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Voltammetric investigation of new boronic ester-substituted triphenylamines-based redox receptors in solution and attached to an electrode surface. Effects of F^- as an anionic guest

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Abstract

Triphenylamines mono-, di- and trisubstituted by boronic ester unit(s) were designed as powerful redox-active receptors for Lewis hard bases like fluoride anion. Their voltammetric behaviour was found to be dramatically changed upon the addition of this halide. Depending on the degree of substitution of triphenylamines, the binding of F^- to the boron atom led to the appearance of one to three new redox system(s). The binding constants determined for their neutral form ranged from 1.0×10^2 to 4.0×10^2 and were dramatically enhanced upon their oxidation into radical cation (3.0×10^5–1.6×10^7). The fixation of such electroactive compounds to the electrode surface has been achieved from the anodic oxidation of a vinyl-substituted bipodal receptor. The polymer films showed a reversible and stable response in a dried organic medium. Unfortunately, the voltammetric changes indicative of a complexation phenomenon were not observed in the presence of F^- and only a degradation of the film electroactivity was noticed.

Keywords: Triphenylamine; Boronic ester; Fluoride; Sensor; Cyclic voltammetry

1. Introduction

Among the neutral anion receptors, electron-deficient groups like boronic acids and esters can strongly bind hard-base anions such as fluoride, resulting in specific orbital changes from sp^2- to the more stable sp^3-hybridised boron [1–4].

With the aim of developing electroactive systems capable of recognizing electrochemically and specifically anionic substrates, some boronic acids and esters have been covalently attached to redox-active units such as ferrocene [3–5], bipyridine metal complex [6,7] and triphenylamines [8]. The anodic behaviour of these moieties was found to be changed upon the addition of F^- to the electrolyte solution. In the case of triphenylamines mono- (**$TPAB_1$**), di- (**$TPAB_2$**) and trisubstituted (**$TPAB_3$**) by a pinacolborane unit (Fig. 1) [8], the binding of F^- to the boron atom of the receptor led to the appearance of one to three new voltammetric peak(s) at less positive potentials assigned to the oxidation of each complexed form into its radical cation. Furthermore, the interaction was specific to F^- because Br^- or Cl^- had no effect on the response of the three triphenylamines. The efficiency of such anion receptors having been demonstrated, this full paper aimed at providing some essential data on the binding event,

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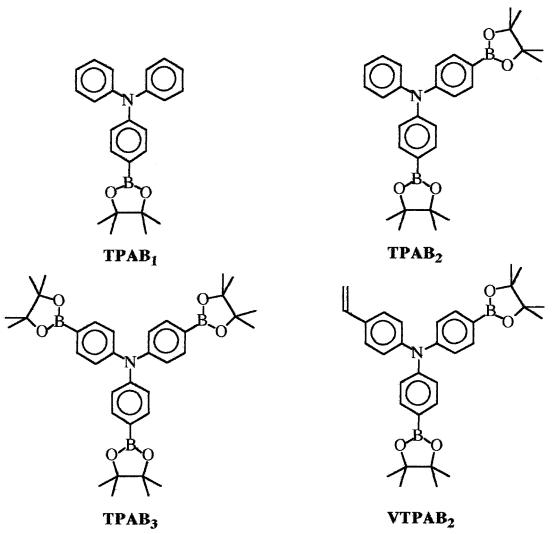
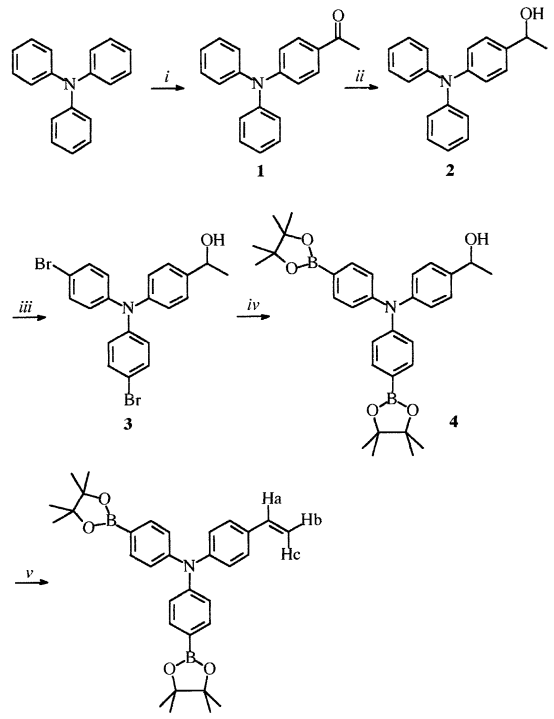


Fig. 1. Pinacol borane-substituted triphenylamines.

such as the equilibrium constants corresponding to the complexation of F^- by the neutral and oxidised forms of the receptor, but also the reversibility of the complexation/decomplexation process. Moreover, the attachment of such functional units to an electrode surface to take advantage of their complexing properties observed in solution is undertaken from the anodic oxidation of the vinyl-substituted bipodal receptor **VTPAB$_2$**. Finally, the effect of a Lewis hard base like fluoride on the voltammetric response of the resulting functionalised polymer film is also presented.



Scheme 1. Synthesis of the vinyl-substituted bipodal redox-active receptor **VTPAB$_2$**. Reagents and conditions: (i) acetic anhydride, toluene, then addition of $SnCl_4$, reflux, 1 h. [9]; (ii) $LiAlH_4$, anhydrous THF, O°C; (iii) Br_2, $CHCl_3$, -20°C; (iv) *n*-BuLi, trimethyl borate, anhydrous diethyl ether, -78°C, pinacol, 25°C; (*v*) $POCl_3$, pyridine, reflux, >12 h.

