Chem. Mater. **1993,** *5,* 1792–1798

Electronic Transitions in Polarons and Bipolarons of Poly(*p*-phenylene) Oligomers

Rajive K. Khanna,* Yong M. Jiang, B. Srinivas, Charles B. Smithhart, and David L. Wertz

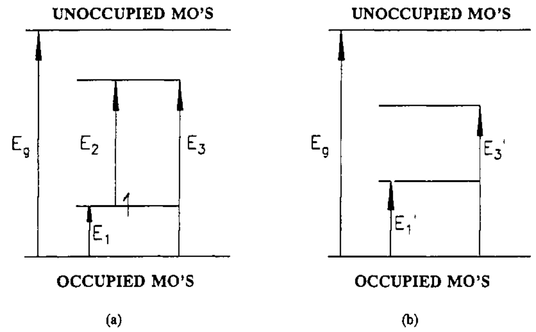
Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, Mississippi 39406–5043

Received September 8, 1993[⊗]

The electronic transitions in radical ions (polarons) and dications (bipolarons) of oligomers of poly(*p*-phenylene) have been measured by laser flash photolysis and steady-state techniques. Plots of the electronic absorption band energies for the polaron and bipolaron are found to be linear functions of inverse chain length. The predicted transitions in the polaron of poly(*p*-phenylene) (PPP), obtained from extrapolations of these plots to infinite chain length, are considerably lower in energy compared to those reported in doped PPP. Interestingly, the transitions observed by us in the radical ions of *p*-quaterphenyl and *p*-sexiphenyl are similar to those observed in highly conducting doped PPP. We have proposed that the polaron is localized to a short segment ($n \sim$ 4–6, where n is the number of phenyl repeat units) of the polymer chain. On the basis of these results, we have concluded that diamagnetic π-stacks of fairly localized polarons could be the conducting entities in doped PPP.

Introduction

Poly(*p*-phenylene), polythiophene, polypyrrole, and other polyaromatics, upon doping (oxidation or reduction), yield highly conducting charge-transfer complexes.[1,2] Defect-state calculations, within the framework of the adiabatic Hückel Hamiltonian with σ-bond compressibility, on doped poly(*p*-phenylene) (PPP) by Brédas *et al*[3,4] predict the formation of polarons (radical ions) at low dopant concentrations. At higher doping levels polarons are suggested to interact to produce correlated pairs of cations or anions (spinless bipolarons). The diffuse reflectance spectrum of undoped PPP shows a broad electronic transition at 3.43 eV derived from the π–π^* transition of the phenylene repeating unit.[5] The formation of polarons and bipolarons, upon doping of this conjugated macromolecule, is predicted to result in the appearance of two doping-induced energy levels, bonding and antibonding, which are about symmetric with respect to the gap center (Figure 1).[3,4] The polaron and bipolaron bonding levels in doped PPP are predicted to be 0.2 and 0.9 eV, respectively, above the top of the valence band.[3,4] Thus, several new electronic transitions are expected in the optical spectrum of doped poly(*p*-phenylene).



(a) (b)

Figure 1. Energy level diagrams for (a) positive polaron and (b) positive bipolaron.

The optical and electronic characteristics of doped PPP have been examined by several research groups with different results. Chance *et al.*[5a] found a strong absorption at 0.6 eV in AsF_5 doped highly conducting (500 S cm^{-1}) PPP. Tieke et al.[6] reported a structure at about 2.5 eV in SbF_5-doped PPP with the absorption band of pure PPP at 3.4 eV being absent. Crecelius *et al.*,[7] utilizing electron energy-loss spectroscopy, observed a strong band at 0.6 eV, at low dopant levels, in AsF_5-doped PPP. They assigned this band to the bonding polaron state in the doped polymer. At higher doping levels, they found a strong band at 1.1 eV and a weak band at ca. 3.00 eV, which they assigned to the bipolaron bonding and antibonding states, respectively. We have examined if the assignments of these bands to polarons and bipolarons is in accord with extrapolations from electronic transitions observed in radical ions and diions of oligomers of PPP.[8] Recently such extrapolations were successfully attempted

---

[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1993.

(1) A number of monographs on the subject of electroactive polymers are available: (a) Skotheim, T. A., Ed. *Handbook of Conducting Polymers*; Mercel Dekker: New York, 1986; Vols. 1, 2. (b) Skotheim, T. A. *Electroresponsive Molecular and Polymeric Systems*; Mercel Dekker: New York, 1991; Vols. 1, 2. (c) Brédas, J. L.; Chance, R. R. *Conjugated Polymeric Materials: Opportunities in Electronic, Optoelectronic, and Molecular Electronics*; Kluwer Academic Publishers: Boston, 1990; NATO ASI Series E: Vol. 182. (d) Frommer, J. E.; Chance, R. R. Electrically Conductive Polymers. In *Electrical and Electronic Properties of Polymers*; Kroschwitz, J. I., Ed.; John Wiley and Sons: New York, 1988.

(2) (a) Brédas, J. L.; Street, G. B. *Acc. Chem. Res.* **1985,** *18,* 309. (b) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988,** *88,* 183.

(3) (a) Brédas, J. L.; Chance, R. R.; Silbey, R. *Phys. Rev. B* **1982,** *26,* 5843. (b) Chung, T.-C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1984,** *30,* 702.

(4) Brédas, J. L.; Thémans, B.; André, J. M. *Phys. Rev. B* **1982,** *26,* 6000.

(5) (a) Chance, R. R.; Baughman, R. H.; Brédas, J. L.; Eckhardt, H.; Elsenbaumer, R. L.; Frommer, J. E.; Shacklette, L. W.; Silbey, R. *Mol. Cryst. Liq. Cryst.* **1982,** *83,* 217. (b) Shacklette, L. W.; Eckhardt, H. Chance, R. R.; Miller, G. G.; Ivory, D. M.; Baughman, R. H. *J. Chem. Phys.* **1980,** *73,* 4098 and references therein.

(6) Tieke, B.; Bubeck, C.; Lieser, G. *Makromol. Chem. Rap. Commun.* **1982,** *3,* 261.

(7) Crecelius, G.; Stamm, M.; Fink, J.; Ritsko, J. *J. Phys. Rev. Lett.* **1983,** *50,* 1498.

