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Conducting polyfurans by electropolymerization of oligofurans†‡

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Polyfurans have never been established as useful conjugated polymers, as previously they were considered to be inherently unstable and poorly conductive. Here, we show the preparation of stable and conducting polyfuran films by electropolymerization of a series of oligofurans of different chain lengths substituted with alkyl groups. The polyfuran films show good conductivity in the order of 1 S cm^{-1} , good environmental and electrochemical stabilities, very smooth morphologies (roughness 1–5 nm), long effective conjugation lengths, well-defined spectroelectrochemistry and electro-optical switching (in the Vis–NIR region), and have optical band-gaps in the range of 2.2–2.3 eV. A low oxidation potential needed for polymerization of oligofurans (compared to furan) is a key factor in achievement of improved properties of polyfurans reported in this work. DFT calculations and experiments show that polyfurans are much more rigid than polythiophenes, and alkyl substitution does not disturb backbone planarity and conjugation. The obtained properties of polyfuran films are similar or superior to the properties of electrochemically prepared poly(oligothiophene)s under similar conditions.

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Introduction

The field of conjugated and electrically conducting polymers continues to attract much attention both scientifically and technologically.¹ Among them, an important class of five-membered unsaturated heterocyclic polymers, such as polypyrrole (PPy),² polythiophene (PT),³ polyselenophene (PSe)⁴ as well as their derivatives, have been extensively studied and applied. Polyfuran (PFu), on the other hand, has scarcely been explored and has not been established as a conductive polymer. This is because of the difficulty in polymerization, the low stability and the poor properties of the polyfuran samples that have been obtained.⁵ The reported electrical conductivities of doped polyfurans were measured in the range of 10^{-5} to $10^{-2} \text{ S cm}^{-1}$,^{5,6} which is significantly lower than the conductivity of polythiophenes electrochemically prepared from a terthiophene (PT₃) (10^0 S cm^{-1})^{3b,7} and thiophene monomers (10^2 S cm^{-1}).^{3b,8} Polyfurans have also been reported as environmentally and electrochemically unstable. For example, the authors noticed

that upon exposure to ambient light and air, films of chemically prepared alkylated polyfuran bleached over a period of hours to days.⁹ Furthermore, the electrochemical redox activity of polyfuran was shown to degrade during cycling in acetonitrile (ACN) solution.¹⁰

Many researchers have tried to overcome preparation problems by varying the conditions of polymerization.^{5,11} The main problem associated with electrochemical polymerization is the high oxidation potential required to polymerize furan, which results in irreversible over-oxidation of the resulting polyfurans.^{5,12} A mixture of trifluoride diethyl etherate and ethyl ether (BFEE/EE) as a solvent was used to reduce this electropolymerization potential.^{11c,d,13} However, the reported conductivities of the resulting polyfurans were small (up to $10^{-2} \text{ S cm}^{-1}$), and their absorption spectra ($\lambda_{\text{max}} = 420 \text{ nm}$)^{11d} reveal a short conjugation length of about eight furan rings.¹⁴ Kanatzidis *et al.*, used terfuran as the starting monomer to lower the potential needed for polymerization to less than 1.0 V (vs. SCE).^{11b} The resulting polyfuran was characterized by a variety of techniques and showed a red shifted absorbance maximum centered at 468 nm. Nevertheless, the polyfuran produced had a low conductivity of $2 \times 10^{-3} \text{ S cm}^{-1}$, which is probably due to defects in the polymer, as were observed by IR spectroscopy. Chemically synthesized polyfuran did not appear to be highly conjugated because of a significant degree of furan ring-opening defects.^{9,15} It is noteworthy that in contrast to polyfurans, the incorporation of furan blocks in conjugated polymers resulted in high quality materials.¹⁶ Overall, despite numerous reports on the preparation of polyfuran (usually

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† This work is dedicated to the memory of Professor Michael Bendikov.

‡ Electronic supplementary information (ESI) available: Full experimental and computational details, synthesis of 1–18, Fig. S1–S26 and Tables S1–S4. See DOI: 10.1039/c4sc02664k

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lacking full characterization),⁵ it appears that there are no reports of polyfurans with properties such as high conductivity, stability, high conjugation length and small number of defects, all of which are required for their application as organic electronic materials.

We previously reported the preparation of long unsubstituted α -oligofurans (Fu₅-Fu₉) and recently alkyl substituted α -oligofurans (Fu_{*n*}-2C₆ (*n* = 4, 6, 8) and Fu₁₆-6C₆) that exhibit higher fluorescence, better packing, greater rigidity, and higher solubility than the corresponding oligothiophenes.^{14,17} We also showed that these oligofurans display good electronic properties, *e.g.*, field effect mobilities and on-off ratios, similar to those of the corresponding oligothiophene analogues.¹⁸ Thus, we surmised that polyfurans would not only possess similar properties, but would have advantages over other conductive polymers. The rigidity of their backbone is expected to enable the introduction of large side substituents without breaking planarity and π -conjugation. Moreover, polyfurans can be synthesized from renewable resources¹⁹ and may be biodegradable.²⁰ Thus, we believe that the reported poor properties, such as low conductivity,⁵ blue-shifted absorption,^{11d} and instability,⁹ of polyfurans were due to defects produced during their preparation rather than intrinsic properties of polyfurans.

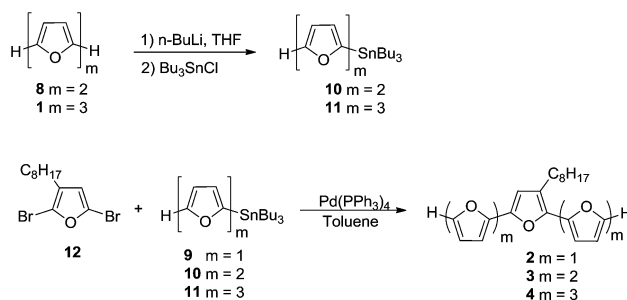
Here we report the first electrochemically-prepared stable and conducting polyfuran films **P1**–**P7** (Chart 1), which possess all the properties necessary to be considered as conducting polymers suitable for applications in organic electronics. These polymers have several advantages over other conjugated polymers, such as rigidity of the backbone and film smoothness. The use of long oligofurans with solubilizing groups, which have relatively low oxidation potential, as the starting monomers for polymerization was the key factor in obtaining polyfuran with improved properties. The electrochemical and spectroelectrochemical behavior, conductivity, electrochemical

stability in air under ambient conditions, as well as the morphology of the prepared polyfuran films were studied and compared with corresponding polythiophene analogues. We also report the development of a synthetic methodology for the preparation of long oligofurans **1**–**7** substituted with solubilizing groups.