2. Experimental

2.1. Synthesis of boronic ester-substituted triphenylamines

Solvents were freshly distilled over 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 Silicycle. Mass spectra were measured with a Varian MAT 311 spectrometer.

The synthesis of different pinacol borane-substituted triphenylamines **TPAB$_1$**, **TPAB$_2$** and **TPAB$_3$** (Fig. 1) has been described previously [8].

VTPAB$_2$ was obtained in five steps from triphenylamine (Scheme 1). In the first step, triphenylamine (Acros, 99%) was converted into 4-acetoxytriphenylamine **1** according to the procedure of Staskun [9].

The reduction of the ketone into the corresponding alcohol **2** was achieved with $LiAlH_4$. In a 250 ml three-necked flask under an argon flow, 4-acetoxytriphenylamine (7.18 g, 25 mmol) dissolved in anhydrous THF (30 ml) was added dropwise to a well-stirred suspension of $LiAlH_4$ (0.95 g, 25 mmol) in THF (50 ml) maintained at 0 °C. Following the addition, the mixture was allowed to slowly warm to room temperature and the progress of the reaction was followed by thin-layer chromatography (eluent: hexanes/ethyl acetate 1:1 (v/v)). Then, the solution was cooled to 0°C and carefully neutralised with water and few drops of aq. NaOH 15%. After extraction with diethyl ether, the organic phase was separated, washed with water, dried with $MgSO_4$ and concentrated to dryness under reduced pressure. The crude product was purified by flash chromatography (eluent: hexanes/ethyl acetate 4:1) to give 1-(4-diphenylamino-phenyl)ethanol **2** (5.73 g, 19.8 mmol) as a white solid.

Yield: 79%; m.p. 102–103°C. ^1H NMR 300 MHz ($CDCl_3$, δ ppm): 1.52 (d, CH_3, [$^3J_{HH} = 6.4$], 3H); 2.13 (s, OH, 1H); 4.86 (q, CH, [$^3J_{HH} = 6.4$], 1H); 7.00–7.30 (m, H_{Ph}, 14H). ^{13}C NMR 75 MHz (δ ppm): 24.98 (CH_3); 70.02 (CHOHCH$_3$); 124.01, 124.16 and 129.23 (C_{Ph}H); 122.76 and 126.44 (C_{Ph}H); 139.97 (C_{Ph}CHOHCH$_3$); 147.72 and 147.83 (NC_{Ph}). MS *m*/*e*: 289.1464 ($M^{+\cdot}$). Calc. 289.1467.

A solution of 1-(4-diphenylaminophenyl)ethanol (5.00 g, 17.3 mmol) in $CHCl_3$ (60 ml) was cooled to −20 °C with a $CH_3CN + CO_2$ bath under stirring. At this temperature, the slow addition of two molar equiv. of Br_2 (1.77 ml, 34.6 mmol) turned the solution green. The progress of the reaction was followed by thin-layer chromatography (eluent: petroleum ether/ethyl acetate 1:1 (v/v)). After 2 h, the mixture was allowed to warm gently to room temperature and extracted with water. Then, the organic phase was separated, dried with $MgSO_4$ and concentrated to dryness under reduced pressure. The crude product was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate 1:1 (v/v)) to give 1-(4-[bis-(4-bromophenyl)-amino]-phenyl)ethanol **3** (6.60 g, 14.8 mmol) as a brown oil.

Yield: 85%. ^{1}H NMR 300 MHz ($CDCl_3$, δ ppm): 1.35 (d, CH_3, [$^3J_{HH} = 6.5$], 3H); 1.54 (s, OH, 1H); 4.29 (q, CH, [$^3J_{HH} = 6.5$], 1H); 6.85 and 7.25 (AA′BB′ system, H_{Ph}, [$^3J_{HH} = 8.8$], 8H); 6.93 and 7.12 (AA′BB′ system, H_{Ph}, [$^3J_{HH} = 8.5$], 4H). ^{13}C NMR 75 MHz (δ ppm): 23.94 (CH_3); 76.63 (CHOHCH$_3$); 115.42 (C_{Ph}Br); 124.42 and 127.30 (C_{Ph}H); 125.54 and 132.36 (C_{Ph}H); 139.65 (C_{Ph}CHOHCH$_3$); 145.94 (NC_{Ph}); 146.56 (NC_{Ph}).

The conversion of the dibrominated triphenylamine into its 'pinacol borane' (4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-substituted analogous was achieved as follows: 1-(4-[bis-(4-bromophenyl)-amino]-phenyl)ethanol (6.50 g, 14.5 mmol) dissolved in anhydrous diethyl ether (50 ml) was cooled to −78°C with a $CH_3COCH_3 + CO_2$ bath under stirring. At this temperature, four molar equiv. of n-BuLi (58 mmol) were added dropwise. After 2 h, the solution was allowed to warm gently to room temperature. After cooling to −78 °C, trimethyl borate (6.47 ml, 58 mmol) was added and the reaction mixture was stirred for 2 h. Then, 4 equiv. of pinacol (6.85 g, 58 mmol) in anhydrous diethyl ether were added to the solution warmed to room temperature. The mixture was stirred for more than 12 h. The solution was then washed with water, the organic phase was separated, dried with $MgSO_4$, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (eluent: diethyl ether/petroleum ether 1:1 (v/v)) to afford 1-4-(bis-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane-2-yl)-phenyl]-amino)-phenyl ethanol **4** (1.71 g, 3.16 mmol) as a yellowish solid.

