with the proposed structures of the polymers **34a–d**, and no evidence of ring opening of the furyl unit in **34d** is seen in the NMR and IR spectra. The molecular weights of **34a–d** are in the range of 8000 g mol^{-1} with polydispersity indices (PDI) of 2. Polymers **34a–c** have band gaps measured at 2.4 eV, while polymer **34d** has its gap at 2.6 eV. Polymers **34a–c** undergo solution doping with $SbCl_5$ to form new low energy bipolaron bands at the expense of the absorption in the UV–VIS. However, polymer **34d** does not oxidatively dope with $SbCl_5$.

Introduction

The synthesis of π-conjugated polymers for applications such as electrochromic windows, flat screen displays, EMI-shielding, and corrosion protection has become an area of intense interest in recent years.[1] However, the drawbacks attributed to many of these systems are their poor processability and in extreme cases, their completely infusible nature. Utilization of electropolymerization/deposition methods can efficiently yield electroactive films, but is limited to specifically designed monomers and is generally of low overall yield. To circumvent these obstacles, a tremendous amount of research has resulted in a number of elegant synthetic means that can be employed efficiently and reliably to afford soluble, high molecular weight conducting polymers.[1b] Polymeric or oligomeric materials that can be spin-coated, solution cast, or even sprayed onto large surface-area electrodes (such as indium-tin oxide (ITO)-coated glass) help alleviate many of the problems associated with attempting large scale electrochemical depositions.

Many groups have fabricated a number of conjugated polymers using both chemical and electrochemical methods that exhibit a variety of electrochromic and electroluminescent properties.[1] These properties are chiefly determined by the polymer band gap (determined as the onset of the π to π* absorption), and the energies for transitions to the charge carrier states in the doped polymers. In general, polymers with band gaps that range through the full visible spectrum are desired because they allow both absorption and emission of all colors. Polyaromatics based on hydrocarbons (*e.g.* *p*-phenylenes, fluorenes) tend to be relatively high gap in nature. There are a number of strategies used for synthesizing lower gap polymers which include increasing electron density along the backbone, often through the inclusion of heterocycles or the linking of multi-ring aromatic or heteroaromatic molecules, and the use of alternating donor–acceptor systems.[2] The first example of a specifically designed low band gap polymer was polyisothianaphthene. This polymer exhibits a band gap of about 1 eV, which is 2 eV lower than poly(*p*-phenylene) and 1 eV lower than polythiophene.[3a] More recently, band gap lowering has been accomplished using donor–acceptor type repeat units.[3b] This strategy employs use of an electron rich heterocycle (donor) in conjugation with an electron poor fragment (acceptor) to effect delocalization of electron density throughout the polymer chain, and band gaps as low as 0.5 eV are claimed. In the spirit of this special issue on electroactive polymers, we introduce some of the general families of variable band gap conjugated polymers, noting systems we have focused on and present new results on polymers synthesized using a combination of fluorene and heteroaromatic repeat units.

Poly(*p*-phenylenes) (PPP's)

Extensive literature has now been developed describing a variety of methodologies for the synthesis of poly(*p*-phenylene)s (PPP's) and their structural derivatives.[4] Being high gap in nature, PPP has found utility as a blue-emitting polymer in polymer light emitting diodes (PLED's).[5] We have developed a class of polyphenylenes that contain portions of disrupted π-conjugation due to deliberate introduction of *meta*-linkages which interrupts the conjugation through the *para*-linkages (**1–3**, Fig. 1), or by introduction of extremely bulky groups

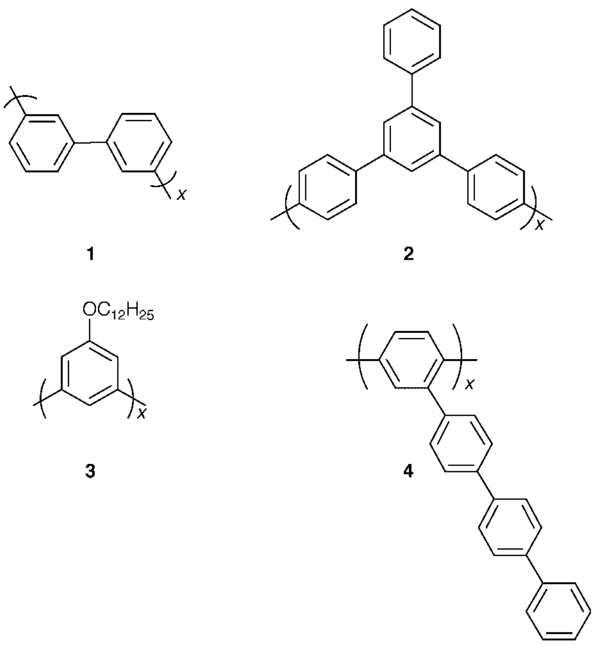


Fig. 1 Poly(*p*-phenylene) repeat units that contain *meta*-linkages **1–3** or bulky substituents **4**.

on the phenylene backbone which causes distortion of the planar conjugation (**4**, Fig. 1).[6] In general, these polymers are blue emitters; however, poly(3,5-didodecyloxy)phenylene synthesized by Ni catalysis in our labs yielded only a faint purple light in emission experiments (**3**, Fig. 1).[6b]

Novak and others have developed elegant routes to water-soluble PPP derivatives by Suzuki coupling[7] of boronic acids and aryl halides using a Pd catalyst which is water-stable.[8] PPP's of this type exhibit similar fluorescence behavior to that of dialkoxy PPP polymers in organic solvents and strongly fluoresce in the blue-green region.[6c,9] Water-soluble PPP's have absorption maxima similar to that of the parent PPP (3.6 eV *vs.* 3.5 eV for PPP) and exhibit bipolaronic charge carrier behavior from observation of two bands at 0.55 and 2.5 eV after electrochemical oxidation at relatively high potentials.

Dioxythiophene based polymers

Electron rich polymers with narrow gaps and low oxidation potentials are on the other end of the structural spectrum. Many researchers have contributed to the development of poly(alkylenedioxythiophene)s based on 3,4-ethylenedioxythiophene (**5**, EDOT, Fig. 2) and 3,4-propylenedioxythiophene (ProDOT, **6**, Fig. 2).[10,11] This family of polymers is interesting due to their reduced band gaps relative to the parent poly(thiophene) derivatives[12] causing the doped conductive polymers to have a relatively low level of visible light absorption. The electron donating ability of the alkylenedioxy fragment significantly raises the HOMO energy levels relative to the unsubstituted polymer while, at the same time, the fused nature of the substituent reduces steric interactions that might disrupt the π conjugation. Another source of conjugation disruption, α,β coupling, is also prevented in the alkylenedioxy substituted thiophenes due to blockage of the 3- and 4-positions as illustrated in Fig. 3 for a heterocycle parent. Due to its chemistry and the properties of its polymer (PEDOT, **7**, Fig. 2), EDOT has served for the preparation of many new derivatives including new fluorene polymers presented here.

Polymers based on terarylene and hybrid systems

A strategy that has proven to be useful in designing polymers which exhibit controllable optoelectronic properties is by exploiting terarylene monomers which contain a central aromatic ring and heterocycles symmetrically placed on either side. Often, a single ring heterocycle will undergo electrochemical polymerization at a potential that is greater than, or equal to, the degradation potential (so called over-oxidation) of the polymer to form defects. It was found that terarylene monomers significantly reduce the oxidation potential needed to effect polymerization, thereby increasing regularity and translating to materials with a higher degree of purity and enhanced redox switching characteristics.

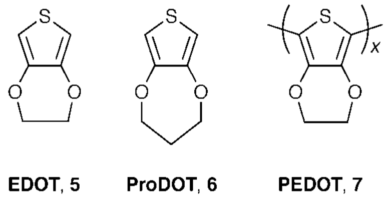


Fig. 2 3,4-Alkylenedioxythiophenes **5–7**.

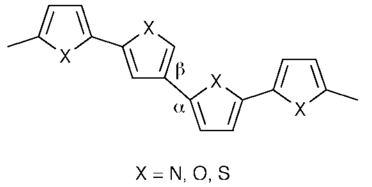


Fig. 3 α,β Linkage defect in polyheteroaromatic polymers.

Pyrroles. Pyrrole has a lower oxidation potential than either furan or thiophene, and polypyrrole has consequently a higher level of electroactivity. A family of bis(pyrrol-2-yl)arylenes that contain phenyl (**8**), 2,5-dialkoxy substituted phenyls (**9**, **10**), naphthyl (**11**), and biphenyl (**12**) are shown in Fig. 4.[13] Electrochemical studies reveal that poly(1,4-bis(pyrrol-2-yl)benzene) poly(**8**) and poly(1,4-bis(pyrrol-2-yl)-2,5-dimethoxybenzene) poly(**9**) exhibit band gaps of 2.4 and 2.3 eV, respectively, which are smaller compared to those for polypyrrole (2.7 eV) and poly(*p*-phenylene) (3.0 eV).

