

Oxidative Coupling of Small Oligothiophenes and Oligopyrroles in Water in the Presence of Cyclodextrin. Flash Photolysis Investigations

P. Hapiot,^{*,†} C. Lagrost,[†] S. Aeiyaeh,[‡] M. Jouini,[‡] and J.-C. Lacroix[‡]

Laboratoire d'Electrochimie Moléculaire et Macromoléculaire, UMR 6510, Synthèse et Electrosynthèse Organiques, Université de Rennes 1, bât. 10C, Campus de Beaulieu, 35042 Rennes Cedex, France, and Interface, Traitement, Organisation et Dynamique des Systèmes (ITODYS), Université Denis Diderot – Paris 7, 1 rue Guy de la Brosse, 75005 Paris, France

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The oxidation of small oligothiophenes (bithiophene and terthiophene) and bipyrroles has been investigated by flash photolysis in aqueous solutions containing hydroxypropyl- β -cyclodextrin (HP β CD), which forms 1:1 host–guest inclusion compounds with the studied oligomers. The photochemical oxidation in the aqueous solution produces the corresponding cation radicals, which are identical to those observed in organic solvents. These cation radicals are rapidly expelled from the cyclodextrin host after their formation. Contrarily to what is generally proposed for oligothiophene cation radicals in the presence of water, these intermediates do not react with water or cyclodextrin and dimerize by a fast “cation radical–cation radical” coupling mechanism as generally observed in organic solvents (kinetics rate constants in the range of $10^9 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$). Interestingly, the consecutive deprotonations of the produced dihydrodimer dication appear to be much faster in water than in organic solvents (generally used for electropolymerization). This point can be a great advantage for the electrosynthesis of the polymer because slow deprotonation reactions are generally responsible for the formation of defects. These reactions were found to be faster during the oxidation of bithiophene than for bipyrrole (in agreement with the higher aromaticity energy of thiophene than of pyrrole) and decrease with the chain length.

Introduction

Organic conductive polymers are an attracting class of materials that combine the optical and electronic properties of semiconductors with the mechanical properties of plastics.^{1,2} Electropolymerization by anodic oxidation of various monomers leading to the growth of such a polymer on the electrode is commonly performed in organic solvents, except for polypyrrole and polyaniline which can be synthesized in aqueous medium.^{3,4} However, considerable advantages such as industrial facilities, low cost of fabrication, and environmental safety can be found in performing this polymerization in water. Thiophene monomers and oligothiophenes do not usually polymerize in aqueous solution, essentially because of their lack of solubility in water and their high oxidation potentials. The influence of water on the polymerization process remains an open question and despite numerous studies, such an effect is still under debate.^{5–10} For thiophenes, the presence of water in the organic media is reported to depress dramatically the efficiency of the electropolymerization,¹¹ and it is believed that the cation radicals resulting from thiophene oxidation can be very reactive toward water molecules.^{12,13} Nevertheless, acidic solutions or anionic micellar solutions have been successfully used to polymerize thiophene derivatives in water.¹⁴ The situation is different for polypyrrole formation. It has been shown that the quality (film adherence, film morphology, conductivity) of the produced polymer was greatly improved when a small quantity (1 wt %)

of water was added in a solution of pyrrole in acetonitrile¹⁵ while dimerization of a pyrrole oligomer (ter-, quarter-, penta-, and heptapyrrole) does not require water addition.^{16,17} On the contrary, the oxidation of bipyrrole in dry acetonitrile does not lead to formation of polypyrrole.¹⁸ Similarly, when protons are present in the solution, several types of polypyrroles are obtained in which acidic environments have a detrimental or favorable effect, depending on the electrolytic media, concentration of acid, and water.^{9a}

The electropolymerization mechanism is a multistep process. It involves the formation of carbon–carbon bonds between two cation radicals and then the release of two protons to rearomatize the produced dihydrodimer dication.^{9,19} This dication is a reactive species that can lead to the formation of defect if the rearomatization reaction is not fast enough. For pyrrole, the favorable effect of the presence of water has been explained by the stronger basicity of water than pyrrole that helps the capture of the released protons.^{9,10} It is generally admitted that the electropolymerization of thiophene and pyrrole compounds follows the same type of mechanism. Therefore, some similarities should exist among oligopyrroles and oligothiophenes, despite that the former ones are considered not to polymerize in water.⁴

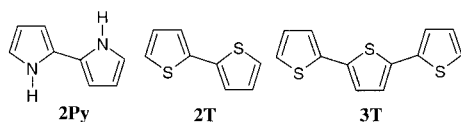
In this context, we recently proposed another strategy to polymerize oligothiophenes in aqueous media, on the basis of the use of cyclodextrin (CD) to improve their solubility.^{20,21} Cyclodextrins are cyclic oligosaccharides with a hydrophobic internal cavity and a hydrophilic outer side. Since the dimensions of bithiophene (**2T**) molecules fit well the size of the inner cavity of β CD and hydroxypropyl- β -cyclodextrin (HP β CD), they form stable 1:1 inclusion compounds, cyclodextrin being the host,

* To whom correspondence should be addressed. E-mail: philippe.hapiot@univ-rennes1.fr.