Results

Synthesis of oligofurans

Oligomers **1**–**5** (Schemes 1 and 2) were synthesized by Stille coupling, oligomer **6** (Scheme 3) was synthesized by Kumada coupling, and oligomer **7** (Scheme 3) was obtained by a combination of Kumada and Ullmann couplings of suitable precursors. Synthesis of compounds **1**, **10** and **11** was reported previously.^{14,21} Synthesis of oligomers **2**, **3**, and **4** (Scheme 1) was achieved by Stille coupling of 2,5-dibromo-3-octylfuran (**12**) with tributyl(furan-2-yl)stannane (**9**), [2,2'-bifuran]-5-yltributylstannane (**10**), and [2,2':5',2''-terfuran]-5-yltributylstannane (**11**), respectively. The precursor 2,5-dibromo-3-octylfuran (**12**) was prepared by bromination of 3-octylfuran with *N*-bromo-succinimide (NBS) with a 68% yield.



Scheme 1

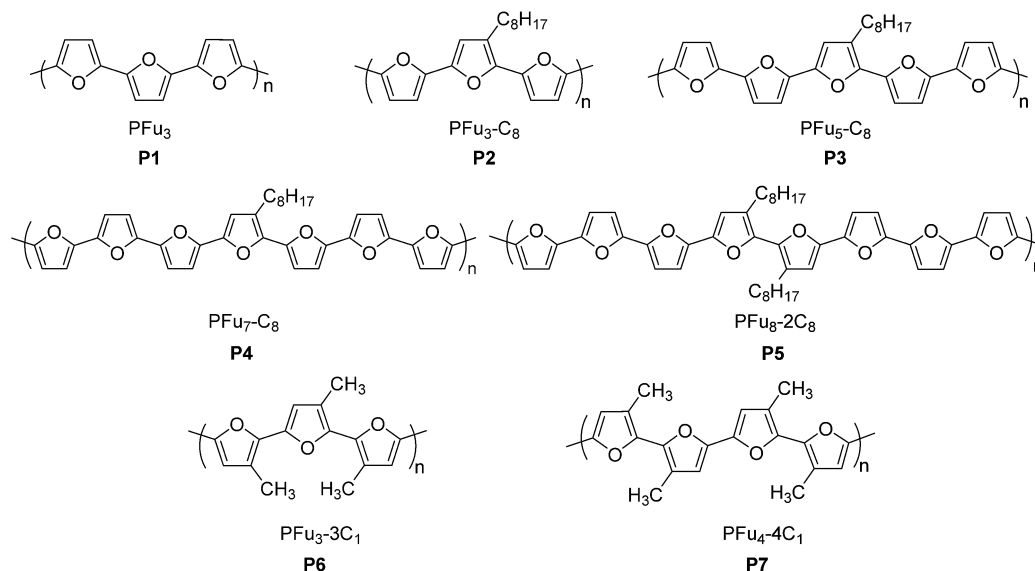
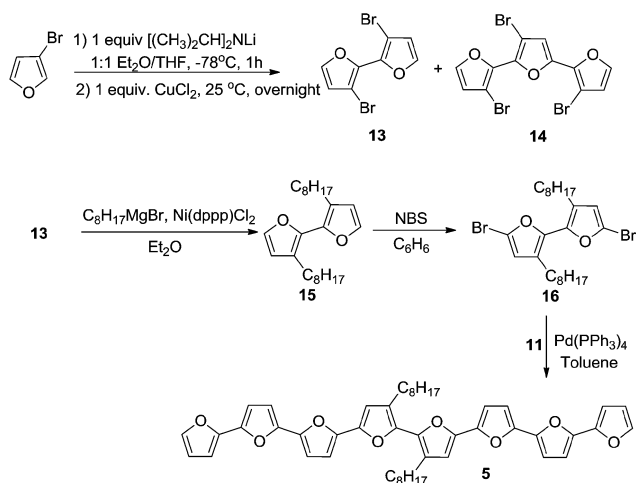
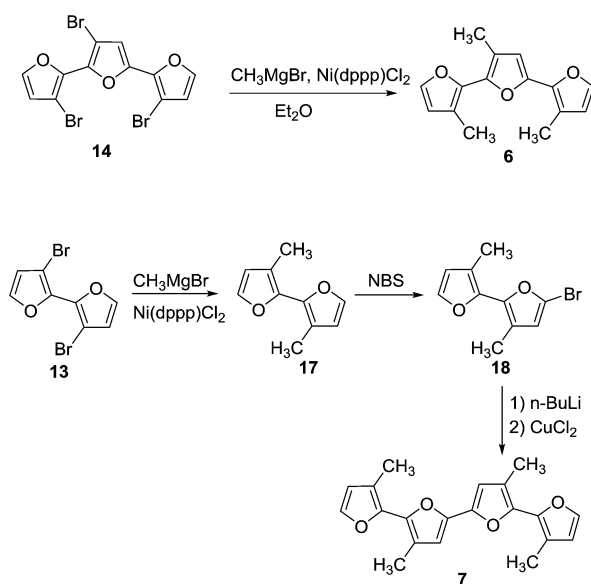


Chart 1 Polymers prepared and studied in this work.





Scheme 2



Scheme 3

For the synthesis of octafuran **5** (Scheme 2), dibromo derivative **13** was prepared using the procedure described in the literature.²² Interestingly, during the course of the reaction, terfuran derivative **14** was also obtained with a 6% yield. Subsequent reaction of compound **13** and octylmagnesium bromide with Ni(dppp)Cl₂ gave 3,3'-dioctyl-2,2'-bifuran (**15**) with a 74% yield. Stille coupling of dibromo derivative **16** (obtained from the bromination of **15** using NBS) with [2,2':5',2''-terfuran]-5-yltributylstannane (**11**) yielded dioctyl-substituted octafuran **5**.

Oligomer **2** has the highest octyl chain to furan ratio (1 : 3), while oligomer **4** has the lowest octyl chain to furan ratio (1 : 7). In order to synthesize polymers having at least a 1 : 1 ratio of alkyl chain to furan ring, bromo groups present in compound **14** were replaced with alkyl chains. Kumada coupling of **14** with methylmagnesium bromide gave compound **6** (Scheme 3) with

a moderate yield of 51%. The tetramethyl quaterfuran **7** (Scheme 3) was synthesized by lithiation of the monobromo precursor **18** followed by coupling with CuCl₂.

Electrochemical polymerization and characterization

Electropolymerization of furan monomer could be achieved only at high potentials (*ca.* 1.8 V *vs.* SCE),^{5,12a} at which point ring opening and irreversible degradation leads to non-conjugated and low quality polyfurans. Thus, the electropolymerization potential needs to be lowered. This is achieved by using oligofurans rather than furan monomer as the repeat units.^{3b,11b,23} Starting from terfuran, the oxidation potential of oligofurans drastically decreases, and the polymerization process proceeds below 1.0 V *vs.* SCE.^{11b} Such low oxidation potentials allowed the preparation of polyfurans reported herein under air at ambient conditions, which can be beneficial for their possible applications.

