

Protonic Doping of Bis-thienylpolyenes and Oligomers of Poly(2,5-thienylenevinylene): Comparison to Oxidative Chemical Doping

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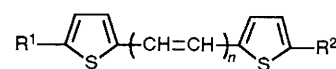
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Protonic doping of polymer oligomers containing thiophene end groups or repeat units yields predominantly bipolaronic charge states.

During the past ten years there has been a wealth of experimental data on the generation of charge states in electroactive oligomers and polymers by various chemical (I₂, FeCl₃, AsF₅, SbCl₅ etc.) or electrochemical redox processes.¹ Considerable work has been done in this area on the polythiophene, poly(*p*-phenylenevinylene) (PPV) and poly(2,5-thienylenevinylene) (PTV) systems.²⁻⁴ As has been stated in a recent review by Patil *et al.*,⁵ spinless bipolarons are the dominant charge carriers in all three systems. However, recent work by Han and Elsenbaumer⁶ has suggested an alternative non-oxidative protonic doping process which yields soluble processible doped polymers in the poly(dialkoxyphenylenevinylene) system. In this approach, protonation occurs on the aromatic ring yielding an initial bipolaron. These workers have claimed, however, based on ESR evidence that the initially formed bipolarons disproportionate by an internal redox mechanism to yield polarons as the primary charge carriers in these conducting polymers. In this communication we report that protonic doping is not limited to polymers with phenyl repeat units, but works equally well for polymers or oligomers containing thiophene repeat units.

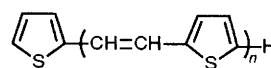
We have previously studied the oxidative (SbCl₅) doping of

α,ω -dithienylpolyenes and a series of poly(2,5-thienylenevinylene) oligomers (dimer, trimer and tetramer).^{7,8} In both cases we found the prevalent charge state to be bipolaronic. However, we were able in these series to obtain polarons if the ratio of oligomer to dopant was carefully controlled. Fichou, Garnier and coworkers^{9,10} have recently reported a similar study for polythiophene oligomers ($n = 3-6$), but found a preference for polaron (P) formation up to the hexamer, where the bipolaron (BP) then became dominant.



1; R¹ = R² = H; n = 6

2; R¹ = R² = Me; n = 6



3; n = 2

4; n = 3

5; n = 4

Table 1 Comparison of optical absorptions (A) for protonically doped species to previous redox assignments

Com- pound	SbCl ₅ Doping ^a		CF ₃ CO ₂ H Doping ^b
	P A/nm	BP A/nm	A/nm
1	760sh, 853, 1154	713, 776	693, 746
2	888, 1167	720, 776	697, 745
3	685, 881, 1007, 1240	643, 1056, 1238	688, 958, 1106, 1302
4^c	725sh, 804, 1460sh	822sh, 904	808, 1154, 1386
5^c	816, 932	984sh, 1105	968, 1072

^a 10⁻⁵ mol dm⁻³ in CH₂Cl₂. ^b 10⁻⁴ mol dm⁻³. ^c For both P and BP absorptions, a near-IR absorption (>1600 nm) exists for which we observe only the leading edge.

Table 2 ESR spectra of protonically doped oligomers

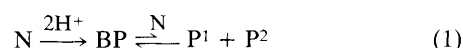
Compound	Spin concentration/mol dm ^{-3a}	
	2 h	24 h
1	2 × 10 ⁻⁸	2 × 10 ⁻⁸
2	6 × 10 ⁻⁸	2 × 10 ⁻⁸
3	1 × 10 ⁻⁷	0
4	5 × 10 ⁻⁷	7 × 10 ⁻⁸

^a ESR signal at mixing too low to measure due to slow nature of CF₃CO₂H doping.

In the present study, bis-thienylpolyenes (*n* = 3–6), and PTV oligomers (dimer, trimer and tetramer), synthesized and characterized in our previous studies,^{7,8} were protonically doped by preparing 10⁻⁴ mol dm⁻³ solutions in neat CF₃CO₂H. The optical absorption and ESR spectra were then continuously monitored for a 24 hour period. The optical absorption data compared to our previous SbCl₅ doping studies, are shown in Table 1. The ESR data is shown in a similar comparative manner in Table 2.

Han and Elsenbaumer⁶ based their assignment of polaronic charge carriers in the protonic doping of PDMPV and PDBPV (dimethoxy- and dibutoxy-PPV) on the observation of three prominent absorption bands (0.6, 0.8 and 1.54 eV) and a strong ESR signal. We recently reported¹¹ a comparison study between protonic and oxidative doping of PDBPV oligomers, which clearly demonstrates that bipolaronic charge carriers dominate even though residual ESR activity survives. We interpreted this data to indicate that P and BP states are in

equilibrium in protonic doping with the latter predominating (>99% in all cases). Thus residual ESR activity is no guarantee that polarons dominate the active charge carriers, and the optical spectra may represent a bipolaronic absorption. In the bis-thienylpolyene and PTV series we find similar behaviour. We conclude that protonic doping of oligomers containing thiophene moieties instead of phenyl repeat units follow similar doping pathways. Where N is the undoped neutral oligomer eqn. (1). One caveat needs to be stressed, however. It does not appear from these preliminary studies that the P–BP mixture obtained upon protonic doping for oligomer containing thiophene rings is as stable as those obtained from PPV-type oligomers and polymers. In the PPV case, we have found that protonically doped solutions are stable for several months, whereas the thiophene containing oligomer doped species begin to decompose after 24 hours. Thus, although it appears that protonic doping may be a general phenomenon for electroactive materials, the stabilities of the doped species may be high dependent on ring structure.



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