[†] Université de Rennes 1.

[‡] Université Denis Diderot–Paris 7.

SCHEME 1



bithiophene being the guest. The electropolymerization of **2T** in aqueous HP β CD solution allows the formation of a polybithiophene composite film.²⁰ Interestingly, experiments performed with quartz crystal microbalance indicate that the reaction could lead to a partial encapsulation of the polymeric chains.²²

Besides the interest in the understanding of these reaction steps to improve the preparation and the properties of new encapsulated polymers, these systems give a unique chance to investigate the effects of water and bases in the polymerization process and to compare the cation radicals reactivity in organic and in aqueous media. In this work, we focus on the reactivity of small oligothiophenes (bithiophene and terthiophene) and bipyrrrole cation radicals in aqueous HP β CD solution. Because of the lack of solubility of oligothiophenes, direct studies in water are difficult to achieve and very little was known about the reactivity of oligothiophenes cation radicals in aqueous media. In the pyrrolic series, the water solubility of bipyrrrole is higher and allows the investigation of the coupling processes in water by electrochemical or radiolytic methods. In these experimental conditions, it was shown that the bipyrrrole cation radical decays by bimolecular reactions (coupling between two cation radicals).¹⁰

In the present work, we used flash photolysis to investigate the homogeneous oxidation of bipyrrrole and small oligothiophenes in water in the presence of HP β CD. To get insight about the water effect, the kinetics decays of the produced cation radicals have been analyzed and compared with the results obtained in organic solvents and in pure water (when the oligomer solubility is high enough). Effects of the complexation by the HP β CD on the different chemical steps were also studied in detail as they play a fundamental role on the structure of the obtained polymers.

Experimental Section

Chemicals. 2,2'-bipyrrrole (**2Py**) was prepared according to a previously described procedure.¹⁶ Bithiophene (**2T**) (Acros), terthiophene (**3T**) (Acros), and hydroxypropyl- β -cyclodextrin (HP β CD) (Aldrich) were used as received. Distilled water, which was used as solvent, was purified with a Millipore system. Formation of the inclusion compounds between **2T** and HP β CD²⁰ and between **2Py** and HP β CD²³ were studied before. The stoichiometry of all these complexes were 1:1 (in the 10^{-2} mol·L⁻¹ HP β CD concentration range) and the association constants were in the range 1000 to 4000 L·mol⁻¹.

Flash Photolysis Experiments. Fresh solutions of **2Py** (10^{-3} mol·L⁻¹) or **2T** (10^{-4} mol·L⁻¹) containing various concentration of HP β CD were prepared as follows: aqueous solutions of **2Py** were prepared by bubbling N₂O in water containing 10^{-1} mol·L⁻¹ of KBr while 10^{-2} mol·L⁻¹ K₂S₂O₈ was added to aqueous HP β CD solutions of **2T**. The pH was adjusted by using KOH or acetic buffer. Irradiations were performed with a Questek Laser 2048 (100–130 mJ, 20–50 ns) using a XeCl mixture ($\lambda = 308$ nm). The detection system consisted of a 150-W Xenon lamp, a 1.5-cm optical path length irradiation quartz cell, a SP 150 spectrograph (ARC), and an intensified diode array system (PG200 pulsed generator, ST-121 controller, and IRY-700 S/RB detector from Princeton Instruments, Inc).

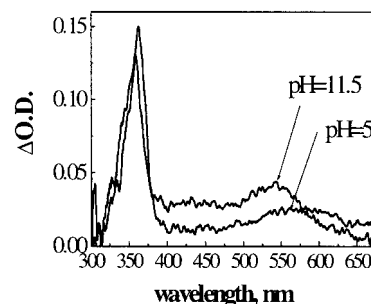
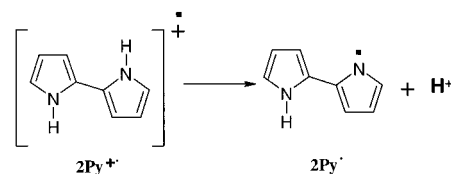


Figure 1. Flash photolysis of **2Py** (10^{-3} mol·L⁻¹) in N₂O-saturated aqueous solution containing 10^{-2} mol·L⁻¹ HP β CD and 10^{-1} mol·L⁻¹ KBr, at pH = 5 and at pH = 11.5 monitored 3 μ s after the LASER pulse (showing the differential absorption spectra of the produced radical species).