Thiophenes. A sample of the body of work of terarylene polymers that incorporate phenyl as the central unit and thienyl units such as thiophene (**13**)[14a–c] or 3,4-ethylenedioxythiophene (EDOT, **14**) are shown in Fig. 5.[14d,e] The electrochemical studies revealed that polymers based on 2,5-disubstituted-1,4-bis(2-thienyl)benzene such as **13** exhibited band gaps at 2.4 to 3.0 eV, but the EDOT-based polymers ranged from 1.4 to 2.3 eV .

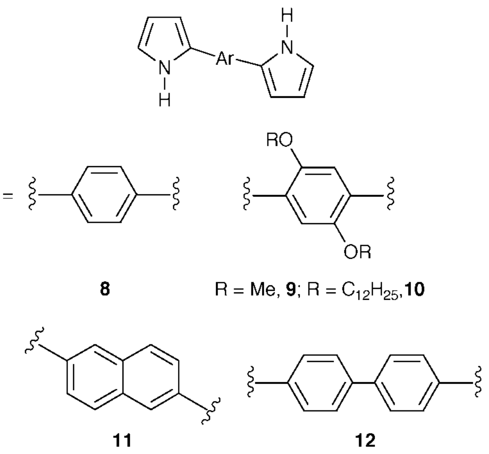
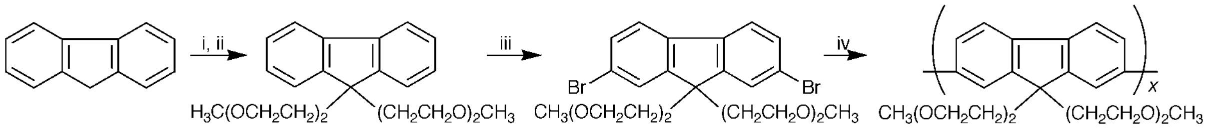
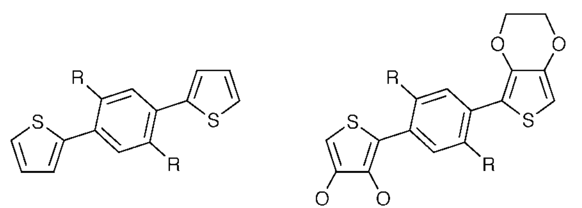


Fig. 4 Bis(pyrrol-2-yl)arylene monomers **8–12**.



(1)

(i) 2 Bu^{n}Li, (ii) 2 Cl(CH_2CH_2O)$_2$$CH_3$, (iii) 2 Br_2/DMF, (iv) $NiCl_2$/Zn/DMF



13

14

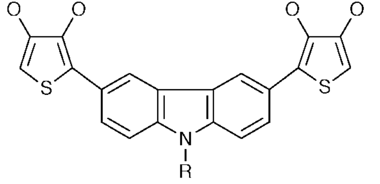
R = H, alkyl, alkoxy

Fig. 5 Bis(thienyl)arylene and bis(EDOT)arylene monomers **13–14**.

Carbazoles. Carbazole is an attractive alternative to phenyl derivatives due to its fused planar, yet synthetically flexible core that can be derivatized.[15] Polycarbazole has the unique feature of undergoing two redox processes yielding three distinct colors. The polymer is colorless when neutral, but turns green at 0.7 V *vs.* SCE and blue at 1.0 V. However, the polymerization of carbazole is slow, and the oxidation potential is high. Multicolored electrochromic polymers based on bis(EDOT)- and bis(pyrrol-2-yl)carbazole monomers (**15** and **16**, respectively) having the structures shown in Fig. 6 are made possible due to the unique electrochemical nature of carbazole.[15]

Fluorene–heterocycle hybrid polymers

Electrochemical synthesis of polyfluorene was first reported by Rault-Berthelot and laid the foundation for the discovery that poly(9,9-disubstituted fluorene)s exhibited reversible p-doped, neutral, and n-doped redox states.[16] One reported *chemical* route to polyfluorene involved oxidative polymerization of fluorene with $FeCl_3$.[17] However, the resulting polymer was partially cross-linked and insoluble with traces of metal residue difficult to remove completely. Other chemical methodologies exploited the use of late transition metal catalysts. For example, Pei used a mixture of $NiCl_2$ and excess Zn in dimethylformamide (DMF) to homopolymerize 2,7-dibromo-9,9-bis(3,6-dioxaheptyl)fluorene in 35% polymer yield [eqn. (1)].[18] Leclerc synthesized acidic copolymers of poly(2,7-fluorenylene) derivatives by Suzuki coupling, and this class of polyfluorene underwent doping with sodium *tert*-butoxide to exhibit electrical conductivities of 10^{-6} to 10^{-5} S cm^{-1}.[19]



R = Me, **15a**; R = (OCH_2)$_2$Et, **15b**

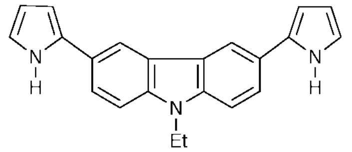


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Fig. 6 Bis(heteroaromatic) carbazole monomers **15–16**.

Poly(alkylfluorene)s have interesting photoluminescent properties as well[20] and have been used as blue light emitting components in PLED's. While the polymer does degrade, it is more light and temperature stable when compared to poly(phenylene vinylene)s. One mechanism of polymer degradation is by oxidation to form carbonyl groups that quench the fluorescence.[21,22] The second mechanism invokes nonradiative relaxation through aggregation of excited states which thereby dampens the emission intensity. It was found that copolymerization of fluorene with various aryl partners allows for tunability of electronic properties and enhanced stabilities. In particular, copolymers of fluorene and anthracene are very thermally robust and still maintain their blue emission. The anthracene unit is not coplanar with the fluorenyl fragment, and thus it is hypothesized that the twisting disfavors the nonradiative relaxation process.[23]

In addition to light emission, fluorene-based polymers exhibit interesting transport properties. For example, fluorene–triarylamine copolymers demonstrate high charge carrier mobilities that approach hole mobilities of the standard glassy films of aryl diamines.[24] Another application of polyfluorenes is in liquid crystal (LC) polymers.[25] This polymer type exhibits well-behaved LC formation, smoothly and reversibly transitioning to an isotropic phase. In the LC state, it cools to form a glass without crystallization.

In this paper, we have incorporated a number of different heterocyclic units along with the fluorene moiety, specifically chosen for their varied electron densities because this methodology could potentially afford rational control of the optoelectronic properties of the resulting polymers. Chemical polymerization was selected for the fluorene–furan and fluorene–thiophene monomers since the products are amenable to a variety of characterization methods. Additionally, higher yields are obtained relative to electrochemical polymerization, which usually affords polymers in only 2–3% monomer-based yield. The Stille reaction using $Cl_2Pd(PPh_3)_2$ as the catalyst couples a halide moiety with a stannyl-based fragment.[26,27] The scope of this chemistry is large and involves reaction of an organic halide,[27a,e] triflate[27b–e] or acid chloride[27e] with an organotin compound to form an organic molecule that contains a new carbon–carbon bond. The Stille reaction is an exceptionally ideal candidate for the synthesis of new electroactive conjugated polymers because the yields are potentially high, the reaction conditions are relatively mild, and the catalyst can tolerate functionalities such as the carbonyl, alkoxy, nitro, and hydroxy groups and tends to have high turn-over rates. Specifically, polymerization is feasible when the appropriate heterocycle, such as thiophene and furan, contains the trialkyltin groups symmetrically on the 2 and 5 positions and the fluorene has the halide groups in the 2 and 7 positions. Moreover, the distannyl and dihalide monomers are straightforward to synthesize, and the monomers are thermally stable. Most notably, Yu has utilized the Stille reaction to prepare a number of heterocycle-based conjugated polymers.[28]

In the case of the fluorene–pyrrole based monomers, electrochemical polymerization was used due to the sensitivity of the polymer catalysts to the pyrrole fragment and the ease of electropolymerization of the bis(pyrrol-2-yl) based monomers. Herein, we overview and report on new results in the preparation of functionalized, fluorene-based materials that display many of the attractive electrochemical and optical properties of the previously reported systems.[29]

Results and discussion

The fluorene–heterocycle polymers that we will discuss are shown in Chart 1. We chose the dihalide fluorenes (**18a**, X = Br; **18b**, X = I) as one set of monomers since the synthesis is efficient and straightforward. The hydrogens on the 9 position of fluorene are sufficiently acidic to undergo successive deprotonations with Bu^{n}Li. The subsequent reaction with three equivalents of bromodecane in THF affords 9,9-didecylfluorene (**17**). The crude material was purified by column chromatography (silica gel) with hexanes, and a colorless oil was obtained in 79% yield. Compound **17** was treated with two equivalents of Br_2 in methylene chloride with 10% I_2 (based on **17**), and 9,9-didecyl-2,7-dibromofluorene (**18a**) was isolated after recrystallization from hexanes in 82% yield. 9,9-Didecyl-2,7-diiodofluorene (**18b**) could be synthesized by similar methods for **18a**.

