

# A new simple synthesis of poly(thiophene-methine)s

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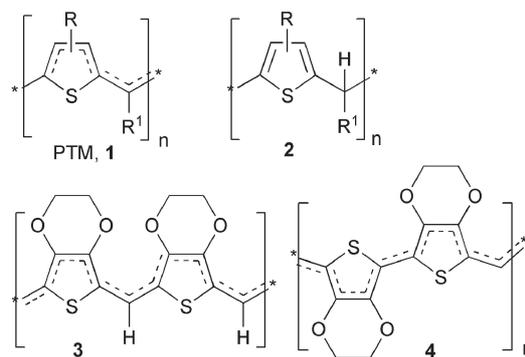
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Acid-promoted polycondensation of 3,4-(ethylenedioxy)-thiophene-2-carbaldehyde leads to a conjugated heavily *p*-doped poly(thiophene-methine), which can be dedoped leading to a low band-gap neutral polymer.

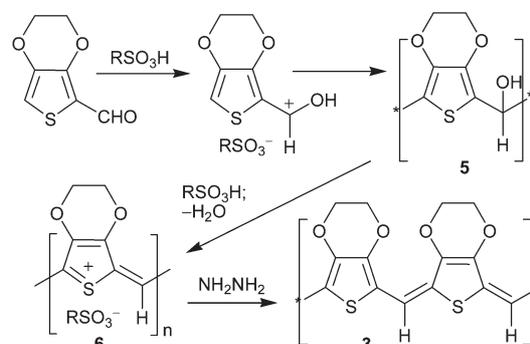
Discovery of conductivity in conjugated polymers and the derived highly promising applications in microelectronics (light-emitting diodes, solar cells, electrochromics, *etc.*) and sensors are among the most outstanding recent achievements of materials chemistry. At the electronic structure level, the most important parameters for fine-tuning the properties of these materials are the energy of their HOMO/LUMO bands and the gap between them (band gap,  $E_g$ ). Controlling these parameters and design of low band-gap polymers has been the subject of major research activities in this field for the last 20 years. The two most successful approaches were (a) alternating donor and acceptor units in the polymer chains,<sup>1–3</sup> and (b) reducing the bond length alternation by stabilizing a quinoid structure, *e.g.*, in poly(isothianaphthalene) by Wudl *et al.*<sup>4</sup> or poly(thiophene-methine) (PTM) by Jenekhe.<sup>5</sup> Although the 0.75 eV band gap value reported for PTM was later shown to be due to partial doping,<sup>6</sup> the theoretical calculations predict a still quite low band gap of 1–1.2 eV for unsubstituted PTM and much lower values (*ca.* 0.5 eV) for some derivatives.<sup>7</sup> At the same time, the most reliable experimental data, available for PTM derivatives (with  $R^1 = \text{Ph}$ ) show electrochemical and optical band gap around 1.9 eV, which might be due to steric hindrances induced by Ph substituents.<sup>8</sup>

The synthesis of PTM derivatives **1** was achieved by polycondensation of substituted thiophenes with aldehydes, followed by bromine or dichlorodicyanobenzoquinone (DDQ) mediated dehydrogenation of the non-conjugated methylene-bridged polymer **2**. Jenekhe *et al.* later observed partial spontaneous dehydrogenation of **2** (possibly, due to oxidation by air).<sup>9</sup> In almost all cases, the aldehyde component was a (substituted) benzaldehyde ( $R^1 = \text{Ph}$ ). Although similar reaction with formaldehyde gives partially dehydrogenated polymer **2** ( $R^1 = \text{H}$ ,  $R = \text{Alk}$ ),<sup>9</sup> fully conjugated PTMs **1** with  $R^1 = \text{H}$ , to the best of our knowledge, are unknown. In the last few years, particular attention in the field of conjugated polymers was paid to the 3,4-(ethylenedioxy)thiophene (EDOT) building unit, due to its exceptional stability and superb donor properties;<sup>10</sup> poly(EDOT), PEDOT, is one of the most industrially successful conducting polymers.<sup>11</sup> Poly(EDOT-methine) (**3**) has been recently identified as an attractive target with predicted band-gap as low as 0.48 eV.<sup>12</sup> This polymer has not been synthesized, although two related

structures, poly(bisEDOT-methine) **4** [prepared by electropolymerization of di(EDOT)-carbinol]<sup>13</sup> and partially dehydrogenated EDOT derivative **2** (with  $R^1 = \text{phenyl}$ ,  $R = 3,4\text{-ethylenedioxy}$  group)<sup>12</sup> are known.