Yield: 21.8%; m.p. 62–63 °C. ^{1}H NMR 300 MHz ($CDCl_3$, δ ppm): 1.13 (s, CH_3, 24H); 1.24 (d, CH_3, [$^3J_{HH} = 6.4$], 3H); 1.41 (s, OH, 1H); 4.17 (q, CH, [$^3J_{HH} = 6.4$], 1H); 6.78 and 6.99 (AA′BB′ system, H_{Ph}, [$^3J_{HH} = 8.5$], 4H); 6.85 and 7.47 (AA′BB′ system, H_{Ph}, [$^3J_{HH} = 8.4$], 8H). ^{13}C NMR 75 MHz (δ ppm): 23.91 (CH_3); 24.89 (CCH$_3$); 77.30 (CH); 83.67 (CCH$_3$); 122.76 and 135.90 (C_{Ph}H); 125.35 and 127.15 (C_{Ph}H); 139.70 (C_{Ph}CHOHCH$_3$); 146.07 (NC_{Ph}); 150.16 (NC_{Ph}). MS m/e: 523.3104 ([M − H$_2$O]$^{+\cdot}$). Calc. 523.3065.

In a 25 ml three-necked flask under an argon flow, 1-4-(bis-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane-2-yl)-phenyl]-amino)-phenyl ethanol (1.00 g, 1.85 mmol) and $POCl_3$ (0.17 ml, 1.85 mmol) were dissolved in distilled pyridine (10 ml). The mixture was heated under reflux for more than 12 h and the solution initially yellow turned progressively brown. The progress of the reaction was followed by thin-layer chromatography using diethyl ether/petroleum ether (1:1 (v/v)) as the eluent. After cooling to room temperature, the solution was extracted with a water/diethyl ether mixture. The aqueous phase was treated with ethyl acetate and then, with dichloromethane. The combined organic phases were dried with $MgSO_4$ and the solvents were evaporated under reduced pressure. The resulting crude product was chromatographed on silica gel (eluent: diethyl ether/petroleum ether 1:1 (v/v)) to give bis-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane-2-yl)-phenyl]-(4-vinylphenyl) amine **VTPAB$_2$** (0.32 g, 0.61 mmol) as a white solid.

Yield: 33%; m.p. 78–79 °C. ^{1}H NMR 300 MHz ($CDCl_3$, δ ppm): 1.26 (s, CH_3, 24H); 5.11 (dd, H_a, [$^3J_{HaHc} = 10.9$, $^3J_{HaHb} = 0.8$], 1H); 5.59 (dd, H_b, [$^2J_{HbHc} = 17.5$, $^3J_{HbHa} = 0.8$], 1H); 6.59 (dd, H_c, [$^2J_{HbHc} = 17.5$, $^3J_{HaHc} = 10.9$], 1H); 6.97 and 7.35 (AA′BB′ system, H_{Ph}, [$^3J_{HH} = 8.6$], 4H); 6.99 and 7.60 (AA′BB′ system, H_{Ph}, [$^3J_{HH} = 8.4$], 8H). ^{13}C NMR 75 MHz (δ ppm): 25.28 (CCH$_3$); 84.05 (CCH$_3$); 113.22 (CHCH$_2$); 123.34 and 136.33 (C_{Ph}H); 125.56 and 127.59 (C_{Ph}H); 133.49 (C_{Ph}CHCH$_2$); 136.53 (CHCH$_2$); 147.05 (NC_{Ph}); 150.33 (NC_{Ph}). MS m/e: 523.3052 (M$^{+\cdot}$). Calc. 523.3065.

2.2. Electrochemical instrumentation and procedures

Tetra-n-butylammonium perchlorate Bu_4NClO_4 from Fluka (puriss, electrochemical grade), triethylamine trihydrofluoride $Et_3N{\cdot}3$ HF and chlorotrimethylsilane Me_3SiCl from Aldrich (98%) were used as received. Acetonitrile (max. 50 ppm water) from Merck and methylene chloride (anhydrous analytical grade) from SDS were used without further purification and stored under dry argon. All electrolytic solutions were dried in situ over neutral alumina from Merck, previously activated at 450°C under vacuum for several hours. They were thoroughly deaerated and kept under a positive pressure of dry argon during each run.

Linear potential sweep cyclic and differential pulse voltammetry experiments were performed with an Autolab PGSTAT 20 potentiostat from Eco Chemie B.V., equipped with General Purpose Electrochemical System GPES software (version 4.5 for Windows). The working electrode was a platinum disk (area: 0.8 mm^2) and

