Intervalence Charge Transfer in Mixed Valence Compound Modified by the Formation of a Supramolecular Complex.

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ABSTRACT: The electrochemical and spectroelectrochemical properties of *N*,*N*-diphenyl-1,4-phenylenediamine (PDA) were investigated in the absence and in the presence of 18-crown-6-ether (18C6) or dibenzo 24-crown-8-ether (DB24C8), in a solution of tetrabutylammonium hexafluorophosphate (TBAPF6) in acetonitrile and in the presence of trifluoroacetic acid (TFA) only for 18C6. In neutral acetonitrile, PDA undergoes two reversible oxidation processes, which lead first to the formation of the cation-radical considered as mixed valence (MV) compound, and then to the dicationic species. When 18C6 is added in the medium and depending on 18C6 concentration, cyclic voltammetry shows a marked shift to more cathodic potentials of the current waves of the second redox process only. This is attributed to a strong interaction between the PDA⁺² dication and two 18C6 molecules, leading to the formation of a supramolecular complex with an association constant value $K_a = 7.0 \times 10^7 \text{ M}^{-2}$. The interaction of 18C6 with PDA⁺² dication



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has a direct effect on the PDA⁺ cation-radical corresponding to a decrease in the lifetime of the MV compound and of the intramolecular electron transfer rate when 18C6 is present. Indeed, it results in a large decrease in the intervalence charge transfer (IV-CT) between the two amine centers in the MV compound ($k_{\rm th} = 1.35 \times 10^{10} \, {\rm s}^{-1}$ in 18C6-free neutral solution containing 5.0 × 10⁻⁴ M PDA, and $k_{\rm th} =$ $3.6 \times 10^9 \text{ s}^{-1}$ in the same medium at [18C6]/[PDA] = 20/1). And the comproportionation constant K_{co} falls from 6.0×10^6 in 18C6-free solution to 1.6×10^3 at [18C6]/[PDA] = 20/1. In acidified acetonitrile and when TFA concentration is increased, PDA still shows the two successive and reversible oxidation processes, but both are shifted to more anodic potentials. However, when 18C6 is added, the two oxidation waves shift to more cathodic potentials, indicating an interaction of all protonated PDA redox states with 18C6, resulting in the formation of supramolecular complexes. In the presence of TFA, the value of K_{co} is decreased to 4.3×10^4 , but it remains unchanged when 18C6 is added, indicating no change in the lifetime of the MV compound. In this medium, IV-CT in the MV compound is greater with 18C6 ($k_{th} = 2.3 \times 10^{10} \text{ s}^{-1}$ for [18C6]/[PDA] = 20/1) than without $(k_{\rm th} = 1.4 \times 10^9 \, {\rm s}^{-1})$, which indicates a more important IV-CT rate when 18C6 is present. The results show for the first time that is it possible to control the IV-CT rate, through the lifetime and the potential range where the MV compound is the most important. This control is not obtained as usual by chemical modification of the structure of the starting molecule, but by varying either the acidity or the 18C6 concentration as external stimuli, which lead to reversible formation/dissociation of a supramolecular complex species. Moreover, we also studied the electrochemical properties of PDA in the presence of wider crown ether such as DB24C8. We showed that PDA undergoes the same electrochemical behavior with DB24C8 than with 18C6 in neutral organic medium ($K_a = 2.9 \times 10^3 \text{ M}^{-1}$). This result suggests that the complexation between the electrogenerated PDA⁺² dication and the crown ethers may occur through face-to-face mode rather than rotaxane mode even with DB24C8 which is supposed to form inclusion complexes.

1. INTRODUCTION

Supramolecular systems that respond to external stimuli (potential,^{1,2} light,^{3,4} chemical,⁵ solvent⁶) by undergoing reversible complexation or translocation are useful for integration into applications such as molecular-based logic gates,⁷ information storage⁸ and processing, or as the active mechanical components in molecular devices⁹ and nanoscale functional materials.¹⁰ Rotaxanes,^{1,4,11,12} pseudorotaxanes,¹³ and catenanes¹⁴ have been advertised as some of the best examples of dynamic supramolecular systems because they can act as molecular 'shuttles' and

undergo long-range motion along a molecular "track".¹⁵ Several groups, that is, Stoddart et al.,¹⁶ Sauvage et al.,¹⁷ Credi et al.,¹⁸ and Brouwer et al.,¹¹ have used chemical, photochemical and electrochemical inputs to trigger changes in supramolecular architectures, and have demonstrated the possibility of reversible control of threading and translocation processes in these