The electrodeposition of polymers **P1–P7** has been performed both potentiodynamically and potentiostatically. The best polyfuran films were obtained using a 0.1–1 mM concentration of the oligomer in an ACN solution containing 0.1 M TBACF₃SO₃ as the electrolyte. In general, for potentiodynamic polymerization, the potential was scanned at 50 mV s^{−1} from −0.2 V to 0.8 V *vs.* Ag/AgCl-wire and for potentiostatic polymerization, a potential of 0.75 V *vs.* Ag/AgCl-wire was applied. Further optimization of polymerization conditions is possible for each of the oligomers (see Table S2, ESI†). Smooth electrodeposition and the growth of insoluble, highly adhesive continuous polymeric films were observed on different types of working electrodes (*i.e.*, ITO-coated glass, Pt-disk, Au-coated quartz crystal and IDA). It is worth noting that the electrodes were not modified and specially cleaned as they were in the preparation of smooth polythiophenes.²⁴ Representative cyclic voltammograms (CV) for the polymerization of **P3** (PFu₅-C₈) on ITO electrode, showing stepwise increases in the current over

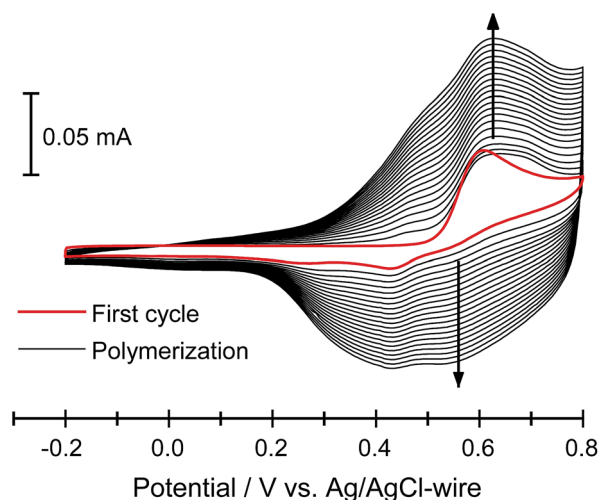


Fig. 1 Electrochemical deposition of **3** (0.1 mM) in 0.1 M TBACF₃SO₃/ACN at 50 mV s^{−1} on an ITO-coated glass slide.



the course of polymerization, are displayed in Fig. 1 (for other polymers see Fig. S3, ESI†).

Oxidation peak potentials are poorly resolved for oligomers 1, 2, 4 and 5 (Fig. S3†). Therefore, the onset potentials for oligomer oxidation (E_{ox}), measured from the first CV curve of the polymerization, were used for comparison between different oligomers (Table 1). As expected, both the introduction of an alkyl group into an oligomer and the elongation of the oligomer decrease the oxidation potential. For example, the E_{ox} for **P1** (PFu₃) is 0.62 V, whereas for **P2** (PFu₃-C₈) and **P3** (PFu₅-C₈), it is 0.51 V and 0.43 V, respectively. Furthermore, polyfurans are obtained at lower oxidation potentials than polythiophenes, as shown by the oxidation onset potential of terfuran, which is 0.33 V lower than that of terthiophene.

It is well known that the electrolyte, solvent, oligomer concentration, and method of electropolymerization drastically affect the quality of the resulting polymeric films.^{1d,23,25} We found that TBACF₃SO₃/ACN electrolyte (see Fig. S4† for others) and concentrations of monomers lower than usually used^{3b,11b} produced better polyfurans. Electrolyte anions and solvent could affect the stability of intermediate σ -dimers, while lower concentrations could reduce π -dimerization of cation radicals that are produced during electropolymerization.^{1d}

CVs of polyfurans in monomer-free TBACF₃SO₃/ACN electrolyte showing broad oxidation and reduction peaks (Fig. 2 and S5†), are similar to those of other conducting polymers.^{1d,3b} It is difficult to determine accurate oxidation potentials for polyfurans from the obtained CVs. Nevertheless, oxidation potentials could be estimated from *in situ* conductivity measurements (see below).

Optical and structural properties

Spectroelectrochemical studies of the electrochemically produced **P1–P7** films on ITO electrodes were performed to evaluate their electronic structure. All prepared polymers exhibited well-defined spectroelectrochemical responses, namely, a reversible and distinct change in the absorption spectrum during the redox processes (doping/dedoping). Fig. 3 shows representative spectroelectrochemical spectra for **P1**, **P2**, and **P6** films (for other polymers see Fig. S8†). During polymer oxidation, the absorption peak of the neutral polymer film at around 460 nm decreases and two peaks at around 750 nm and 1250 nm develop. In addition, the isosbestic point is observed at

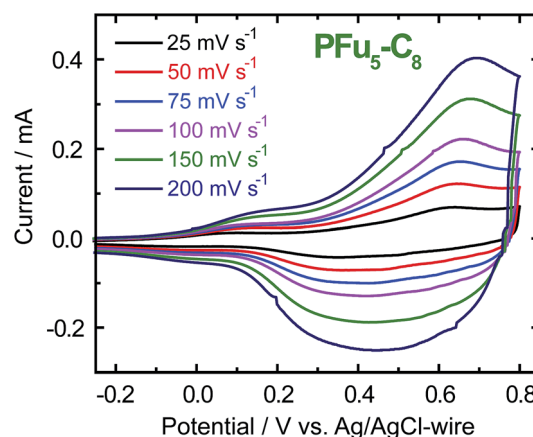


Fig. 2 CV of **P3** film on an ITO coated glass electrode in monomer-free 0.1 M TBACF₃SO₃/ACN electrolyte at different scanning rates.

ca. 530 nm for **P1–P5** and at ca. 550 nm for **P6** and **P7**. Importantly, the presence of one isosbestic point indicates interconversion between neutral and cation-radical (polaron) states.²⁶ Only the 0.7 V spectral trace of **P6** (Fig. 3c) shows beginning of bipolaron formation, which is consistent with the decrease in electrical conductivity (see below).

The measured λ_{max} values of neutral polyfurans are in the range of 456–466 nm (Table 2). This range is red-shifted compared with most of previously reported values of <420 nm.^{10c,11a,c,d,12b} This suggests that much longer effective conjugation lengths are obtained in the current work. We note that Kanatzidis *et al.* reported^{11b} an absorption maximum of 468 nm for PFu₃. However, their spectrum lacks vibronic shoulders, which are observed in all our spectra. We estimate the effective conjugation length in prepared polyfurans to be more than 25 furan units, as can be deduced from extrapolation of the λ_{max} values of α -oligofurans (see Fig. S25†).

The optical band gaps of polyfurans estimated from the absorption spectra (Table 2) for unsubstituted **P1** and partially alkyl substituted **P2–P5** are ca. 2.3 eV. By contrast, for polyfurans **P6** and **P7** substituted with one methyl group per furan ring, the band gaps are decreased to ca. 2.2 eV. This observation is consistent with DFT calculations, which showed that alkyl substitution reduces band gaps (Table 2 and S3†). Moreover, calculations (Table 2) showed that this reduction in band gap occurs because of the increase in the highest occupied crystal orbital (HOCO) energy (*i.e.* the energy of the valence band), which is partially offset by an increase in the lowest occupied crystal orbital (LUCO) energy (*i.e.* the energy of the conduction band). Consequently, the oxidation potential of alkyl-substituted polyfurans decreased. The increase of the HOCO energy is consistent with the electron donating property of alkyl groups.