SCHEME 2



For the acquisition, the pulse width was set to 100 ns and the delay after the laser pulse was adjusted as short as possible to avoid the observation of laser flash. Spectra were averaged 10 times to improve the ratio signal/noise. For kinetic experiments, the detection system consisted of a Jobin–Yvon high-intensity monochromator and a Hamamatsu photomultiplier.¹⁰ The signal were digitized with a Nicolet 450 digital oscilloscope and analyzed by a PC. The Gepasi 3.0 software[©] was used to extract by a fitting procedure the deprotonation kinetics rate constants from the flash photolysis experiments.²⁴

Results and Discussion

Identification of the First Intermediates Produced by Irradiation of Bipyrrrole, Bithiophene, and Terthiophene in Water with and without Cyclodextrin. β -cyclodextrins have a suitable cavity size for incorporation of small oligothiophenes or oligopyrroles.²⁵ In the present study, we used hydroxypropyl- β -cyclodextrin, which is more soluble in water than the unsubstituted β -cyclodextrin. Small oligothiophenes are insoluble in water (solubility in the range of 10^{-7} to 10^{-6} mol L⁻¹) but quite soluble in the presence of HP β CD (up to several 10^{-2} mol L⁻¹ for bithiophene). Bipyrrrole is sufficiently soluble in pure water to allow a comparison of its behavior in the presence of cyclodextrin and in pure water. The stoichiometry of all these complexes were found to be 1:1 for concentrations of HP β CD in the 10^{-2} molar range and the oligomers concentrations used in this work.^{20,23}

Differential spectra recorded 3 μ s after irradiation of a **2Py**–HP β CD solution at different pH are shown in Figure 1. They exhibit a sharp peak around 360 nm and a broad band centered at 540–580 nm. The same spectra were obtained in the presence or in the absence of cyclodextrin indicating that the same intermediates are produced. Comparison of these transient spectra with those obtained with pulse radiolysis experiments²³ allows us to ascribe the spectra observed at low pH to the cation radical **2Py**^{•+} and at higher pH to the neutral radical **2Py**[•], arising from the deprotonation of cation radical (Scheme 2). (Cation radicals of bipyrrrole are weak acids in water with, for instance, a pK_a of 8.7 for methylbipyrrrole.¹⁰)

Since the maximum absorption shows a linear dependence with the energy of the excitation pulse, it can be concluded that

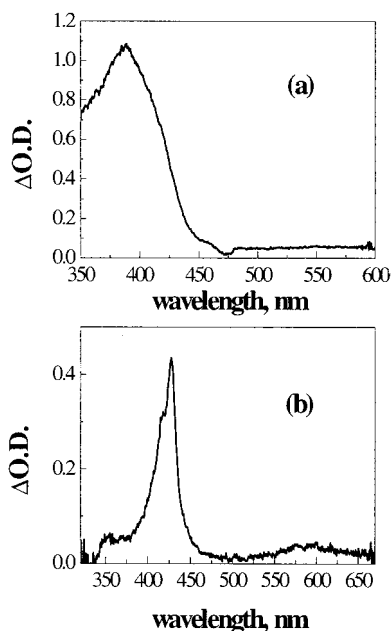
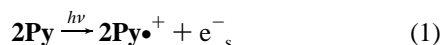


Figure 2. (a) Flash photolysis of aqueous solution of **2T** (10^{-4} mol·L $^{-1}$), HPβCD (3×10^{-4} mol·L $^{-1}$) recorded 500 ns after the LASER pulse, showing differential absorption spectrum of produced transient species. (b) Differential absorption spectrum of **2T** $^{\bullet+}$ recorded in the same experimental conditions except 5 μs after the laser pulse in the presence of the quencher K₂S₂O₈ (10^{-2} mol·L $^{-1}$).

a monophotonic process is mainly involved in the photochemical production of radical species. For values of energy of the excitation pulse similar to those used in this work, it has been shown that photochemical production of terthiophene cation radicals in dichloromethane solution did not involve the triplet state but a direct monophotonic ionization of terthiophene.²⁶ Because bipyrrrole is easier to oxidize than terthiophene,¹⁰ it is likely that the formation of the initial radical cation occurs by a similar process in water:



To limit the possibility of a recombination process between the solvated electrons and reduced species, experiments have been performed in saturated-N₂O (+KBr 10^{-1} mol·L $^{-1}$) aqueous solution.²⁷

