

## Research Article

# Solvent Effects on the Electrochemical Behavior of TAPD-Based Redox-Responsive Probes for Cadmium(II)

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Two tetraalkylated phenylenediamines (TAPD) **1** and **2** have been prepared by reductive alkylation of *para*-dimethylaminoaniline with furfural or thiophene 2-carboxaldehyde, respectively. Their chelation ability has been evaluated as electrochemical guest-responsive chemosensors for Cd(II) in acetonitrile (ACN), dimethylformamide (DMF), propylene carbonate (PC), and nitromethane (NM). The voltamperometric studies showed that these compounds are able to bind the Cd(II) cation with strong affinities except in DMF. The redox features of the chemosensors changed drastically when they are bounded to Cd(II) to undergo important anodic potential peak shifts comprised between ca. 500 and ca. 900 mV depending on the solvent. The addition of ~4–10% molar triflic acid (TfOH) was found to be necessary to achieve rapidly the cation chelation which is slow without the acid. The electrochemical investigations suggested the formation of 1:2 stoichiometry complexes  $[\text{Cd}(\text{L})_2]^{2+}$ . The results are discussed in terms of solvent effects as a competitive electron donating ligand to the cation. The reaction coupling efficiency (RCE) values were determined and were also found to be solvent-dependent.

## 1. Introduction

Metallic ions are widely present in the biological systems and play many important roles [1, 2]. Some others are toxic but are tolerated at low levels such as nickel or cobalt because of their interventions in some biological processes [3]. Other cations can cause major health damage if they are present even in trace amounts such lead(II) and cadmium(II) [4, 5]. Indeed, lead is known to cause saturnism when it is present at high concentration in biological medium [6, 7]. Cadmium has been reported to block calcium channels in sensory neurons and prevents regular central system functioning [8]. Many researchers have been consequently devoted to the development of methods for the determination of these cations.

In living organisms, biological receptors like those found in enzymes or neurons bind selectively to a cation to achieve some goals most of the times in reversible processes. Contrarily, most of the synthetic receptors do not work that way;

they tightly bind to cations in nonreversible processes [9]. Only few attempts have been directed at the elaboration of reversible chemosensors useful for the detection and eventually the delivery cations such as calcium ions when they are photochemically or electrochemically triggered [10, 11]. The first class of chemosensors relies on chromogenic guest-responsive transducers whose properties change when they are linked to cations. The second class of chemosensors depends on reversible electrochemical transducers to achieve the chelation of ions in a chemical reversible manner.

In the last two decades, electroactive chemosensors have been built by using reversible systems. The detection or release of guest ions is monitored through the modification of the electrochemical features of redox centers. For instance, Pearson and Hwang were pioneers in the field and reported many TAPD-based chemosensors formed by crown ethers as ionophore sites and phenylenediamine moiety as a transducer capable of detection of alkaline or alkaline earth

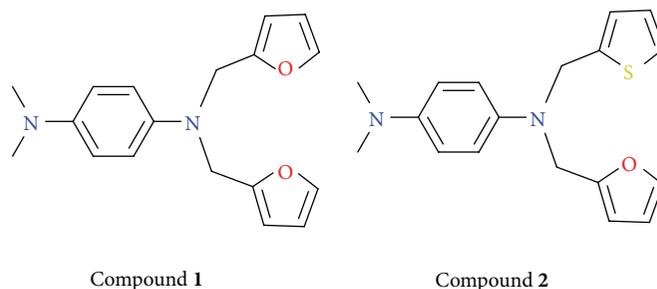


FIGURE 1: Structures of the TAPD-based chemosensors **1** and **2**.

cations [12]. In a similar way, Sibert and coworkers prepared chemosensors containing crown thiaethers as hosting sites to selectively recognize noble and heavy-metal ions such as platinum(II) and mercury(II) [13, 14]. Recently, our group reported the preparation of new chemosensors which are able to chelate metal ions in solution [15, 16]. Bhattacharyya et al. also recently reported the preparation and the electrochemical study of a novel water-soluble redox active and selective chelator for calcium based on organometallic derivative [17]. Thus, as chelation took place in solution, the thermodynamics and kinetics of the electron transfer are solvent-dependent and so should be the chemosensor electrochemical features prior to and after the cadmium(II) chelation process. For example, Pirson and Huyskens have studied the effect of the solvent in the complexation of same anions and cations by substituted benzoic acid ligands [18]. They concluded that the acetonitrile and nitrobenzene had influence on the stability constants of the formed complexes. Besides, Coetzee and Sharpe reported the interaction between acetonitrile and anions or cations [19]. Moreover, Wang et al. [20] demonstrated the influence of various organic solvents on the electrochemical activity of redox moiety. To our best knowledge there are no reports on the study of complexation dependence on the solvent for TAPD systems. This work is intended to fill in this gap.