Interestingly, the peak of neutral polyfuran films shows red-shifted shoulders (Fig. 3 and S8†), probably because of the vibronic coupling.²⁷ The presence of vibronic coupling may indicate that the polymer backbone is highly rigid, planar and effectively π -conjugated. We have shown that oligofurans exhibit high rigidity,^{14,28} as evident from calculated twisting

Table 1 Onset potentials for 1–7 and T3 oligomer oxidation (E_{ox})

Oligomer	E_{ox} , ^a V vs. Ag/AgCl-wire
Fu ₃ (1)	0.62
Fu ₃ -C ₈ (2)	0.51
Fu ₅ -C ₈ (3)	0.43
Fu ₇ -C ₈ (4)	0.40
Fu ₈ -2C ₈ (5)	0.37
Fu ₃ -3C ₁ (6)	0.44
Fu ₄ -4C ₁ (7)	0.41
T ₃	0.95

^a For approximate oxidation peak potentials see Table S1.



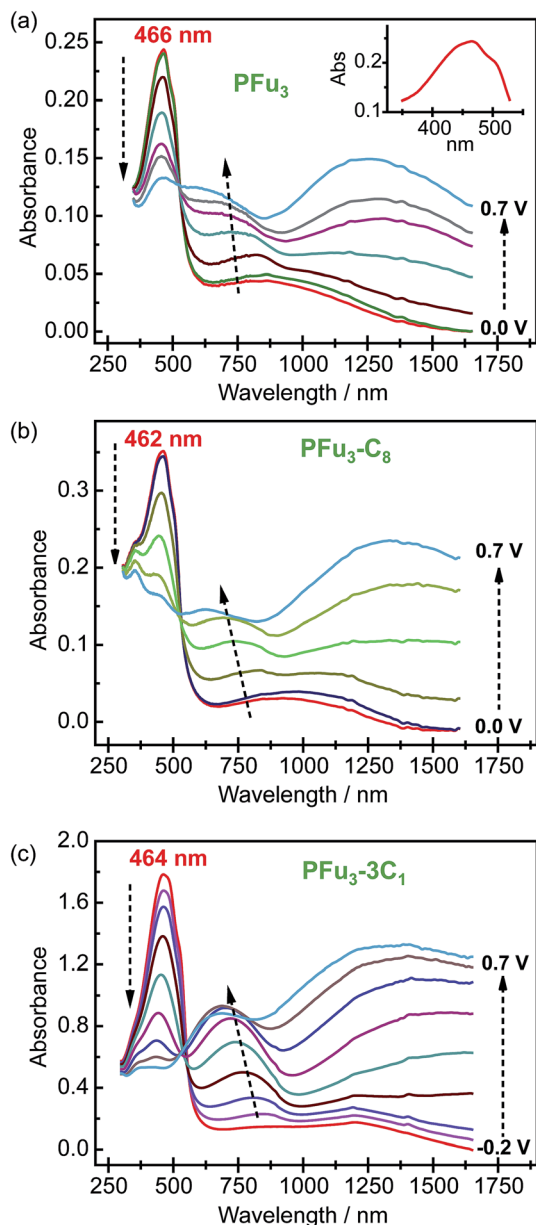


Fig. 3 Spectroelectrochemistry of (a) **P1**, (b) **P2**, and (c) **P6** on an ITO coated glass electrode in monomer-free 0.1 M TBACF₃SO₃/ACN electrolyte. Inset (a) shows closer look on the vibronic shoulders of the main absorption peak of **P1** at 0.0 V. Stated potentials are vs. Ag/AgCl-wire.

potentials which are higher than for oligothiophenes. Similar computational results have been recently shown for polyfurans.²⁹ Consequently, the π -conjugation and planarity of polyfurans should not be distorted by various substitution of the polyfuran backbone as strongly as it is in the polythiophene family. Indeed, DFT geometry optimization (PBC/B3LYP/6-31G(d)) of polyfurans **P1–P7** shows that the polyfuran backbone remains planar upon alkyl substitution (Fig. 4a and S10†). In contrast, in polythiophene PT₄-4C₁, which is a thiophene analogue of **P7**, the polymer backbone deviates strongly from planarity (Fig. 4b), distorting the π -conjugation. As a consequence, the calculated band gap for PT₄-4C₁ increases to 2.9 eV

from 2.0 eV for planar unsubstituted polythiophene.^{29,30} Whereas measured optical and calculated band gaps for polyfurans **P1–P7** are not increased upon alkyl substitution.

IR spectroscopy

Structural defects in the conjugated backbone of polyfuran can be revealed by IR spectroscopy.³² Previously reported polyfurans showed defects, such as ring-opening and β -coupling, which were observed by stretching vibrational modes of the aliphatic C–H bond (~ 2900 cm^{−1}), carbonyl C=O bond (~ 1720 cm^{−1}), and O–H bond (~ 3500 cm^{−1}).^{10b,11a–c} The measured ATR-FTIR spectra of **P1** and **P3** films on Pt-foil (Fig. 5a and b) show little structural defects for **P1** and almost none for **P3** and are in good agreement with the calculated spectrum of model Fu₂₀ (Fig. 5c, Table S4 and Fig. S12†) and with previous IR data.^{10b,11c,33} The IR spectra of **P1** and **P3** are similar, showing the same bands except for the aliphatic C–H stretching mode of the octyl substituents at around 2900 cm^{−1}.

In situ conductivity

The conductivity of conjugated polymers strongly depends on many factors, particularly the method of preparation, the presence of impurities, humidity, and the measurement technique.^{1b} Owing to their simplicity as well as their ability to obtain a potentiodynamic response, *in situ* conductivity measurements using an interdigitated array (IDA) microelectrode³⁴ or two-band electrode³⁵ have found wide use.³⁶ However, obtaining the absolute value of polymer film conductivity is not straightforward because it depends on many factors that are hard to define, such as non-trivial geometrical factor of the electrode, non-linear dependence of the conductance on film thickness, and undefined contact resistances. Thus, we report conductance values in comparison to that of poly(terthiophene) (PT₃), which was electrochemically prepared and measured under the same setup. Additionally, we compare the conductance values of our polyfurans to those of drop-cast commercial poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) film on the same type of electrode. The conductivity of electrochemically prepared PT₃ film^{7a} and that obtained from commercial PEDOT:PSS³⁷ is estimated to be on the order of 1 S cm^{−1}.