As mentioned above, the solubility of bithiophene in water is too weak to allow flash photolysis investigations without cyclodextrin. Therefore, experiments have been carried out with HPβCD concentrations higher than 3×10^{-4} mol·L $^{-1}$. Absorption spectra monitored just after (500 ns) the laser pulse ($\lambda = 308$ nm) in a deaerated aqueous **2T**–HPβCD solution display a broad and intense band around 385 nm. This absorption remains visible 400 μs after the laser pulse (Figure 2a) and corresponding to the triplet state of the bithiophene, **³2T**.²⁸ Under air, the decay of **³2T** becomes much faster (<10 μs) in agreement with the fact that bi- and terthiophene are potent singlet oxygen sensitizers.²⁹ After 10 μs, an intense peak at 420 nm and a weaker broad band at 580 nm are observed and are ascribed to the bithiophene cation radical, **2T** $^{\bullet+}$, absorption.²⁸ Experiments making use of a strong oxidant like potassium persulfate, K₂S₂O₈, as an aqueous phase quencher were also carried out. In that case, the triplet absorption is rapidly converted to another one displaying features of **2T** $^{\bullet+}$, showing that an electron transfer occurs from **³2T** to the ground-state S₂O₈²⁻ (see Figure 2b). The same experiments have been

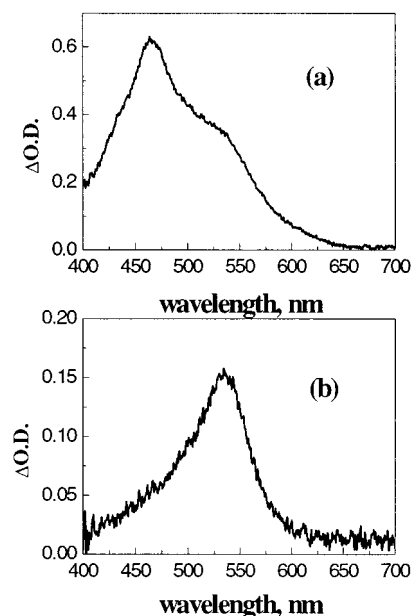


Figure 3. (a) Flash photolysis experiments of aqueous solution of **3T** (2×10^{-4} mol·L $^{-1}$), HPβCD (7×10^{-3} mol·L $^{-1}$), showing differential absorption spectrum of produced transient species, monitored 3 μs after the LASER pulse. (b) Differential absorption spectrum of **3T** $^{\bullet+}$ recorded in the same experimental conditions except 10 μs after the laser pulse in the presence of the quencher K₂S₂O₈ (2×10^{-2} mol·L $^{-1}$).

performed with higher concentrations of HPβCD (up to 10^{-1} mol·L $^{-1}$) and similar absorptions have been observed. In addition, we also observed that the **³2T** lifetime increases indicating a protective effect of the HPβCD toward the excited state, phenomenon which is well-documented in the cyclodextrin literature.^{25,30}

Parallel experiments have been also achieved with terthiophene **3T**. Since the water solubility of **3T** is lower than that of **2T**, we used higher HPβCD concentrations. Similarly to the **2T** behavior, a large absorption around 460 nm is visible just after the pulse corresponding to the triplet state **³3T** of terthiophene (Figure 3a).²⁵ A long-lived species (>800 μs), insensitive to the presence of oxygen, absorbing at 535 nm is also observed and can be ascribed to the cation radical **3T** $^{\bullet+}$.²⁵ In presence of 2×10^{-2} mol·L $^{-1}$ of persulfate, the absorbance of **³3T** disappears in less than 5 μs, **³3T** being converted into the cation radical **3T** $^{\bullet+}$ whose absorption is located at 535 nm (Figure 3b).

From these first experiments, we can conclude that the photochemical oxidation of **2Py**, **2T**, and **3T** in water and in aqueous cyclodextrin leads to the formation of their corresponding cations radicals, showing that the same chemical intermediates are produced by flash photolysis in aqueous media as in acetonitrile. Moreover, the presence of HPβCD in the solution does not result in any modification of the nature of the produced species.