The aim of this work is to study the solvent effects on the electrochemical behavior of **1** and **2** (Figure 1) during the chelation of cadmium(II) following several works devoted to the development of TAPD-based chemosensors for bivalent cations which have been mostly studied in acetonitrile. The electrochemical investigations were conducted by means of cyclic voltammetry (CV) in acetonitrile (ACN), dimethylformamide (DMF), propylene carbonate (PC), or nitromethane (NM), solvents commonly used for electrochemical measurements, aiming to draw some conclusions in the solvent effects on the chemosensors chelating ability.

## 2. Materials and Methods

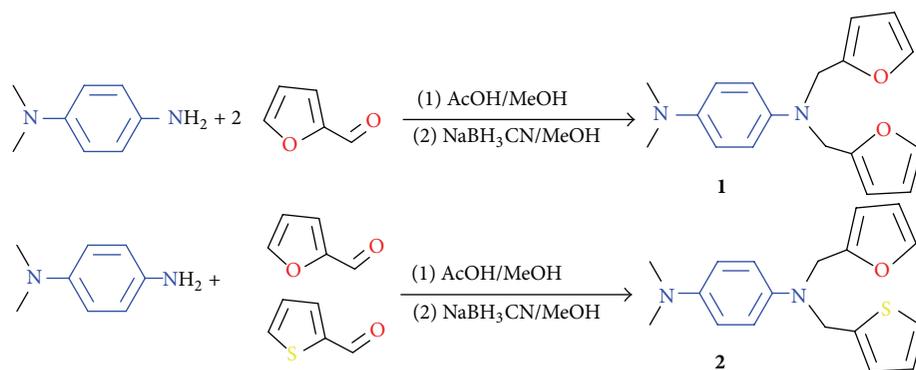
**2.1. Reagents and Chemicals.** 4-Dimethylaminoaniline (97%), sodium cyanoborohydride (95%), sodium bicarbonate ( $\geq 95\%$ ), glacial acetic acid ( $\geq 99\%$ ), cadmium perchlorate hydrate ( $\text{Cd}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ ), tetrabutylammonium tetrafluoroborate ( $\text{TBABF}_4$ ,  $\geq 99\%$ ), triflic acid ( $\geq 99\%$ ), and HPLC grade methanol were purchased from Sigma-Aldrich and used

without further purification. Aldehydes (furfural, 99%, and thiophene-2-carboxaldehyde, 98%) were freshly distilled before use. PC and NM were purchased from Merck and were distilled and stored in dark; AnhydroScan ACN, DMF, and dichloromethane were purchased, respectively, from LabScan and Sigma-Aldrich and used as received without further purification. A stock solution of cadmium 0.1 M is prepared by dissolving the corresponding amount in acetonitrile.

**2.2. Apparatus.** Proton and carbon 13 NMR spectra were recorded on a Bruker Avance 300 MHz apparatus in  $\text{CDCl}_3$ . Chemical shifts are given in ppm relative to TMS as internal reference. IR spectra were measured on a Perkin Elmer ATR Alpha spectrophotometer. The electrochemical experiments were conducted in the corresponding solvent containing 0.1 M  $\text{TBABF}_4$  as supporting electrolyte, at ambient temperature and at a scan rate of  $0.1 \text{ Vs}^{-1}$ . A Radiometer Analytical POL-150 with MED-150 stand-controlled three-electrode glass cell fitted with a carbon glassy disk as a working electrode (3 mm-diameters), a platinum wire as a counter electrode, and an SCE (3 M KCl) electrode as a reference electrode was used for the electrochemical measurements. Data acquisition was performed with TraceMaster 5 software for CV experiments and treated using Kaleidagraph 4.0 software package. The working electrode was polished using  $0.3 \mu\text{m}$  slurry of alumina at the beginning of each experiment.

**2.3. Preparation and Physicochemical Characterization of Chemosensors.** The compounds were prepared according to published procedure [15, 16]. The reaction was performed in round bottom flask maintained under argon atmosphere at room temperature and shielded from the light with an aluminum foil. Briefly, compound **1** (**2**) was obtained by mixing 2.0 mmol of 4-dimethylaminoaniline, 8.0 mmol of furfural (4.0 mmol of furfural and 4.0 mmol of thiophene-2-carboxaldehyde), and 10.0 mmol of acetic acid in methanol (50 mL). After 12 h stirring, 2.0 mmol of sodium cyanoborohydride was added and stirring was kept for a further 4 h. The mixture was quenched with 50 mL of a saturated sodium bicarbonate solution and extracted twice with 20 mL of dichloromethane. The organic phase was washed twice with 10 mL of distilled water, dried over magnesium sulfate, and evaporated to dryness (Scheme 1).

The oily brown residue was purified on silica gel eluted by 30:70 ethyl acetate/cyclohexane leading to solid product



SCHEME 1: Synthetic route to TAPD derivatives via reductive alkylation reaction.