Fig. 6 shows simultaneous measurements of CV and conductance of **P1–P4**, **P6** and **P7** films. All obtained polyfurans show maximum conductances comparable to those of PT₃ and PEDOT:PSS films (Table 3, Fig. S15†). Thus electrical conductivities of doped polyfurans are in the order of 1 S cm^{−1}. This conductivity is much higher than most published values, which range from 10^{−2} to 10^{−5} S cm^{−1}.⁵

Each polymer undergoes transition to conductive state at different potentials (Fig. 6 and S15†). We used the potential at half-maximal conductance (for the forward scan) (E_{hc}) for comparison between polymers. As evident from Table 3, E_{hc} depends on the degree of alkyl substitution, *i.e.*, E_{hc} decreases with increasing degree of alkyl substitution (Table 3). For example, the value of E_{hc} for fully methylated polyfuran **P6** is 0.39 V is lower than that of the unsubstituted **P1**. Since, the transition to conductive state is associated with the oxidation of a



Table 2 Experimental and calculated electronic and optical properties for neutral P1–P7

Polymer	λ_{\max} , nm	Optical band gap ^a , eV	E_g (calc) ^b , eV	HOCO (calc) ^b , eV	LUCO (calc) ^b , eV
PFu ₃ (P1)	466	2.31	2.41	−4.36	−1.95
PFu ₃ -C ₈ (P2)	462	2.31	2.35	−4.20	−1.85
PFu ₅ -C ₈ (P3)	463	2.32	2.37	−4.23	−1.88
PFu ₇ -C ₈ (P4)	458	2.29	2.38	−4.29	−1.90
PFu ₈ -2C ₈ (P5)	460	2.31	2.36	−4.23	−1.88
PFu ₃ -3C ₁ (P6)	464	2.22	2.25	−4.02	−1.78
PFu ₄ -4C ₁ (P7)	456	2.22	2.26	−4.03	−1.77
PT ₃ ^c	475	2.02	2.05	−4.61	−2.56

^a The optical band gaps were obtained from the extrapolation of the linear part of the $(\alpha h\nu)^2$ vs. $h\nu$ plot to $(\alpha h\nu)^2 = 0$, where α is the absorption coefficient. ^b Calculated using the PBC/B3LYP/6-31G(d) level. ^c For comparison, PT₃ was prepared and measured in this work at same conditions as polyfurans.

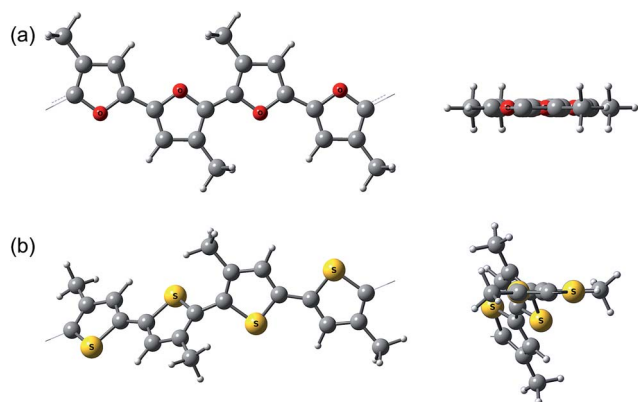


Fig. 4 Calculated (PBC/B3LYP/6-31G(d)) geometry of (a) P7 and (b) polythiophene analog of P7, PT₄-4C₁. A side view and a view along the polymer backbone.

conjugated polymer, we can conclude that the oxidation potential of polyfurans is also decreased by alkyl substitution. This is in the agreement with DFT calculations, which show increase in energy of the HOCO as the degree of alkyl substitution increases (Table 2 and S3†). Furthermore, for polyfurans, the E_{hc} potentials are lower than that of PT₃ but higher than that of PEDOT, which is consistent with the higher oxidation potential of PT₃ (ref. 38) and the lower oxidation potential of PEDOT.³⁹

We observe that the conductivity of fully methylated polyfurans P6 and P7 reaches maximum at 0.5 V and 0.6 V, respectively, and decreases at higher potentials. This observation may suggest that the charge carriers are polarons. Upon further electrochemical oxidation, their conductivity decreases (reversibly) as bipolarons are formed. However, this behavior is not observed in polyfurans P1–P4 due to degradation of the polyfuran films at potentials above 0.8 V, where their conductivity decreases irreversibly.

Electrochemical stability

The electrochemical stability of conducting polymers is of utmost importance for their use in electrochemical systems, such as batteries, electrocatalytic materials, sensor devices, and other electronic components.⁴⁰ Electrochemical degradation of

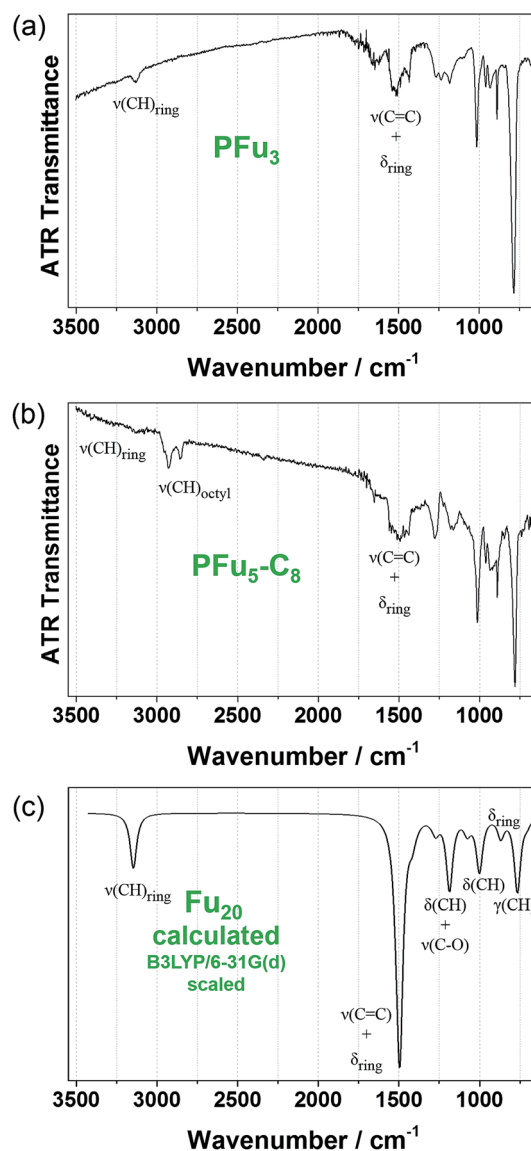


Fig. 5 Experimental FTIR-ATR spectra: (a) of P1 and (b) of P3 films electrodeposited on platinum foil. (c) DFT B3LYP/6-31G(d) calculated IR spectrum of Fu₂₀ (frequencies were scaled by 0.96 (ref. 31)).

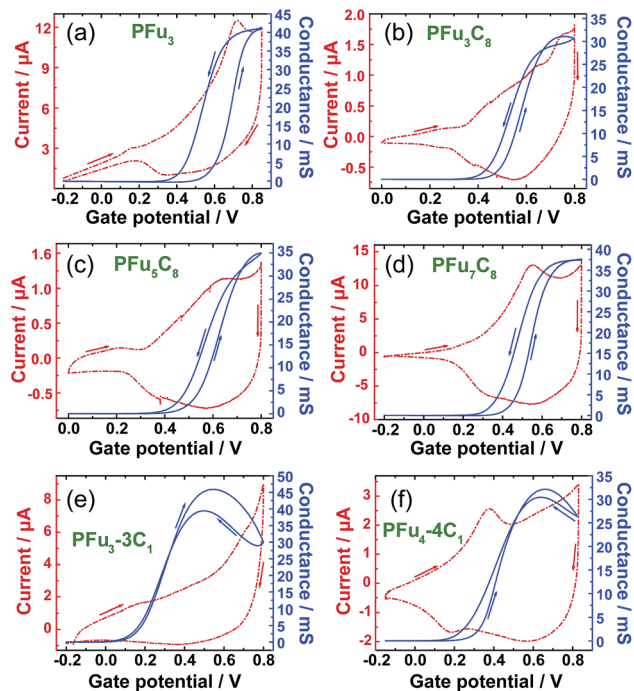


Fig. 6 Cyclic voltammograms (dashed line) and *in situ* conductance measurements (solid line) for: (a) P1, (b) P2, (c) P3, (d) P4, (e) P6 and (f) P7 in monomer-free TBACF₃SO₃/ACN using a 10 μm interdigitated array gold microelectrode. Sweep rates are 10 mV s⁻¹ for cyclic voltammograms with a 10 mV probe potential for conductivity measurements. Stated potentials are vs. Ag/AgCl-wire.