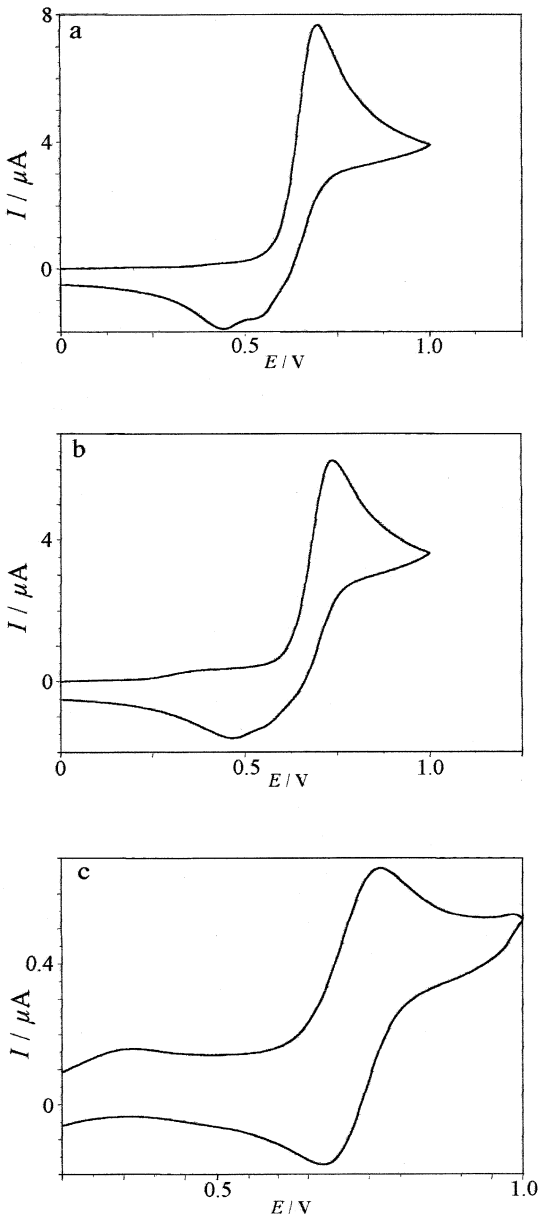


Fig. 2. Cyclic voltammograms in $CH_3CN + 0.1$ M Bu_4NClO_4 of: (a) **TPAB$_1$** (2 mM); (b) **TPAB$_2$** (2 mM); and (c) **TPAB$_3$** (1.5 mM). Potential scan rate: 0.1 V s^{-1}.

the counter electrode was a glassy carbon rod. All potentials were relative to the system 0.1 M $AgNO_3$ | Ag in acetonitrile. Solution resistance was compensated by positive feedback and the accuracy of the corrections was tested with ferrocene at different concentrations.

3. Results and discussion

3.1. Voltammetric behaviour of the boronic ester-substituted triphenylamines

As expected, the electrochemical behaviour of triphenylamines mono- and disubstituted by boronic ester groups in $CH_3CN + 0.1$ M Bu_4NClO_4 is similar to that obtained for other triphenylamines [10–13]. At 0.1 V s^{-1}, **TPAB$_1$** and **TPAB$_2$** are irreversibly oxidised at $E_{pa} = 0.69$ and 0.74 V, respectively, and the backward scan shows small cathodic peaks located at 0.44 and 0.54 V for **TPAB$_1$** and 0.47 and 0.56 V for **TPAB$_2$** (Fig. 2). A one-electron reversible process was observed at $E^{\circ\prime} = 0.65_5$ V for **TPAB$_1$** and 0.70_5 V for **TPAB$_2$** when the scan rate was increased to 5 V s^{-1}. Moreover, the ratio $I_{pa}/v^{1/2}$ (where I_{pa} is the anodic peak current intensity and v is the potential scan rate) was found to decrease with increasing v and E_{pa} was positively shifted of about 20 mV for a ten-fold increase in v (Fig. 3). For scan rates larger than 0.4 V s^{-1}, E_{pa} was approximately constant. Thus, these results are consistent with a second-order ECE mechanism in which the unstable electrogenerated radical cation leads to a dimer that is more easily oxidisable than the starting material [13]. Experimentally, the dimerisation constant k_d of each triphenylamine can be determined from the variation of E_{pa} with v [14] (Eq. (1)).

$$k_d = 0.80 \frac{F}{RT} \frac{v_i}{C^0} \quad (1)$$

where v_i is the scan rate measured at the intersection between the two linear parts of the $E_{pa} - \log v$ experimental diagram (Fig. 3) and C^0 is the bulk concentration of the substituted triphenylamine. So, values of 2.6×10^3 l mol^{-1} s^{-1} and 2.4×10^3 l mol^{-1} s^{-1} were extracted for **TPAB$_1$** and **TPAB$_2$**, respectively. Compared to those reported in the literature for other substituted triphenylamines [12,15], it could be concluded that the presence of electron-withdrawing boronate groups increased the coupling probability between two radical cations, resulting in a larger dimerisation constant. Indeed, triphenylamines mono- or disubstituted by an electron-donating methoxy group were characterised by a small k_d (lower than 6×10^{-1} l mol^{-1} s^{-1}) whereas the presence of nitro groups led to k_d larger than 10^4 l mol^{-1} s^{-1}.

In contrast with the voltammetric behaviour of **TPAB$_1$** and **TPAB$_2$**, the tri-*para*-substituted triphenylamine **TPAB$_3$** exhibited, whatever the scan rate, a reversible oxidation step at $E^{\circ\prime} = 0.72$ V corresponding to the formation of a stable radical cation (Fig. 2c). Furthermore, the ratio $I_{pa}/v^{1/2}$ was roughly constant within the scan rate range investigated (0.01–10 V s^{-1}).

3.2. Effect of F^- on the voltammetric response of the boronic ester-substituted triphenylamines

Owing to the electronic communication between the boronic ester unit(s) and the redox center, it is expected that the binding of a hard base like F^- leads to the modification of the electrochemical response of the receptor. The effect of this halide has been analysed in CH_2Cl_2 because of the ability of this solvent to stabilise radical cations [16]. As clearly evidenced by differential pulse voltammetry (DPV), the initial redox system assigned to the oxidation of the substituted triphenylamine into its corresponding radical cation was decreased in intensity upon the addition of F^- while one or several new peak(s) emerged at less positive potentials (Fig. 4). Those were assigned to the oxidation of each complexed form of triphenylamines and their lower potential was explained by the stabilisation of the radical cation upon the binding of F^- to the boron atom.

The presence of the pinacolborane group was essential for electrochemically sensing F^- because the voltammetric response of an unsubstituted triphenylamine was found to be unmodified after the addition of this halide. Moreover, as demonstrated in our preliminary paper [8], no changes were noticed when F^- was replaced by Br^- or Cl^-. All these results are thus consistent with a specific recognition of F^- by **TPAB$_n$** (with n ranging from 1 to 3).