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Figure 1. Oxidation and interaction equilibria of PDA in neutral acetonitrile with and without 18C6.

self-assembled structures. For such uses, various macromolecules, able to form complexes through weak intermolecular bounds, are employed, such as cryptands,^{19,20} cyclodextrins,²¹ hemispherands,²² or calixarenes.²³

The macrocyclic crown ether compounds, first synthesized by Pedersen^{24,25} are receiving increasing attention because of their ability to form complexes with alkali-metal cations through hydrogen bound interactions. Nevertheless, investigations on supramole-cular complexes of crown ethers with organic molecules $^{26-33}$ are of particular interest because the positive charge of the organic molecule can be modified by protonation (pH variation)^{32a} and also by oxidation reaction.⁹ As an example, the interaction between secondary ammonium salts and crown ethers is generally acid-base controlled and may occurs through different modes of supramolecular interactions (face-to-face²⁸ or rotaxane^{27,29,30}). Generally, when phenyl moieties are present as terminal groups in secondary dialkylammonium salt guests they can act as stoppers to trap crown ether on the axle.^{31,29f} The 24-crown-8-ether derivatives are the most used macrocycles hosts to form rotaxanes;³¹ and for crown ethers with less than 24 atoms in their macrorings, the rotaxane formation is far from being accepted. Indeed, recent results suggest that smaller cavities are supposed to form only face-to-face complex with secondary dialkylammonium salts.²⁸ However, it should be noted that Zhang et al.³¹ have found that secondary dialkylammonium salts can thread through the cavity of benzo-21-crown-7-ether (B21C7) to form more strongly [2]-pseudorotaxane- and [2]-rotaxane-type structures than the those with dicyclohexyl-24-crown-8-ether (DC24C8).

Besides, mixed-valence species (MV),^{34–37} that is, systems that contain an element which exists in more than one oxidation state have interesting conductivity,^{34j} magnetic³⁴ⁱ and spectral properties.^{34k} Measuring the activation barriers for intervalence charge transfer (IV-CT) in MV compounds is of particular interest, because electron migration is a fundamental process in the operation of many systems, including catalysts, light-activated devices, non-linear optical materials, etc. Therefore, numerous investigations have been devoted to purely organic Robin/Day³⁸ molecules, and

particularly organic diamines with different substituents, to understand and control the IV-CT process in the MV compounds of these molecular models. The cation-radical of these organic diamines is described as the MV state (+1 and 0 state);^{35–37} where the comproportionation constant K_{co} ,³⁹ which indicates the MV stability, is measured by different techniques, such as electrochemistry and UV—vis, IR, and Raman spectroscopies.^{35,36} In previous work, Lambert and Nöll⁴⁰ succeeded in changing the IV-CT process by varying π -electron spacers in triarylamines. Nishiumi et al.^{35,36} modulated it by introducing substituents into one or other of the phenyl moieties of *N*,*N*-diphenyl-1,4-phenylenediamine (PDA). In these cases, modulation was obtained by chemical modification of the structure of the starting amine derivatives.

In this work, we demonstrated that 18-crown-6-ether (18C6) (Figure 1) can be used to modulate the stability of the cationic species and allows a gradual control of the IV-CT process in the MV compound generated by electrochemical oxidation of PDA (Figure 1). The high comproportionation constant is decreased by the presence of 18C6; this is the consequence of the formation of a supramolecular complex between 18C6 and the PDA⁺² dication. In acetonitrile, this complex is highly stable and is formed after cation-radical oxidation at higher potential, whereas it dissociates on the backscan at low potential. Varying the solution acidity can modify the potential range where the MV compound predominates. Consequently, both 18C6 concentration and acidity can be used as external stimuli to easy control of this range and of the lifetime of the MV compound.

Moreover and for comparison purpose, the results obtained on the electrochemical behavior of PDA with dibenzo-24-crown-8-ether (DB24C8) (Figure 1) are reported. The nature of the interaction between each of the crown ethers and PDA⁺² dication is discussed and highlight the face-to-face interaction rather than the rotaxane interaction in both systems.