TABLE 1: Thermodynamics data for the first and second peaks: anodic  $E_{pa}$  and cathodic  $E_{pc}$  potential values, peaks separation  $\Delta E$ , half-wave potential  $E_{1/2}$ , and the current ratio  $i_{pc}/i_{pa}$  for compounds **1** and **2** measured in ACN, PC, NM, and DMF.

Compound	Compound	1st peak of oxidation				2nd peak of oxidation				
		$E_{pa}^{(a)}$	$E_{pc}^{(a)}$	$\Delta E_p^{(b)}$	$E_{1/2}^{(c)}$	$i_{pc}/i_{pa}$	$E_{pa}^{(a)}$	$E_{pc}^{(a)}$	$\Delta E_p^{(b)}$	$E_{1/2}^{(c)}$
ACN	<b>1</b>	358	259	99	308	1.03	912	765	147	838
	<b>2</b>	355	263	92	309	1.04	942	775	167	858
PC	<b>1</b>	315	218	97	266	0.98	882	700	182	791
	<b>2</b>	327	216	111	271	0.99	918	735	183	826
NM	<b>1</b>	330	233	97	281	1.02	947	794	153	870
	<b>2</b>	306	204	102	255	1.00	922	753	169	837
DMF	<b>1</b>	365	267	98	316	1.04	970	676	294	823
	<b>2</b>	370	267	103	318	0.99	965	706	259	835

<sup>(a)</sup>  $E_p$  measured (mV) versus SCE;  $E_{pc}$  are extracted for curves in Figure 2.

<sup>(b)</sup>  $\Delta E_p = E_{pa} - E_{pc}$ .

<sup>(c)</sup>  $E_{1/2} = E_{pa} - \Delta E_p/2$ .

which was characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, and infrared spectroscopy. The characteristics are summarized below.

**Compound 1** ( $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2$ ): yield: 61%; mp: 49–51°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta/\text{ppm}$ : 2.75 (s, 6H,  $\text{CH}_3$ ), 4.27 (s, 4H,  $\text{CH}_2$ ), 6.03 (d, 2H, furan,  $^3J_{\text{H-H}} = 3$  Hz), 6.19 (dd, 2H, furan,  $^3J_{\text{H-H}} = 3$  Hz), 6.65 (d, 2H,  $^3J_{\text{H-H}} = 9$  Hz,  $\text{CH}_{\text{arom.}}$ ), 6.80 (d, 2H,  $^3J_{\text{H-H}} = 9$  Hz,  $\text{CH}_{\text{arom.}}$ ), 7.23 (s, 2H, furan);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz)  $\delta/\text{ppm}$ : 40.7, 47.4, 106.7, 109.1, 113.9, 115.9, 140.2, 140.7, 143.5, 151.6; IR  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2964 (CH), 2896 (CH), 1514 (C=C), 1250 (C-N), 1070 (C-C), 1056 (C-C), 810 (C-O).

**Compound 2** ( $\text{C}_{18}\text{H}_{20}\text{N}_2\text{OS}$ ): yield: 65%; mp: 58–59°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta/\text{ppm}$ : 2.77 (m, 6H,  $\text{CH}_3$ ), 4.27 (s, 2H,  $\text{CH}_2$ , furan), 4.48 (s, 2H,  $\text{CH}_2$ , thiophene), 6.06 (d, 2H,  $^3J_{\text{H-H}} = 3$  Hz, furan), 6.21 (d, 2H,  $^3J_{\text{H-H}} = 3$  Hz, furan), 6.65 (d, 2H,  $^3J_{\text{H-H}} = 10$  Hz,  $\text{CH}_{\text{arom.}}$ ), 6.80 (d, 2H,  $^3J_{\text{H-H}} = 10$  Hz,  $\text{CH}_{\text{arom.}}$ ), 7.08 (d, 1H,  $^3J_{\text{H-H}} = 2$  Hz,  $\text{CH}_{\text{arom.}}$ ), 7.17 (s, 1H, furan), 7.17 (m, 1H, furan);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.1 MHz)  $\delta/\text{ppm}$ : 41.8, 48.2, 50.7, 107.9, 110.2, 114.9, 117.3, 124.4, 125.2, 126.5, 141.0, 141.8;  $\nu_{\text{max}}/\text{cm}^{-1}$ : IR3663 (CH), 2972 (CH), 1514 (C=C), 1393 (C-N), 1248 (C-C), 809 (C-O), 720 (C-S).

### 3. Results and Discussion

**3.1. Electrochemistry of the Uncoordinated Chemosensors.** CVs of **1** and **2** investigated in the different solvents except in DMF exhibit two oxidation peaks. This electrochemical behavior is similar to that reported for tetramethylated *para*-phenylenediamine (TMPD) [21] which is generally attributed, respectively, to the formation of a TAPD $^{+}$  radical-cation and TAPD $^{2+}$  (Figures 2(a) and 2(b)).

