

New Boronic-Acid- and Boronate-Substituted Aromatic Compounds as Precursors of Fluoride-Responsive Conjugated Polymer Films

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New electropolymerizable aromatic compounds (i.e. pyrrole, thiophene, aniline) bearing boronic acid and ester substituents have been synthesized and their electrochemical behavior has been investigated. Functionalized polythiophene and polypyrrole films could be anodically generated in acetonitrile, whereas the polyaniline derivative was elec-

troformed in an acidic aqueous solution. The electrochemical responses of some of these materials were changed when fluoride ions were added to the electrolytic solutions. The strongest modifications, caused by binding of fluoride by the immobilized boron, were observed for the polypyrrole derivative in hydroorganic media.

Introduction

In recent years, cation recognition by functionalized redox-active polymer-film-coated electrodes has been a subject of considerable interest. For example, much work has been devoted to the sensing properties of certain linear polyether- or crown-ether-functionalized conjugated polymers.^[1–8] In contrast, redox-active polymer-film-based selective anion detection has surprisingly been largely ignored, even though an extensive range of receptors have been used in anion transport and sensing.^[9,10] Among such receptors, Shinkai and co-workers have demonstrated that boronic acid and boronate groups are able to strongly bind hard-base anions such as F^- , resulting in specific orbital changes from sp^2 - to the more stable sp^3 -hybridized boron.^[11–14] In the case of a boron site being covalently bound to ferrocene, the boron– F^- interaction was found to perturb the electrochemical signal of the electroactive moiety in solution. This encouraging result was clearly indicative of an anion-recognition phenomenon. However, the immobilization of these functional groups on electrode surfaces has not hitherto been achieved. In continuation of our investigations concerning the development of new sensory materials, we describe here the synthesis of various boronic-acid- and boronate-substituted electropolymerizable aromatic compounds with the aim of electrochemically generating new anion-sensitive layers. Precursors differing in the nature and length of the spacer arm between the monomeric unit and the boron site were chosen, as such parameters have strong effects on the electropolymerization process and the electroactivity of the resulting conjugated polymers, and are also central to fast and sensitive recognition. Thus, the electronic and/or conformational changes induced by boron–fluoride binding can be expected to be detectable through the modification of a characteristic (e.g. electrochemical) response of the conjugated polymer, pro-

vided that the binding site is in close proximity to the polymer.

Results and Discussion

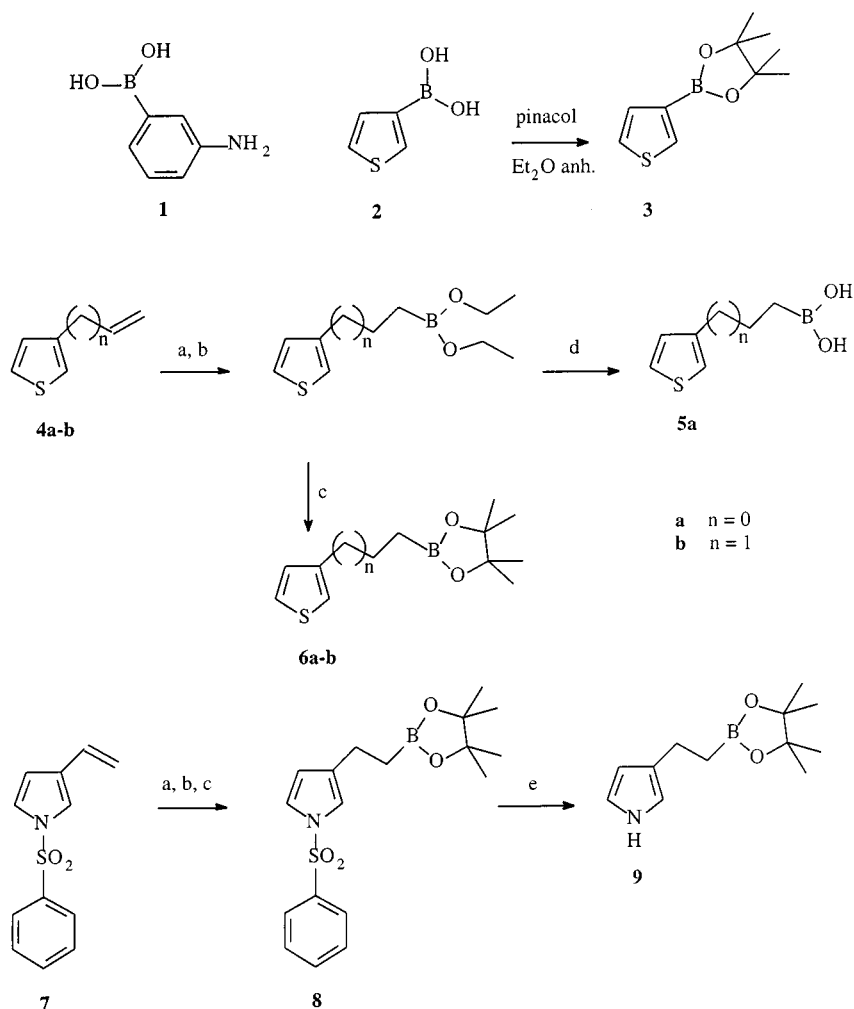
Synthesis of Monomers

With a view to electrochemically generating versatile conjugated polymer films showing electroactivity in organic and aqueous media, the functionalization of various electropolymerizable aromatic units, specifically aniline, pyrrole, and thiophene, by a boronic acid group or its protected form, “pinacol borane” (4,4,5,5-tetramethyl-1,3,2-dioxaborolane), was envisaged. Direct attachment of the functional group to the aromatic ring was considered in the cases of 3-substituted aniline and thiophene. 3-Aminophenylboronic acid (**1**) and thiophene-3-boronic acid (**2**) are commercially available, while the boronate derivative **3** of thiophene could easily be obtained in 90% yield by reaction of **2** with pinacol in anhydrous diethyl ether (Scheme 1).

The incorporation of an alkyl spacer arm between the aromatic ring and the recognition site was achieved by hydroboration of the appropriate alkenes.^[15] Thus, 3-vinyl-^[16] (**4a**) and 3-allylthiophene^[17] (**4b**) were treated with diisopinocampheylborane^[18] (IPC_2BH), previously prepared from (+)- α -pinene and borane–dimethyl sulfide, to give the diethyl boronate derivatives (Scheme 1). Treatment with aqueous acid or pinacol yielded **5a** and **6a–b**, respectively, in 22–26% overall yield. The same protocol was used for the vinyl derivative of the protected pyrrole **7**, which was synthesized in four steps from pyrrole.^[19,20] Deprotection of the functionalized pyrrole was carried out electrochemically at -2.45 V (vs. 10^{-1} M Ag^+/Ag) using pyrene as a redox mediator. Compared to the classical chemical deprotection method (i.e. using concentrated aqueous NaOH solution), this procedure was found to be more efficient.