Table 3 Conductance and half-maximal conductance potential (E_{hc}) for forward scan in P1–P4, P6, P7, PT₃ and PEDOT

Polymer	Conductance (max), mS	E_{hc}^a , V
PFu ₃ (P1)	43	0.69
PFu ₃ -C ₈ (P2)	32	0.58
PFu ₅ -C ₈ (P3)	38	0.62
PFu ₇ -C ₈ (P4)	37	0.55
PFu ₃ -3C ₁ (P6)	46	0.30
PFu ₄ -4C ₁ (P7)	32	0.44
PT ₃	42	0.87
PEDOT	>72 ^b	−0.21
PEDOT:PSS ^c	50	—

^a Half-maximal conductance potential (vs. Ag/AgCl-wire) for the forward scan. ^b Limited by the resistance of the IDA electrode contacts (Fig. S15). ^c Drop-cast film.

conductive polymers, such as polypyrrole, polythiophene, and polyaniline, has been studied extensively.⁴⁰ However, very little has been reported on the electrochemical degradation of polyfuran.^{10b,11c}

(a) Redox current stability. The electrochemical cyclability of the polyfurans was tested using cyclic voltammetry between −0.3 to 0.7 V vs. Ag/AgCl-wire in a monomer-free TBACF₃SO₃/ACN electrolyte solution for up to 2000 cycles in the air under ambient conditions (Fig. 7). Polyfurans P1 and P3 show reasonable electrochemical stability, with oxidation current

remaining at *ca.* 50% after 1000 cycles. This is considerably better than the values reported for polyfurans retention of redox activity (40–50% over 100 cycles).^{10b,11c} In order to properly compare the stability of polyfurans with that of PT₃, the potential scan window was shifted by 0.2 V towards higher potentials. The reasoning for this stems from the fact that PT₃ has a higher oxidation potential.^{3b,41} Under these conditions, polyfurans showed slightly better stability than PT₃ (Fig. 7c), because PT₃ undergoes faster degradation due to higher applied potential that is required to induce its conductivity. Furthermore, as shown in Fig. S13,† the addition of 1% v/v water to the electrolyte solution had a small effect on the electrochemical stability of polyfuran P3. As expected, the electrochemical stability upon cycling over 0.0–0.5 V was much higher (Fig. S14†). P1 and P3 show only a 25% reduction in oxidation current after 10 000 cycles (Fig. S14a and c†).

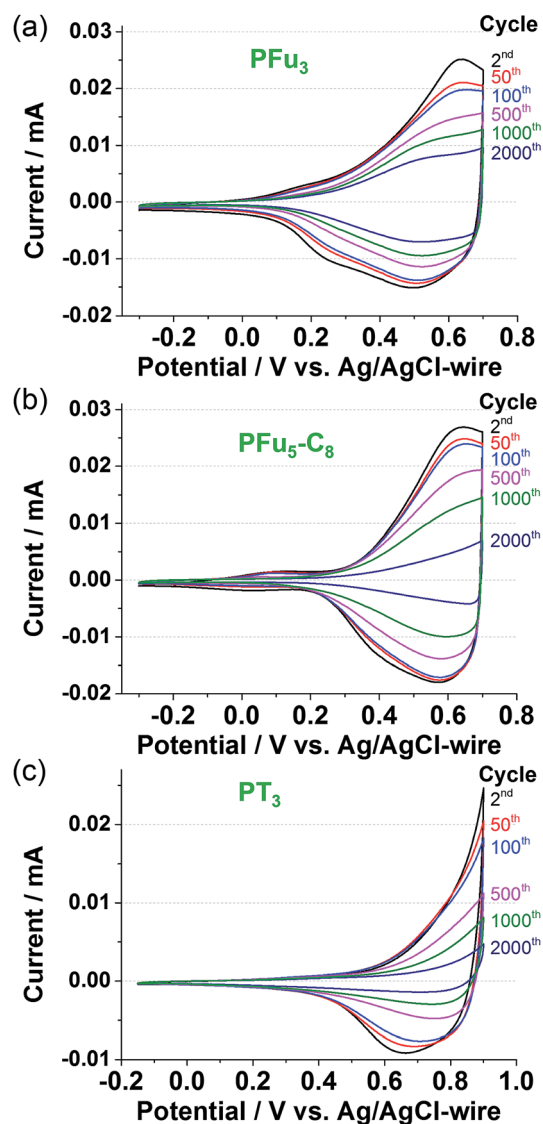


Fig. 7 Long term CV at 100 mV s⁻¹ of polymer films: (a) P1, (b) P3, and (c) PT₃ on Pt-disk electrode in monomer-free 0.1 M TBACF₃SO₃/ACN electrolyte.



(b) Optical switching and stability. Optical switching was measured for doped **P1**, **P3**, and **PT₃** at the maximum absorption peak wavelength in the NIR region (see spectroelectrochemistry above), within which the degraded and non-electroactive polyfurans show no absorbance. The stability of optical switching was evaluated by applying repetitive potential pulses (10 s length) of 0.0 V and 0.7 V for polyfurans, and 0.0 V and 0.9 V for **PT₃** for prolonged time (2 h) (Fig. 8). For complete doping and achievement of maximal NIR absorbance, higher potential was needed for **PT₃**.

The degraded optical activities (*i.e.*, difference in transmittance of undoped and doped state) obtained after 120 min of cycling (for a total of 360 cycles) were found to be 39%, 45%, and 51% for **P1**, **P3** and **PT₃** of the starting activity, respectively. Thus, polyfurans **P1** and **P3** showed only slightly lower stabilities compared with **PT₃**, but are much better than that reported for a PFu/PEDOT device.^{10c}

(c) Stability in conductive state. The stability of the conductive state of the **P1**, **P3** and **PT₃**, was tested on an IDA electrode by applying a constant potential for a prolonged time (up to 18 h) in air under ambient conditions (Fig. 9). A potential of 0.7 V was used for polyfurans **P1** and **P3**. For polythiophene **PT₃**, a potential of 0.9 V was used. These potentials correspond to slightly lower potential at which the polymers exhibit maximum conductance (Fig. 6).