When the potential reverse sweep is poised to approximately 0.5 V, the first monoelectronic peak is reversible (Figure 3) and this is due to the stability of the generated radical-cation allowing more accurate determination of  $i_{pc}$ . The second oxidation peak is irreversible probably due to the deactivation of the generated dication, which is highly reactive, by the nucleophilic impurities present in the medium. In DMF, this peak involves also the oxidation of furan and/or thiophene ring. Table 1 summarized the thermodynamic data of compounds **1** and **2**. As it appears in this table, one can observe that the  $i_{pc}/i_{pa}$  ratio is close to the unity confirming the reversibility of the electron transfer of the first peak [22]. Moreover, at the same concentration, the intensity of the oxidation peak current for compound **1** and compound **2** decreases from ACN to PC. These results, in agreement

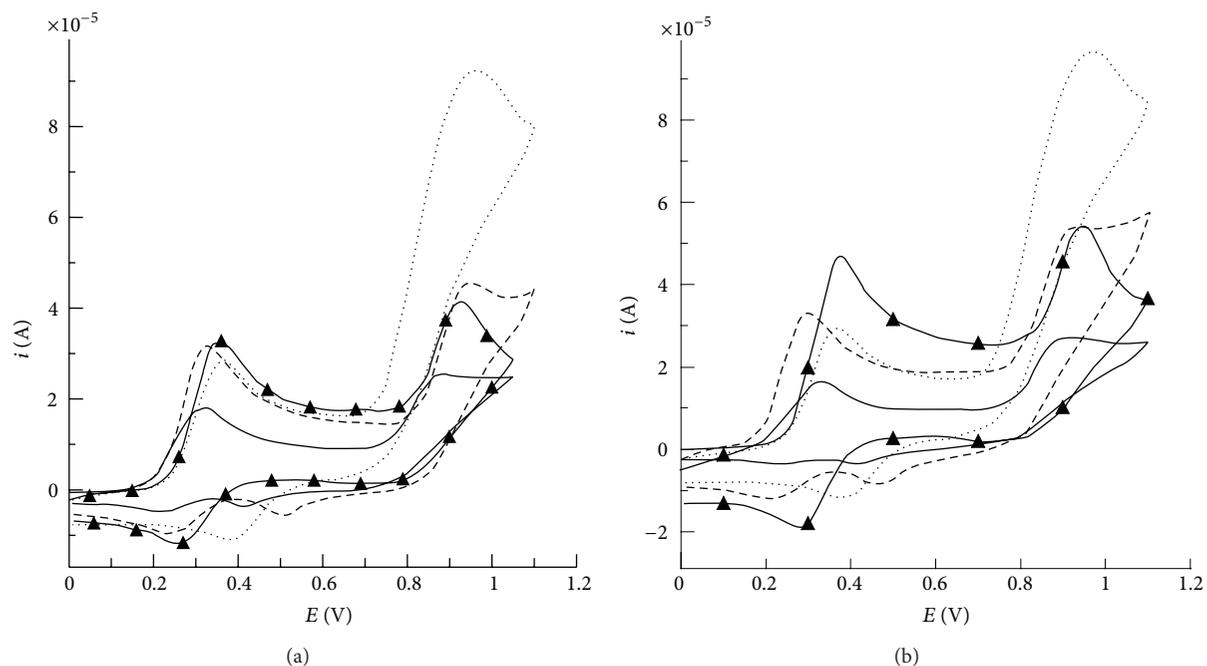


FIGURE 2: CVs showing the first and second oxidation stages of 1 (a) and 2 (b) at 2.0 mM concentration; the curves were recorded in ACN ( $-\blacktriangle-$ ), in DMF ( $\bullet\bullet\bullet$ ), in NM ( $- - -$ ), and in PC ( $-$ ) containing 0.1 M TBABF<sub>4</sub>. Working electrode: glassy carbon ( $\Phi = 3$  mm); reference electrode: SCE (KCl 3 M); scan rate:  $0.1 \text{ V s}^{-1}$ .