0897-4756/93/2805-1792$04.00/0

with doped polythiophene and doped polyacetylene oligomers.[9,10]

We have measured the absorption spectra of radical cations, radical anions and dications of several oligomers (n = 1–6) of poly(p-phenylene), by generating the radical cations in MeCN solvent by a simple laser flash photolysis (LFP) method using ceric ammonium nitrate (CAN) as a photochemical oxidant,[11] radical anions by reduction of the oligomers with alkali metals in deaerated THF, and dications by oxidation of the oligomers with excess $SbCl_5$ in dry and deaerated methylene chloride. We find that the plots of the electronic band energies, thus obtained for the radical ions and diions, are linear functions of inverse chain length. Our attempts to determine the electronic and geometric properties of the polarons and bipolarons in doped PPP, from such correlations, are described.

Experimental Section

General Considerations. All UV–vis spectra were recorded on a Perkin-Elmer Lambda 6 Model 80524P spectrophotometer. Infrared spectra were recorded on a Mattson Polaris FT-IR Model NU-1000 spectrophotometer. Near-IR spectra were obtained on a Bruker IFS88 spectrometer with FT Raman and IR microscopy. Photoluminescence studies were performed on a Spex Fluorolog-2 spectrofluorimeter. ^{1}H and ^{13}C NMR spectra were obtained on a 300-MHz Bruker AC-300 spectrometer. ^{13}C solid-state NMR spectra were obtained on a 200-MHz Bruker MSL-200 cross-polarization, magic angle spinning (CP/MAS) NMR spectrometer. Elemental analyses were provided by Galbraith Laboratories, Knoxville, TN. GC-MS spectra were obtained on a Hewlett-Packard MS Model 5985B and GC Model 5840A GC/MS system with 9876A Hewlett-Packard interface.

X-ray diffraction patterns were obtained on a Philips Electronics PW 1710 powder diffractometer with theta compensator, Cu Kα radiation, and a graphite monochromator using the step-scan method. Samples were hand ground to a fine powder and lightly compacted into standard sample cassettes.

Materials. Acetonitrile (MeCN) was dried over CaH_2 and distilled under argon (Ar) atmosphere. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride. All the solvents were stored over fresh molecular sieves. p-Quaterphenyl (QP) and p-sexiphenyl (SP) were synthesized by literature procedures.[12,13] Lithium metal wire ($^1/_8$-in. diameter) was purchased from Lithium Corporation of America. All other chemicals were purchased from Aldrich Chemical Co. and used as such.

p-Quaterphenyl (QP):[12] white solid mp 316–317 °C, lit.[12] 318–320 °C; IR(KBr) 3038, 3034, 1491, 1002, 827, 754, 689, 459 cm^{-1}; ^{13}C NMR (CP/MAS) δ 137.15 (nonprotonated carbons), 129.51 (meta carbons), 126.29 (ortho and para carbons). Anal. Calcd for $C_{24}H_{18}$: C, 94.08%; H, 5.92%. Found: C, 93.90%; H, 5.93%.

p-Quinquephenyl (QQP): A solution of 4-bromobiphenyl (11.501 g, 50 mmol) in dry THF (50 mL) was very slowly added under Ar atmosphere in a three-neck round-bottom flask containing magnesium powder (1.222 g, 50 mmol) at room temperature. After a 30-min reflux, the mixture was cooled to room temperature and transferred into another three-neck round-bottom flask containing 1,4-dibromobenzene (6.011 g, 25 mmol) and nickel catalyst, Ni(dppp) (0.141 g, 0.25 mmol), in dry THF (30 mL). The reaction mixture was stirred at room temperature overnight. The mixture was refluxed for another 2 h, cooled, acidified with 150 mL of 10% HCl and extracted with 125 mL of benzene. The organic layer was washed with 5% sodium bicarbonate, dried over sodium sulfate, and evaporated. The residue was extracted with boiling dioxane and the crude product was purified by sublimation (350 °C, 4 mmHg) and recrystallization from 1,2,4-trichlorobenzene. The crystals (light yellow) were washed with hot benzene again and were dried in vacuum oven (70 °C, 25 mmHg) for 2 days. Yield: 0.912 g, 10%; mp 390 °C, lit.[12] 395 °C; IR (KBr) 3058, 3029, 1479, 1400, 1000, 818, 757, 688, 466 cm^{-1}; ^{13}C NMR (CP/MAS) δ 136.90, 129.31, 126.27. Anal. Calcd for $C_{30}H_{22}$: C, 94.20%; H, 5.80%. Found: C, 94.02%; H, 6.20%.

p-Sexiphenyl (SP):[13] Light-green fluorescent crystals mp >430 °C, lit.[12] 465–467 °C; ^{13}C NMR (CP/MAS) δ 136.92–126.29 (broad); mass spectrum m/e (rel intensity) 459 (29.3, M + 1), 458 (73.2, M), 456 (36.6, M − 2), 321 (26.8), 243 (28.0), 241 (18.3), 225 (25.6), 211 (19.5), 196 (31.7), 182 (36.6), 149 (100), 137 (19.5), 112 (18.3), 99 (21.9), 77 (19.5), 69 (31.7), 55 (41.5). Anal. Calcd for $C_{36}H_{26}$: C, 94.28%; H, 5.72%. Found: C, 93.99%; H, 5.80%.

Generation of Radical Ions and Dications. Radical cations were generated in dry, deaerated MeCN by LFP technique utilizing ceric ammonium nitrate (CAN) as a photochemical oxidant. The laser flash photolysis apparatus was the same as described elsewhere.[14] Experiments were carried out in static systems with samples contained in suprasil cells. These were deoxygenated by bubbling with argon. Laser dose attenuation experiments were routinely carried out. In typical experiments, LFP of CAN (0.05–0.5 mM) at 351 nm in dry deaerated MeCN in the presence of an aromatic hydrocarbon substrate (0.02–5.0 mM) yielded the absorption spectrum of the transient radical cation of the hydrocarbon, which was recorded 200 ns–2.0 μs after the laser pulse. The initial concentration of the $NO_3^{\bullet}$ (1.5–15 μM), under our reaction conditions, is considerably lower than that of the substrate hydrocarbon. None of the substrate hydrocarbons absorb substantially at 351 nm, and thus they do not yield any transients in the absence of CAN.