As shown in Fig. 9, polyfurans **P1** and **P3** show much higher stabilities toward continuous potential application than **PT₃**, whose lower stability is likely due to the high potential (0.9 V) needed for oxidation (doping), which in turn, is expected to break the conjugation of the backbone *via* side reactions.⁴²

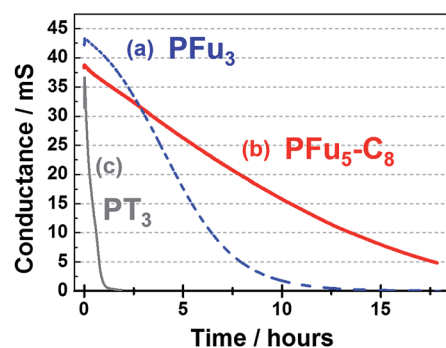


Fig. 9 Stability of the conductive state of polymer films: (a) **P1** at 0.7 V, (b) **P3** at 0.7 V, and (c) **PT₃** at 0.9 V on an IDA electrode in monomer-free 0.1 M TBACF₃SO₃/ACN electrolyte.

Thus, the lower potential required for doping the polyfurans is advantageous because it minimizes the occurrence of backbone degradation under ambient conditions.

Morphology

Polymer morphology has a significant effect on polymer charge-transport properties.^{1b} Controlled film thickness, surface smoothness, and uniformity are important considerations for application of conductive polymers in thin film devices (where high surface area is not required, such as sensing), including photovoltaic cells and OFETs. Electrochemical deposition has some advantages over solution processing of conjugated polymers. It combines polymer formation and deposition in one-step and bypasses the need for polymer isolation and purification. As such, it has found use in fabrication of organic electronic devices.⁴³ However, it is difficult to obtain smooth and homogeneous thin films by electropolymerization, necessitating the optimization of electrodeposition.^{1d} For example, the root mean square roughness (r_{rms}) of **PT₃** on ITO is 173 nm (Fig. S18†) and **PT** on ITO is 25–174 nm.²⁴ To the best of our knowledge, the lowest r_{rms} value obtained for electrodeposited PEDOT films in organic media is 46 nm.^{25c} Smooth polythiophene films were obtained after modification of the working electrode,^{24,44} while smooth electrodeposited PEDOT films were obtained from microemulsions in aqueous solution.⁴⁵ The polymer precursor approach (*i.e.*, use of inert polymer with pendant electroactive monomer units) was proposed to obtain thin films of less than 100 nm with controllable thickness.⁴⁶ The drawback of this method, however, is that prior polymer synthesis is necessary.

As can be seen in Fig. 10 showing SEM and AFM images of representative example of **P3** on HOPG electrode (for the additional images of polyfurans on different electrodes see ESI†), the prepared polyfuran films show excellent surface smoothness and complete coverage of all working electrodes used. In contrast, polythiophene exhibits separate islands of film and areas of bare electrode surface (see Fig. S17† for similarly prepared **PT₃**).⁴⁷ Additionally, polyfuran films have high adhesion to the electrode surface and are not easily detached. For example, they cannot be pulled off by sticking adhesive tape to

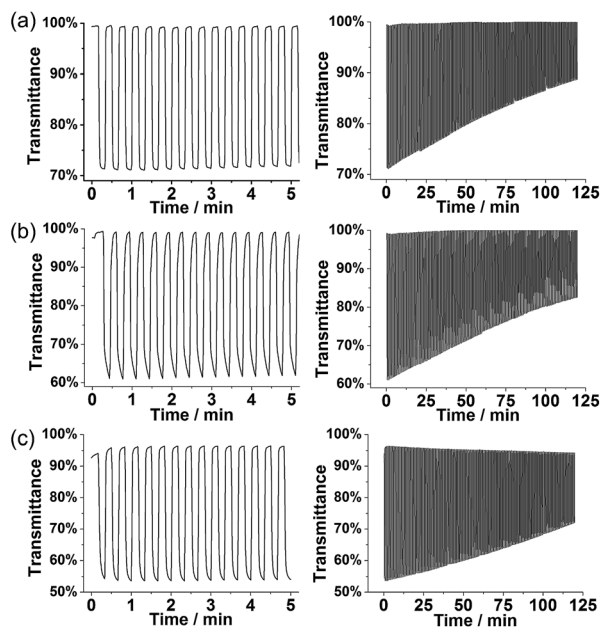


Fig. 8 Optical switching and stability of polymer films: (a) **P1** at 1250 nm, (b) **P3** at 1350 nm, and (c) **PT₃** at 1275 nm on ITO coated glass electrodes in monomer-free 0.1 M TBACF₃SO₃/ACN electrolyte. Voltage pulses of 0.0 V and 0.7 V (for **P1** and **P3**) and of 0.0 V and 0.9 V (for **PT₃**) were applied for 10 s.



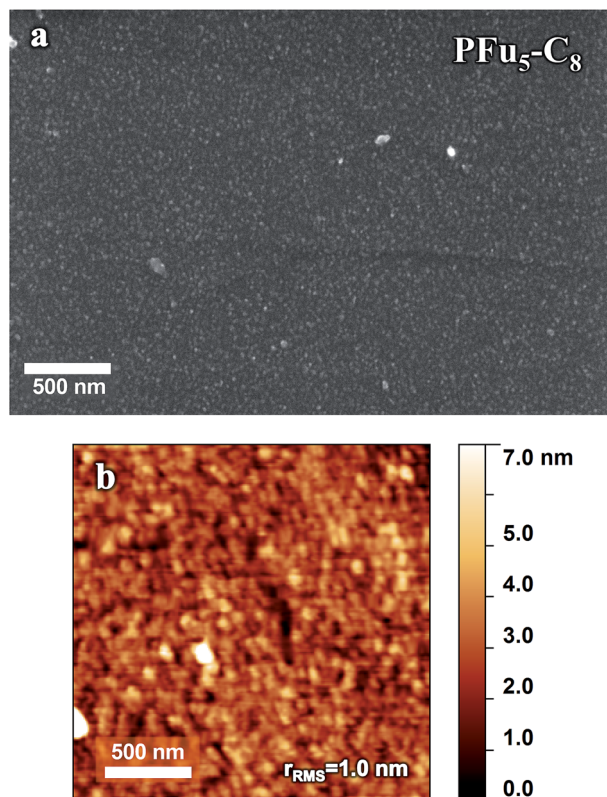


Fig. 10 (a) SEM and (b) AFM images of **P3** film prepared on a HOPG electrode by CV polymerization using potential scanning from -0.2 V to 0.78 V for 1 cycle of 0.2 mM of monomer **3** in 0.1 M TBACF₃SO₃/ACN electrolyte. Film thickness is 10 nm.

the electrode, as in case of poly(3-methylthiophene) films.⁴⁸ Additionally, films were found to be completely insoluble in organic solvents, such as THF and toluene.