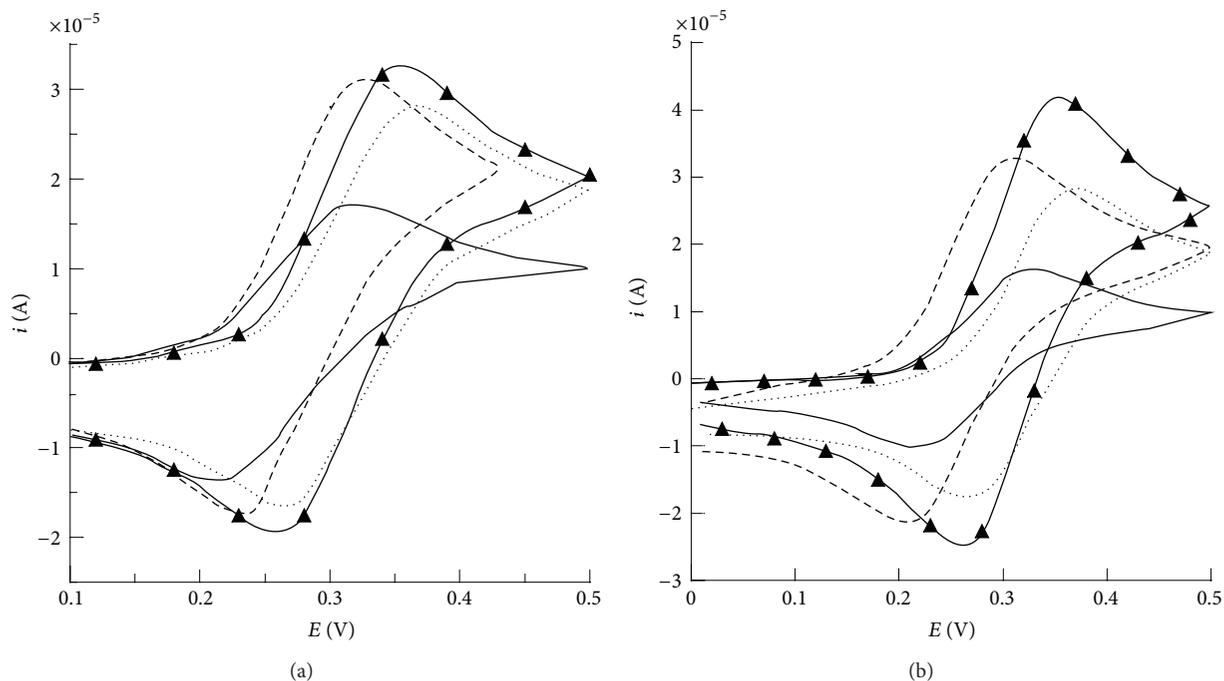


FIGURE 3: CVs of compounds with sweep poised at 0.5 V for 1 (a) and 2 (b) in ACN ( $-\blacktriangle-$ ), in DMF ( $\bullet\bullet\bullet$ ), in NM ( $- - -$ ), and in PC ( $-$ ) containing 0.1 M TBABF<sub>4</sub>, scan rate:  $0.1 \text{ V s}^{-1}$ . Working electrode: glassy carbon; reference electrode: SCE (KCl 3 M); concentration: 2.0 mM.

with those reported in the literature, could be explained by using the Randles-Sevcik and Stokes-Einstein equations which correlate the peak current upon the solvent viscosity [23, 24]. Thus, viscosity increase from ACN to PC leads to a decrease in the intensity of the peak current. Moreover, the

current intensity is dependent on the diffusion coefficient of the compounds in each solvent which could explain the changes in current intensities [25].

Additionally, one can see in Table 1 that the oxidation potential peaks of the two compounds also depend on the