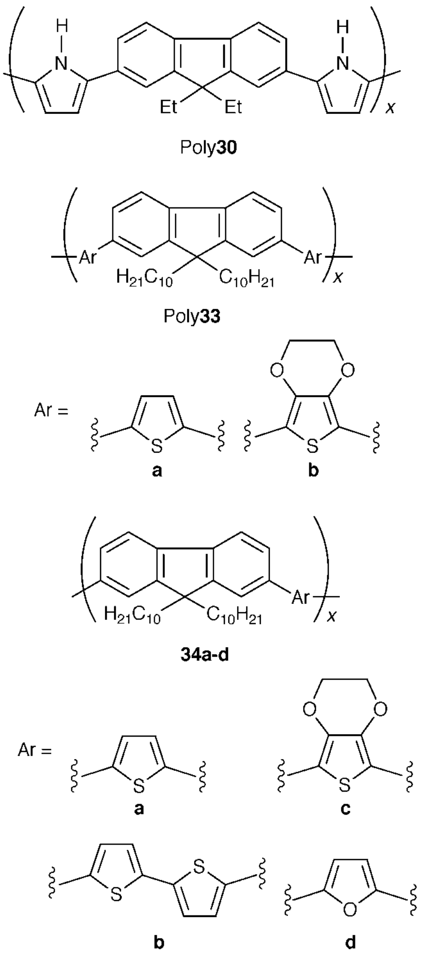
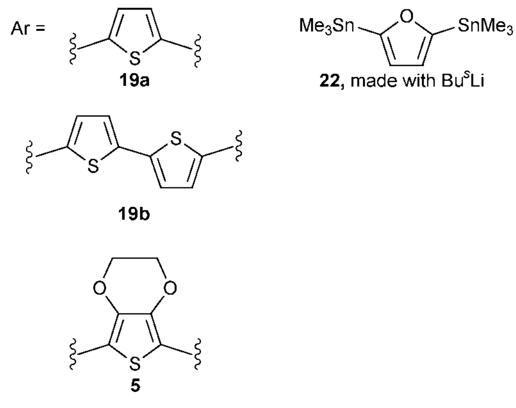


Chart 1 Fluorene–heterocycle hybrid polymers **30**, **33** and **34**.

The stannyl coupling partner monomers are shown in eqn. (2).[30] Reaction of thiophene (**19a**), 2,2′-bithiophene (**19b**) and 3,4-ethylenedioxythiophene (EDOT, **5**) with two equivalents of Bu^{n}Li in hexanes generated their respective dilithio salts (**20a–c**) which were not isolated. Tetramethylethylenediamine (TMEDA) was used to chelate the lithium cations and to enhance the nucleophilicity of **20a–c**. Subsequent treatment of **20a–c** with two equivalents of trimethyltin chloride in hexanes afforded 2,5-bis(trimethylstannyl)thiophene (**21a**), 5,5′-bis(trimethylstannyl)-2,2′-bithiophene (**21b**) and 2,5-bis(trimethylstannyl)EDOT [**21c**, eqn. (2)] as solids in 60 to 75% yields.

$$\text{H-Ar-H} \xrightarrow[\text{2 TMEDA, hexanes}]{\text{2 Bu}^n\text{Li}} \underset{\mathbf{20}}{\text{Li-Ar-Li}} \xrightarrow[\text{hexanes}]{\text{2 Me}_3\text{SnCl}} \underset{\mathbf{21}}{\text{Me}_3\text{Sn-Ar-SnMe}_3} \qquad (2)$$



19a

19b

5

22, made with Bu^{s}Li

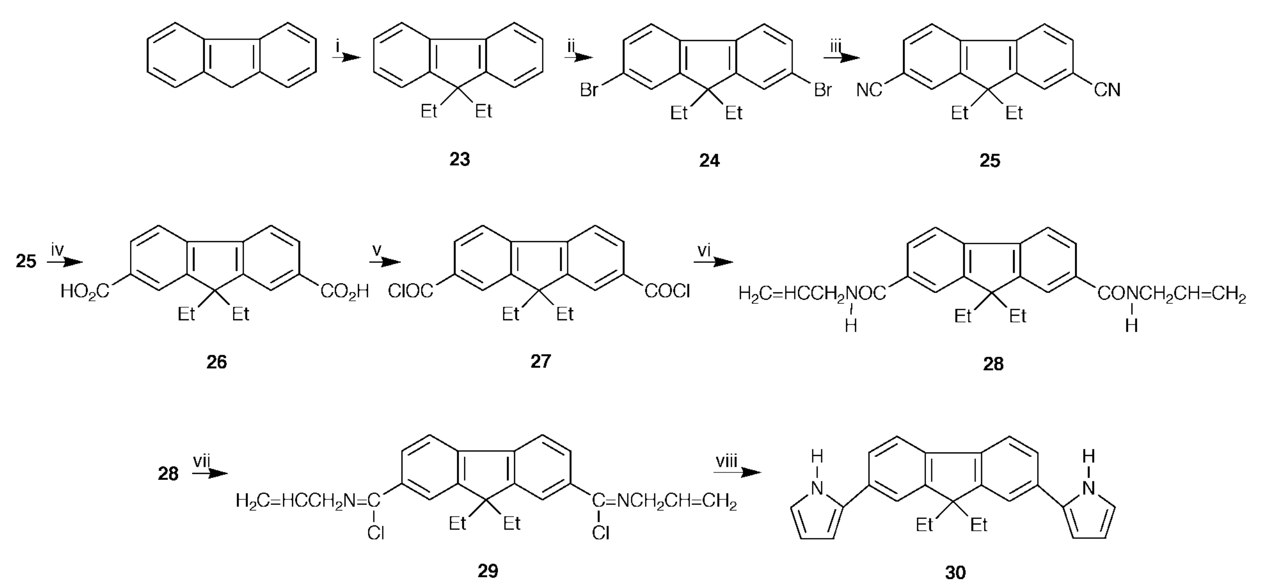
Similar reaction conditions were employed for the furan analogue. However, higher yields of 2,5-bis(trimethylstannyl)furan (**22**) were obtained when the stronger base *sec*-butyllithium was used. Compound **22** was isolated as a colorless oil after two distillations in 52% yield.

The synthesis of 9,9-diethyl-2,7-bis(pyrrol-2-yl)fluorene (**30**, BP-DEF) was carried out by two different procedures. The first was developed by Engel in accordance to the general pathway in Scheme 1.[31] The compound 9,9-diethylfluorene-2,7-dicarboxylic acid dichloride (**27**, Scheme 1) is an important intermediate. Deprotonation of fluorene with 2.5 equivalents of Bu^{n}Li followed by addition of three equivalents of bromoethane afforded 9,9-diethylfluorene (**23**). Bromination of **23** to give the dibromo analogue **24** followed by aromatic nucleophilic substitution with excess CuCN in DMF afforded the dicyanofluorene complex **25**, which was converted to the diacid **26** with H_3PO_4. Subsequent treatment of **26** with thionyl chloride afforded **27** in an overall yield of 26% based on fluorene.

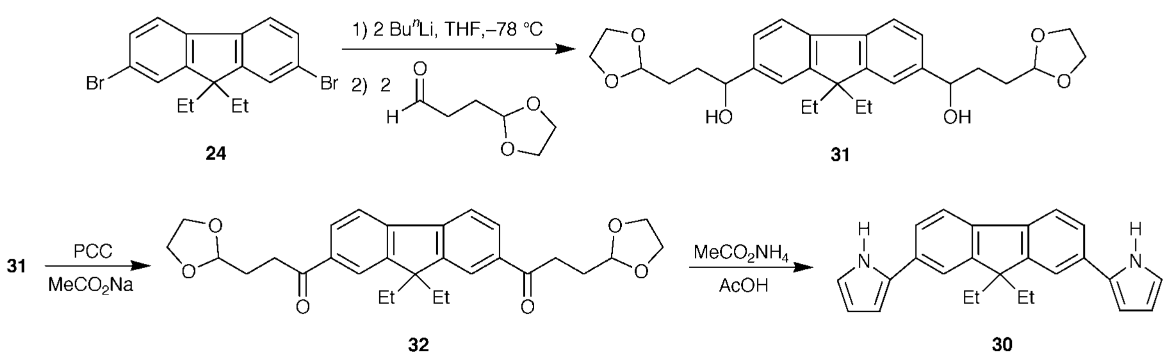
The reaction of **27** with two equivalents of allylamine yielded the fluorenedicarboxylic acid diallylamide **28**. Treatment of **28** with six equivalents of phosgene afforded the bis[*N*-allylimino(chloro)methyl]fluorene **29**, which was used without isolation and cyclized under basic conditions to give BP-DEF **30** in an overall yield of 64% based on **27**.

A second procedure for the preparation of BP-DEF was modeled after work done by Lucchesini (Scheme 2).[32] 9,9-Diethyl-2,7-dibromofluorene (**24**) was metallated with Bu^{n}Li and reacted with two equivalents of 1,3-dioxolane-2-propanal to give the dioxolanol derivative **31**, which was used without purification in the next step. Reaction of **31** with pyridinium chlorochromate (PCC) and sodium acetate yielded the oxidized product **32** which was refluxed in acetic acid with ammonium acetate for 18 h to afford BP-DEF **30** in 20% overall yield. A comparison of both synthetic routes revealed that the yield for BP-DEF by the Engel method was 30% based on **24**, while the yield from the Lucchesini route was 20% based on **24**. Therefore, we chose to use Engel's route in large scale preparations.