Radical anions were generated by reduction of the oligomers with alkali metals under argon atmosphere.[11] Approximately 5.0 μmol of the substrate hydrocarbon, an equimolar amount of the alkali metal, and 4 mL of dry THF were placed in a silicon-septa-sealed long-neck quartz fluorescence cell. The mixture was purged with dry argon, and the cell was placed in a Branson 5200 ultrasonic bath. The formation of the radical anion was indicated by a color change to purple or violet. The absorption spectrum was recorded immediately after the radical anion was formed.

Dications of the oligomers were generated by oxidation of the oligomers with excess $SbCl_5$ in CH_2Cl_2.[15] A solution of the substrate hydrocarbon (0.2 mM) in dry, deaerated CH_2Cl_2 (4.0 mL) was placed in a silicon-septa-sealed long-neck quartz cell, equipped with a small Teflon-coated magnetic bar. $SbCl_5$ (0.25 mL) was added using a glass microsyringe in a N_2 filled glovebox. The solution was stirred for 2 min, and the absorption spectrum was immediately recorded.

Results and Discussion

Electronic Transitions in Neutral Oligomers. The stationary absorption spectra of the neutral oligomers show broad transitions[5,16] derived from the π–π^* transition of the phenylene moiety. The energy gaps between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) in neutral oligomers (E_n, Table I), calculated from these transitions, decrease with chain length. It is interesting to note that in contrast to the absorption spectra, the emission spectra

---

[8] Such extrapolations with neutral oligomers are often found to be linear in $1/n$ (where n is the number of repeating units): Schaffer, H. E.; Chance, R. R.; Knoll, K.; Schrock, R. R.; Silbey, R. *J. Chem. Phys.* **1991**, *94*, 4161 and references therein.

[9] (a) Casper, J. V.; Ramamurthy, V.; Corbin, D. *J. Am. Chem. Soc.* **1991**, *113*, 600. (b) Guay, J.; Kasai, P.; Diaz, A.; Wu, R.; Tour, J. M.; Dao, L. H. *Chem. Mater.* **1992**, *4*, 1097.

[10] Bally, T.; Roth, K.; Tang, W.; Schrock, R. R.; Knoll, K.; Park, L. Y. *J. Am. Chem. Soc.* **1992**, *114*, 2440.

[11] Khanna, R. K.; Jiang, Y. M.; Creed, D. *J. Am. Chem. Soc.* **1991**, *113*, 5451.

[12] Taylor, S. K.; Bennett, S. G.; Heinz, K. J.; Lashley, L. K. *J. Org. Chem.* **1981**, *46*, 2194.

[13] Kovacic, P.; Lange, R. M. *J. Org. Chem.* **1964**, *29*, 2416.

[14] Khanna, R. K.; Armstrong, B.; Cui, H.; Tanko, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 6003.

[15] Spangler, C. W.; Rathunde, R. A. *J. Chem. Soc., Chem. Commun.* **1989**, 26.

[16] Brédas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 6555.

Table I. Energies of the Electronic Transitions (electronvolts) in Radical Ions and Dications of Oligomers of Poly(*p*-phenylene)[a]

oligomer chain length	neutral[b] E_n	radical ions[c] E_1	radical ions[c] E_2	dication E_1'
2	4.92	1.86 ($2^{\bullet+}$) 1.96 ($2^{\bullet-}$) 1.95 ($2^{\bullet-}$)^{d}	3.30 ($2^{\bullet+}$) 3.10 ($2^{\bullet-}$) 3.08 ($2^{\bullet-}$)^{d}	2.06
3	4.43	$<$1.40 ($3^{\bullet+}$)^{e} 1.40 ($3^{\bullet-}$) 1.40 ($3^{\bullet-}$)^{d}	2.70 ($3^{\bullet+}$) 2.60 ($3^{\bullet-}$) 2.58 ($3^{\bullet-}$)^{d}	1.78
4	4.15	$<$1.40 ($4^{\bullet+}$)^{e} 1.05 ($4^{\bullet-}$) 1.02 ($4^{\bullet-}$)^{d}	2.60 ($4^{\bullet+}$) 2.37 ($4^{\bullet-}$) 2.41 ($4^{\bullet-}$)^{d}	1.68
5	4.00	0.90 ($5^{\bullet-}$)	2.29 ($5^{\bullet-}$)	1.59
6	3.90	0.81 ($6^{\bullet-}$)	2.25 ($6^{\bullet-}$)	1.54

[a] Radical cations are generated by laser flash photolysis of solutions of polyphenyls and ceric ammonium nitrate in MeCN at 351 nm. Radical anions are generated by reduction of the hydrocarbons with lithium metal in THF. Dications are generated by oxidation of the oligomers with excess $SbCl_5$ in CH_2Cl_2. [b] Values from ref 5b and 16. [c] Energies calculated from observed transitions. The absorption spectra of $2^{\bullet+}$ and $3^{\bullet+}$ are similar to those previously obtained by radiolytic methods (refs 25 and 26). The absorption spectra of $2^{\bullet-}$, $3^{\bullet-}$, and $4^{\bullet-}$ are similar to those measured by Buschow et al.[29] [d] Values from ref 29. [e] Absorption extends beyond the spectral range of the monitoring system.

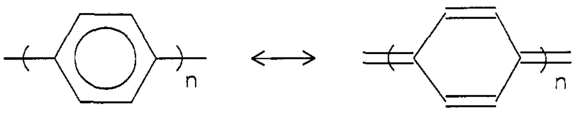


Figure 2. Benzenoid and quinoid structures of polyphenyls.

of these oligomers, measured by us in cyclohexane, show well-defined vibrational structure. Such deviations from the mirror image rule indicate a different arrangement of nuclei in the excited state as compared to the ground state. It is well established that the ground states of the oligomers of PPP have a nonplanar benzenoid structure. For example the neighboring phenyls in biphenyl are twisted with a rotation angle of 10°.[17] Apparently, the structured emission in these oligomers arises from the planar-quinoid excited state.[18] Thus the neutral oligomers, upon photoexcitation, undergo a structural change from the benzenoid to the quinoid form (Figure 2). The emission bands shift to longer wavelengths and show less structure with increasing chain length. This suggests that the excited states of larger oligomers may be less planar in comparison to smaller oligomers.