Our approach contrasts with the chemical modification of the structure of the diamine compounds reported before^{34,36,40} and seems a promising advance for the design of new types of switchable molecular devices.

2. EXPERIMENTAL SECTION

2.1. Chemicals. *N*,*N*-Diphenyl-1,4-phenylenediamine (PDA) was purchased from Aldrich. It was dissolved in ethanol, stirred and recovered as slightly gray crystals. These were filtered and dried in vacuum. 18-crown-6-ether (Aldrich) and dibenzo 24-crown-8-ether (Aldrich) were used as received. Acetonitrile (Aldrich, HPLC grade) and the supporting electrolyte, tetrabuty-lammonium hexafluorophosphate (TBAPF₆) (Aldrich, electrochemical grade), were used without further purification. Trifluoroacetic acid (TFA) (Sigma Aldrich, 99%) was used as received.

2.2. Electrochemistry. Electrochemical analyses were carried out in a one-compartment three-electrode cell using an EGG 273A potentiostat. A 0.07 cm² glassy carbon disk, a Pt grid, and a saturated calomel electrode (SCE) were used as working electrode, counter-electrode and reference electrode, respectively. The working electrode was polished carefully with diamond paste (3 and 1 μ m), rinsed in acetone with ultrasonic stirring and then air-dried immediately prior to use.

Cyclic voltammetry (\overline{CV}) was carried out in acetonitrile, containing PDA and 0.1 M TBAPF₆ with or without TFA and crown ether, at potential scan rates in the 20–200 mV s⁻¹ range.

2.3. Spectroelectrochemistry. In situ spectroelectrochemical measurements were carried out on 18C6 at room temperature in the same solution used for electrochemical measurements. The necessary amount of solid crown ether was added to the solution



Figure 2. Cyclic voltammograms of 5.0×10^{-4} M PDA in acetonitrile containing 0.1 M TBAPF₆ at scan rates from 10 to 200 mV s⁻¹ and T = 25 °C.

to obtain a given [18C6]/[PDA] ratio. The very small volume effect on the total volume of the solution (10 mL) was neglected. The UV-vis spectroelectrochemical experiments were carried out using a photodiode array UV-visible-NIR spectrometer MCS 501 UVNIR (Carl Zeiss). The light sources were halogen CLH 500 20 W and deuterium CLD 500 lamps with an optical fiber 041.002-UV SN 012105 using a 1 mm quartz cell (Hellma) and an automatic shutter. For this experiment, we used a Pt grid as working electrode, Ag/AgCl as reference electrode and a platinum wire as counter-electrode.

3. RESULTS AND DISCUSSION

3.1. Electrochemistry in Neutral Acetonitrile. Cyclic voltammograms of PDA in acetonitrile containing 0.1 M TBAPF₆ show (Figure 2) two reversible one-electron oxidation processes at scan rates between 10 and 200 mV s⁻¹. The first anodic peak corresponds to the formation of PDA⁺ cation-radical and the second to the PDA⁺² dication species. The electrochemical behavior of PDA in the absence of crown ether (Figure 2) is similar to that reported by Nishiumi et al. 36,37 Under our conditions, the standard potential values are 445 mV for the first transfer and 846 mV for the second (Table 1).⁴¹ The standard potential splitting ΔE_{t} , corresponding to the difference between the two standard potentials and related to the interaction intensity between redox sites, is 401 mV; and the comproportionation equilibrium constant³⁹ (K_{co}) is 6.0 \times 10⁶, indicating the high stability of the PDA^{+.} cation-radical. This corresponds to a large electron delocalization between the two amine centers in the MV compound and supports the high IV-CT rate constant $k_{
m th}$ = 1.35 imes 10^{10} s⁻¹ calculated from spectroelectrochemical data (Tables 2 and 3), according to the approach described by Lambert et al. 40,42

The cyclic voltammograms of PDA in the presence of 18C6 (Figure 3) do not show any marked change in the shape and the standard potential of the first transfer process, suggesting no significant interaction between 18C6 and neutral or the MV compound under these conditions.^{43,44} The peak potential of the second redox process changes significantly, falling by about 210 mV at a [18C6]/[DPA] ratio of 20/1 (Table 1), indicating that the dication forms more easily when 18C6 is present. This is due to a thermodynamically favorable interaction with the dication^{45–49} and results from the formation of a hydrogen