In contrast to the synthesis of BP-DEF, the previously reported bis(2-thienyl)-9,9-didecylfluorene (**33a**, BTDF, Scheme 3) and bis(3,4-(ethylenedioxy)-2-thienyl)-9,9-didecylfluorene (**33b**, BEDOT-DF, Scheme 3) were synthesized by the Stille coupling reaction of **18a** and two equivalents of Ar-SnBu$^n{}_3$.[29] Therefore, versatile and straightforward synthetic



Scheme 1 Synthesis of 9,9-diethyl-2,7-bis(pyrrol-2-yl)fluorene (**30**). *Reagents and conditions*: (i) 2.5 Bu^{n}Li, THF, 3 EtBr; (ii) 2 Br_2, CH_2Cl_2; (iii) excess CuCN, DMF; (iv) H_3PO_4, 170 °C; (v) 2 $SOCl_2$, DMF; (vi) 2 $NH_2CH_2CH{=}CH_2$, NEt_3, C_6H_6; (vii) 6 $COCl_2$, DMF; (viii) 2 Bu^{t}OK, THF–DMF.

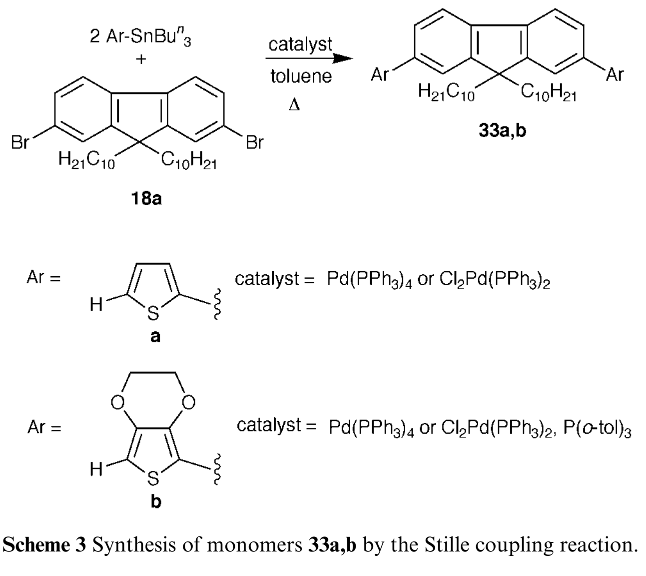


Scheme 2 Alternate synthesis of **30**.

routes to derivatized heterocycle–fluorene monomers are accessible.

Electropolymerization of bis(2-heterocycle)-2,7-fluorene hybrid monomers

The repeated potential scan electrochemical polymerization of 10 mM BP-DEF in 0.1 M tetrabutylammonium perchlorate–acetonitrile (TBAP–CH_3CN) is shown in Fig. 7. The first scan



Scheme 3 Synthesis of monomers **33a,b** by the Stille coupling reaction.

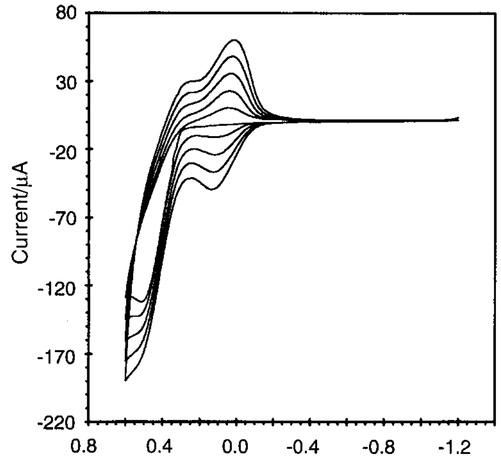


Fig. 7 Repeated potential scan electrochemical polymerization of 10 mM BP-DEF on Pt in 0.1 M TBAP–CH_3CN at a scan rate of 100 mV s^{-1}.

of the polymerization shows no current response until initial oxidation of the monomer occurs with an onset at 0.34 V. At this potential, the oxidative polymerization is initiated, and the oxidation proceeds until the potential is reversed at 0.6 V and is lower than that for the oxidation of the monomer. Upon further scanning to a more negative potential, the reduction of poly(BP-DEF) occurs. After the scan reached

−1.20 V, the potential scan was reversed in the oxidative direction, upon which an oxidative process at a lower potential than the monomer's occurs, which is attributed to the oxidation of the surface adhered polymer. This is followed by oxidation of the monomer initiating at 0.30 V, oxidative polymerization, and potential scan reversal to allow for reduction of the polymer. Subsequent scanning led to an increase in current response for the electrochemical processes due to the deposition of conducting polymer onto the surface of the electrode.

The oxidative electrochemical polymerization of BP-DEF was performed in other electrolytic solutions such as tetrabutylammonium hexafluorophosphate ($TBAPF_6$)–CH_3CN, tetrabutylammonium tetrafluoroborate ($TBABF_4$)–CH_3CN, tetraethylammonium tosylate (TEATOS)–CH_3CN, and $LiN(SO_2CF_3)_2$–CH_3CN. The solvent system that led to the lowest oxidation potential was TEATOS–CH_3CN, but polymerization proceeded sluggishly. It was found that BP-DEF in $TBAPF_6$–CH_3CN, $TBABF_4$–CH_3CN, and $LiN(SO_2CF_3)_2$–CH_3CN led to monomer oxidation values equivalent to that of BP-DEF in 0.1 M TBAP–CH_3CN.

The oxidation potential for BP-DEF is lower than that observed for bis(pyrrol-2-yl)biphenyl (BPBP, **12**, Fig. 4). This may be attributed to the increased coplanarity of the fused fluorene compared to that of the biphenyl. Substitution of the fluorene with two ethyl groups enhanced the solubility of the monomer relative to the solubility of BPBP. The monomer BP-DEF dissolved readily at room temperature in order to give a 10 mM concentration in acetonitrile, whereas BPBP required refluxing in acetonitrile in order to attain a saturated solution with a concentration of approximately 10 mM.

Cyclic voltammetry of poly(BP-DEF)

Poly(BP-DEF) in TBAP–CH_3CN, $TBAPF_6$–CH_3CN, and $TBABF_4$–CH_3CN exhibits multiple polymer half wave redox processes ($E_{1/2,p1}$, $E_{1/2,p2}$). The cyclic voltammogram of poly(BP-DEF) on a Pt button electrode in 0.1 M TBAP–CH_3CN is shown in Fig. 8. The first electrochemical redox process is narrow, whereas the second is complex and likely contains two separate redox peaks.

We hypothesize two reasons for this redox response. One possibility is that the electropolymerization leads to different conjugated structures within the polymer, possibly through coupling at the β positions of the pyrrole breaking the conjugation of the chain. We note that this behavior is electrolyte dependent, and when TEATOS was used as electrolyte, only one redox process was observed. Secondly, as it is well known that the morphology of electrochemically prepared films evolve during deposition, it is possible that a highly ordered layer having a low oxidation potential deposits first. This inner portion of the film would provide the sharp redox process with an $E_{1/2,p1}$ of +0.05 V. Further film deposition occurs with a more disordered morphology (likely containing a higher defect density), and a multiple redox response is observed and found at a higher potential ($E_{1/2,p2} = +0.5$ V). However, through the use of the electrochemical quartz crystal microbalance, both processes do involve doping of the polymer as each process is accompanied by a corresponding mass increase due to dopant anion insertion.

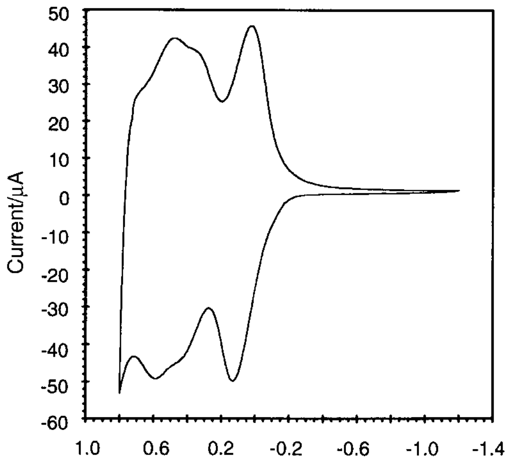


Fig. 8 Cyclic voltammetry of poly(BP-DEF) on Pt in 0.1 M TBAP–CH_3CN at a scan rate of 100 mV s^{-1}.

For poly(BP-DEF) polymerized from $TBAPF_6$–CH_3CN and $TBABF_4$–CH_3CN and cycled in $TBAPF_6$–CH_3CN and $TBABF_4$–CH_3CN, respectively, the polymer redox processes were very unstable. Over the duration of ten redox cycles between 0.0 V and 1.0 V, the lower potential polymer redox process shifted to a higher oxidation potential while the second redox process shifted to a higher potential until it became undetectable. For poly(BP-DEF) prepared from TEATOS–CH_3CN, cycling afforded only one broad peak. The system with the most stable redox properties was poly(BP-DEF) prepared from TBAP–CH_3CN and cycled in TBAP–CH_3CN. For this system, both redox processes were stable with essentially no change in the peak current for polymer oxidation occurring for over 100 cycles. In order to test that the polymer was adhered to the electrode surface, cyclic voltammograms were obtained as a function of scan rate. Linear dependency of the scan rate with the current indicated that these systems were surfaced adhered.[33] For poly(BP-DEF) in TBAP–CH_3CN, both redox processes were found to exhibit a linear response of the current *vs.* scan rate.