We have checked by cyclic voltammetry that the different complexed species were reversibly oxidised, i.e. the peak-to-peak separation was about 60–70 mV and $I_{pa}/I_{pc} \approx 1$. So, in these conditions, the fluoride complexation by **TPAB$_n$** can be described by the various equilibria depicted in Scheme 2. The F^--binding constant K_m corresponding to the neutral form of **TPAB$_n$** was determined for each susbtituted triphenylamine from DPV data (see Appendix A) and the calculated values are summarised in Table 1. Moreover, the binding constant corresponding to the oxidised form of **TPAB$_n$**, K'_m, was easily obtained from the ratio K'_m/K_m expressed as a function of the formal potentials of complexed and free forms (Eq. (2)).

$$\frac{K'_m}{K_m} = \exp\left[\frac{F}{RT}(E^{\circ\prime}{}_{m-1} - E^{\circ\prime}{}_m)\right] \quad (2)$$

Expectedly, it appears that the complexes produced between the **TPAB$_n$** radical cation and F^- were about 10^3–5×10^4-fold more stable than those formed with the neutral species. It must be pointed out that a weaker enhancement binding upon electron transfer has been reported for ferrocene boronic acid [4], which indicates that **TPAB$_n$** is a more powerful F^- redox-active receptor.

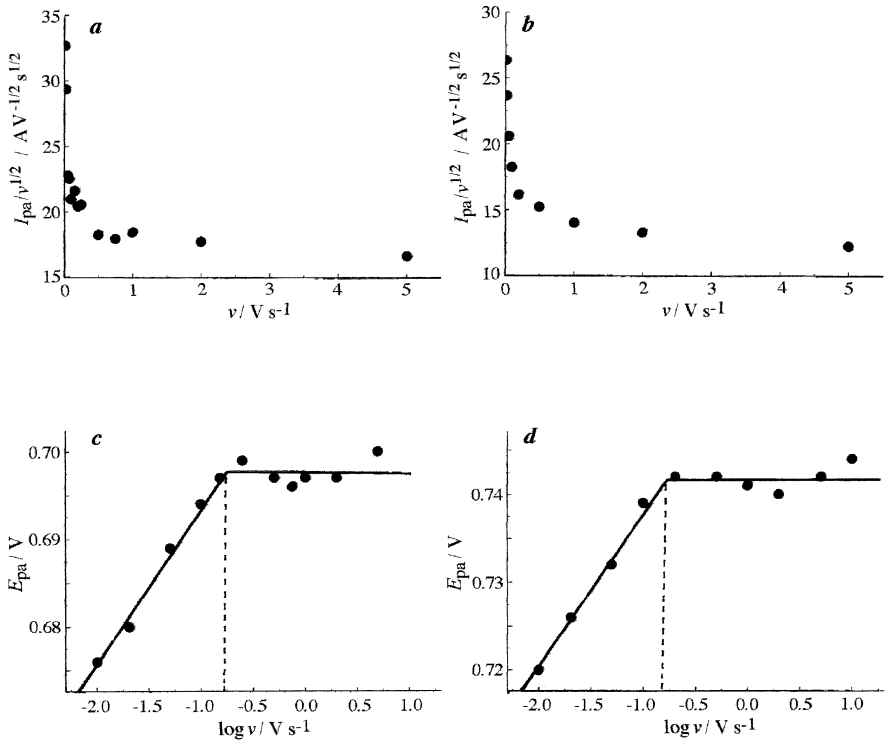


Fig. 3. $I_{pa}/v^{1/2} - v$ and $E_{pa} - \log v$ plots for (a, c) **TPAB$_1$**; and (b, d) **TPAB$_2$** at 2 mM in $CH_3CN + 0.1$ M Bu_4NClO_4.

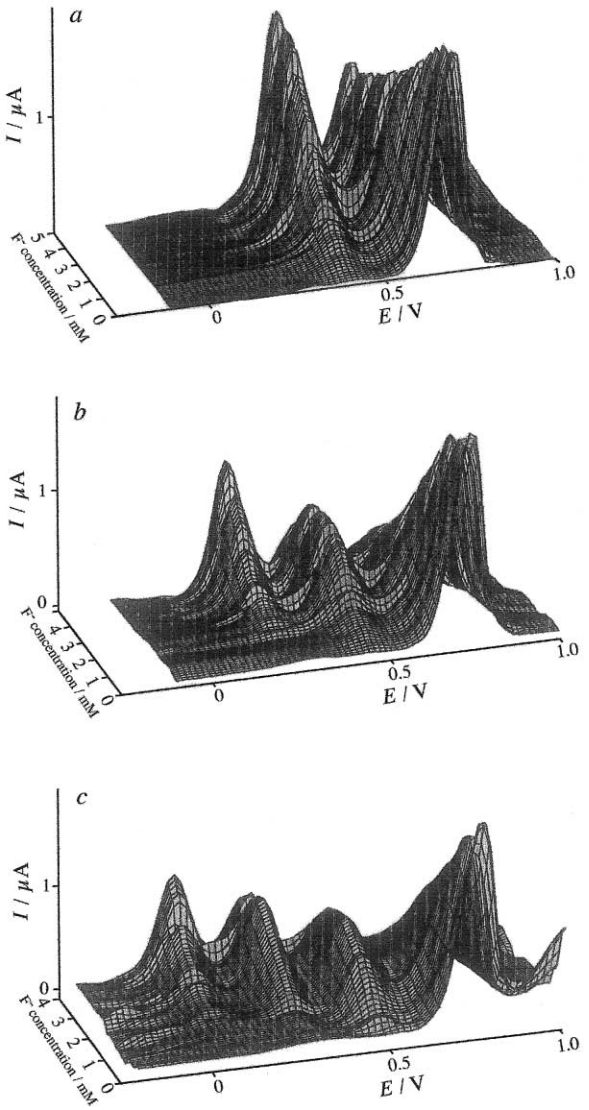
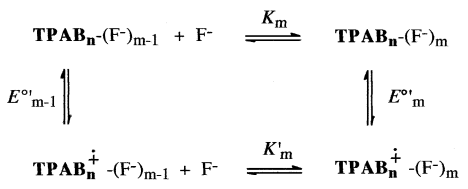