Crystallographic data on biphenyl[17] and biphenyl radical anions[19,20] also indicates an increased admixture of the quinoidal resonance form in the doped oligomer.[21] This change in structure, upon doping or photoexcitation, from the benzenoid to the quinoid form is expected to result in a narrowing of the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of these oligomers.

Electronic Transitions in Radical Ions. Baciocchi et al.[22] had demonstrated earlier that radical cations of aromatic hydrocarbons can be generated by utilizing ceric ammonium nitrate as a photochemical oxidant. We have utilized this technique to generate transient radical cations of oligomers of *p*-phenylene in acetonitrile (MeCN) by a simple laser flash photolysis (LFP) method.[11] Excimer laser excitation (351 nm, 10 ns, 20 mJ) of CAN in dry MeCN yields the highly oxidizing $NO_3^{\bullet}$ (λ_{max} at 602, 640, and 675 nm) which, in the presence of an oxidizable substrate, decays rapidly with concomitant appearance of absorption attributed to the radical cation of the substrate.[23] The electron affinity of $NO_3^{\bullet}$ is 3.7 eV, and this method can, for example, be used to generate even benzene (B) radical cation (Figure 3). The transient absorption spectrum shown in Figure 3 could also be assigned to the benzene radical cation–benzene sandwich type complex.[24] The energies of the electronic transitions observed in the radical cations of biphenyl (BP, Figure 4), *p*-terphenyl (TP), and *p*-quaterphenyl (QP, Figure 5), generated by this method, are listed in Table I. We were unable to generate the radical cations of quinquephenyl and sexiphenyl by this method due to the insolubility of these oligomers in MeCN. The spectra of $BP^{\bullet+}$ and $TP^{\bullet+}$ obtained by us are very similar to those previously measured by Shida and Hamill[25] in CCl_4 glass by radiolytic methods ($BP^{\bullet+}$, λ_{max} at ca. 380 and 690 nm; $TP^{\bullet+}$, λ_{max} at ca. 480 and 1000 nm) and by Arai et al[26] in 1,2-dichloroethane by the pulse-radiolysis method ($BP^{\bullet+}$, λ_{max} at ca. 380 and 690 nm; $TP^{\bullet+}$, λ_{max} at ca. 460 and 965 nm).

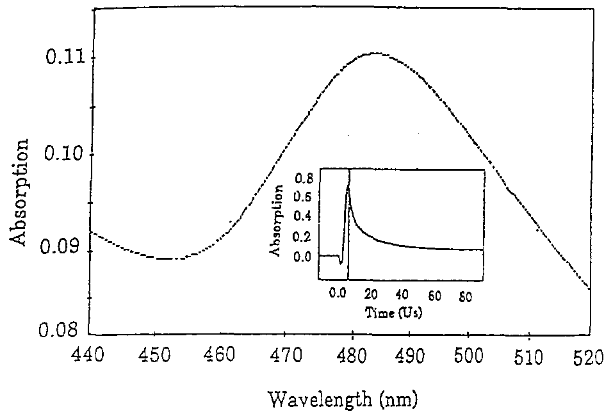


Figure 3. Transient absorption spectrum recorded upon laser flash photolysis of 1.0 M benzene and 0.2 mM CAN in dry MeCN 100 ns after the laser pulse. The insert shows a decay trace for the same sample at 480 nm.

The radical anions of polyphenyls, generated by reduction of the oligomers with alkali metals at 30 °C in

---

(17) (a) Charbonneau, G. P.; Delugeard, Y. *Acta Crystallogr., Sect. B* **1977**, *33*, 1586. (b) Calleau, H.; Baudour, J. L.; Zeyen, G. M. E. *Acta Crystallogr., Sect. B* **1979**, *35*, 426.

(18) Lokowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983; pp 7–9.

(19) Noordik, J. H.; Schreurs, J.; Gould, R. O.; Mooij, J. J.; de Boer, E. *J. Phys. Chem.* **1978**, *82*, 1105.

(20) de Boer, E.; Klaasen, A. A. K.; Noordik, J. H. *Pure Appl. Chem.* **1979**, *51*, 73.

(21) Similar geometrical changes to quinoidal form, upon doping, are predicted from *ab initio* SCF-LCAO-MO calculations in *p*-quaterphenyl.[4]

(22) Baciocchi, E.; Giacco, T. D.; Murgia, S. M.; Sebastiani, G. V. *J. Chem. Soc., Chem. Commun.* **1987**, 1246 and references therein.

(23) The pseudo-first-order rate constants for the formation of radical cations are in excess of 1×10^8 s^{-1}. The absorption bands attributed to each radical cation decay with identical kinetics. In our hands, the radical cations have lifetimes up to a few microseconds, and their decay is mixed order. Under comparable conditions the lifetimes increase with increasing conjugation: $B^{\bullet+}$ (0.2 μs); $BP^{\bullet+}$ (0.6 μs); $TP^{\bullet+}$ (3.5 μs); $QP^{\bullet+}$ (5.0 μs).

(24) (a) The benzene cation radical–benzene dimer is characterized by two bands: one at ca. 465 nm and the other at ca. 925 nm (charge resonance band): Badger, B.; Brocklehurst, B. *Trans. Faraday Soc.* **1969**, 2582. We are unable to confirm the presence of the low-energy band due to the spectral limitations of our system. (b) Recently, Arnautov et al. obtained a similar spectrum of benzene radical cation (broad band at λ_{max} 430 nm) in a mixture of butylpyridinium chloride and $AlCl_3$: Sergei A. Arnautov, The Institute of Chemical Physics, Russian Academy of Sciences, Moscow 117971, private communications.

(25) (a) Shida, T.; Hamill, W. H. *J. Chem. Phys.* **1966**, *44*, 2375. (b) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988.

(26) Arai, S.; Ueda, H.; Firestone, R. F.; Dorfman, L. M. *J. Chem. Phys.* **1969**, *50*, 1072.