Redox activity and electrochromism of electropolymerized films

In order to elucidate the evolution of electronic structure upon oxidation of the polymer, spectroelectrochemical analysis was performed. Fig. 9 represents the spectroelectrochemical analysis of poly(BP-DEF) in TBAP–CH_3CN. The UV–Vis–NIR spectrum of the polymer was obtained upon sequentially stepping the oxidation potential in 0.05 V increments. In the fully reduced form (−1.0 V), there is only one absorption with an onset at 2.4 eV representative of the E_g and a peak at 3.0 eV. Upon oxidation of the polymer, two lower energy absorptions become evident with peaks at 1.2 and 2.2 eV. These lower energy transitions represent the bipolaronic bands located between the valence and conduction bands.

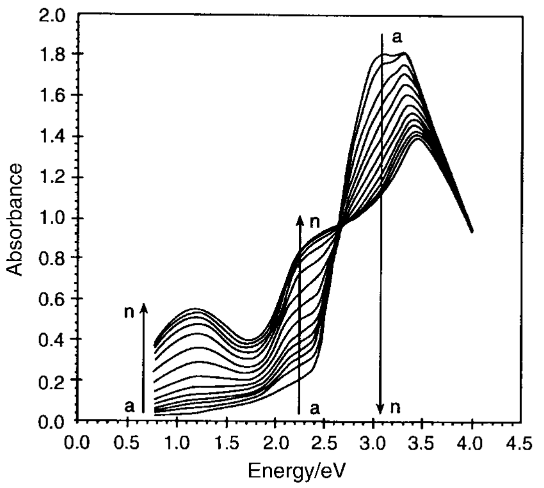


Fig. 9 Spectroelectrochemical analysis of poly(BP-DEF) in 0.1 M TBAP–CH_3CN at applied potentials of (a) −1.0 V, (b) 0.45 V, (c) 0.50 V, (d) 0.55 V, (e) 0.60 V, (f) 0.65 V, (g) 0.70 V, (h) 0.75 V, (i) 0.80 V, (j) 0.85 V, (k) 0.90 V, (l) 0.95 V, (m) 1.00 V, and (n) 1.10 V *vs.* Ag/Ag^+.

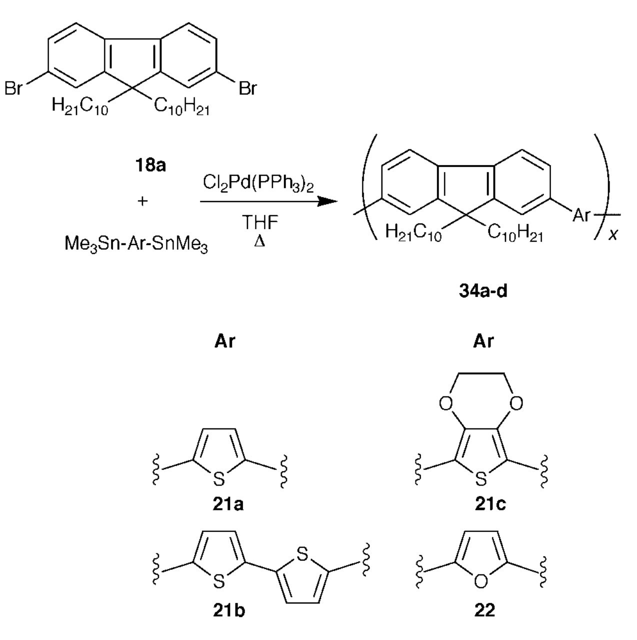
The E_g for poly(BPB) (**8**, Fig. 4) occurs at the same energy as poly(BP-DEF). However, even though the band gaps are identical, the λ_{max} for both systems are not. Poly(BPB) has a λ_{max} at 2.8 eV, whereas poly(BP-DEF) has a λ_{max} located at 3.0 eV. This is as expected since poly(BP-DEF) contains a biphenyl conjugated core. Therefore, the electronic band structure of poly(BP-DEF) should more closely resemble poly(*p*-phenylene).

Soluble fluorene–heterocycle hybrid polymers

The polymerizations of **18a** with the distannyl derivatives **21** were carried out under an argon atmosphere by refluxing a THF solution of the desired monomers in the presence of 5 mol% $Cl_2Pd(PPh_3)_2$ for 24 hours to yield alternating copolymers of didecylfluorene with thiophene (**34a**), bithiophene (**34b**), and EDOT (**34c**) as shown in Scheme 4. The resulting polymers were precipitated into methanol, redissolved in THF, and reprecipitated into hexane. Polymers **34a–c** are highly soluble in many organic solvents such as THF, chloroform, and dichloromethane, and optical quality films are readily cast or spin-coated from such polymer solutions.

For the furan-containing polymer **34d**, THF must be freshly distilled from Na–benzophenone ketyl immediately before use, and the monomers and catalyst carefully dried. As the monomers are oily at room temperature, they were dried separately and added as a solution in THF to the catalyst. The reaction vessel was shielded from the light and heated to reflux and monitored until a black precipitate formed. The mixture was filtered hot, and the filtrate was concentrated and poured into MeOH to form a yellow–green solid. The solid was redissolved in dichloromethane and reprecipitated in MeOH to yield polymer **34d** which is highly soluble in THF and benzene. The polymers were repeatedly submitted for elemental analysis, but the results were consistently inaccurate relative to the expected values.[34]

Both ^{1}H and ^{13}C NMR spectra are consistent for each of the proposed structures for polymers **34a–d**. The ^{1}H NMR spectrum of polymer **34d** in benzene-d_6 reveals four aromatic hydrogens as expected for the repeat unit shown in Fig. 10, which correspond to the furyl and three fluorenyl hydrogens (H_1 to H_4). The other hydrogens are related by symmetry. The resonances in the upfield region are consistent for the decyl groups on the 9 position on the fluorenyl fragment. The aromatic region of the $^{13}C\{^{1}H\}$ NMR spectrum of polymer **34d** contains 8 out of 9 resonances due to the residual C_6D_5H interference at 128.0 ppm. Furthermore, there are no downfield resonances in the $^{13}C\{^{1}H\}$ NMR spectrum for the carbonyl carbons.



Scheme 4 Synthesis of soluble fluorene–heterocycle hybrid polymers **34a–d** by the Stille coupling reaction.

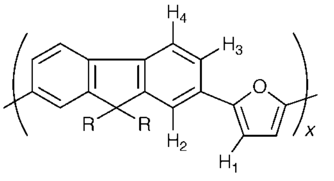
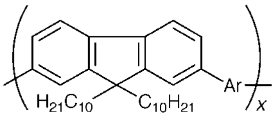


Fig. 10 The four inequivalent hydrogens in polymer **34d**. $R = C_{10}H_{21}$.

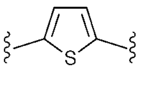
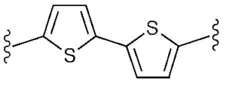
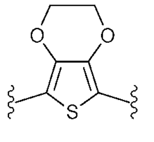
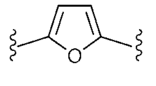
Molecular weights were obtained for polymers **34a–d** by gel permeation chromatography (GPC) using polystyrene standards (Table 1). Polymers **34a**, **34b**, and **34d** were relatively modest in molecular weight with M_n values of 8100, 8700, and 8750 g mol^{-1} and M_w values (PDI) of 17 400 (2.15), 19 800 (2.27), and 23 250 g mol^{-1} (2.65), respectively. Polymer **34c** continually proved to be of much lower molecular weight (M_n ~2000–2500 g mol^{-1}), and variation of polymerization conditions showed little effect on the molecular weight. The cause of the poor polymerization performance can likely be traced back to the instability of the bis-stannyl monomer **21c**, which slowly decomposes upon exposure to air. The loss of the trialkylstannyl units would greatly disrupt the required stoichiometric balance that is required for the synthesis of high molecular weight materials through the generation of end-capping (loss of one group) and inactive monomers (loss of both groups).

It is well established that polymers which contain 2,5-disubstituted furan fragments will often ring-open in acidic media to afford carbonyl groups. For example, we found that poly[1,4-bis(2-furyl)phenylene] undergoes ring opening and exhibits a medium intensity absorbance at 1680 cm^{-1} in the IR spectrum.[35] For polymer **34d**, there is no evidence of ring opening due to the absence of carbonyl stretching frequencies in the IR and the absence of carbonyl ^{13}C resonances in the NMR spectrum.