Fig. 4. Three-dimensional view of differential pulse voltammograms DPV in $CH_2Cl_2 + 0.1$ M Bu_4NClO_4 of: (a) **TPAB$_1$**; (b) **TPAB$_2$**; and (c) **TPAB$_3$** at 1 mM, as a function of the $Et_3N{\cdot}3$ HF concentration (from 0 to 5 mM). DPV parameters: modulation time, 0.1 s; interval time, 1 s; modulation amplitude, 50 mV.



Scheme 2. General square scheme for the F^- complexation by boronic ester-substituted triphenylamines. The formal potentials $E°'_{m-1}$ and $E°'_m$ were extracted from DPV of Fig. 4.

3.3. Reversibility of the fluoride complexation/decomplexation process

Generally, the development of a sensory device for long-term uses requires that the properties of the sensing element are not irremediably changed after the binding event, i.e. the original signal is recovered without significant loss of intensity. In the contrary case, the system can function only if a preferentially mild and fast method yields the original signal. Taking into account the latter feature, chlorotrimethylsilane Me_3SiCl seemed to be an efficient reagent to cleave the boron-fluoride bond of complexed **TPAB$_n$**. As shown in Fig. 5 for **TPAB$_1$**, the redox system attributed to the complexed form totally disappeared after the addition of Me_3SiCl and the initial peak was restored with the same intensity but shifted 50 mV towards less positive potentials. The reason for such a shifting is not elucidated but it is possible that the silane derivative also interacts with nitrogen of the substituted triphenylamine [17] resulting in the modification of its anodic behaviour. Similarly to **TPAB$_1$**, the DPV data obtained with **TPAB$_2$** and **TPAB$_3$** were consistent with the conversion of the various complexed forms into their free form after the addition of Me_3SiCl. Thus, all these results demonstrate that the decomplexation process can be chemically achieved without significantly lowering the redox properties of the receptor.

3.4. Anodic electropolymerisation of *VTPAB$_2$*. Effect of fluoride

In the light of the promising sensing potentialities exhibited by **TPAB$_n$** in homogeneous phase, the immobilisation of such a redox-active receptor onto an electrode surface has been considered, using the vinyl-substituted bipodal triphenylamine **VTPAB$_2$** as the starting precursor. The cyclic voltammogram of the latter in acetonitrile medium showed two irreversible anodic peaks at 0.60 and 0.74 V (0.1 V s^{-1}) (Fig. 6a). Repetitive potential cycling between 0 and 1.0 V led to the formation of an electroactive polymer film poly(**VTPAB$_2$**), as revealed by the increase of the second anodic peak and its corresponding cathodic component emerging on the reverse scan. After several cycles, the modified electrode was transferred to a monomer-free electrolyte solution and showed a perfectly reversible redox system at 0.61 V (Fig. 6b). As already reported for other vinyl-substituted electroactive compounds [18–20], the polymerisation mechanism has chain propagation character and yields a polystyrene-like polymer. So, the material electroactivity is due to the electron hopping between the neutral triphenylamine and its radical cation species. The films could be repeatedly cycled without apparent decrease of their electroactivity (Fig. 6b), provided that the elec-

Table 1
Binding constants corresponding to the complexation of F^- by the neutral and oxidised forms of three substituted triphenylamines

	K_1	K'_1	K_2	K'_2	K_3	K'_3
TPAB$_1$	2.4×10^2	1.6×10^7	–	–	–	–
TPAB$_2$	2.8×10^2	1.2×10^7	3.9×10^2	1.1×10^6	–	–
TPAB$_3$	2.1×10^2	0.9×10^7	1.6×10^2	3.0×10^5	1.0×10^2	3.4×10^5

trolytic medium was thoroughly dried with activated neutral alumina. Under these conditions, the peak-to-peak separation (ΔE_p) was close to 20 mV and the half-height peak width ($\Delta E_{p/2}$) was 300 mV at 0.05 V s^{-1}. Theoretically, values of 0 and 90 mV are expected for surface-immobilised redox species with a monoelectronic Nernstian-type reaction [21]. The larger $\Delta E_{p/2}$ value would be indicative of strong repulsive interactions between electroactive centers [22]. Moreover, the fixation of the receptor to the electrode surface was also proved by the proportionality between I_{pa} and the scan rate up to 1 V s^{-1}. When studied in CH_2Cl_2, poly(**VTPAB$_2$**) was characterised by a less reversible and more distorded system ($\Delta E_p \approx 100$ mV at 0.05 V s^{-1}).

The effect of F^- on the electrochemical behaviour of poly(**VTPAB$_2$**) is illustrated in Fig. 7. In dried CH_3CN, the anodic peak was greatly decreased in size and broadened upon the addition of this halide. The film electroactivity was even totally lost from a certain F^- concentration, for example 5 mM with a film electrosynthesised using 150 mC cm^{-2}, and not subsequently restored in a solution without fluoride. The same trend was observed for other polymer thicknesses and in previously dried CH_2Cl_2. Consequently, the voltammetric changes caused by F^- in homogeneous phase (namely, decrease of the initial system together with the emergence of new redox system(s)) were not seen in heterogeneous phase. As the degradation of the electroactive properties was irreversible, it could be concluded that poly(**VTPAB$_2$**) was not suitable for electrochemically sensing F^-. The strong F^--induced electroactivity decrease was thought to be ascribed to a film conductivity lowering caused by the large repulsive interactions between the sterically hindered triphenylamine units. Nevertheless, a partial solubilisation of the F^--complexed film could also account for the voltammetric data.