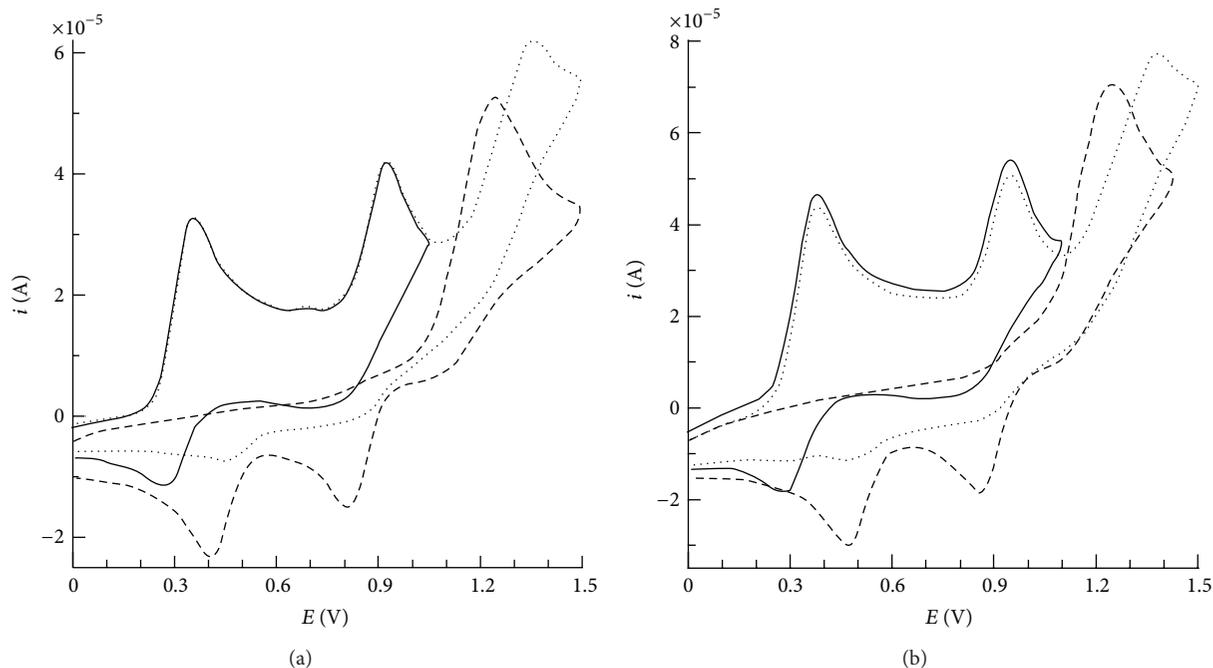


FIGURE 4: (a) CV curves of 2.0 mM of chemosensor 1 in absence (—: inversion potential  $E_i = 1$  V; •••: inversion potential  $E_i = 1.5$  V) and in presence of 1.0 mM of  $\text{Cd}^{2+}$  (---). (b) CV curves of 2.0 mM of chemosensor 2 in absence (—: inversion potential  $E_i = 1$  V; •••: inversion potential  $E_i = 1.5$  V) and in presence of 0.5 equivalent of  $\text{Cd}^{2+}$  (---). Voltammograms were recorded in ACN containing 0.1 M  $\text{TBABF}_4$  as supporting electrolyte. Working electrode: glassy carbon; reference electrode: SCE (KCl 3 M); scan rate:  $0.1 \text{ V s}^{-1}$ .

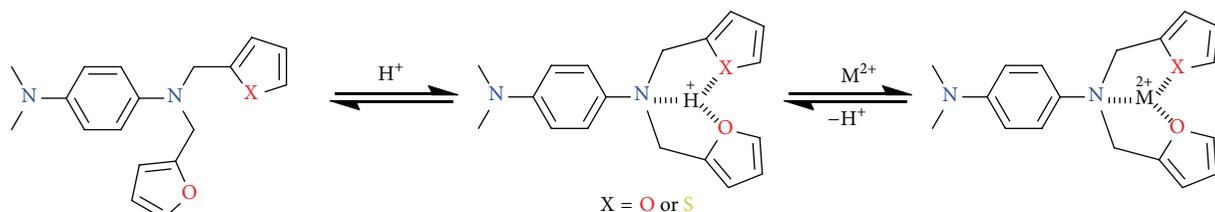
solvent in which the studies were carried out. For instance, in the case of **1** (**2**), the difference of the oxidation peak potentials which could be observed comparatively in any two different solvents is at most 40 mV (50 mV). However, one can note that compounds **1** and **2** can be more easily oxidized in NM and PC than in ACN or DMF. Thus, the oxidation potential is close to 358 mV for compound **1** in ACN while in PC it is only 315 mV. This behavior could be due to donor-acceptor interaction between the studied components and the solvent [26]. Participation of liquid junction potential could be involved. For any couple of these solvents it is comprised between 0 and 10 mV [27].

The study of the scan rate effect carried out on the first oxidation peak shows that the current intensity increases with the scan rate in the range of  $0.05\text{--}0.5 \text{ V s}^{-1}$ . The linear plot of the logarithm of the first peak current as a function of logarithm of scan rate is close to 0.5 indicating a diffusion-controlled electron reaction [28].

**3.2. Electrochemistry of the Chemosensors in Presence of Cadmium.** CVs recorded in presence of 0.5 equivalent of  $\text{Cd}(\text{II})$  show that chemosensors are capable of binding to this ion except in DMF. Indeed, it is noticeable on the curves of Figures 4(a) and 4(b) that the addition of 0.5 equivalent of  $\text{Cd}(\text{II})$  leads to a total disappearance of the two oxidation peaks characteristic of the uncoordinated chemosensors. This behavior corresponds mostly to a chemical interaction in solution between chemosensors and  $\text{Cd}(\text{II})$  as it has been previously reported [12–17]. Indeed, after the addition of cadmium

cation, the lone pair of electrons on the nitrogen is involved in the complexation reaction with the metal leading to the disappearance of the two oxidation peaks and a new one is observed at more anodic potential which is different from that of the aromatic ring of thiophene or furan. In our point of view and in comparison with works reported by Amatore group [11, 17] and Sahli et al. [15, 16], this peak is probably due to the oxidation of the complex **1**- $\text{Cd}(\text{II})$  or **2**- $\text{Cd}(\text{II})$ . When the scanning is realized at more anodic potential in absence of  $\text{Cd}(\text{II})$ , one can observe a different oxidation peak, which is irreversible, corresponding to the oxidation of furan or thiophene ring (dotted voltammograms) [29, 30].