Table 1. Standard Potentials of First and Second Redox Processes of PDA for 0.1 M TBAPF₆ in Acetonitrile with or without TFA or 18C6 ([18C6]/[PDA] = 20/1)

		E° (mV/SCE) without 18C6	E° (mV/SCE) for[18C6]/[PDA] = 20
neutral acetonitrile	first charge transfer E_1°	445	445
	second charge transfer E_2°	846	634
acetonitrile containing trifluoroacetic acid	first charge transfer $\stackrel{{}_\circ}{E_1}$	624	554
	second charge transfer E_2°	898	828

Tał	ole 2.	Absorpti	on Maxima	Observed	l for	PDA	Transcient	: S	pecies i	in I	Difl	ferent	Me	edia	ı wit	h or	' with	lout	180	26
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	withou	at 18C6	with	18C6
	cation-radical	dication	cation-radical	dication
Wavelength (wavenumber) in Neutral ACN	387 nm (25840 cm ⁻¹) 697 nm (14347 cm ⁻¹)	526 nm (19011 cm ⁻¹)	387 nm (25840 cm ⁻¹) 697 nm (14347 cm ⁻¹)	539 nm (18553 cm ⁻¹)
Wavelength (Wavenumbre) in TFA-ACN	389 nm(25707 cm ⁻¹) 704 nm (14205 cm ⁻¹)	507 nm (19724 cm ⁻¹)	389 nm (25707 cm ⁻¹) 704 nm (14205 cm ⁻¹)	517 nm (19342 cm ⁻¹)

Table 3.	Band Sh	ape Data for t	the IV-CT	of PDA MV	Compound	Obtained	under D	ifferent Ex	perimental	Conditions
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medium	$r/\text{\AA}$	$v_{\rm max}/{\rm cm}^{-1}$	$\nu_{1/2}/\mathrm{cm}^{-1}$	$\varepsilon/\mathrm{M}^{-1}~\mathrm{cm}^{-1}$	V/cm^{-1}	α	$\Delta G^*/\mathrm{J}~\mathrm{M}^{-1}$	$k_{\rm th}/{\rm s}^{-1}$
Neutral acetonitrile	5.56	14347	$6.22 imes 10^3$	$6.22 imes 10^3$	$2.75 imes 10^3$	1.93×10^{-1}	1.35×10^3	$1.35\times10^{1}0$
[18C6]/[PDA] = 20 in neutral acetonitrile	5.56	14347	6.33×10^3	4.40×10^3	2.34×10^3	$1.63 imes 10^{-1}$	$1.62 imes 10^3$	3.60×10^9
TFA - acetonitrile	5.56	14205	5.85×10^3	$3.71 imes 10^3$	2.06×10^3	$1.44 imes 10^{-1}$	$1.81 imes 10^3$	$1.44 imes 10^9$
[18C6]/[PDA] = 20 in TFA - acetonitrile	5.56	14205	7.56×10^3	$5.81 imes 10^3$	$2.93 imes 10^3$	$2.05 imes 10^{-1}$	$1.24 imes 10^3$	$2.27 imes 10^{1}0$



Figure 3. Cyclic voltammograms of 5.0×10^{-4} M PDA in acetonitrile containing 0.1 M TBAPF₆ with and without 18C6, at scan rate 50 mV s⁻¹ and T = 25 °C at different [18C6]/[PDA] ratios.

bound-based supramolecular complex between 18C6 and the PDA⁺² dication species. At even high 18C6 concentration (i.e., [18C6]/[PDA] = 200/1, results not shown) ΔE decreases further, but the two redox processes do not overlap totally, showing that the MV compound persists, in a more restricted potential range. The PDA^{+2} dication interaction with 18C6 dramatically affects the comproportionation constant. Indeed, at [18C6]/[PDA] = 20/1, K_{co} is estimated to be 1.6×10^3 , corresponding to a decrease of about 3 orders of magnitude. This decrease indicates a large drop in the stability of the MV compound when 18C6 is present. The same interaction results also in a decrease in the electron delocalization between the two amine centers, indicated by a lower IV-CT rate constant $k_{\rm th}$ = 3.6 \times 10⁹ s⁻¹ at [18C6]/[PDA] = 20/1 (Tables 2 and 3). Consequently, when the 18C6 concentration is increased in this medium, (i) the lifetime of the MV compound falls, (ii) the MV compound exists only in a more restricted potential range, and (iii) the IV-CT rate constant decreases.