4. Conclusions

As demonstrated in this paper, the sensing properties of a redox-active receptor can be greatly diminished after its immobilisation onto an electrode surface. Indeed, the remarkable voltammetric effects observed

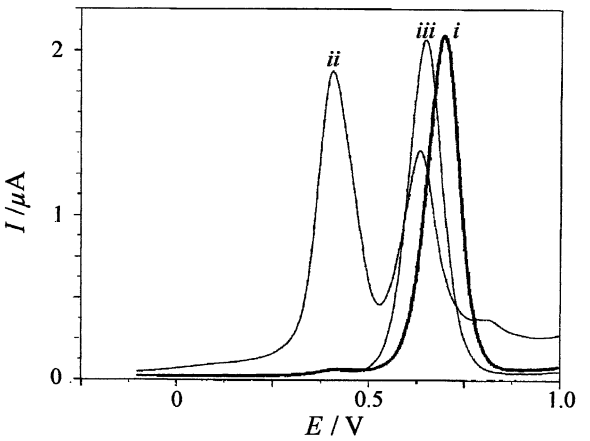


Fig. 5. DPV in $CH_2Cl_2 + 0.1$ M Bu_4NClO_4 of **TPAB$_1$** (1 mM) before (i) and after addition of 5 mM $Et_3N{\cdot}3$ HF (ii) and then 10 mM Me_3SiCl (iii).

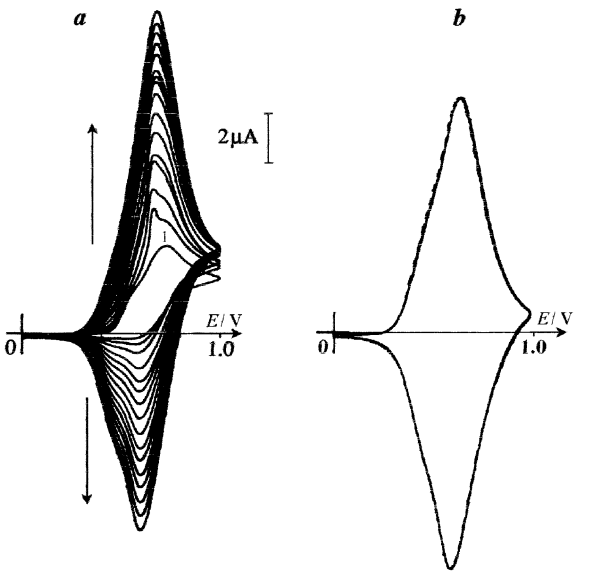


Fig. 6. (a) Potentiodynamical electropolymerisation of **VTPAB$_2$** at 5 mM in $CH_3CN + 0.1$ M Bu_4NClO_4 and (b) response of the resulting polymer film in the same electrolytic solution; first cycle (—) and tenth cycle (— —). Potential scan rate: 50 mV s^{-1}.

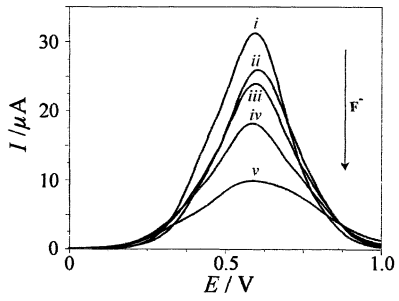


Fig. 7. DPV of a poly(**VTPAB$_2$**) film (electropolymerisation charge, 150 mC cm^{-2}) in CH_3CN + 0.1 M Bu_4NClO_4 without (i) and with 0.1 mM (ii), 0.5 mM (iii), 1.0 mM (iv) and 2.0 mM (v) of $Et_3N{\cdot}3$ HF.

with **TPAB$_n$** in the presence of fluoride are changed into a total and irreversible degradation of the receptor electroactivity with poly(**VTPAB$_2$**).

It seems obvious that the recognition pathway in heterogeneous phase is dependent on a large number of not easily controllable parameters, such as the analyte diffusion and the transport of electrons through the film as well as on the stability of charge carriers and the polymer structure. In contrast, the situation is considerably simplified when both the receptor and the anionic guest are in solution. Generally, such a feature is not raised in the literature and most of concerned papers have dealt with recognition events occurring in homogeneous phase. In our case, different strategies could be applied in order that the immobilised receptor retains its original characteristics, including the chemical polymerisation of **VTPAB$_2$** with α,α′-azoisobutyronitrile (AIBN) or benzoyl peroxide [23] (influence on the cross-linking and the polymerisation degree) or introduction of the boronic ester-substituted triphenylamine units into a backbone of conjugated polymer [24].

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Appendix A

The binding constants K_m corresponding to the free and complexed neutral forms of **TPAB$_n$** (with $n = 1$–3) can be determined from the DPV anodic peak currents I_{pa} of each redox system, assuming that the diffusion coefficients of the free and complexed forms are nearly equal.

For **TPAB$_1$**, the F^- binding constant K_1 is given by

$$K_1 = \frac{[\mathrm{TPAB_1} - (\mathrm{F^-})]}{[\mathrm{TPAB_1}][\mathrm{F^-}]} \tag{A1}$$

where $[\mathrm{TPAB_1} - (\mathrm{F^-})]$, $[\mathrm{TPAB_1}]$ and $[\mathrm{F^-}]$ correspond to the F^--complexed **TPAB$_1$**, free **TPAB$_1$** and free fluoride concentrations, respectively (the standard concentration used is 1 mol dm^{-3}).