Additionally, temporal monitoring of the  $\text{Cd}(\text{II})$  chelation reaction of the chemosensors revealed that the reaction is slow leading to complete disappearance of the chemosensors' signals after 45–60 min even if 1.0 equivalent of  $\text{Cd}(\text{II})$  is added. When 4 to 10% molar TfOH is added, this cation chelation is accelerated and a purple coloration of the solution is noticed. On the other hand, one can observe that the addition of small amounts of TfOH does not affect the electrochemical features of the chemosensors (figure not shown); since TfOH is a weak acid in organic solvents ( $\text{pK}_a = 0.7$  in ACN) [31], the protonated amounts of **1** and **2** should remain very low and the oxidation currents are unaltered. Besides, the addition of an increasing quantity of acid (up to 20%) does not affect the electrochemical behavior of TAPD compounds, nor are the potentials or the currents of the peaks altered. The presence of the acid seems indeed to be necessary to achieve rapidly the complexation reaction. One can hypothesize that the protons from TfOH protonate the aromatic nitrogen bearing the



SCHEME 2: Conformational changes of the chemosensors by protonation followed by proton-cation exchange reaction.

two other chelating rings inducing a conformational change, which is thermodynamically unfavoured, followed by a proton-metal exchange giving more rapidly the  $[\text{Cd}(\text{L})_2]^{2+}$  complexes. In both cases, at least a nitrogen atom is protonated (Scheme 2) [32].

During the reverse scan, two cathodic peaks are visible in ACN, NM, or PC corresponding to the two-stage reduction of dication peaks. Indeed, due to the positive charges on compounds **1** and **2** after the anodic electron transfer, one can suggest the release of Cd(II) in solution from the inner sphere of the complex by electrostatic repulsion between the positive charges on the phenylenediamine moiety and on Cd(II) leading to  $\mathbf{1}^{2+}$  and  $\mathbf{2}^{2+}$  which are reducible during the reverse potential scan. The dication reduction gives radical-cation  $\mathbf{1}^{\bullet+}$  or  $\mathbf{2}^{\bullet+}$  leading to neutral species after a second electron transfer. Moreover, the reduction of  $\mathbf{1}^{\bullet+}/\mathbf{2}^{\bullet+}$  into the neutral form occurs at higher potentials than of the uncoordinated chemosensors because the recomplexation reaction displaces the interfacial equilibrium, facilitating thus the electron transfer [33]. The chelating abilities of the chemosensors are thus restored. Furthermore, the cathodic current increase may be due to the introduction of perchlorate ions; that is, cadmium perchlorate was used, having a more stabilizing effect on the organic dication than tetrafluoroborate from the supporting electrolyte. On the other hand, the gradual addition of Cd(II) to solutions of the chemosensors showed that the current of the two oxidation peaks of ligand dropped gradually and completely vanished when 0.5 equivalent of the cation is added suggesting a total complexation of the ligands so it can be concluded that the complex stoichiometry is 1 : 2.

When the chelation of Cd(II) by the chemosensors is attempted in DMF (Figure 5), the voltammetric curves showed a decreasing of the current intensity and exhibited also a slight shift of oxidation peak potential in the presence of 0.5 equivalent of Cd(II) toward anodic value suggesting a chemosensor-cation interaction and a solvent-cation interaction, respectively. These interactions remain weak even when 1.0 equivalent of Cd(II) is added. These relatively weak potential shifts (125 mV for **1** and 48 mV for **2**) suggest a possible competition between the ligand and DMF which is a good electron-donating ligand for Cd(II). This behavior is in agreement with the studies by Jorge and Stradiotto [34], who reported that DMF is able to complex Sn(II) by removal of ACN molecules. The addition of a small amount of acid to the Cd/ligand in DMF solution does not improve the complexation process.

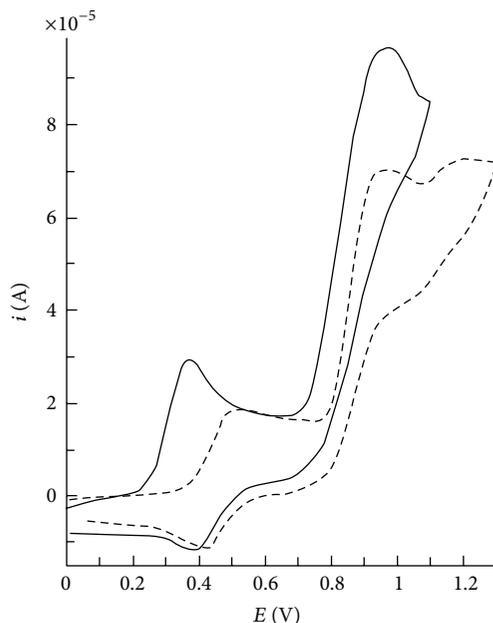


FIGURE 5: CV of 2.0 mM of chemosensor **1** in absence (—) and in presence of 1.0 equivalent  $\text{Cd}^{2+}$  (2.0 mM) (---) recorded in DMF containing 0.1 M TBABF<sub>4</sub>. Working electrode: glassy carbon; reference electrode: SCE (KCl 3 M); scan rate: 0.1 V s<sup>-1</sup>.