The steric and electronic effects of the substituents on the electropolymerization efficiency, as well as on the electroactive and recognition properties of the corresponding

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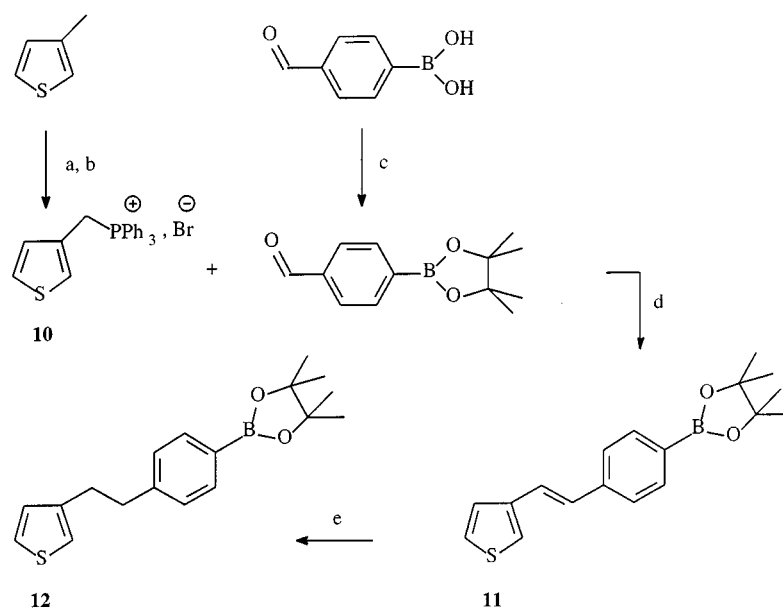
Scheme 1. Reagents and conditions: (a) Ipc_2BH (1.2 equiv.), THF, -40°C , then addition of the vinylated compound, room temp., 24 h; (b) acetaldehyde (10.0 equiv.), 0°C , 24 h; (c) pinacol (1.0 equiv.), THF, room temp., 24 h; (d) 1 M HCl; (e) pyrene (20%), reduction at -2.45 V (vs. $10^{-1}\text{ M Ag}^+/\text{Ag}$) in $\text{CH}_3\text{CN} + 10^{-1}\text{ M Bu}_4\text{NClO}_4$

polymers, were also examined by introducing a phenyl ring in the spacer arm, in some cases in conjunction with an ether group. The isomerically pure *trans* compound **11** was prepared in 42% yield by means of a Wittig reaction between *p*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde and triphenyl(3-thienylmethyl)phosphonium bromide (**10**) using lithium diisopropylamide as the base (Scheme 2).^[21] As observed previously for thiophenes bearing arylsulfonamide substituents in their 3-positions,^[22] only the *trans* isomer was detected when a short spacer was used. Catalytic hydrogenation of **11** yielded **12**, in which the “pinacol borane” moiety is electronically insulated from the thiophene ring.

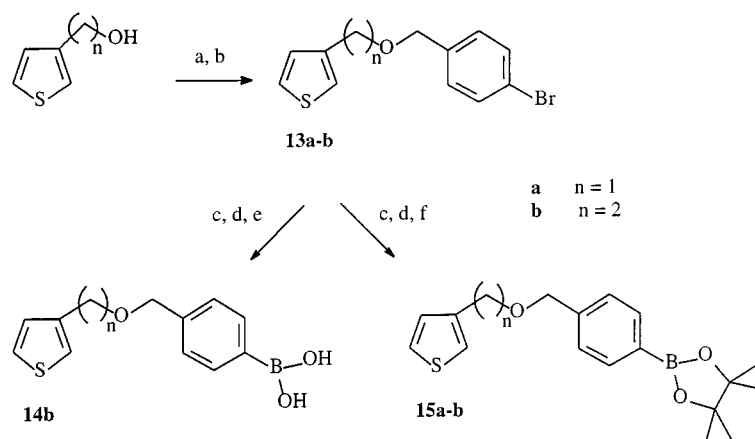
Compounds **13a–b**, incorporating an ether function, were readily obtained (80–92% yield) by condensation of 3-thienylalkoxides with *p*-bromobenzyl bromide (Scheme 3) according to a similar procedure developed by Garnier and co-workers.^[23] The Grignard reagents prepared from **13a–b** were treated with trimethyl borate to give the dimethyl boronate derivatives, which were then converted to the required monomers in about 25% yield by treatment with aqueous acid or pinacol.

Anodic Behaviour of Boronic-Acid- and Boronate-Substituted Aromatic Compounds – Effect of F^- on the Oxidation of the Aniline Derivative

Cyclic voltammetric characterization of the five-membered heterocycles in $\text{CH}_3\text{CN} + 10^{-1}\text{ M Bu}_4\text{NClO}_4$ revealed an irreversible oxidation peak E_{pa} in the range 1.40–1.60 V (at 100 mV s^{-1}) for the thiophene derivatives, whereas **9** was oxidized at a lower potential of 0.82 V (Table 1). Compared with its analogues, the easier oxidation of **11** may be rationalized in terms of charge delocalization along the alkene. From the data gathered in Table 1, it is apparent that the nature and length of the substituent grafted to the thiophene ring has a significant effect on E_{pa} . Firstly, the slightly less positive oxidation potential exhibited by the boronic esters can be ascribed to a decrease in the electron-withdrawing character of the boron atom. Moreover, the introduction of an ethyl spacer between the thiophene and the boronic unit can be seen to contribute to the decrease in E_{pa} , whereas no such clear changes are observed for a propyl spacer (**3** compared to **6b**). In fact, the electronic effect of the boronic group on the oxidation of the thio-



Scheme 2. Reagents and conditions: (a) *N*-bromosuccinimide, CCl_4 , $h\nu$; (b) PPh_3 , DMF; (c) pinacol (1.1 equiv.), Et_2O , room temp., overnight; (d) lithium diisopropylamide (1.3 equiv.), EtOH , reflux, 2–3 h; (e) 10% Pd/C, MeOH, H_2 (50 atm), overnight



Scheme 3. Reagents and conditions: (a) *t*BuOK (1.2 equiv.), THF, room temp., 15 min; (b) *p*-bromobenzyl bromide (1.3 equiv.), THF, reflux, 4 h; (c) Mg, THF, reflux, 1–2 h; (d) B(OMe)_3 , THF, -78°C , 1–2 h, then room temp., overnight; (e) 1 M HCl; (f) pinacol (1.1 equiv.), THF, room temp., 12 h

phene ring is seen to be strongly attenuated with a short linear chain, whereas the more flexible propyl spacer facilitates direct interaction between the boronic group and the oxidizable ring. The E_{pa} values exhibited by **6a** and **12** may be explained in terms of the steric hindrance and electron-withdrawing character of the phenyl group. As has already been demonstrated for oxyalkyl-substituted polythiophenes,^[24] the steric effect of the phenyl group may be negated by incorporating an ether function in the spacer arm.