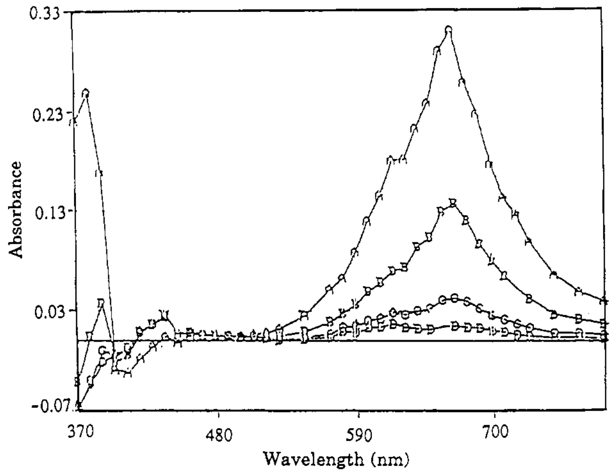


Figure 4. Absorption spectra recorded upon laser flash photolysis of 5.1 mM biphenyl and 0.56 mM CAN in dry MeCN. Points were recorded 200 ns (A), 800 ns (B), 1.4 μs (C), and 2.0 μs (D) after the laser pulse.

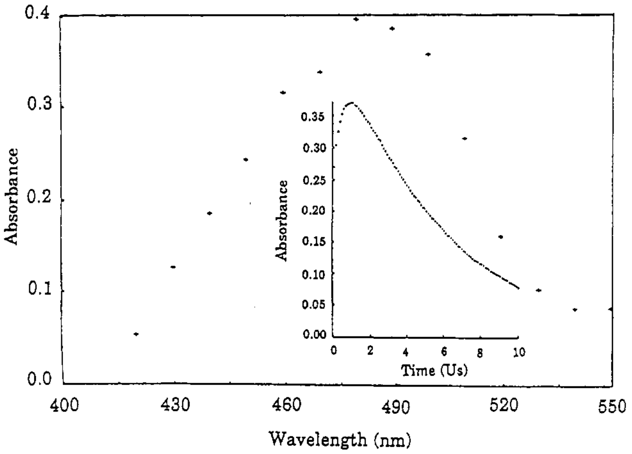


Figure 5. Transient absorption spectrum recorded upon laser flash photolysis of *p*-quaterphenyl (1.0 mM) and CAN (0.2 mM) in dry MeCN 1.0 μs after the laser pulse. The insert shows a decay trace for the same sample at 470 nm. Another band which grows beyond the spectral range of our monitoring system (>900 nm) is also observed for this species.

deaerated THF, display absorption characteristics similar to those of the corresponding radical cations. This is in accord with earlier observations on radical ions of alternant hydrocarbons.[27] All substrate hydrocarbons are soluble in THF and the optical spectra of lithium-doped QP, QQP, and SP are shown in Figure 6 (UV–vis region) and Figure 7 (near-IR region). The absorption spectra show two pairs of absorption bands, one pair in the UV–vis region separated by ca. 1600 cm^{-1} and the other in the near-IR region also separated by the same value. The sideband absorptions are consistent with a C═C vibrational stretching mode of planar–quinoid radical ions which is strongly coupled to the electronic structure.[28] These vibronic transitions in the radical ions are reminiscent of the vibrational structure in the emission spectra of neutral oligomers. The spectra of lithium salts of $BP^{\bullet-}$, $TP^{\bullet-}$, and $QP^{\bullet-}$ measured by us are very similar to those previously reported by Buschow et al.[29] for these species in THF at room temperature (Table I).

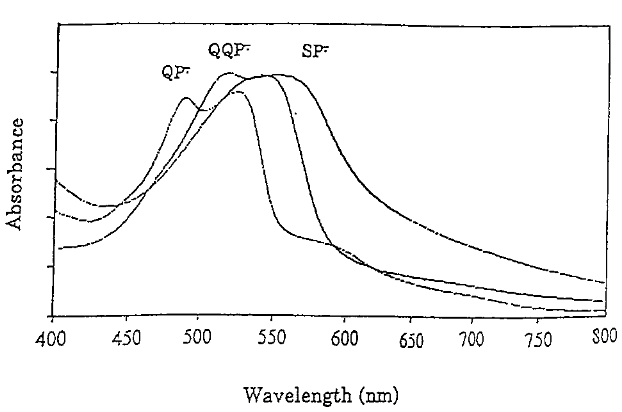


Figure 6. Absorption spectra of lithium salts of *p*-quaterphenyl (QP), *p*-quinquephenyl (QQP) and *p*-sexiphenyl (SP) radical anions in dry THF in the UV–vis range.

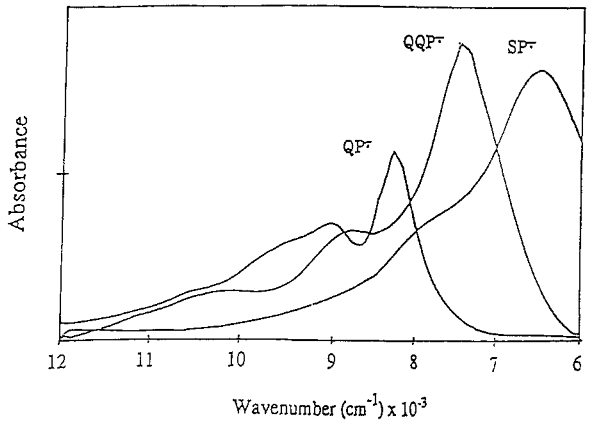


Figure 7. Absorption spectra of lithium salts of *p*-quaterphenyl (QP), *p*-quinquephenyl (QQP) and *p*-sexiphenyl (SP) radical anions in dry THF in the near-IR range.

The absorption bands in the optical spectra of potassium-doped oligomers are slightly blue shifted in comparison to the lithium-doped oligomers. Buschow et al.[29] had demonstrated earlier, from electrical conductance measurements, that potassium salts of $BP^{\bullet-}$ and $TP^{\bullet-}$ are ion-paired in THF at room temperature, but lithium salts are completely dissociated. The energies of the electronic transitions (0–0 bands) in lithium salts of $BP^{\bullet-}$, $TP^{\bullet-}$, $QP^{\bullet-}$, $QQP^{\bullet-}$, and $SP^{\bullet-}$ are listed in Table I.