**3.3. Reaction Coupling Efficiency.** Depending on the solvent and the chemosensor, potentials of the first oxidation peak of ligands **1** and **2** and the one corresponding to the complex oxidation are reported in Table 2. As shown in Table 2, one can remark that except in DMF the shift of the potential after the complexation varies from ca. 500 to ca. 900 mV and can be correlated to the stability of the formed complex. These observations are in agreement with works of Beer et al. showing that the stability of the complexes is proportional to the shifts of oxidation potentials of various ferrocene-based ligands [35]. Due to the difficulty of determining  $E_{1/2}^3$  since the third peak is irreversible, the values of  $\Delta E_{1/2} = E_{1/2}^3 - E_{1/2}^1$  should stay very close to  $\Delta E_p = E_p^3 - E_p^1$  as it is for the first and the second peaks for both compounds. Indeed, the peak potential depends on the electron transfer rate constant and following chemical reactions [36]. This system is considered electrochemically reversible at 0.1 V/s. This is demonstrated by a low peak to peak separation (less

TABLE 2: Potentials of first oxidation peak,  $E_p^1$ , and complex oxidation peak  $E_p^3$ ,  $\Delta E$ , and the logarithm of the reaction coupling efficiency (log RCE) for compounds **1** and **2** in the presence of 0.5 equivalent of  $\text{Cd}^{2+}$  in ACN, NM, PC, and DMF containing 0.1M TBABF<sub>4</sub>.

	$E_p^1$ <sup>(a)</sup>	$E_p^3$ <sup>(a)</sup>	$\Delta E$ <sup>(b)</sup>	$-\log \text{RCE}$ <sup>(c)</sup>
ACN				
<b>1</b>	353	1247	-894	14.9
<b>2</b>	312	118	-864	14.4
NM				
<b>1</b>	330	1218	-888	14.8
<b>2</b>	306	1094	-788	13.1
PC				
<b>1</b>	315	1188	-873	14.6
<b>2</b>	327	884	-502	8.4

<sup>(a)</sup>  $E_p$  measured (mV) versus SCE.

<sup>(b)</sup>  $\Delta E = E_p^1 - E_p^3$ .

<sup>(c)</sup>  $\log \text{RCE} = \Delta E/60$ .

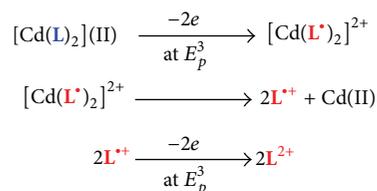
than 111 mV). Degradation rate after the second electron transfer was not determined precisely so  $\Delta E_{1/2}$  cannot be deduced directly from  $\Delta E_p$ . However, we can infer that  $\Delta E_{1/2}$  is equal to  $\Delta E_p$  since the oxidation potential is lowered when chemical reaction displaces the electrochemical equilibrium.

Since the  $E_p^3$  peak of oxidation corresponds to the oxidation of the complexes  $[\text{Cd}(\text{L})_2]^{2+}$  ( $\text{L} = \mathbf{1}$  or  $\mathbf{2}$ ), to the radical-cation and subsequent dissociation of the radical-cation complex  $[\text{Cd}(\text{L}^{\bullet})_2]^{2+}$  into  $\text{Cd}(\text{II})$  and free oxidized forms of **1** or **2**, due to the electrostatic repulsion between these two positively charged species [15, 16]. At this potential, the released radical-cation undergoes a second one-electron transfer to its dication according to Scheme 3.

Beer and coworkers described the reaction coupling efficiency (RCE) as the ratio of  $K_{\text{ox}}/K_{\text{red}}$  which are, respectively, the complex stability constants for a given ligand in its oxidized and reduced forms. The RCE can be easily determined from corresponding difference between the oxidation potentials of the uncoordinated and coordinated host and is a very useful tool to evaluate and compare the redox-active ligands efficiency toward metal chelation. This relation can be reasonably applied to determine the RCE [35–37] since one-electron exchange is sufficient for the dissociation of the complex as previously reported in the case of ferrocene-based chemosensors [38–40]. Very high values of RCE imply that the reaction is complete, which is observed for ACN, NM, and PC and not chelation attempted in DMF. In addition, one can note through this table and the results obtained from cyclic voltammetry investigations that chemosensor **1** binds more efficiently to cadmium than chemosensor **2**, probably because compound **1** has two more donating sites than one sulfur and one oxygen atoms in compound **2**.

## 4. Conclusions

Cyclic voltammetry of two new chemosensors investigated in ACN, NM, PC, and DMF showed that these compounds



SCHEME 3: Oxidation of the complexes  $[\text{Cd}(\text{L})_2]^{2+}$  and their dissociation at the oxidation potential  $E_p^3$ .

exhibit two oxidation waves corresponding to a 2-electron transfer from the phenylenediamine moiety. It was also demonstrated using CV that these compounds constituted good ligands for cadmium(II) in solution and the affinity toward this metal depends strongly of the nature of solvent used, and complexes were formed in 1:2 stoichiometry. Moreover, it was shown that this complexation reaction starts after 45 to 60 min under open circuit conditions due to electrogenerated protons but it can be tremendously accelerated by addition of catalytic amount of TfOH. RCE values showed that ligand binds tightly to the cation except in DMF and the complexes are more stable with ligand **1** than with **2**.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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