It was found that the thiophene and pyrrole derivatives could be anodically electropolymerized in thoroughly dried acetonitrile containing Bu_4NClO_4 or Bu_4NPF_6 as the supporting electrolyte. The boronate-substituted compounds proved to be the most efficiently electropolymerized, probably as a result of the strong adsorption of the boronic acid containing derivatives on the drying agent used in situ (i.e. alumina). Compounds **5a**, **11**, and **14b** could not be electropolymerized, irrespective of the experimental conditions. In

fact, their oxidation rendered the electrode passive after a few potential scans without the apparent formation of a deposit. The ClO_4^- or PF_6^- -doped films were potentiodynamically electroformed with an anodic limit close to the irreversible oxidation peak potential of the monomer, e.g. 0.75 V vs. 10^{-1} M Ag^+/Ag for **9**. For example, the successive cyclic voltammograms recorded for **9** showed the emergence of new redox systems attributable to the doping-undoping process of the electroformed polymer (Figure 1).

In contrast to the facile electropolymerization of the five-membered heterocycles, **1** was found to be inefficiently electropolymerized in aqueous solution containing 5×10^{-1} M H_2SO_4 . Nevertheless, the process was strongly promoted when F^- was added to the electrolyte (Figure 2). No such effect was observed with Cl^- or with unfunctionalized polyaniline in the presence of F^- . This catalytic phenomenon can only be explained in terms of an enhanced reactivity of **1** stemming from a boron– F^- interaction. Thus, the elec-

Table 1. Voltammetric data of boronic-acid- and boronate-substituted aromatic compounds and their corresponding polymers in $\text{CH}_3\text{CN} + 10^{-1} \text{ M Bu}_4\text{NClO}_4$ (electroformation charge: 65 mC cm^{-2}); potential scan rate: 100 mV s^{-1} ; reference electrode: $10^{-1} \text{ M Ag}^+/\text{Ag}$

Compound	$E_{\text{pa}} [\text{V}]^{[\text{a}]}$	$E^{\circ'}$ polymer $[\text{V}]^{[\text{c}]}$
1	0.44 ^[b]	0.25 and 0.44 ^[b]
2	1.60	0.69
3	1.61	0.83
5a	1.47	— ^[d]
6a	1.43	0.52
6b	1.62	0.86
9	0.82	−0.35 −0.08 ^[e]
11	1.04 and 1.14	— ^[d]
12	1.58	0.77
14b	1.56	— ^[d]
15a	1.53	0.65
15b	1.50	0.56

[a] Anodic peak potential relative to the compound at $2 \times 10^{-2} \text{ M}$. — [b] vs. SCE in $\text{H}_2\text{O} + 5 \times 10^{-1} \text{ M H}_2\text{SO}_4$. — [c] Average of anodic and cathodic peak potentials corresponding to the p-doping/undoping process. — [d] Passivation of the electrode occurred. — [e] vs. SCE in $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (1/1 v/v) + $5 \times 10^{-1} \text{ M LiClO}_4$.

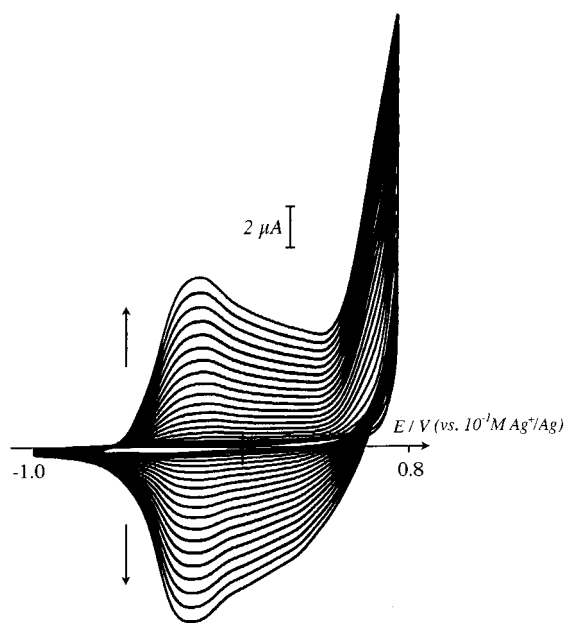


Figure 1. Successive cyclic voltammograms of **9** (10^{-2} M) in $\text{CH}_3\text{CN} + 10^{-1} \text{ M Bu}_4\text{NPF}_6$ (final electropolymerization charge: 70 mC cm^{-2}); potential scan rate: 100 mV s^{-1}

trogenerated polymer may be considered as being self-doped. The binding of F^- was confirmed by recording ^{11}B -NMR spectra (96 MHz) of **1** in solution before and after the addition of KF. In H_2O , containing $5 \times 10^{-1} \text{ M H}_2\text{SO}_4$, the ^{11}B signal of **1** was observed at $\delta = 27.7$ vs. $\text{BF}_3 \cdot \text{Et}_2\text{O}$. Upon addition of KF (from 0 to 3 equiv.), another signal emerged at $\delta = 3.4$, the magnitude of which increased with the amount of F^- added. These results are thus perfectly consistent with a transformation from sp^2 - to sp^3 -hybridized boron upon binding of F^- .