Affinity Constant Calculation. The voltammograms obtained for 10^{-3} M PDA at [18C6]/[PDA] = 10/1 show no change in the position of the potential peaks when the scan rate is increased from 20 to 200 mV s⁻¹ (Figure 4). This indicates that under these conditions, there is no kinetic effect on complexation between the different PDA species and 18C6. Consequently, when CV is used, the interaction between PDA⁺² and 18C6 is faster than a sweep rate as high as 200 mV s⁻¹.^{41,50} In order to evaluate the affinity of 18C6 toward PDA and its oxidation products, different 18C6 concentrations were used to estimate the association constants (K_a). For this purpose, we can assume a reversible E–C mechanism for an electrochemical reaction (E) corresponding to the oxidation of the MV compound followed by a chemical reaction (C) corresponding to the interaction of the dication with 18C6 (Figure 1). For this type of mechanism, the association constant (K_a) can be evaluated from the plot of the formal potential⁵¹ ΔE_p



Figure 4. Cyclic voltammograms of 10^{-3} M PDA in acetonitrile containing 0.1 M TBAPF₆ in solutions at [18C6]/[PDA] = 10/1 ratio, for scan rates from 20 to 200 mV s⁻¹ and T = 25 °C.



Figure 5. Plot of $\Delta E_p = (E_{p^{2ox(free)}} - E_{p^{2ox(compl)}})$ vs (log [18C6]) for 5×10^{-4} M PDA in acetonitrile containing 0.1 M TBAPF₆ at scan rate 50 mV s⁻¹.

versus total 18C6 concentration in solution (eq 1)

$$\Delta E_{\rm p} = E_{\rm p(free)} - E_{\rm complex} = 0.0592 \log(1 + K_{\rm a} [\rm{CE}]_{\rm total}^{p}) \qquad (1)$$

where $[CE]_{total}$ is the total 18C6 concentration, $E_{p(free)}$ is the oxidation peak potential of PDA⁺ cation-radical in 18C6-free solution and $E_{complex}$ is the oxidation peak potential of PDA⁺ cation-radical in the presence of a given 18C6 total concentration.

 K_a is the association constant of equilibrium 3 in Figure 1 and p is the stoichiometry of 18C6 in the complex:

$$K_{a} = \frac{\left[\left(\text{PDA}^{++}: p \times \text{CE}\right)\right]_{eq}}{\left[\text{PDA}^{++}\right]_{eq}\left[\text{CE}\right]_{eq}^{p}}$$



Figure 6. Cyclic voltammograms of 5.0×10^{-4} M PDA in acetonitrile containing 0.1 M TBAPF₆ with and without DB24C8, at scan rate 50 mV s⁻¹ and T = 25 °C at different [DB24C8]/[PDA] ratios.

Usually, we operate with a large excess of 18C6, and in this case the term " $K_a \times [CE]_{total}^p$ " is larger than unity; thus eq 1 can be simplified as follows:

$$\Delta E_{\rm p} = E_{\rm p(free)} - E_{\rm complex} = p \times 59.2 \log(K_{\rm a}[{\rm CE}]_{\rm total}) {\rm mV} \qquad (2)$$

In this case a 10-fold increase in [18C6] leads to a $p \times 59.2$ mV increase in ΔE_p at 298 K. Consequently, a plot of ΔE_p versus $\log[CE]_{total}$ should lead to a linear correlation, the slope of which gives the stoichiometry, "p"; while the association constant (K_a) can be calculated from the intercept.