Electronic Transitions in Dications. The dications of oligomers of PPP (n = 2–6), generated by the oxidation of the oligomers with excess $SbCl_5$ at 30 °C in dry, deaerated CH_2Cl_2, are stable on the time scale (1–2 h) of our experiments. The UV–vis spectra of these dications show a strong band in the visible region (Figure 8) and the electronic band energies (Table I) decrease with chain length. It is pertinent to note that the spectra of TP^{2+} and QP^{2+} measured by us in CH_2Cl_2 are similar to the previously reported spectra of TP^{2-} (λ_{max} at ca. 1.92 eV) and QP^{2-} (λ_{max} at ca. 1.60 eV), respectively, in 2-methyltetrahydrofuran.[30]

Correlation of Energy Gaps with Chain Length. It is apparent from Table I that the energies of the transitions observed in the radical ions and the dications of oligomers of PPP decrease with chain length. We recognize that the band model shown in Figure 1 was developed for mac-

---

[27] Dorfman, L. M. *Acc. Chem. Res.* **1970**, *3*, 224.

[28] Ingabas, O.; Gustafsson, G. *Synth. Met.* **1990**, *37*, 195 and references therein.

[29] Buschow, K. H. J.; Dielman, J.; Hoijtink, G. J. *J. Chem. Phys.* **1965**, *42*, 1993.

[30] (a) Hoijtink, G. J.; Zandstra, P. J. *Mol. Phys.* **1960**, *3*, 371. (b) Buschow, K. H. J.; Dieleman, J.; Hoijtink, G. J. *Mol. Phys.* **1963**, *7*, 1.

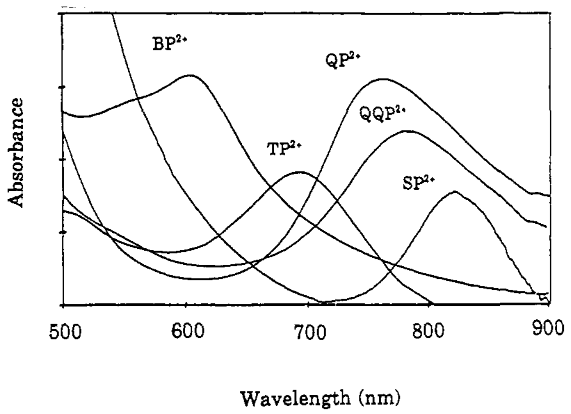


Figure 8. Absorption spectra of dications of biphenyl (BP), *p*-terphenyl (TP), *p*-quaterphenyl (QP), *p*-quinquephenyl (QQP), and *p*-sexiphenyl (SP) generated by oxidation of the oligomers with excess $SbCl_5$ in CH_2Cl_2.

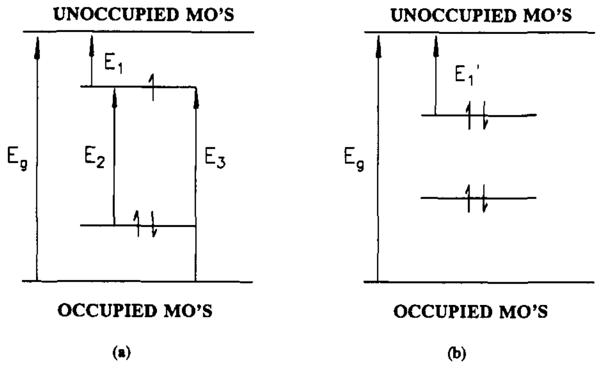


Figure 9. Energy level diagrams for (a) negative polaron and (b) negative bipolaron.

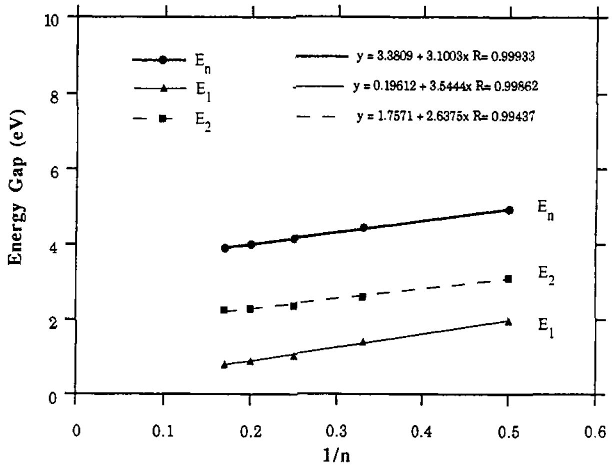


Figure 10. Plot of dependence of electronic band energies for oligomers of poly(*p*-phenylene) as a function of inverse chain length, n^{-1}; (●) E_n for neutral oligomers; (▲) E_1 for radical ions; (■) E_2 for radical ions.

romolecules with large number of π-orbitals per chain and neglects Coulombic interactions and states within the bands which in short-chain oligomers could give rise to other discrete electronic transitions. However, we believe that as a first approximation the band model is useful for examining trends in the energies of the electronic transitions in short-chain oligomers. Recently, this model was successfully used to predict trends in the electronic transitions in the radical cations of oligothiophenes.[9] On the basis of this model, the low-energy transitions observed in the spectra of radical cations can be assigned to the valence band to the singly occupied molecular orbital (SOMO) energy gap (E_1, Figure 1) and the band in the UV–vis spectra of radical cations can be assigned to the SOMO to LUMO transition (E_2, Figure 1). Since for radical anions the two MOs in the gap contain three electrons (two electrons in the bonding orbital and one electron in the antibonding orbital), the lowest energy transition observed in these species can be assigned to the SOMO-to-conduction band energy gap (E_1, Figure 9) and the high-energy transition to the HOMO to SOMO energy gap (E_2, Figure 9). Due to the pairing properties of alternant hydrocarbons, the valence band to SOMO and the SOMO-to-LUMO transitions in the radical cations are expected to occur at the same energies as the SOMO–conduction band and HOMO–SOMO transitions, respectively in the radical anions. Our assignments of the observed transitions are in accord with those proposed by Hoijtink et al.[29,30] in radical anions of $BP^{•-}$, $TP^{•-}$, and $QP^{•-}$. Furthermore, theoretical calculations also indicate that the transitions E_1 and E_2 in radical ions should have the largest oscillator strengths.[31,32] The electronic transitions observed in the dications may be assigned to the valence band to the LUMO (E_1') energy gap (Figure 1). In accord with the theoretical predictions,[3,4] the energies of the E_1' transitions in dications are larger than the energies of the E_1 transitions in the corresponding radical ions. The plots of the energies of the observed electronic transitions in the radical ions and the π–π* transitions (E_n) in the neutral oligomers vs 1/*n* (where *n* is number of phenyl units in the oligomer) are shown in Figure 10. All three plots yield good straight lines. The extrapolations of these plots to infinite chain length (1/*n* = 0) yield values of E_n = 3.38 eV, E_1 = 0.20 eV, and E_2 = 1.76 eV for the undoped and the doped polymer. The predicted value for the undoped polymer (E_n) is in accord with that observed in poly(*p*-phenylene) at 3.43 eV.[5b] The two different transitions observed by Chance[5a] at 0.6 eV and Tieke[6] at 2.5 eV in p-doped PPP can now be assigned to the valence band to the SOMO (E_1, Figure 1) and the SOMO to the LUMO (E_2, Figure 1) transitions, respectively, in the polaron of PPP. A plot of E_1' energy gap in dications vs 1/*n* yields a good straight line (Figure 11) with an intercept (1/*n* = 0) of 1.28 eV. This predicted bipolaron bandgap is in accord with that observed and assigned to the bipolaron bonding state by Crecelius[7] (1.1 eV) and predicted by Brédas[4] from MO calculations (0.9 eV) in highly p-doped PPP.