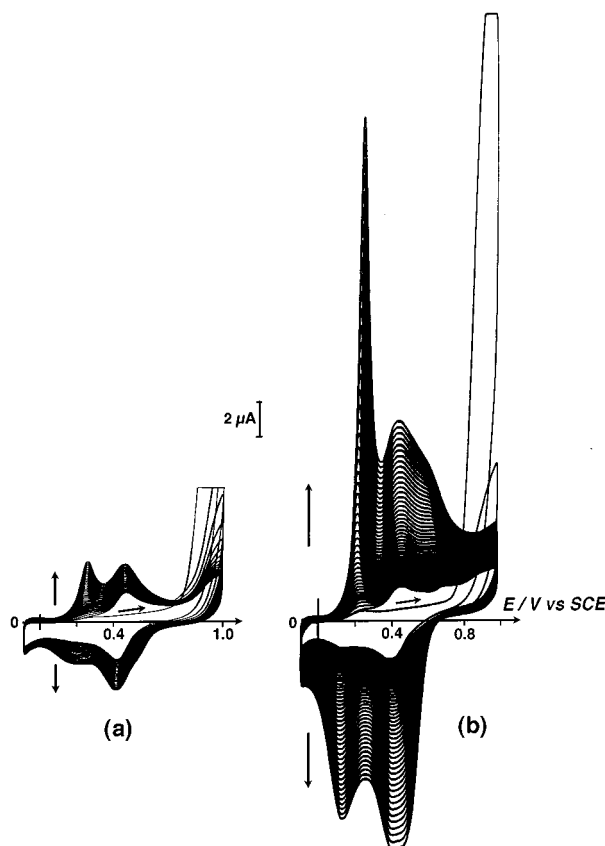


Figure 2. Successive cyclic voltammograms of **1** (10^{-1} M) (a) in the absence and (b) in the presence of 10^{-1} M KF ; electrolyte: $\text{H}_2\text{O} + 5 \times 10^{-1} \text{ M H}_2\text{SO}_4$; potential scan rate: 100 mV s^{-1}

Electrochemical Characteristics of the Electroformed Polymers: Effect of F^-

Following their electrosynthesis, the substituted polythiophene and polypyrrole films were examined in monomer-free acetonitrile solutions. They exhibited stable reversible redox systems corresponding to the p-doping/undoping process (Table 1) and the doping level was deduced from the cyclic voltammograms to be in the range 0.15–0.30. Additionally, below -2.2 V , a moderately stable n-doped state was observable for some polythiophenes, such as poly(**6a**) (Figure 3, a). The electrochemical behaviour of the polythiophene films proved to be very sensitive to substituent effects. As shown in Figure 4, the electronic and steric properties of the substituents exerted similar effects as in the monomers.

In contrast to the polythiophene films, the 3-substituted polypyrrole electroformed from **9** remained electroactive in aqueous media. However, its electroactivity was weaker and less reversible than in organic electrolytes, probably owing to the presence of the hydrophobic pinacol moiety. A better electrochemical response was observed in hydroorganic media, such as $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (Figure 3, b). In this medium, the addition of KF led to a decrease of the p-doping/undoping system at -0.11 V vs. SCE, while a new redox peak emerged at -0.37 V , the magnitude of which increased with the F^- concentration. For a film electropolymerized using a charge of 70 mC cm^{-2} , only the second system was ob-

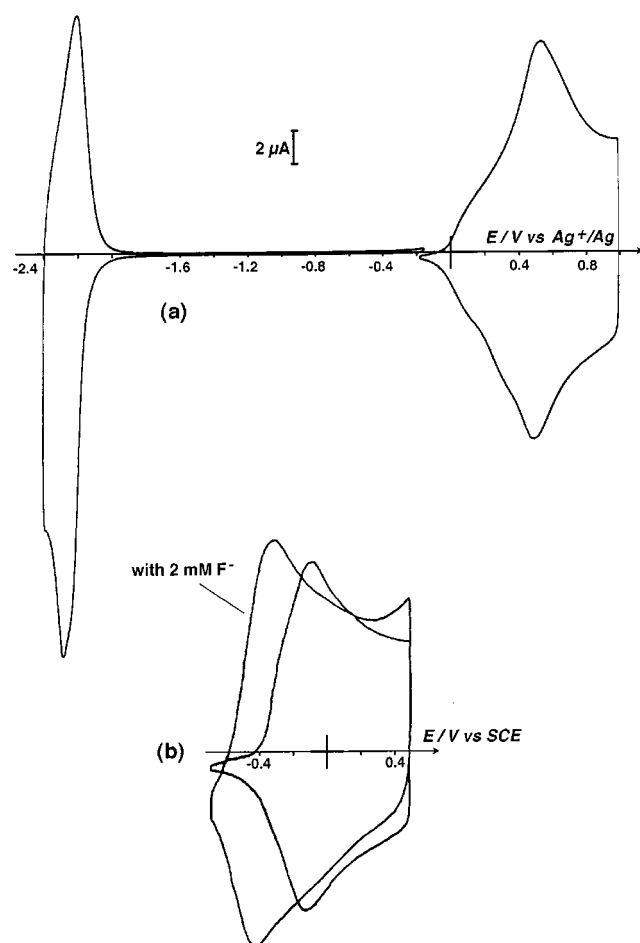


Figure 3. Cyclic voltammograms of (a) poly(6a) in CH₃CN + 10⁻¹ M Bu₄NClO₄ and (b) poly(9) in H₂O/CH₃CN (1:1, v/v) + 5 × 10⁻¹ M LiClO₄ in the absence and presence of 2 mM KF; electroformation charge of the polymers: 65 mC cm⁻²; potential scan rate: 100 mV s⁻¹

served at a high F⁻ concentration, e.g. 2 mM (Figure 3, b). It must be pointed out that the electrochemical response of poly(9) was not modified when F⁻ was replaced by Cl⁻ or Br⁻ up to tested concentrations of 20 mM. Moreover, the interaction with F⁻ was specific to the boronate-containing polymers; the voltammetric responses of the unfunctionalized polymer films were found to be unaffected by the presence of this anion. Thus, all these results are consistent with a selective electrochemical recognition of F⁻ by poly(9). The negative shift of the redox potential indicates that the F⁻-bound polymer is more easily oxidizable. This may be rationalized in terms of stabilization of the F⁻-bound to the boron atom by the positive charges along the backbone of the oxidized polymer.