Here we report the first and straightforward synthesis of a fully conjugated poly(thiophene-methine) **3** with an unsubstituted methine unit, based on acid-catalyzed polycondensation of readily available EDOT-2-carbaldehyde. A related  $\text{POCl}_3$ -promoted reaction was previously patented for pyrrol-2-carbaldehyde,<sup>14</sup> although it gave an ill-defined polymer containing cross-links and NH-dehydrogenated pyrrol units.<sup>15</sup> We found that refluxing EDOT-2-carbaldehyde in  $\text{CHCl}_3$  with excess of methanesulfonic (or toluenesulfonic) acid under nitrogen for 12 h results in the formation of a black precipitate, which was filtered and thoroughly washed with  $\text{CHCl}_3$ . The yield of the well-dried product corresponds to nearly quantitative ( $\sim 90\text{--}100\%$ ) formation of the structure **6** incorporating one  $\text{RSO}_3^-$  anion per each thiophene unit (Scheme 1). Such a high doping level has not been observed in polythiophene materials; the most electron rich polythiophene, PEDOT, can accept no more than one charge per three units, even when doped with bromine.<sup>16</sup> It is, therefore, not surprising that



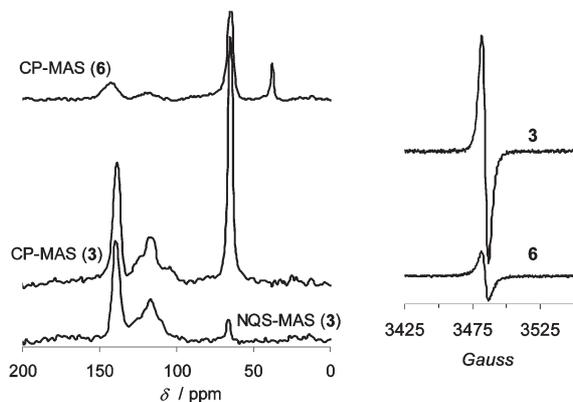
Scheme 1 Synthesis of poly(EDOT-methine).

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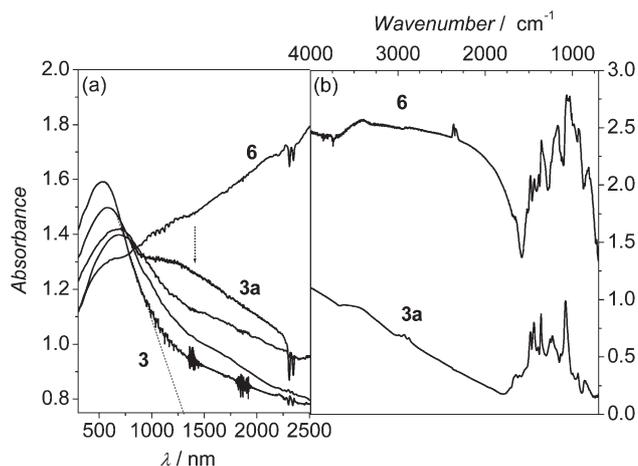
treatment of **6** with water results in partial dedoping as observed in experimental weight loss of 25–30% (dedoping and dissolution of short oligomers). As prepared polymer **6** is a semiconductor with room temperature conductivity of  $(1\text{--}3) \times 10^{-3} \text{ S cm}^{-1}$  (two-probe method), this value is similar to those observed in other poly(thiophenemethine)s.<sup>8,13</sup> In contrast to other doped polythiophenes, the ESR signal of **6** is quite weak and symmetric ( $g$ -value 2.004, Fig. 1b), which can be explained by preferable bipolaronic (closed shell) structure at so high a doping level. Nevertheless, the solid state CP-MAS  $^{13}\text{C}$  NMR spectrum of as-prepared polymer **6** (Fig. 1a) is very broad, especially for  $\text{sp}^2$  carbons (presumably due to paramagnetic broadening). The only sharp signals are from  $\text{OCH}_2$  (66 ppm) and  $\text{CH}_3\text{SO}_3$  (39 ppm) carbons, isolated from the spin-localizing conjugated backbone.