Interestingly, the predicted transitions in the polaron of PPP are considerably lower than those experimentally observed by Chance[5a] and Crecelius.[7] In fact the transition observed by Chance[5a] in doped PPP is very similar to the E_1 transition observed by us in radical ions of *p*-sexiphenyl (*n* = 6) and the transition observed by Tieke[6] is very similar to the E_2 transition observed by us in the radical ions of *p*-quaterphenyl (*n* = 4). Thus, although the energy gaps in radical ions of oligomers of PPP narrow with an increase in chain length, they reach a limiting value for *n* ~ 4–6. This indicates that for longer chain lengths the extent of spin and charge delocalization becomes independent of the extent of conjugation, and therefore the *E* vs 1/*n* plots are expected to level off at some point and meet the abscissa horizontally. This deviation also suggests that the polaron

---

[31] Fesser, K.; Bishop, A. R.; Campbell, D. K. *Phys. Rev. B* **1983**, *27*, 4804.

[32] Sum, U.; Fesser, K.; Büttner, H. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 957.

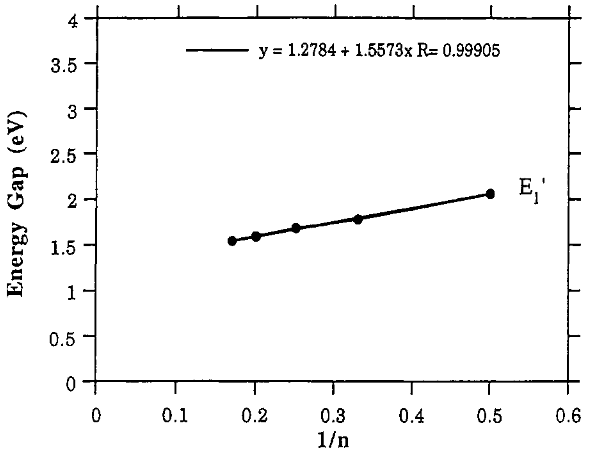


Figure 11. Plot of dependence of first electronic transitions (E_1') in dications of oligomers of poly(*p*-phenylene) as a function of inverse chain length, n^{-1}.

in PPP has limited delocalization length involving 4–6 phenyl units. Thus the planar polaron is confined to a short segment of the polymer chain by twisted benzenoid chains. These results and conclusions are in agreement with MO calculations by Brédas on doped PPP which predict the extension of the polaron charged defect to be over about five rings.[3,4]

We emphasize that our experiments in dilute solutions may not necessarily reflect the situation in the solid state where strong interchain interactions may prevail. It is well established that planar π-radical cations form sandwich type complexes with corresponding neutrals where charge and spin are delocalized over several molecules, resulting in slightly shifted electronic transitions.[33] Thus, higher energy electronic transitions observed in p-doped crystalline PPP compared to those predicted from results in dilute solutions could be due to the formation of polaron–neutral complexes. However, formation of such complexes is probable only if PPP chains are very well stacked in the polymer matrix.

We have examined the undoped oligomers of PPP by the X-ray powder diffraction technique to determine the extent of stacking of the molecules in the crystal lattice. The X-ray powder diffraction patterns obtained for biphenyl (BP), *p*-terphenyl (TP), QP, QQP, and SP exhibit several intense, narrow peaks. The peaks characterized by the largest *d* spacings (9.44, 13.3, 17.28, 22.92, and 26.44 Å for BP, TP, QP, QQP, and SP, respectively) correspond to one of the unit-cell dimensions in the crystals of these compounds, which have previously been identified as monoclinic.[34–36] It is interesting to note that a plot of d_{max} vs the numbers of phenyl units (n) in the oligomer yields an excellent straight line (correlation coefficient, r = 0.9974). This linear correlation suggests that this unit cell dimension reflects the numbers of phenyl units, linked through their para positions, in these oligomers. The average length of the phenyl unit in these oligomers, obtained from the slope of this linear plot, is 4.36 Å. The X-ray diffraction patterns for all the oligomers exhibit the most intense peak in the region of 4.4–4.6 Å. A similar intense peak was reported by Marvel and Hartzell[37] in the diffractogram of PPP. This intense peak has been suggested to be due to the stacking of the lamellae in these aromatic compounds. The width of this peak increases with an increase in chain length, which suggests that although the lamellae lie nearly coplanar in the smaller molecules, the stacking becomes less regular as the length of the oligomer increases. This is in agreement with the previously reported rotation angles between neighbouring phenyls of 10° and 22° in biphenyl and poly(*p*-phenylene), respectively.[17,38]

Although these results do not rule out the formation of polaron–neutral complexes in doped PPP, they indicate that the formation of such complexes is more probable in the smaller oligomers. We have observed that the fluorescence emission spectra of crystalline (suspensions in water) oligomers (n = 3–6) of PPP do not show broad bands typical of excimer emissions but display bands with well-defined vibrational structure, similar to those observed in cyclohexane solutions. Since excimer as well as radical ion–neutral complex formation is expected to be preferred in molecules with planar geometries, formation of these species in polyphenyls may be hindered due to the twisted geometries of these molecules. These results, coupled with the fact that the shifts in electronic transitions of radical cations due to the formation of sandwich type complexes are usually small, leads us to believe that polaron-neutral complex formation cannot account for the *large differences* in the observed and the predicted energy gaps in the doped polymer. The localization of the charged defect to a short segment ($n \sim$ 4–6) of the polymer chain appears to be a more plausible explanation. It is pertinent to note that Guay et al.[9b] recently demonstrated that the polarons in doped polythiophene are delocalized over a chain length of ca. 12 monomer units. Bally *et al.*[10] have also predicted, from MNDO calculations, a similar levelling effect on electronic band energies of polyene radical cations where this flattening is expected to set in as the chain length increases beyond ~15 double bonds. Tolbert[39] recently demonstrated that the soliton in polyacetylene is also localized to a polyene length of ca. 30 carbon atoms.