The effect of F⁻ on the other functionalized polymers was also investigated. The results obtained for the polythiophene derivatives in acetonitrile using Bu₄NF were not wholly satisfactory owing to the well-known instability and hygroscopic nature of the fluoride salt.^[25] Generally, reactions that have been reported to proceed in the presence of Bu₄NF have involved hydrated F⁻ or bifluoride ions. In view of the lack of electroactivity of these materials in aqueous media, we did not test the effect of F⁻ under such con-

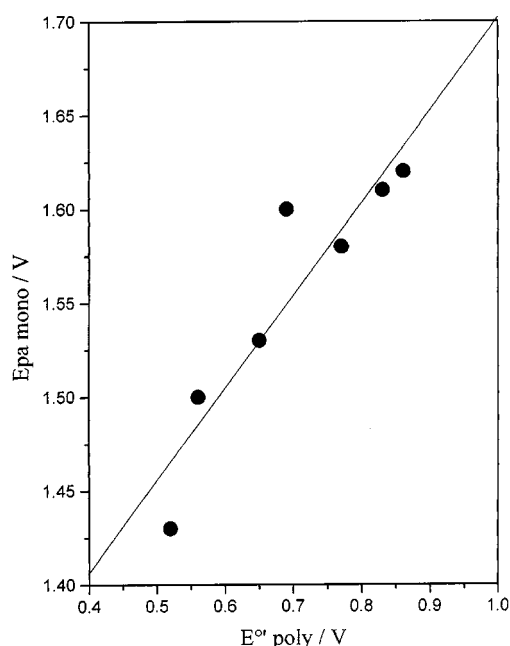


Figure 4. E_{pa} of the thiophene derivatives as a function of E° corresponding to the p-doping/undoping process of their respective polymers; data were extracted from Table 1

ditions. For the polyaniline derivative, it was found that films electrosynthesized in the presence of various amounts of KF showed different electrochemical responses when cycled in a weakly acidic buffer at pH = 4.0 (Figure 5, a). These observations suggest that the interaction in solution between the boron atom and fluoride ion has a modifying effect on the structural arrangement of the resulting polymer. Moreover, the response of a poly(1) film electrosynthesized in the absence of KF was also modified, albeit to a lesser extent, upon addition of this salt to a buffered solution (Figure 5, b). In this case, the binding event apparently induces a post-polymerization modification of the polymer structure. However, the electrochemical perturbations caused by the boron–fluoride interaction were lower in magnitude than those observed for the polypyrrole system. Indeed, the polypyrrole response was strongly shifted when only 2 mM KF was added to the electrolytic solution (Figure 3, b), whereas with poly(1) the effect of F⁻ only became electrochemically detectable above 5 mM. Further work is necessary to assess the effect of the film thickness on the sensitivity of these two potential sensor materials.

Conclusions

Of the various boronic-acid- and boronate-functionalized conjugated polymer films described here, the polypyrrole derivative poly(9) has been shown to exhibit the most significant and interesting recognition properties towards F⁻. Thus, the electrochemical response of this polymer was strongly modified in the presence of this anion, whereas Cl⁻ or Br⁻ had no effect. Such specific changes may be ascribed to electronic and/or conformational perturbations caused by the interaction between the immobilized boron atoms and fluoride ions. UV/Vis spectroelectrochemical experi-

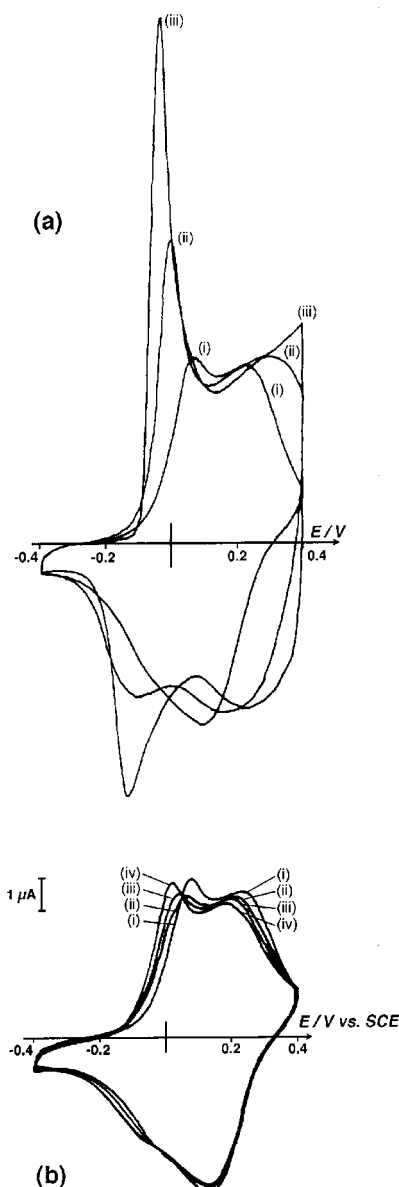


Figure 5. (a) Cyclic voltammograms in an acetate buffer at pH = 4.0 of poly(**1**) films electrosynthesized in 5×10^{-1} M H_2SO_4 containing (i) **1** at 10^{-1} M, (ii) KF at 2×10^{-1} M, and (iii) KF at 4×10^{-1} M; (b) effect of the F^- concentration in an acetate buffer at pH = 4.0 on the electrochemical response of a poly(**1**) film electrosynthesized in the absence of this anion; KF at (i) 0 M, (ii) 5×10^{-3} M, (iii) 10^{-2} M, and (iv) 2×10^{-2} M; potential scan rate: 20 mV s^{-1} ; electroformation charge of the polymers: 125 mC cm^{-2}

ments are currently in progress aimed at providing further information on the effect of F^- . Several parameters, such as the nature and length of the spacer arm between the boron atom and the monomer, need to be optimized in order to obtain a sensory material capable of operating over a wide F^- concentration range. Moreover, considering some potential technological applications, an enhancement of the electroactive properties of poly(**9**), as well as those of the polythiophene derivatives, in aqueous media would be required. The introduction of oligooxyethylene segments in the spacer or the electrochemical copolymerization of the functionalized pyrrole with unsubstituted pyrrole might be

possible ways of improving the hydrophilicity of these materials.

Experimental Section

Synthesis of Monomers

General: All organic reactions were carried out under nitrogen. Solvents were freshly distilled from Na or P_2O_5 prior to use. — ^1H - and ^{13}C -NMR spectra were recorded in CDCl_3 solution with a Bruker AC 300 spectrometer using TMS as an internal reference. — Melting points were determined with an Electrothermal® melting point apparatus. — Silica gel (70–230 mesh) for column chromatography was purchased from Merck. — Mass spectra were measured with a Varian MAT 311 spectrometer. — The boronic-acid-substituted compounds **1** and **2** are commercially available (Lancaster; 98%) and were used without further purification.