In our case, the plot of the formal potential (ΔE_p) versus $\log[CE]_{total}$ (Figure 5) exhibits typically the behavior described above, and the slope is about 110 mV, which corresponds to p = 2, and means that one dication interacts with two 18C6 molecules as shown in Figure 1; and the corresponding association constant (K_a) was calculated to be $7.0 \times 10^7 \text{ M}^{-2}$. This value indicates clearly the formation of very stable hydrogen bound-based supramolecular complex between the PDA⁺² dication and two 18C6 molecules, where each of the two amine groups of the dication is surrounded by one 18C6 molecule (Figure 1).

The cyclic voltammograms of PDA in the presence of DB24C8 (Figure 6) show the same behavior than the one observed in the presence of 18C6 with the negative potential shift of only the second current wave when DB24C8 is present. For the same [crown ether]/[PDA] ratio, the potential shift is a little higher with 18C6 than with DB24C8, which indicates a more important interaction of PDA⁺² dication with 18C6. The value of the affinity constant of DB24C8 with PDA⁺² dication was equal to 2.9×10^3 for a 1:1 stoichiometry.

The fact that there is no interaction between the monocharged MV compound and each of the crown ethers is surprising since generally they interact with monocharged cations.^{26–33} The interaction is apparently prevented even between the MV compound and DB24C8 which has a large cavity, adapted to thread secondary amines containing aromatic moeties such as phenyl rings.^{29e,30,31} This means that an insuperable barrier hinders the complex formation with the MV compound; whereas, it does not exist in the interaction between PDA⁺² dication and the same crown ethers. The main difference is that a unique positive charge is delocalized on the MV compound as proposed above; whereas, in the PDA⁺² dication the two positive charges are located on each nitrogen atom of the two secondary amines. As a consequence, if the interaction of the mono charged MV compound with the crown ether occurs through a lateral



Figure 7. Cyclic voltammograms of 10^{-3} M PDA in acetonitrile containing 0.1 M TBAPF₆ with increasing TFA concentration, at scan rate 100 mV s⁻¹ and T = 25 °C.

face-to-face mode; the charge delocalization makes it difficult for crown ether to reach the partially charged amine groups to form the complex. On the contrary, the two localized positive charges in the PDA⁺² dication make its affinity rather high to overcome this barrier. This suggests that the localization of the charge on the nitrogen atom of a secondary amine seems to be a necessary driving force to lead to the interaction with crown ether.

This thermodynamically favorable complexation results probably from face-to-face interaction (Figure 1) and not through the inclusion of PDA⁺² dication in the cavity of the crown ether even in the case of DB24C8, the cavity of which is sufficiently large to generally allow rotaxane formation.^{30b}

3.2. Electrochemistry in Acetonitrile Containing TFA. When trifluoroacetic acid is added to 10^{-3} M PDA in acetonitrile containing 0.1 M TBAPF₆, the cyclic voltammograms of PDA still show the same two reversible oxidation processes (Figure 7) but both redox waves are progressively shifted to more anodic potentials as the TFA concentration increases, leveling off at about 1 M. At this ratio, the standard potentials are 624 and 898 mV for the first and second redox processes (Table 1), which correspond to shifts of about 180 and 60 mV, respectively, compared to their values in neutral acetonitrile solution. This is not unexpected: the result suggests that the two amine groups are protonated but that the oxidation of the MV compound is less affected than that of neutral PDA. In this medium, the potential splitting ΔE is 274 mV, and the corresponding comproportionation constant K_{co} is 4.3 \times 10⁴, which indicates that the MV compound is less stable than in neutral acetonitrile. The IV-CT rate constant (Tables 2 and 3) decreases to $k_{\rm th} = 1.4 \times 10^9 \, {\rm s}^{-1}$ indicating less electron delocalization between the two amine sites.

Moreover, in TFA-acetonitrile solution and in the presence of 18C6, the potentials of both redox processes are similarly shifted cathodically (Figure 8) to 554 mV and 828 mV for the first and second, respectively, at [18C6]/[PDA] = 20/1 (Table 1). This indicates that 18C6 interacts with both the initial PDA and with its oxidation products (Figure 9). The thermodynamically favorable interaction between 18C6 and each of the charged PDA products is possible due to their initially protonated state. Consequently, supramolecular complexes are formed with each of these products in TFA-acetonitrile solution. Since the standard potential splitting ΔE does not vary with 18C6 concentration, the comproportionation constant K_{co} of the MV compound remains the same whatever the [18C6]/[PDA] ratio. This indicates clearly that the stability of the MV compound in

TFA-acetonitrile is almost the same with or without 18C6, and that 18C6 shifts the MV potential range without significantly changing its lifetime. On the contrary, this behavior results in an increase in the IV-CT rate constant to $k_{\rm th} = 2.3 \times 10^{10} \, {\rm s}^{-1}$ for [18C6]/[PDA] = 20/1 (Tables 2 and 3) indicating more electron delocalization between the two amine centers.