The thickness of prepared polyfuran films can be easily controlled and tailored for the specific application. For instance, the film thickness of **P3** linearly depends on the number of CV cycles used in the polymerization (Fig. 11). The thickness of 10 nm on HOPG electrode was obtained after 1 cycle (Fig. 10), 45 nm after 5 cycles (Fig. S19†) and 90 nm after 10 cycles (Fig. S20†). The films show full coverage of electrodes with very smooth and homogeneous morphology. Although the r_{rms} value for the 10 nm thick film was only 1 nm, it increased with film growth, as evidenced by the r_{rms} values of 3.5 nm and 5 nm for 45 and 90 nm thick films, respectively (Fig. S20†). For polyfuran films with thickness above 50 nm, formation of globular structures on the top of smooth film is observed on both HOPG and ITO electrodes (see Fig. S20–S22†). Polyfuran film roughness on an ITO electrode (Fig. S21–S22†) is higher than on HOPG and is due to inherent higher roughness of the electrode (*i.e.*, $r_{\text{rms}} = 4.6$ nm for bare ITO, Fig. S23†).

Discussion

Overall, we have shown that by careful selection of starting oligomers and electropolymerization conditions (*i.e.*,

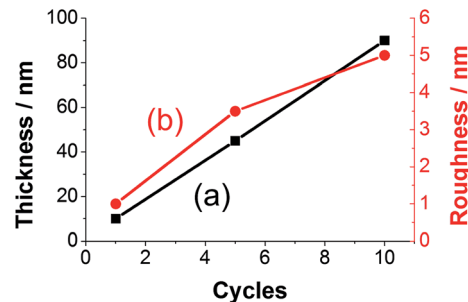


Fig. 11 Dependence of (a) thickness and (b) roughness on number of CV cycles used for polymerization of **P3** on HOPG electrode.

electrochemical method, monomer concentration, electrolyte and solvent), polyfurans of good quality are obtained. By lowering the polymerization potential using long oligofurans as the starting monomers, the polyfurans could be prepared in open air under ambient conditions.

The measured high conductivity on the order of 1 S cm^{-1} for doped polyfuran films may be attributed to better quality of the prepared polyfurans when compared with previous reports.⁵ This increased quality is manifested in the longer effective conjugation lengths (estimated to be above 25 furan units based on oligomer data, Fig. S25†) revealed by absorption spectra of the reduced (dedoped) polyfuran films, which show considerable red-shifted (456 – 466 nm) absorption maxima compared to most reported polyfurans.^{11a,c,d,12b} Additionally, IR spectroscopy showed almost no structural defects, including ring opening and β -coupling in the backbone. Moreover, absorption spectra of the neutral polyfurans show vibronic coupling, indicative of well-ordered, planar, and rigid polymers. Although similar vibronic coupling is also observed in highly conductive samples of PT⁴⁹ and PEDOT,^{27b} they were not previously observed in electrochemically prepared polyfurans. Furthermore, the measured conductivity of polyfurans is comparable to the conductivity of electrochemically prepared poly(oligothiophene)s.^{7a} Thus, we are convinced that the previously reported low conductivities⁵ are due to preparation problems, and are not an intrinsic property of polyfurans.

We have studied the effect of alkyl substitution on the properties of polyfurans. DFT calculations predict reductions of the band gaps, as well as oxidation potentials of polyfurans, with increasing alkyl substitution ratio (see Table S3†). Indeed, compared to **P1**, we experimentally observe a reduction of around 0.08 eV (Table 2) in optical band gaps in fully methylated polyfurans **P6** and **P7**. Although we cannot reliably measure the oxidation potentials from cyclic voltammetry, we do qualitatively observe that the onset of the broad oxidation peak is shifted to lower potentials for **P6** and **P7**. Another estimation of oxidation potentials can be obtained from the potential at half-maximum conductance E_{hc} , which is significantly decreased upon alkyl substitution (*e.g.*, $E_{\text{hc}} = 0.69$ V vs. Ag/AgCl-wire for PFu₃ (**P1**) and $E_{\text{hc}} = 0.30$ V for PFu₃-3C₁ (**P6**)). Furthermore, E_{hc} for polyfurans is lower than that of PT₃ ($E_{\text{hc}} = 0.87$ V). Therefore, when compared to polythiophenes, a lower oxidation potential of polyfurans serves as an advantage. The



lower doping potential minimizes the occurrence of the destructive side reactions (e.g., with water and oxygen). Moreover, oligofurans show lower oxidation potential compared to oligothiophenes, as evidenced by the onset potentials for oligomer oxidation (0.62 V for terfuran and 0.95 V for terthiophene).

As shown by DFT calculations²⁹ and absorption spectra (Fig. 4 and S11†), polyfurans have the further advantage of being more rigid than polythiophenes. High rigidity of polyfurans is also consistent with the experimental observation that regioirregular methylated polyfurans **P6** and **P7** show lower band gaps and oxidation potentials. This is advantageous for future development of furan-based polymers, where regioregular arrangement of different functional groups (otherwise needed in the case of polythiophenes to keep the efficient π -conjugation, e.g., rrP3HT)⁵⁰ is no longer mandatory.

We have carefully studied the stability of electrochemical, optical, and conductive properties of polyfurans in open air under ambient conditions. The stability of the redox activity and conductivity over time showed that polyfurans are actually more stable than polythiophene PT₃ under similar conditions. This stability is attributed to lower potential needed for doping of polyfurans. The optical switching stability of polyfurans is found to be comparable with that of PT₃, and it is much better than the previously reported stability of the optical switching of a PFu/PEDOT device at 415 nm. Previous studies showing optical switching degradation after only 90 s then is likely attributable to the polyfuran's poor quality, as suggested by the low absorption maximum ($\lambda_{\text{max}} = 420$).^{10c} Therefore, we believe that the earlier reported instabilities of polyfurans are also due to problems in their preparation.

We have identified two phases of the polyfuran film growth. Initially (up to ca. 50 nm thickness), we observe a smooth thin film covering the whole electrode surface is formed. As the film continues to grow, globular bumps and aggregates are observed on top of the smooth film surface. As a result, the roughness of the surface increases. For instance, in **P3** on HOPG, the r_{rms} value was ca. 5 nm for the underlying film and ca. 17 nm for the full scanned area (Fig. S20†). The formation of the structures on top of homogenous film is consistent with electrochemical polymerization where a new polymer forms at surface points with a higher conductivity.

It is worth noting that prepared polyfuran films have lower roughness than most other electrochemically-prepared films under similar conditions,^{24,25c,44–46} i.e., in organic media electrolyte, in ambient environment, without electrode surface modifications and extensive electrode cleaning. This is certainly an advantage for technological applications of polyfurans.

Conclusion

Using long oligofurans as precursors, we were able to obtain and thoroughly characterize polyfuran films with different alkyl substitutions that exhibit high stability, are spectroelectrochemically active, show good conductivity in the open air under ambient conditions, and have smooth morphology. These properties are considerably improved from any other known polyfuran prepared electrochemically. Additionally, we showed

that polyfurans exhibit high rigidity, which allows many different substituents to be introduced without distorting the planarity and conjugation of the polyfuran backbone. We showed that regioirregular alkyl-substituted polyfurans do not lose their conjugation, and moreover exhibit reduced band gaps.

Polymerization of oligofurans using considerable lower potential than parent furan allowed us to obtain stable polyfurans with very good properties. This is in contrast to the previous belief that polyfurans are intrinsically unstable and possess low conductivity. We believe that this work will establish polyfurans as a fundamental series of conductive polymers with important properties, opening up future applications for polyfurans as conductive polymers.

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