3: At room temperature, **2** (1.28 g, 10.0 mmol) and anhydrous pinacol (1.30 g, 11.0 mmol) were mixed in anhydrous diethyl ether (10 mL) and the reaction mixture was stirred for 24 h. After washing with water, the ether phase was dried with MgSO_4 and concentrated to dryness in vacuo to give **3** in 90% yield. White solid; m.p. 82°C . — ^1H NMR (300 MHz): $\delta = 1.24$ (s, 12 H, CH_3), 7.24 (dd, $^3J = 4.9 \text{ Hz}$, $^4J = 2.7 \text{ Hz}$, 1 H, CH), 7.32 (dd, $^3J = 4.9 \text{ Hz}$, $^4J = 1.0 \text{ Hz}$, 1 H, CH), 7.83 (dd, $^4J = 2.7 \text{ Hz}$, $^4J = 1.0 \text{ Hz}$, 1 H, CH). — MS: $m/z = 210.0864 [\text{M}^+]$; calcd. 210.0886.

Hydroboration of Alkenes: The functionalized monomers containing an alkyl chain were prepared by hydroboration^[15] of 3-vinylthiophene, 3-allylthiophene, and 1-(phenylsulfonyl)-3-vinylpyrrole. Ipc_2BH was used as a regio- and stereoselective hydroboration agent. It was prepared from (+)- α -pinene and borane–dimethyl sulfide according to a known procedure.^[18] **4a** and **4b** were synthesized in two steps in yields of 70% and 40% from 3-(2-hydroxyethyl)-thiophene and 3-bromothiophene, respectively, according to previously described procedures.^[16,17] **7** was prepared in 55% overall yield from pyrrole.^[19,20] All these reagents exhibited physical characteristics similar to those reported in the literature. — For the synthesis of “pinacol borane”-substituted compounds, the typical procedure was as follows: 5 mmol of the alkene was added dropwise to a well-stirred white suspension of Ipc_2BH (1.70 g, 6.0 mmol) in anhydrous THF (8 mL) maintained at -40°C . Following the addition, the reaction mixture was allowed to very slowly warm to room temperature and stirring was continued for 24 h. The mixture was then cooled to 0°C , whereupon freshly distilled acetaldehyde (50.0 mmol) was added. After 24 h, the excess acetaldehyde was removed in vacuo and a solution of recrystallized pinacol (5.0 mmol) in anhydrous THF (5 mL) was added. The resulting mixture was stirred for 24 h and then the THF was evaporated in vacuo. The residue was transferred to a Büchi kugelrohr apparatus in order to distil off (+)- α -pinene and pinacol, and then the “pinacol borane”-substituted crude product was purified by column chromatography (silica gel).

6a: Eluent: CH_2Cl_2 /petroleum ether, 1:1. Colorless oil. Yield: 26%. — ^1H NMR (300 MHz): $\delta = 1.06$ (t, $^3J = 7.9 \text{ Hz}$, 2 H, CH_2B), 1.11 (s, 12 H, CH_3), 2.67 (t, $^3J = 7.9 \text{ Hz}$, 2 H, Th- CH_2), 6.83–6.86 (m, 2 H, Th-H), 7.10 (dd, $^3J = 4.9 \text{ Hz}$, $^4J = 3.0 \text{ Hz}$, 1 H, Th-H). — ^{13}C NMR (75 MHz): $\delta = 24.6, 24.8, 83.1, 119.4, 125.0, 128.2, 144.8$. — ^{11}B NMR (96 MHz): δ (vs. external $\text{BF}_3 \cdot \text{Et}_2\text{O}$) = 33.8. — MS: $m/z = 223.0969 [\text{M} - \text{CH}_3]^+$; calcd. 223.0964.

6b: Eluent: Diethyl ether/petroleum ether, 1:1. Colorless oil. Yield: 22%. — ^1H NMR (300 MHz): $\delta = 1.17$ (t, $^3J = 7.6 \text{ Hz}$, 2 H,

CH₂B), 1.25 (s, 12 H, CH₃), 1.57 (qt, ³J = 7.6 Hz, 2 H, CH₂), 2.62 (t, ³J = 7.6 Hz, 2 H, Th-CH₂), 6.84–6.92 (m, 2 H, Th-H), 7.18–7.22 (m, 1 H, Th-H). – ¹³C NMR (75 MHz): δ = 24.8, 25.4, 32.8, 82.9, 120.0, 124.9, 128.4, 143.0.

8: Eluent: CH₂Cl₂. Colorless oil. Yield: 23%. – ¹H NMR (300 MHz): δ = 1.01 (t, ³J = 7.8 Hz, 2 H, CH₂B), 1.15 (s, 12 H, CH₃), 2.50 (t, ³J = 7.8 Hz, 2 H, Py-CH₂), 6.16 (dd, ³J = 3.3 Hz, ⁴J = 1.5 Hz, 1 H, Py-H), 6.89 (dd, ⁴J = 2.2 Hz, ⁴J = 1.5 Hz, 1 H, Py-H), 7.05 (dd, ³J = 3.3 Hz, ⁴J = 2.2 Hz, 1 H, Py-H), 7.43–7.55 (m, 3 H, Ph-H), 7.79–7.82 (m, 2 H, Ph-H). – ¹³C NMR (75 MHz): δ = 21.1, 24.8, 83.1, 114.8, 116.9, 120.8, 126.7, 129.3, 132.0, 133.6, 139.3. – MS: *m/z* = 361.1534 [M⁺]; calcd. 361.1519.

Compound **8** was electrochemically deprotected using pyrene as a redox mediator. At 2 × 10^{−2} M in 10^{−1} M Bu₄NClO₄/CH₃CN, **8** showed an irreversible cathodic peak at −2.87 V vs. 10^{−1} M Ag⁺/Ag (100 mV s^{−1}), which was assigned to cleavage of the S–N bond. In order to avoid the formation of by-products at this highly negative potential, pyrene at 4 × 10^{−3} M was added to the electrolytic medium and the cleavage peak potential was lowered to −2.50 V. – The preparative-scale cathodic reduction of **8** was performed at −2.45 V in 10^{−1} M Bu₄NClO₄/CH₃CN, thoroughly dried with alumina. The progress of the reaction was followed by thin-layer chromatography (eluent: CH₂Cl₂) and the quantity of electricity passed. After the passage of 2 F per mol, the starting product had been entirely consumed and the electrolytic solution was then filtered in order to remove alumina. The solvent was evaporated and the residue was taken up in CH₂Cl₂ and chromatographed on silica gel (eluent: CH₂Cl₂/diethyl ether, 1:1) to remove the electrolyte. A second column chromatography (eluent: CH₂Cl₂) was required to separate **9** from pyrene.