The reaction most likely proceeds through an expected protonated poly(thiophenecarbinol) intermediate **5** (Scheme 1). The protonation of OH group and subsequent dehydration should afford a conjugated polycation (presented by a resonance form **6**). Treatment of the doped polymer **6** with hydrazine results in dedoping. This is accompanied by weight loss of 41–50% due to counter-ion removal (calc. 39%) and partial dissolution of short oligomers. Elemental analysis of the dedoped sample matches well the structure **3**; the residual nitrogen content of 0.45% is expected due to a hydrazone formation at the terminal aldehyde group, from which the lower limit of molecular weight of 6 000 (40 units) can be deduced.<sup>†</sup> Hydrazine dedoping results in the expected drop of conductivity (to  $\sim 10^{-6} \text{ S cm}^{-1}$ ). The conductivity can be partially regained by redoping in iodine vapor ( $\sigma_{\text{rt}} = 4 \times 10^{-4} \text{ S cm}^{-1}$ ), and stronger oxidants (bromine) restore the original conductivity ( $1.3 \times 10^{-3} \text{ S cm}^{-1}$ ).

The solid state CP-MAS  $^{13}\text{C}$  NMR spectrum of the dedoped polymer **3** (Fig. 2) shows aliphatic carbon at 66 ppm (from ethylenedioxy bridge), a methine signal at 105 ppm and two signals at 117 and 139 ppm, which can be attributed to C-2 and C-3 carbons of the thiophene ring. All signals are observed at the expected chemical shifts, and disappearance of the first two signals in NQS (non-quaternary signals suppression)  $^{13}\text{C}$  NMR spectrum supports their assignment to  $\text{CH}_2/\text{CH}$  carbons. Interestingly, the NMR signals of **3** are sharper than those of **6**, even though the ESR signal of the former is stronger. We rationalize this ESR signal by partial doping of **3** by air,<sup>17</sup> as also observed for PEDOT.<sup>16</sup>



**Fig. 1** (a) CP-MAS and NQS-MAS  $^{13}\text{C}$  NMR of the polymers **6** ( $\text{R} = \text{CH}_3$ ) and **3**. (b) ESR spectra of **6** and **3** (10 mg samples).

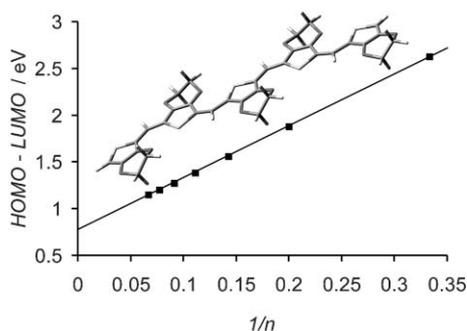


**Fig. 2** (a) UV-Vis-NIR spectra of **6**, partially doped **3a** (processed in air) and **3** (processed under  $\text{N}_2$ ; different ) and in Nujol oil. (b) FTIR spectra of polymers **6** and **3a** in KBr.

The low band-gap properties of poly(EDOT-methine) are manifested in optical absorption spectra (Fig. 2). The broad and intense “conductance band” in the doped polymer **6** spreads from Vis to mid-IR region, with on-set below  $1500 \text{ cm}^{-1}$  ( $<0.2 \text{ eV}$ ). This band disappears during the dedoping, revealing the characteristic band of the neutral polymer **3**. Complete dedoping of **6** cannot be achieved in air, which explains the residual long wavelength absorption of **3a** (dedoped in ambient atmosphere). This absorption can be further suppressed by performing the dedoping procedure under  $\text{N}_2$  (curves **3a**  $\rightarrow$  **3**, Fig. 2a), while an extreme caution against oxygen should be taken for the complete dedoping (curve **3**). Although such behavior hinders an accurate determination of the band gap of **3**, nevertheless, the on-set absorption at *ca.* 1300 nm corresponding to  $E_g$  of 0.95 eV can be estimated (Fig. 2a). Unfortunately, the extremely low solubility of **6** and **3** precludes (spectro)electrochemical characterization.