Taking into account the mass conservation for fluoride,

$$[\mathrm{F^-}]_{tot} = [\mathrm{F^-}] + [\mathrm{TPAB_1} - (\mathrm{F^-})] \tag{A2}$$

where $[F^-]_{tot}$ is the total fluoride concentration, K_1 can be re-written

$$K_1 = \frac{[\mathrm{TPAB_1} - (\mathrm{F^-})]}{[\mathrm{TPAB_1}]([\mathrm{F^-}]_{tot} - [\mathrm{TPAB_1} - (\mathrm{F^-})])} \tag{A3}$$

or

$$\frac{1}{K_1} = \frac{[\mathrm{TPAB_1}]}{[\mathrm{TPAB_1} - (\mathrm{F^-})]}[\mathrm{F^-}]_{tot} - [\mathrm{TPAB_1}] \tag{A4}$$

This parameter can be expressed as a function of the DPV anodic peak currents I_{pa} assigned to the free and complexed **TPAB$_1$** forms (Eq. (A5)).

$$\frac{1}{K_1} = \frac{I_{pa}(\mathrm{TPAB_1})}{I_{pa}(\mathrm{TPAB_1} - (\mathrm{F^-}))}[\mathrm{F^-}]_{tot} - [\mathrm{TPAB_1}]_0 \frac{I_{pa}(\mathrm{TPAB_1})}{I^0_{pa}(\mathrm{TPAB_1})} \tag{A5}$$

where $I^0_{pa}(\mathrm{TPAB_1})$ is the anodic peak current recorded in the absence of fluoride and $[\mathrm{TPAB_1}]_0$ is the initial **TPAB$_1$** concentration.

For **TPAB$_2$**, the constants attributed to the binding of one and then two fluoride anions can be expressed as follows:

$$K_1 = \frac{[\mathrm{TPAB_2} - (\mathrm{F^-})]}{[\mathrm{TPAB_2}][\mathrm{F^-}]} \tag{A6}$$

$$K_2 = \frac{[\mathrm{TPAB_2} - (\mathrm{F^-})_2]}{[\mathrm{TPAB_2} - (\mathrm{F^-})][\mathrm{F^-}]} \tag{A7}$$

where $[\mathrm{TPAB_2}]$, $[\mathrm{TPAB_2} - (\mathrm{F^-})]$ and $[\mathrm{TPAB_2} - (\mathrm{F^-})_2]$ are the free **TPAB$_2$**, one and two F^--complexed **TPAB$_2$** concentrations, respectively. Considering the mass conservation for fluoride,

$$[\mathrm{F^-}]_{tot} = [\mathrm{F^-}] + [\mathrm{TPAB_2} - (\mathrm{F^-})] + \frac{1}{2}[\mathrm{TPAB_2} - (\mathrm{F^-})_2] \tag{A8}$$

it can be easily established that

$$\frac{1}{K_1}=\frac{I_{pa}(TPAB_2)}{I_{pa}(TPAB_2-(F^-))}[F^-]_{tot}-[TPAB_2]_0 \times\frac{I_{pa}TPAB_2}{I^0_{pa}(TPAB_2)}\left(1+\frac{1}{2}\frac{I_{pa}(TPAB_2-(F^-)_2)}{I_{pa}(TPAB_2-(F^-))}\right) \quad (A9)$$

and

$$\frac{K_2}{K_1}=\frac{I_{pa}(TPAB_2-(F^-)_2)I_{pa}(TPAB_2)}{I^2_{pa}(TPAB_2-(F^-))} \quad (A10)$$

$TPAB_3$ is characterised by three binding constants (Eqs. (A11), (A12) and (A13))

$$K_1=\frac{[TPAB_3-(F^-)]}{[TPAB_3][F^-]} \quad (A11)$$

$$K_2=\frac{[TPAB_3-(F^-)_2]}{[TPAB_3-(F^-)][F^-]} \quad (A12)$$

$$K_3=\frac{[TPAB_3-(F^-)_3]}{[TPAB_3(F^-)_2][F^-]} \quad (A13)$$

with $[TPAB_3]$, $[TPAB_3-(F^-)]$, $[TPAB_3-(F^-)_2]$ and $[TPAB_3-(F^-)_3]$ are the free **$TPAB_3$**, one, two and three F^--complexed **$TPAB_3$** concentrations, respectively. The value of the first binding constant is extracted from Eq. (A14) and the two following ones are then easily deduced.

$$[F^-]_{tot}=[F^-]+[TPAB_3-(F^-)]+\frac{1}{2}[TPAB_3-(F^-)_2]+\frac{1}{3}[TPAB_3-(F^-)_3] \quad (A14)$$

$$\frac{1}{K_1}=\frac{I_{pa}(TPAB_3)}{I_{pa}(TPAB_3-(F^-))}[F^-]_{tot}-[TPAB_3]_0 \times\frac{I_{pa}(TPAB_3)}{I^0_{pa}(TPAB_3)}\left(1+\frac{1}{2}\frac{I_{pa}(TPAB_3-(F^-)_2)}{I_{pa}(TPAB_3-(F^-))}+\frac{1}{3}\frac{I_{pa}(TPAB_3-(F^-)_3)}{I_{pa}(TPAB_3-(F^-))}\right) \quad (A15)$$

$$\frac{K_2}{K_1}=\frac{I_{pa}(TPAB_3-(F^-)_2)I_{pa}(TPAB_3)}{I^2_{pa}(TPAB_3-(F^-))} \quad (A16)$$

$$\frac{K_3}{K_2}=\frac{I_{pa}(TPAB_3-(F^-)_3)I_{pa}(TPAB_3-(F^-))}{I^2_{pa}(TPAB_3-(F^-)_2)} \quad (A17)$$

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