9: Brownish oil. Yield: 58%. – ¹H NMR (300 MHz): δ = 1.04 (t, ³J = 8.1 Hz, 2 H, CH₂B), 1.15 (s, 12 H, CH₃), 2.55 (t, ³J = 8.1 Hz, 2 H, Py-CH₂), 6.00–6.04 (m, 1 H, Py-H), 6.47–6.50 (m, 1 H, Py-H), 6.57–6.61 (m, 1 H, Py-H), 8.02 (s, 1 H, NH). – ¹³C NMR (75 MHz): δ = 21.6, 25.2, 83.4, 108.7, 114.9, 117.9, 126.7. – MS: *m/z* = 221.1584 [M⁺]; calcd. 221.1587.

The boronic-acid-substituted thiophene **5a** was prepared in a similar manner as **6** and **8**, but the mixture was treated with aqueous acid instead of pinacol, as described below. After removal of the excess acetaldehyde, the mixture was diluted with pentane (5 mL) and then treated with 1 M aqueous HCl. The organic layer was separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were then extracted with 3 M aqueous NaOH solution. The alkaline solution was acidified to pH = 1 with 1 M HCl, which resulted in precipitation of the boronic acid derivative. The collected yellowish solid could be recrystallized from water but its purification proved rather intricate. Yield: 25%. – ¹H NMR (300 MHz): δ = 1.06 (t, ³J = 7.9 Hz, 2 H, CH₂B), 2.67 (t, ³J = 7.9 Hz, 2 H, Th-CH₂), 5.15 [s, 2 H, B(OH)₂], 6.83–6.86 (m, 2 H, Th-H), 7.10 (dd, ³J = 4.9 Hz, ⁴J = 3.0 Hz, 1 H, Th-H). – FT-IR (KBr): ν_{OH} = 3250 cm^{−1}.

“Pinacol Borane”-Substituted Thiophenes Containing One Phenyl

Group: The synthesis of the phosphonium salt **10** from 3-methylthiophene has been described previously by Greenwald et al.^[21] *p*-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde could easily be prepared from a stirred solution of *p*-formylbenzeneboronic acid (Lancaster; 97%) and pinacol (1.1 equiv.) in anhydrous diethyl ether. The mixture was allowed to react at room temperature overnight. After washing with water, the organic phase was separated, dried with MgSO₄, and concentrated under reduced pressure to give the expected product in quantitative yield. The

latter was used directly for the next step. – In a 25-mL three-necked flask, **10** (0.49 g, 1.1 mmol) and *p*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (0.26 g, 1.1 mmol) were dissolved in 10 mL of freshly distilled absolute EtOH. Lithium diisopropylamide (0.16 g, 1.5 mmol) was added dropwise at room temperature and the mixture was then refluxed for 2–3 h. After cooling to room temperature, the solution was poured into water (10 mL) and extracted with diethyl ether. The organic phase was separated, dried with MgSO₄, and concentrated to dryness. The crude product was chromatographed on silica gel (eluent: diethyl ether/petroleum ether, 1:10) to give 0.15 g (0.5 mmol) of **11** as a yellow powder. Yield: 42%. – ¹H NMR (300 MHz): δ = 1.27 (s, 12 H, CH₃), 6.88 and 7.12 (AB system, ³J = 16.3 Hz, 2 H, vinyl-H), 7.17–7.28 (m, 3 H, Th-H), 7.40 and 7.71 (AA'BB' system, ³J = 8.1 Hz, 4 H, Ph-H). – Reduction of the alkene was performed as described below. A well-stirred and deaerated solution of **11** (0.2 g, 0.6 mmol) in anhydrous MeOH (20 mL) was hydrogenated overnight under a hydrogen pressure of 50 atm in the presence of 10% Pd/C (0.1 mmol). The resulting mixture was then filtered through Celite, which was carefully washed with MeOH. The combined filtrate and washings were concentrated to dryness and the residue was purified by column chromatography (eluent: diethyl ether/petroleum ether, 1:1) to give 0.17 g (0.5 mmol) of **12** as a yellowish solid. Yield: 83%; m.p. 77–78 °C. – ¹H NMR (300 MHz): δ = 1.32 (s, 12 H, CH₃), 2.92 (m, 4 H, CH₂), 6.87 (dd, ⁴J = 3.0 Hz, ⁴J = 1.2 Hz, 1 H, CH), 6.90 (dd, ³J = 5.0 Hz, ⁴J = 1.2 Hz, 1 H, CH), 7.20 (dd, ³J = 5.0 Hz, ³J = 3.0 Hz, 1 H, CH), 7.18 and 7.73 (AA'BB' system, ³J = 8.0 Hz, 4 H, Ph-H). – ¹³C NMR (75 MHz): δ = 24.9, 32.0, 37.2, 83.7, 120.5, 125.3, 128.0, 128.3, 135.0, 142.0, 145.1. – ¹¹B NMR (96 MHz): δ (vs. external BF₃·Et₂O) = 30.9.

Thiophene Derivatives Containing Both a Phenyl and an Ether

Group: In a first step, 25.0 mmol of 3-thienylmethanol (Lancaster; 97%) or 3-thienylethanol (Fluka; 98%) was added to a solution of *t*BuOK (3.37 g, 30.0 mmol) in THF (50 mL). After stirring for ca. 15 min, a solution of *p*-bromobenzyl bromide (Acros; 98%) (32.5 mmol, 8.13 g) in THF (40 mL) was added and the reaction mixture was refluxed for 4 h. It was then cooled to room temperature and treated with diethyl ether/1 M aq. HCl. The organic phase was separated, washed with water, dried with MgSO₄, and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography (eluent: diethyl ether/petroleum ether, 1:1) to afford ca. 6.0 g (20 mmol) of **13** in good yield.

13a: Yellowish liquid. Yield: 92%. – ¹H NMR (300 MHz): δ = 4.40 (s, 2 H, CH₂O), 4.48 (s, 2 H, OCH₂Ph), 6.92–7.25 (m, 3 H, Th-H), 7.13 and 7.40 (AA'BB' system, ³J = 8.4 Hz, 4 H, Ph-H).

13b: Colorless liquid. Yield: 78%. – ¹H NMR (300 MHz): δ = 2.95 (t, ³J = 6.8 Hz, 2 H, CH₂), 3.68 (t, ³J = 6.8 Hz, 2 H, CH₂O), 4.47 (s, 2 H, OCH₂Ph), 6.95–7.02 (m, 2 H, Th-H), 7.17 and 7.45 (AA'BB' system, ³J = 8.4 Hz, 4 H, Ph-H), 7.23–7.27 (m, 1 H, Th-H). – ¹³C NMR (75 MHz): δ = 30.6, 70.5, 72.0, 121.1, 125.2, 128.4, 129.1, 131.3, 137.3, 139.0.