Table 1 Molecular weight values for polymers **34a–d**



34a-d

	Ar	M_n/g mol^{-1}	M_w/g mol^{-1}	PDI
a		8100	17 400	2.15
b		8700	19 800	2.27
c		This polymer was not stable for analysis		
d		8750	23 250	2.65

Redox and electrochromic properties of soluble fluorene–heterocycle hybrid polymers

The investigation of the electrochemical and optical properties of polymers **34a–c** was carried out. Films of **34a–c** were cast on platinum, gold, and vitreous carbon electrodes and their electrochemical behaviors probed utilizing cyclic voltammetric (CV) methods in 0.1 M TBAP–CH_3CN solutions. Films of polymers **34a–c** displayed well-defined oxidative and reductive electrochemical processes. It is interesting to note that while the general CV shape for a film of polymer **34b** is similar to that of its electrosynthesized counterpart,[29] its redox processes occur at potentials *ca.* 100 mV lower. This may be due to the fact that the chemically synthesized polymer is likely to be of much higher molecular weight than the corresponding electropolymerized material and thus stabilizes the oxidized species better.

Spectroelectrochemical studies were conducted on polymer films cast onto ITO-coated glass to reveal a more detailed picture of polymer oxidation. Fig. 11 shows the results obtained for oxidation of a film of **34b** on an ITO-coated glass slide. Potentials were sequentially stepped between −0.25 V and +0.88 V (*vs.* Ag/Ag^+) with UV–Vis–NIR spectra taken at selected potentials within this range. For the reduced form of the polymer, the onset for the π–π* absorption can be found at 2.25 eV. The main π–π* absorption in the neutral polymer continually decreases as new, low energy transitions, attributed to polaron and bipolaron levels, grow in with increased polymer oxidation. Table 2 lists the values for the respective transitions obtained from optoelectrochemical analyses for the three polymers.

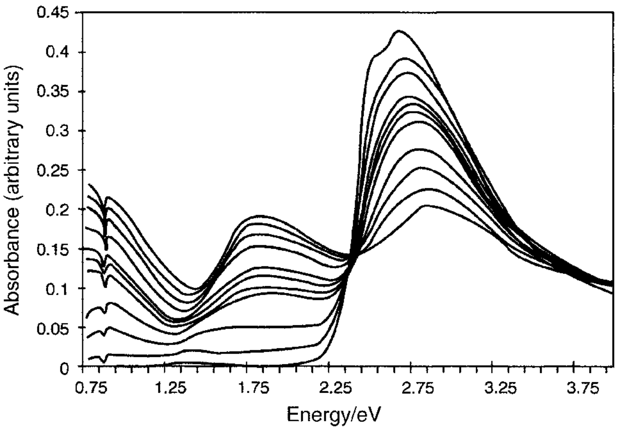
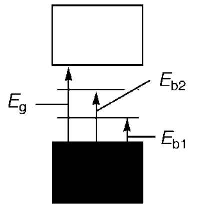


Fig. 11 Spectroelectrochemical analysis of a film of **34b** cast onto an ITO-coated electrode in 0.1 M TBAP–CH_3CN electrolyte. The applied potentials for each spectrum are (a) −0.25 V, (b) +0.53 V, (c) +0.60 V, (d) +0.65 V, (e) +0.69 V, (f) +0.71 V, (g) +0.73 V, (h) +0.75 V, (i) +0.78 V, (j) +0.81 V, (k) +0.85 V, and (l) +0.88 V.

Table 2 Energy values for various interband transitions determined by spectroelectrochemical analysis



Polymer	$E_{b1}{}^a$	$E_{b2}{}^a$	$E_g{}^{ab}$
34a	0.65	1.95	2.50
34b	0.75	1.80	2.32
34c	0.65	1.95	2.15

[a] Energies are in eV. [b] Values taken as the onset of the transition.

Solution doping experiments were performed, employing the same UV–Vis–NIR spectrophotometer used for optoelectrochemical studies, to investigate polymer switching by chemical oxidants/reductants. In a typical experiment, small aliquots of a 2% $SbCl_5$–CH_2Cl_2 solution were added to a dilute polymer solution ($\sim 10^{-5}$ M) with spectra acquired upon each subsequent addition of dopant solution. As in the spectroelectrochemical experiments, the absorption due to the main π–π* transition decreases with formation and growth of the lower energy absorptions.[11,14c,36] It should be noted that this doping can be rapidly and completely reversed by bubbling ammonia vapors through the polymer solution. Surprisingly, polymer **34d** does not undergo solution doping with $SbCl_5$, despite high concentrations of dopant. The UV–Vis absorbance spectrum of a 1 μM solution of polymer **34d** in THF reveals two peak maxima at 425 nm (2.92 eV) and at 452 nm (2.74 eV). The luminescence spectrum of **34d** in THF shows a typical broad emission with a peak maximum at 475 nm with a shoulder at 500 nm, and the spectrum is consistent with the absorbance as shown in Fig. 12.

Experimental

General

Polymerization reactions were performed using standard high-vacuum and Schlenk techniques. Tetrahydrofuran was vacuum distilled from Na–benzophenone ketyl. Benzene-d_6, chloroform-*d*, methylene chloride, fluorene, and methanol were used as received. The reagents $Cl_2Pd(PPh_3)_2$ and $SbCl_5$ were purchased from Aldrich and used as received. ^1H (300 MHz) and $^{13}C\{^1H\}$ (75 MHz) NMR spectra were recorded on a Varian Gemini 300 spectrometer at 23 °C. Absorption spectra were recorded on a Varian Cary 5E UV/Vis/NIR spectrophotometer. Emission data was recorded on a SPEX F-112 fluorimeter, and IR spectra as KBr pellets were recorded on a Mattson Instruments (Madison, WI) Research Series-1 FT IR spectrometer with a deuterated triglycine sulfate (DTGS) detector. Molecular weight determinations were done by GPC and were run on a Millipore Waters Model 590 pump with an ABI Analytical Kratos Division Spectroflow 757 Absorbance Detector. The calibration was made with a series of monodispersed polystyrene standards in THF. Bis(trimethylstannyl)furan was prepared by the literature method.[30] Elemental analyses were performed by Robertson Microlit Laboratories, Inc.

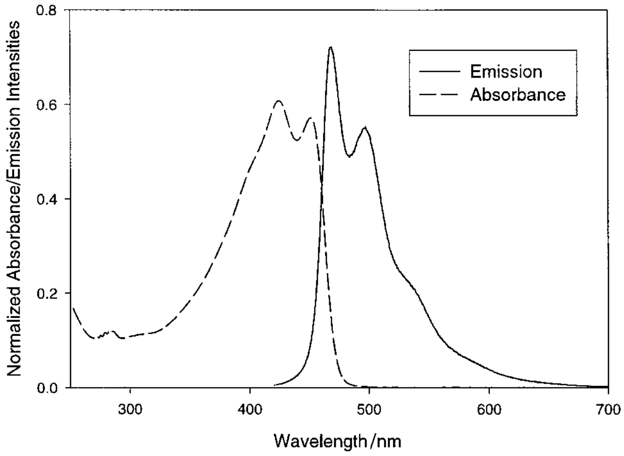


Fig. 12 Absorbance and emission spectra of **34d**.

9,9-Didecylfluorene (17)[37a]

Bu^{n}Li (9.4 mL, 1.6 M in hexanes, 15 mmol) was added to a solution of fluorene (1.0 g, 6.0 mmol) in THF (50 mL) at −60 °C over a period of 5 min. The resulting solution was stirred at −60 °C for 1 h. A solution of 1-bromodecane (2.7 mL, 18 mmol) in THF (10 mL) was added dropwise, and the solution was stirred at −60 °C for 20 min. Ammonium chloride (5 g) in H_2O (30 mL) was added, the organic layer was separated and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the crude oily product was purified by column chromatography using hexane as the eluent. Yield 79%. ^1H NMR δ ($CDCl_3$): 7.76–7.67 (m, 2H, arom H), 7.34–7.27 (m, 6H, arom H), 1.97–1.91 (m, 4H, CH_2), 1.25–1.02 (m, 28H, CH_2), 0.84 (t, $J=6.6$ Hz, 6H, CH_3), 0.65–0.61 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR δ ($CDCl_3$): 150.6, 141.0, 126.9, 126.6, 122.8, 119.6, 55.0, 40.4, 31.9, 30.0, 29.3, 23.7, 22.7, 14.1. HRMS Calcd for $C_{33}H_{50}$ 446.3912 ($M^+ + 1$), found 446.4001.