This clearly indicates that, varying the acidity and/or the 18C6 concentration makes it possible to modulate the rate of the IV-CT process, the lifetime and the potential range of the MV compound.

3.3. In Situ Spectroelectrochemistry. 18C6 induces important modifications in the voltammograms of PDA. It should also cause some differences in the UV–visible spectra, which allow determination of the IV-CT band of the MV compound. UV–visible spectra were studied in situ, in the presence and in the absence of 18C6 during potential sweep between –500 and 1200 mV versus Ag/AgCl, in neutral and acidified acetonitrile. Absorption maxima are summerized in Table 2.

In 18C6-free acetonitrile containing 5 10^{-4} M PDA (Figure 10), when the potential is scanned between -500 and 700 mV, the spectrum shows two absorption maxima at 387 and 697 nm



Figure 8. Cyclic voltammograms of 10^{-3} M PDA in acetonitrile containing 1 M TFA and 0.1 M TBAPF₆ in the absence of 18C6 and in the presence of increasing 18C6 concentration, at scan rate 100 mV s⁻¹ and T = 25 °C.

(Figure 11), observed on the forward and backward scans and attributed to the cation-radical. The band at 697 nm is assigned to the IV-CT excitation associated with a photoexcited electron transfer from a neutral amine center to a cation-radical amine center in the MV compound.^{36,37} When the potential is increased from 700 to 1200 mV, both peaks disappear and a new one appears at 526 nm, corresponding to the $\pi - \pi^*$ transition in the PDA⁺² dication^{36,37} (Figure 11). This peak disappears during the backward scan.

In the same medium and at ratio [18C6]/[PDA] = 20/1 (Figure 12), when the potential is scanned from -500 to 700 mV, the spectrum still shows the same absorption peaks at almost the same wavelengths. This confirms that there is no interaction between the MV compound and 18C6, as reported by the electrochemical results. However, when the potential exceeds 700 mV, the peak which was at 526 nm is red-shifted by 13 to



Wavelength / nm

Figure 10. In situ spectroelectrovoltammogram of 5.0×10^{-4} M PDA in acetonitrile containing 0.1 M TBAPF₆ at 50 mV s⁻¹ scan rate. Full 3D spectra at varying potential.



Figure 9. Oxidation and interaction equilibria of PDA in acetonitrile in (A) absence and (B) presence of 18C6.



Figure 11. Spectra of 5.0×10^{-4} M PDA in acetonitrile containing 0.1 M TBAPF₆. Blue line: At maximum absorption for PDA⁺ cation-radical (with or without 18C6); red line: at maximum absorption for PDA⁺² dication without 18C6. Black line: At maximum absorption for PDA⁺² dication at [18C6]/[PDA] = 20/1.



Figure 12. In situ spectroelectrovoltammogram of 5.0×10^{-4} M PDA and 0.1 M TBAPF₆ in acetonitrile at [18C6]/[PDA] = 20/1 and 50 mV s⁻¹ scan rate. Full 3D spectra at varying potential.

539 nm in the presence of 18C6 (Figure 11). This shift is already observed at [18C6]/[PDA] = 1/1 and remains constant for higher ratios. This observation indicates that the dication interacts with 18C6 (Figure 9), in good agreement with the previous electrochemical results.

The in situ UV—visible spectrum (not showed) of PDA in 1 M TFA acetonitrile exhibits almost the same two absorption maxima 389 nm instead of 387 and 704 nm instead of 697 nm (Table 2), which were attributed to the cation-radical. This indicates that TFA does not significantly affect the IV-CT band. The absorption maximum of the second oxidation species (Table 2) is observed at 507 nm, which corresponds to a blue shift of 20 nm when compared to the value measured in neutral acetonitrile; probably due to the protonation of the second oxidation product in the presence of TFA.