The boronic acid and ester derivatives were synthesized using the Grignard reagent of **13** and trimethyl borate, followed by treatment with aqueous acid or pinacol, respectively. Thus, a solution of **13** (10.0 mmol) in anhydrous THF (10 mL) was slowly added to a well-stirred suspension of magnesium (11.0 mmol) in THF (1–2 mL). The mixture was heated under reflux for 1–2 h with activation by a few drops of dibromoethane until the Grignard reagent had been formed. The Grignard reagent was then carefully and slowly poured into a solution of trimethyl borate (2.0 equiv., Fluka; 99%) in THF (20 mL) maintained at −78 °C by means of

an acetone/liquid air bath. After 1–2 h at this temperature, the reaction mixture was allowed to slowly warm to room temperature and stirring was continued overnight. Then, a solution of pinacol (1.1 equiv., 1.30 g, 11.0 mmol) in anhydrous THF (11 mL) was added and the reaction was allowed to proceed for 12 h. Thereafter, diethyl ether (50 mL) was added and the resulting mixture was washed with water. The organic phase was dried with MgSO_4 and concentrated to dryness under reduced pressure. The crude product was purified by column chromatography (eluent: diethyl ether/petroleum ether, 1:1) to give **15** in 25% yield.

15a: Yellow oil. – ^1H NMR (300 MHz): δ = 1.25 (s, 12 H, CH_3), 4.44 (s, 2 H, CH_2O), 4.47 (s, 2 H, OCH_2Ph), 6.95 (dd, 3J = 5.0 Hz, 4J = 1.3 Hz, 1 H, CH), 7.07 (dd, 4J = 3.0 Hz, 4J = 1.3 Hz, 1 H, CH), 7.15 (dd, 3J = 5.0 Hz, 3J = 3.0 Hz, 1 H, CH), 7.27 and 7.72 (AA'BB' system, 3J = 8.1 Hz, 4 H, Ph-H). – ^{13}C NMR (75 MHz): δ = 24.9, 67.3, 71.9, 83.8, 122.9, 126.0, 127.0, 127.4, 135.0, 139.3, 141.4. – ^{11}B NMR (96 MHz): δ (vs. external $\text{BF}_3\cdot\text{Et}_2\text{O}$) = 30.8. – MS: m/z = 315.1223 [$\text{M} - \text{CH}_3$] $^+$; calcd. 315.1226.

15b: Colorless oil. – ^1H NMR (300 MHz): δ = 1.30 (s, 12 H, CH_3), 2.89 (t, 3J = 6.8 Hz, 2 H, CH_2), 3.62 (t, 3J = 6.8 Hz, 2 H, CH_2O), 4.49 (s, 2 H, OCH_2Ph), 6.98 (dd, 3J = 5.0 Hz, 4J = 1.3 Hz, 1 H, CH), 7.02 (dd, 4J = 2.9 Hz, 4J = 1.3 Hz, 1 H, CH), 7.25 (dd, 3J = 5.0 Hz, 3J = 2.9 Hz, 1 H, CH), 7.28 and 7.80 (AA'BB' system, 3J = 7.6 Hz, 4 H, Ph-H). – ^{13}C NMR (75 MHz): δ = 25.4, 31.3, 71.0, 73.3, 84.2, 121.7, 125.7, 127.0, 129.0, 135.5, 139.7, 142.2. – ^{11}B NMR (96 MHz): δ (vs. external $\text{BF}_3\cdot\text{Et}_2\text{O}$) = 30.6. – MS: m/z = 344.1622 [M^+]; calcd. 344.1617.

The boronic acid **14b** was prepared in a similar manner as **5a**, but using 1 M HCl solution in place of pinacol. As for **5a**, the purification of this product was rather intricate. It was obtained as a yellowish solid. Yield: 25%. – ^1H NMR (300 MHz): δ = 2.89 (t, 3J = 6.8 Hz, 2 H, CH_2), 3.62 (t, 3J = 6.8 Hz, 2 H, CH_2O), 4.49 (s, 2 H, OCH_2Ph), 4.51 [s, 2 H, $\text{B}(\text{OH})_2$], 6.98 (dd, 3J = 5.0 Hz, 4J = 1.3 Hz, 1 H, CH), 7.02 (dd, 4J = 2.9 Hz, 4J = 1.3 Hz, 1 H, CH), 7.25 (dd, 3J = 5.0 Hz, 3J = 2.9 Hz, 1 H, CH), 7.28 and 7.80 (AA'BB' system, 3J = 7.6 Hz, 4 H, Ph-H). – FT-IR (KBr): ν_{OH} = 3200 cm^{-1} .

Electrochemical Experiments and Instrumentation: Tetra-*n*-butylammonium tetrafluoroborate (Bu_4NBF_4) (Fluka) was recrystallized three times from methanol/water (1:1, v/v) and then dried for 48 h in vacuo. Tetra-*n*-butylammonium perchlorate (Bu_4NClO_4) and tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) (Fluka) were used as received (puriss, electrochemical grade). All salts were stored in a vacuum desiccator over silica gel. Acetonitrile (Merck; max. 50 ppm water) was used without further purification and was stored under dry argon. All electrolytic solutions were dried in situ with neutral alumina (Merck), previously activated at 450 °C in vacuo for several hours. The solutions were thoroughly deaerated and kept under a positive pressure of dry argon throughout each run. – Cyclic voltammetry measurements were performed in a classical three-electrode cell. The working electrode was a platinum disc (area: $8 \times 10^{-1} \text{ mm}^2$) and the counter electrode was a glassy carbon rod. All potentials were referenced to the system $10^{-1} \text{ M Ag-NO}_3/\text{Ag}$ in acetonitrile. The cell was connected to an EGG PAR

model 173 potentiostat and monitored with an EGG PAR model 175 signal generator and an EGG PAR model 179 digital coulometer. Cyclic voltammograms were plotted with an X-Y Sefram type TGM 164 recorder. – The preparative-scale electrochemical reduction of **8** was performed using a Tacussel potentiostat/galvanostat type PJT 120–1 connected to a U-shaped two-compartment cell (total volume 100 mL). The working and counter electrodes were made of platinum and glassy carbon plates (area 10 cm^2), respectively.

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