Charge Carriers in Doped PPP. Our assignment of the strong absorption band at 0.6 eV observed by Chance et al.[5a] in AsF_5-doped highly conducting (500 S cm^{-1}) PPP to polarons suggests that polarons are the principle charge carriers in highly conducting doped PPP. Furthermore, our results demonstrate that the extent of delocalization of the polaron in PPP is about 4–6 phenyl rings. This is also in accord with the fact that high conductivities in AsF_5-doped PPP are observed for doping levels of about 0.4 mol of AsF_5/mol of phenylene repeat unit.[5a] Since 1.5 mol of AsF_5 is required to generate one unit of charge (eq 1), doping levels of 0.4 mol AsF_5/mol of repeat unit

$$2Ar + 3AsF_5 \rightarrow 2Ar^{\bullet+} + 2AsF_6^- + AsF_3 \qquad (1)$$

corresponds to the generation of a polaron delocalized over about four phenyl rings (1.5/0.4) in the doped polymer. Thus it appears that fairly localized polarons are responsible for the high electronic conductivities in doped PPP. These results and conclusions appear to be inconsistent

---

[33] (a) Badger, B.; Brocklehurst, B. *Trans. Faraday Soc.* **1969**, *65*, 2576, 2588. (b) Badger, B.; Brocklehurst, B. *Trans. Faraday Soc.* **1970**, *66*, 2989.

[34] Rietveld, H. M.; Maslen, E. N.; Clews, C. J. B. *Acta Crystallogr.* **1970**, *B26*, 693.

[35] Toussaint, C.; Vos, G. *J. Chem. Soc. B* **1966**, 813.

[36] Toussaint, C. *Acta Crystallogr.* **1966**, *21*, 1002.

[37] Marvel, C. S.; Hartzell, G. E. *J. Am. Chem. Soc.* **1959**, *81*, 448.

[38] Brédas, J. L.; Chance, R. R.; Silbey, R.; Nicolas, G.; Durand, P. *J. Chem. Phys.* **1982**, *77*, 371.

[39] Tolbert, L. M. *Acc. Chem. Res.* **1992**, *25*, 561 and references therein.

with the absence of Pauli susceptibility in highly conducting doped PPP, a fact which suggests that bipolaron migration is responsible for the "spinless" conductivity in this polymer.[40] However, Miller *et al.*[41] recently demonstrated that cation radicals of oligomers of thiophene rapidly dimerize (reversibly) in dilute solutions to yield diamagnetic π-dimers. Since in the solid state the concentration of radical cations, at high doping levels, is expected to be very high, interactions between *planar* radical cations on neighboring chains could lead to the formation of diamagnetic π-stacks.[42] The radical cation dimer complexes of this type are well-known in viologens[43a] and Wurster's blue.[43b] The optical spectra of cation radical π-dimers show slightly shifted absorption bands as compared to the corresponding radical cations,[41,42] which may explain the slight differences in the spectral characteristics of the *p*-quaterphenyl radical ions (in solution) and the highly conducting doped PPP (in solid state). In doped PPP, the formation of polaron diamagnetic π-stacks would be highly favored in an intercalant structure (stage 1 structure analogous to polyacetylene and graphite) in which the molecular plane is perpendicular to the intercalant plane. In fact, such an intercalant structure has been suggested for potassium-doped PPP.[44] Although the highest dopant level observed for AsF_5 (0.42 mol of AsF_5/mol of phenyl repeat unit) is less than that indicated in stage 1 structures of acceptor-doped polyacetylene and graphite, an analogous intercalant structure with dopant density lower than graphite in the intercalant plane can be envisioned for AsF_5-doped PPP.[44] Thus, diamagnetic π-stacks (similar to those present in conducting charge-transfer salts[45]) of fairly localized polarons can be an alternative to diamagnetic bipolarons as an explanation for the absence of Pauli susceptibility in highly oxidized PPP and could be the conducting species in this and other conjugated polymers.[46]

Acknowledgment. Support of this research by the National Science Foundation EPSCoR program and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We thank professor David Creed for many helpful discussions.

Supplementary Material Available: Transient absorption spectrum of the radical cation of *p*-terphenyl, X-ray powder patterns of oligomers (n = 2–6) of poly(*p*-phenylene), plot of the largest *d* spacings in powder X-ray diffractograms as a function of chain length, fluorescence emission spectra of polyphenyls (n = 2–5) in cyclohexane and in the solid state (suspensions in water) (5 pages). Ordering information is given on any current masthead page.

---

[40] Brédas, J. L.; Chance, R. R.; Silbey, R. *Phys. Rev. B* **1982**, *26*, 5843.

[41] Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 2728.

[42] Diamagnetic π-stacks of ion radicals are reported in the following: Penneau, J.-F.; Miller, L. L. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 986. Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, *5*, 620.

[43] (a) Evans, J. C.; Evans, A. G.; Nouri-Sorkhabi, N. H.; Obaid, A. Y.; Rowlands, C. C. *J. Chem. Soc., Perkin Trans.* **1985**, 315 and references therein. (b) Soos, Z. G.; Bondeson, S. R. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1983; pp 193–257 and references therein.

[44] Shacklette, L. W.; Chance, R. R.; Ivory, D. M.; Miller, G. G.; Baughman, R. H. *Synth. Met.* **1979**, *1*, 307.

[45] Ferraro, J. R.; Williams, J. M. *Introduction to Synthetic Electrical Conductors*; Academic Press: New York, 1987.

[46] Conductive, discotic liquid crystal stacks of porphyrins are also reported: Schouten, P. G.; Matthijs, P. D.; Fox, M. A.; Pan, H.-L. *Nature* **1991**, *353*, 736.