9,9-Didecyl-2,7-dibromofluorene (18a)[37b]

Bromine (0.22 mL, 4.0 mmol) in CH_2Cl_2 (5 mL) was added quickly to a stirred solution of **17** (1.0 g, 2.2 mmol) and I_2 (1.1 mg, 0.34 mmol) in CH_2Cl_2 (15 mL) at room temperature. The reaction mixture was stirred at room temperature for 20 h. An aqueous solution of $NaHSO_3$ (15 mL, 15%) was added, and the resulting two phases were stirred until the color disappeared (30 min). The organic layer was separated, washed with water, and dried over $MgSO_4$. The volatiles were removed under reduced pressure, and the crude product was recrystallized from hexane. Yield 81.5%, mp 38 °C. ^1H NMR δ ($CDCl_3$): 7.52–7.41 (m, 6H, arom H), 1.94–1.87 (m, 4H, CH_2), 1.84–1.25 (m, 28H, CH_2), 0.58 (t, $J=6.7$ Hz, 6H, CH_3), 0.64–0.54 (m, 4H, CH_2). $^{13}C\{^1H\}$ δ ($CDCl_3$): 152.5, 139.0, 130.1, 126.2, 121.5, 121.1, 55.6, 40.1, 31.9, 29.8, 29.5, 29.20, 29.21, 23.6, 22.6, 14.1. Anal. Calcd for $C_{33}H_{48}Br_2$: C, 65.56; H, 8.00. Found: C, 65.40; H, 8.27%.

9,9-Didecyl-2,7-diiodofluorene (18b)[37c]

A mixture of red fuming nitric acid (0.04 mL) and sulfuric acid (96%, 0.4 mL) was added dropwise at 40 °C to a stirred mixture of **17** (1.0 g, 2.2 mmol), finely divided iodine (0.43 g, 1.7 mmol) and acetic acid (10 mL). The reaction mixture was stirred at 40 °C for 1.5 h, and the oily product was partitioned between diethyl ether (100 mL) and H_2O (30 mL). The organic layer was separated and washed with 5% $NaHSO_3$ (50 mL), H_2O (50 mL), and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography using petroleum ether as eluent to yield a colorless oil in 40% yield. ^1H NMR δ ($CDCl_3$): 7.64 (d, $J=7.2$ Hz, 2H, arom H), 7.63 (s, 2H, arom H), 7.39 (d, $J=8.4$ Hz, 2H, CH_2), 1.91–1.85 (m, 4H, CH_2), 1.25–1.04 (m, 28H, CH_2), 0.85 (t, $J=6.8$ Hz, 6H, CH_3), 0.62–0.50 (m, 4H, CH_2). $^{13}C\{^1H\}$ δ ($CDCl_3$): 152.5, 139.7, 136.0, 132.0, 121.5, 93.1, 55.5, 40.0, 31.9, 29.8, 29.5, 29.3, 29.1, 23.6, 22.6, 14.1. Anal. Calcd for $C_{33}H_{48}I_2$: C, 56.73; H, 6.92. Found: C, 57.10; H, 7.04%.

9,9-Diethylfluorene (23)

Bu^{n}Li (9.4 mL, 1.6 M solution in hexane, 15 mmol) was added to a solution of fluorene (1.0 g, 6.0 mmol) in THF (50 mL) at −60 °C over a period of five minutes. The resulting orange solution was stirred at −60 °C for 1 hour. A solution of bromoethane (1.34 mL, 18.0 mmol) in 10 ml of THF was added, and the red solution was stirred for 20 minutes. Ammonium chloride (5 g) in H_2O (30 mL) was added, and the organic layer was separated and dried over $MgSO_4$. The volatiles were removed under reduced pressure, and the crude oily product was purified by column chromatography on silica gel using hexane as the eluent. Yield 79%. ^1H NMR δ ($CDCl_3$): 7.69 (m, 2H), 7.32–7.30 (m, 6H), 2.02 (q, $J=7.2$ Hz, 4H), 0.31 (t, $J=7.3$ Hz, 6H). $^{13}C\{^1H\}$ NMR δ ($CDCl_3$): 149.8, 141.4, 126.9, 122.8, 119.5, 56.0, 32.7, 8.4. Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found C, 91.96; H, 8.46%.

9,9-Diethyl-2,7-dibromofluorene (24)

A solution of bromine (0.47 mL, 0.30 mmol) in methylene chloride (4 mL) was added to a solution of **23** (1.0 g, 4.4 mmol) and I_2 (1.1 mg, 4.4 mmol) in CH_2Cl_2 (18 mL) at room temperature. The mixture was shielded from the light and stirred for 24 h. An aqueous solution of sodium bisulfite (15%, 10 mL) was added, and the two phases were stirred until the color disappeared. The organic layer was separated, washed with water, and dried over $MgSO_4$. The volatiles were removed under reduced pressure, and the crude product was recrystallized from hexane to give white crystals. Yield 79%, mp 155–156 °C. ^1H NMR δ ($CDCl_3$): 7.33–7.31 (m, 6H), 2.02 (q, $J=7.3$ Hz, 4H), 0.31 (t, $J=7.3$ Hz, 6H). $^{13}C\{^1H\}$ NMR δ ($CDCl_3$): 149.7, 141.4, 126.9, 126.7, 124.2, 122.8, 119.5, 55.9, 32.7, 8.4. Anal. Calcd for $C_{17}H_{16}Br_2$: C, 53.71; H, 4.24. Found C, 53.44; H, 4.19%.

9,9-Diethyl-2,7-dicyanofluorene (25)

A mixture of copper(I) cyanide (0.80 g, 8.9 mmol) and **24** (1.0 g, 2.6 mmol) in DMF (25 mL) was refluxed for 24 h. The mixture was poured into a solution of ammonia (20 mL, 15%) to form a precipitate. The solid was collected by filtration and washed with an ammonia solution followed by water. The solid was recrystallized from acetone to give yellow crystals. Yield 69%, mp 163–164 °C. ^1H NMR δ ($CDCl_3$): 7.70 (d, $J=8.4$ Hz, 4H), 7.66 (s, 2H), 2.08 (q, $J=7.3$ Hz, 4H), 0.30 (t, $J=7.3$ Hz, 6H). $^{13}C\{^1H\}$ NMR δ ($CDCl_3$): 151.2, 143.7, 131.6, 126.7, 126.2, 121.3, 119.9, 119.0, 57.0, 32.2, 8.2. Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.28. Found C, 83.89; H, 6.17; N, 10.36%.

9,9-Diethylfluorene-2,7-dicarboxylic acid (26)

A mixture of **25** (1.0 g, 2.0 mmol) and phosphoric acid (17.17 mL) in water (2.55 mL) was stirred under nitrogen at 170 °C for 24 h. The mixture was poured into hot water to precipitate the diacid **26**, which was isolated by filtration and washed repeatedly with water. The crude product was recrystallized from methanol to give white prisms. Yield 80%, mp 324 °C. ^1H NMR δ (DMSO-d_6): 8.06–7.99 (m, 6H), 2.51 (s, 2H), 2.13–2.09 (m, 4H), 0.19 (t, $J=7.2$ Hz, 6H). $^{13}C\{^1H\}$ NMR δ (DMSO-d_6): 167.4, 150.4, 144.1, 130.4, 128.8, 123.8, 120.7, 55.9, 31.4, 8.2. HRMS Calcd for $C_{19}H_{18}O_4$: 311.1283 (M + 1), found 311.1281.

9,9-Diethylfluorene-2,7-dicarboxylic acid dichloride (27)

A mixture of **26** (1.0 g, 3.2 mmol) and thionyl chloride (12 mL) in anhydrous DMF (0.1 mL) was stirred at room temperature for 12 h and stirred at 50 °C for 1 h. Excess thionyl chloride was removed under reduced pressure. The crude product was taken up in chloroform and was treated with activated charcoal, filtered, and recrystallized from chloroform to give yellow–green crystals. Yield 83%, mp 110–112 °C. ^1H NMR δ ($CDCl_3$): 8.21 (d, $J=7.8$ Hz, 2H), 8.11 (s, 2H), 7.92 (d, $J=8.4$ Hz, 2H), 2.16 (q, $J=7.2$ Hz, 4H), 0.31 (t, $J=7.2$ Hz, 6H). $^{13}C\{^1H\}$ NMR δ ($CDCl_3$): 168.3, 152.0, 146.2, 133.3, 131.4, 125.8, 121.3, 56.9, 32.2, 8.4. HRMS Calcd for $C_{19}H_{16}O_2Cl_2$: 346.0527 (M + 1), found 346.0554.

9,9-Diethylfluorene-2,7-dicarboxylic acid diallylamide (28)

A solution of **27** (1.0 g, 2.8 mmol) in dry benzene (30 mL) was added slowly with vigorous stirring to a solution of allylamine (0.34 g, 6.0 mmol) and triethylamine (0.6 g, 6 mmol) in dry benzene (10 mL). The mixture was stirred at room temperature for 8 h and heated for 1 hour at 50 °C. The mixture was cooled and the precipitate was collected by filtration and washed with benzene. Recrystallization from methanol afforded colorless needles. Yield 80%, mp 218–219 °C. ^{1}H NMR δ ($CDCl_3$): 7.83 (s, 2H), 7.76 (br s, 4H), 6.35 (s, 2H), 6.05–5.94 (m, 2H), 5.30 (d, $J=17.0$ Hz, 2H), 5.21 (d, $J=9.9$ Hz, 2H), 4.13 (t, $J=5.4$ Hz, 4H), 2.10 (q, $J=7.2$ Hz, 4H), 0.25 (t, $J=7.2$ Hz, 6H). $^{13}C\{^1H\}$ NMR δ ($CDCl_3$): 167.3, 151.1, 143.6, 134.1, 133.8, 125.8, 121.9, 120.1, 116.8, 56.7, 42.5, 32.5, 8.4. HRMS Calcd for $C_{25}H_{28}O_2N_2$: 389.2229 (M + 1), found 389.2225.