The large values of K_{co} obtained in neutral solution with and without CE, indicate the high stability of the mixed valence cation radical species. The presence of the absorption band at 697 nm (Figure 11) in neutral medium with and without CE confirms the

mixed valence nature of the cation radical. Furthermore, this band matches with Gaussian shape at higher energy region, whereas it does not overlap with a Gaussian shape on the low-energy one. This result indicates that MV cation radical is classified as Class II rather than Class III system. Moreover, the data listed in table 3 shows that, $V \ll v_{\rm max}$ in all the studied media, which confirms a regime of relatively weak electronic coupling between the redox sites corresponding to Class II system.³⁴⁶

When 18C6 is added ([18C6]/[PDA] = 20/1), the two absorption maxima (Table 2) of the first oxidation product are not significantly modified. This does not mean that 18C6 does not interact with the MV compound. Indeed, the interaction was confirmed by electrochemical investigations, which show that all PDA species interact with 18C6 in this medium. Probably the MV compound, free and interacting with 18C6, has the same absorption spectrum, and both forms are protonated with at least three positive charges (Figure 8). This situation is very favorable to allow strong interactions.

Nevertheless and just as observed in neutral acentonitrile, we also observe a red shift of the absorption maximum of the second oxidation product, from 507 nm in 18C6-free solution to 517 nm when 18C6 is present at [18C6]/[PDA] = 20/1 (Table 2). This red shift confirms that 18C6 interacts strongly with the second oxidation product.

The localization of the charge on each of the two nitrogen atoms results in a favorable interaction strongly supported by the red-shift observed for the dication absorption peak when crown ether is present.

4. CONCLUSION

The possibility of forming supramolecular complex based on weak intermolecular interactions is used for the first time to successfully modify the charge distribution between a pair of aromatic (redox) centers in a mixed-valence compound of PDA a purely organic Robin/Day molecule. The intensity of this interaction can be modulated by changing either the acidity of the solution and/or the concentration of the crown ether macrocycle as external stimuli.

The addition of 18C6 in neutral acetonitrile does not modify the lower limit value of the of MV potential range, but decreases its upper limit. Consequently, the comproportionation constant and the IV-CT rate constant are lowered, indicating a large decrease of the MV stability and lifetime and less electron delocalization between its two amine centers when 18C6 is present. The same results are observed for DB24C8 with lower amplitude indicating a less important effect with DB24C8. This has been attributed to the formation of a reversible supramolecular complex between each of the crown ether and the dication, following the oxidation of the crown ether-free MV compound. The supramolecular complex is very stable at high potential values $(K_a = 7.0 \times 10^7 \text{ M}^{-2} \text{ for } 18\text{C}6/\text{PDA} \text{ system and } K_a =$ $2.9 \times 10^3 \,\mathrm{M^{-1}}$ for DB24C8/PDA system) and dissociates at low potentials. The complex structure corresponds to face-to-face mode and not to rotaxane one even with DB24C8.

When TFA is added, the MV potential range is gradually shifted to more anodic values; whereas the addition of 18C6 gradually shifts it to more cathodic values. Both waves shift results from a strong interaction of the oxidation products with 18C6 corresponding to the formation of hydrogen bound-based supramolecular complexes between 18C6 molecules and each of the PDA species: the starting molecule and its two oxidation products. In this medium, the comproportionation constant of the MV compound remains the same whatever the [18C6]/ [PDA] ratio, suggesting that the MV compound is stable with or without 18C6, but the addition of 18C6 significantly increases the IV-CT rate constant between the two amine centers.

In situ UV-visible absorption spectroscopy confirms the interaction of 18C6 with initial PDA and its oxidation products in TFA acetonitrile medium and with only the second PDA oxidation product in neutral acetonitrile. When 18C6 is present, the IV-CT rate constant decreases in neutral acetonitrile, whereas it increases in TFA-acetonitrile.

To the best of our knowledge, this work shows for the first time the possible control of the IV-CT process, the lifetime and the potential range of the MV compound. This control is not obtained as usual by chemical modification of the structure of the starting molecule, but simply by varying medium acidity or crown ether concentration as external stimuli, which leads to a more or less favorable formation of reversible hydrogen bound basedsupramolecular complex.

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