The vibrational spectra of **6** and **3** are consistent with the polymers structure: a strong band at *ca.*  $1070 \text{ cm}^{-1}$  due to C–O vibration of substituents, and thiophene features at  $\sim 1360$  and  $\sim 1440 \text{ cm}^{-1}$  were observed in both polymers (Fig. 2b). Interestingly, the aromatic C–C vibration (observed as a strong band at  $\sim 1650 \text{ cm}^{-1}$  in PEDOT) is extremely weak in both samples, suggesting highly delocalized structure. Furthermore, Raman spectrum of **3** ( $1427$  and  $1530 \text{ cm}^{-1}$ ) also shows no aromatic C–C bonds. Two strong IR bands at  $1350$  and  $1167 \text{ cm}^{-1}$  in polymer **6** are due to  $\text{CH}_3\text{SO}_3^-$  dopant and vanish in the dedoped sample **3**.

To rationalize the observed properties of the new polymer **3**, we performed density functional theory (DFT) calculations of the geometry and electronic structure of EDOT-methine oligomers with  $n = 3\text{--}15$  (with H terminal groups). The geometry optimization at the B3LYP/3-21G\* level shows all-*trans* conformation of the thiophene rings, similar to the unsubstituted PTM. Recalculation with 6-31G(d) basis set and the frequency check (for  $n = 3, 5$ ) shows this conformation is the minimum. Bond length analysis shows an alternation of “aromatic-like” and “quinoid-like” thiophene rings even for the longest oligomer with  $n = 15$  (thiophene C3–C4 bond length alters between 1.368 and 1.405 Å). Although nearly-planar geometry is predicted for the



**Fig. 3** HOMO-LUMO gap vs. inverse number of units for the oligomers **3** ( $n = 3$ – $15$ ) and an optimized structure of the pentamer of **3**. [calculated at B3LYP/6-31G(d)//B3LYP/3-21G\* level].

backbone (the dihedral angle between the thiophene rings does not exceed  $2^\circ$ ), the steric effect of the ethylenedioxy substituents is revealed by increased thiophene–methine–thiophene angle of *ca.*  $133^\circ$  (Fig. 3). The intramolecular S...O contacts ( $\sim 2.8$  Å) are shorter than the sum of van der Waals radii (3.2 Å), similar to those in PEDOT (2.9 Å) where they are believed to be attractive.<sup>18</sup> These geometric features of **3** are similar to recent calculations at the semiempirical AM1 level.<sup>12</sup> The projection of the DFT-derived HOMO–LUMO vs.  $1/n$  plot (Fig. 3) suggests a gap of  $\sim 0.8$  eV for  $n = \infty$ , which is close to the optical band-gap, although larger than 0.48 eV earlier predicted from extended Hückel calculations.<sup>12,†</sup>

To conclude, we have demonstrated a simple and convenient synthetic route to poly(thiophene methine)s and prepared the first fully conjugated PTM with unsubstituted methine unit. The optical absorption and DFT calculations suggest the band-gap of  $\leq 1$  eV. Furthermore, the exceptionally high doping level found in **6** could be important for applications in capacitor/batteries materials. Synthesis of soluble analogues of polymer **3** and development of their applications as  $\pi$ -functional materials is now in progress in our lab.

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## Notes and references

† Synthesis of **6** and **3**: To a stirred solution of EDOT-2-carbaldehyde (250 mg, 1.47 mmole) [prepared by formylation of EDOT-Li with *N*-methylformanilide] in  $\text{CHCl}_3$  (25 ml) at room temperature, methanesulfonic acid (155 mg, 1.56 mmole) was added under nitrogen atmosphere. After stirring at room temperature for 1 h, the solution mixture was refluxed overnight (12 h). The black precipitate was filtered and washed thoroughly with  $\text{CHCl}_3$  to afford **6** (319 mg, 88%). Dedoping **6** with hydrazine (2 ml) in ethanol (or MeCN) solution results in polymer **3**, which was washed with ethanol and water, and dried in vacuum to afford 190–210 mg of **3** [this step should be done under  $\text{N}_2$  to prevent redoping with air]. Anal. Calcd for  $[\text{H}-(\text{C}_7\text{H}_5\text{O}_2\text{S}-0.75\text{H}_2\text{O})_{40}-\text{CH}=\text{NNH}_2]$ : C, 50.20; H, 3.97; N, 0.42; S, 19.14. Found: C, 49.85; H, 2.98; N, 0.45; S, 18.95.

‡ The wavefunction stability was checked for oligomers up to  $n = 13$ .

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