9,9-Diethyl-2,7-bis(pyrrol-2-yl)fluorene (30, Engel)[31]

A mixture of **28** (1.0 g, 2.6 mmol), phosgene (14.2 mL) and anhydrous DMF (0.1 mL) was stirred for 10 h at room temperature. The mixture was heated to 40 °C for 1 h. The solvent was removed under reduced pressure, and crude 9,9-diethyl-2,7-bis[*N*-allylimino(chloro)methyl]fluorene (**29**) was used without isolation for the next step. A solution of crude **29** in THF (50 mL) was added dropwise to a solution of potassium *tert*-butoxide (1.6 g, 1.4 mmol) in dry THF (30 mL) held at a temperature between −10 °C and 0 °C under nitrogen. The mixture was stirred for 1 h, and the mixture was poured into ice and extracted with diethyl ether (50 mL). The organic phase was dried with $MgSO_4$, the volatiles were removed under reduced pressure, and the residue was purified by column chromatography. The first eluent was hexane, and a second column was run with hexane–ethyl acetate (5:3) to yield **30**. Yield 80%, mp 278–279 °C. ^{1}H NMR δ ($CDCl_3$): 8.51 (br s, 2H), 7.65 (d, $J=7.8$ Hz, 2H), 7.45 (d, $J=7.8$ Hz, 2H), 7.41 (s, 2H), 6.89 (s, 2H), 6.58 (s, 2H), 6.33 (s, 2H), 2.05 (q, $J=7.2$ Hz, 4H), 0.34 (t, $J=7.2$ Hz, 6H). $^{13}C\{^1H\}$ NMR δ ($CDCl_3$): 150.6, 139.6, 132.7, 131.4, 122.7, 119.8, 118.7, 118.1, 110.2, 105.8, 56.2, 33.0, 8.5. HRMS Calcd for $C_{25}H_{24}N_2$: 352.1939 (M^+), found 352.1942.

1,3-Dioxolane-2-propanal (Lucchesini)[32]

A solution of 2-(2-bromoethyl)-1,3-dioxolane (2.0 g, 11 mmol) in THF (6 mL) was added dropwise to a suspension of magnesium turnings (0.48 g, 20 mmol) in THF (10 mL) under nitrogen and allowed to cool for 1 hour. Anhydrous DMF (1 mL) was added to the Grignard reagent over 10 min. The mixture was stirred for 90 min at room temperature, and citric acid (2.3 g) in water (7 mL) was added. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 × 10 ml). The organic layers were combined, dried over $MgSO_4$, and the solvents evaporated. The residue was purified by flash chromatography using hexane–ethyl acetate (5:2) as the eluent. Yield 37% bp 85–90 °C. ^{1}H NMR δ ($CDCl_3$): 9.75 (s, 1H), 4.96 (t, $J=3.6$ Hz, 1H), 3.97–3.82 (m, 4H), 2.57–2.51 (m, 2H), 2.07–2.01 (m, 2H). $^{13}C\{^1H\}$ NMR δ ($CDCl_3$): 201.4, 102.6, 64.7, 37.3, 26.0.

9,9-Diethyl-2,7-bis[3-(1,3-dioxolan-2-yl)propanoyl]fluorene (32)

Bu^nLi (4.9 mL, 1.6 mol) was added to a solution of **24** (1.0 g, 2.6 mmol) in dry THF at −70 °C, and the mixture was stirred for 1 hour. 1,3-Dioxolane-2-propanal (0.85 g, 6.5 mmol) was added dropwise, and the resulting mixture was stirred for 1 h at −30 °C. The mixture was warmed to room temperature, and saturated ammonium chloride (5.5 mL) was added. The organic layer was separated and the aqueous layer was extracted with diethyl ether (40 mL), the organic layers were combined and dried over $MgSO_4$, and the volatiles were removed to afford **31**. A solution of **31** in anhydrous methylene chloride (5 mL) was added to a suspension of pyridinium chlorochromate (PCC, 1.94 g, 9.00 mmol) and sodium acetate (0.28 g, 3.4 mmol) in methylene chloride (5 mL). The mixture was stirred for 90 min at room temperature followed by addition of further PCC (0.2 g). The mixture was stirred for 60 min. Saturated sodium hydrogen carbonate (20 mL) was added to the solution until evolution of CO_2 ceased. The slurry was filtered, and the residue was washed with methylene chloride (50 mL). The filtrate was concentrated under reduced pressure, and the crude **32** was used directly for the next step.

9,9-Diethyl-2,7-bis(pyrrol-2-yl)fluorene (30, Lucchesini)[32]

A solution of crude **32** (0.50 g, 1.2 mmol) and ammonium acetate (2.2 g, 2.8 mmol) in acetic acid (10 mL) was refluxed for 18 h under nitrogen. Acetic anhydride was added until **32** was consumed as monitored by TLC (hexane–ethyl acetate, 5:3). The mixture was poured into water (30 mL), neutralized with sodium hydrogen carbonate and extracted with methylene chloride (30 mL). The combined organic layers were dried with $MgSO_4$, and volatiles were removed under reduced pressure. The crude **30** was purified by flash chromatography (silica gel, hexane–ethyl acetate, 5:3). Yield 20%, mp 278–279 °C. ^{1}H NMR δ (DMSO-d_6): 11.31 (s, 2H), 7.71 (d, $J=7.5$ Hz, 4H), 7.67 (s, 2H), 7.58 (d, $J=8.1$ Hz, 2H), 6.86 (s, 2H), 6.57 (s, 2H), 6.13 (s, 2H), 2.08 (q, $J=7.2$ Hz, 4H), 0.28 (t, $J=7.0$ Hz, 6H). $^{13}C\{^1H\}$ NMR δ (DMSO-d_6): 149.8, 138.4, 131.6, 131.5, 122.2, 119.7, 119.1, 117.5, 109.1, 105.5, 55.5, 32.0, 8.5. HRMS Calcd for $C_{25}H_{24}N_2$: 352.1939 (M^+), found 352.1942.

Polymers 34a–c

The experimental details are similar to those of **34d**.

Polymer 34a

A mixture of **21a** (0.29 g, 0.68 mmol) and **18a** (0.40 g, 0.67 mmol) was dissolved in THF (30 mL) and $Cl_2Pd(PPh_3)_2$ (25 μg) was added. The mixture was refluxed overnight and poured into water, and the solid was collected and reprecipitated into CH_2Cl_2 (0.21 g, 60%).

Polymer 34b

A mixture of **21b** (0.76 g, 1.5 mmol) and **18a** (0.91 g, 1.5 mmol) was dissolved in THF (40 mL) and $Cl_2Pd(PPh_3)_2$ (32 μg) was added. The mixture was refluxed overnight and poured into water, and the solid was collected and reprecipitated into CH_2Cl_2 (0.52 g, 57%).

Polymer 34c

A mixture of **21c** (0.49 g, 1.1 mmol) and **18a** (0.60 g, 1.0 mmol) was dissolved in THF (30 mL) and $Cl_2Pd(PPh_3)_2$ (25 μg) was added. The mixture was refluxed overnight and poured into water, and the solid was collected and reprecipitated into CH_2Cl_2 (0.63 mg, 11%).

Polymer 34d

A mixture of 9,9-didecyl-2,7-dibromofluorene **18a** (1.36 g, 2.25 mmol) and bis(trimethylstannyl)furan (0.94 g, 2.4 mmol) was placed under vacuum for 1 h and freshly distilled THF (30 mL) was added. The solution was added by syringe to $Cl_2Pd(PPh_3)_2$ (0.035 g, 0.050 mmol), and the mixture was shielded from the light and heated to reflux for 7 d. The darkened mixture was cooled to room temperature and concentrated to *ca.* 20 mL and poured into MeOH (150 mL). A lime green solid formed and was isolated by vacuum filtration. The solid was partially dissolved in CH_2Cl_2 (300 mL) and filtered. The filtrate was concentrated to *ca.* 150 mL and poured into MeOH (500 mL). The green–yellow solid was collected and dried under high vacuum (1.05 g, 90.9%). ^{1}H NMR δ (C_6D_6): 8.07 (m, 1H, arom H), 7.85 (m, 1H, arom H), 7.66 (m, 1H, arom H), 6.64 (m, 1H, arom H), 2.21 (m, 4H, CH_2), 1.15 (br s, 28H, CH_2), 0.86 (m, 6H, CH_3), 0.4 (m, 4H, CH_2). $^{13}C\{^1H\}$ δ (C_6D_6): 154.9, 152.5, 141.2, 130.8, 124.1, 120.6, 118.6, 108.2, 56.2, 41.3, 32.6, 30.8, 30.4, 30.1, 24.7, 23.4, 14.7, 1.7. Anal. Calcd for $C_{37}H_{50}O$: C, 87.00; H, 9.90. Found: C, 64.43; H, 7.44%. Duplicate analyses of a spectroscopically pure sample gave low carbon and hydrogen content values.[34]

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