2Py $^{\bullet+}$ Kinetics Decays. Figure 4 displays the differential spectra recorded a long time after the pulse (1 ms) of a **2Py** solution in acidic and basic media. In acidic media, a residual absorption around 360 nm corresponding to coupling products (neutral quaterpyrrole, **4Py**) is observed,³¹ while no such absorption is noticeable in experiments performed in basic media. These results agree well with experiments previously reported in acetonitrile.¹⁰ Only the cation radicals, but not the neutral radicals, have been shown to produce higher oligopyrroles, explaining the inhibition of pyrrole polymerization by

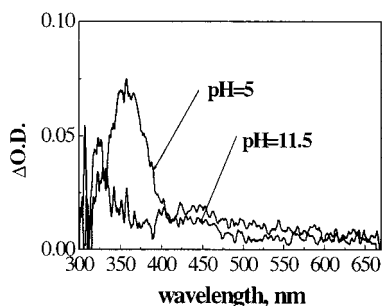


Figure 4. Flash photolysis of N_2O -saturated aqueous solution of 2Py ($10^{-3} \text{ mol}\cdot\text{L}^{-1}$), $\text{HP}\beta\text{CD}$ ($10^{-2} \text{ mol}\cdot\text{L}^{-1}$), and $10^{-1} \text{ mol}\cdot\text{L}^{-1}$ KBr showing differential absorption spectra recorded 1 ms after the LASER pulse at $\text{pH} = 5$ and at $\text{pH} = 11.5$.

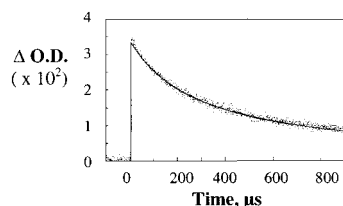


Figure 5. Decay of 2Py^+ monitored at 580 nm in N_2O -saturated aqueous solution containing $10^{-1} \text{ mol}\cdot\text{L}^{-1}$ KBr , $10^{-3} \text{ mol}\cdot\text{L}^{-1}$ 2Py at $\text{pH} = 5$. The line is the second-order fit.

strong bases. The variations of the transient absorption were studied as a function of time in both acidic and basic media.

At low pH ($\text{pH} = 5$), that is, under such experimental conditions as 2Py^+ is produced, the absorbance decay monitored at 580 nm is found to fit a second-order law (Figure 5). The value of the kinetics rate constants of the carbon–carbon bond formation was derived from the decay, and no variation of the value was found with the different energy pulses (variation of the cation radical concentration), confirming the second-order nature of the decay. A (pseudo) first-order reaction should be observed if the cation radical reacted with water, $\text{HP}\beta\text{CD}$, or with neutral oligomers that are all present in large excess versus the produced radical cation. Since the decays fit a second-order law, we deduced that the former processes do not occur in our systems (or have only minor contributions) and that the cation radicals decay via a cation radical–cation radical coupling process (dimerization). This result is in agreement with previously published electrochemical investigations where it was found that the carbon–carbon bond formation occurs through the same coupling mechanism.¹⁰ In pure water (without cyclodextrin), a value of $2k_{\text{dim}} = 9 \times 10^8 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ is found. After addition of $8 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ of $\text{HP}\beta\text{CD}$, the kinetics rate constant is almost unchanged ($2k_{\text{dim}} = 7.8 \times 10^8 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$),³² showing that the presence of cyclodextrin has no influence on the cation radical decaying process and suggesting that the cation radical is not included inside the cyclodextrin host. Indeed, if the cation radical was included inside the cyclodextrin, a shielding effect because of $\text{HP}\beta\text{CD}$ would prevent the cation radical from reacting with another molecule.³³ Consequently, the absence of such an effect indicates that the coupling between two cation radicals occurs outside the cyclodextrin cavity, and thus the cation radical is rapidly expelled outside the cyclodextrin after its formation.

2Py^+ Kinetics Decays. At higher pH, the cation radical 2Py^+ is rapidly deprotonated to produce a neutral radical 2Py^\bullet .²³ We found that 2Py^\bullet also decays by a bimolecular process. However, on the contrary to the measured dimerization rate of the cation radical that was not sensitive to the concentration of cyclodextrin, the second-order decay of 2Py^\bullet was strongly dependent

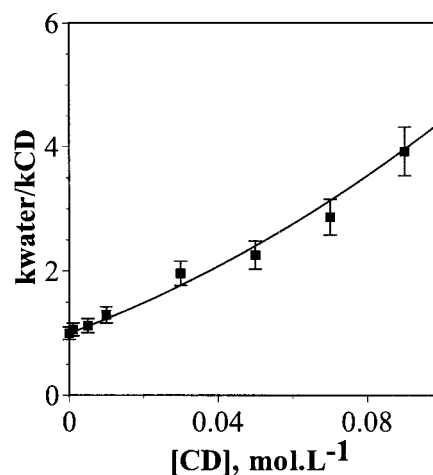
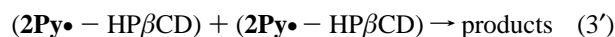
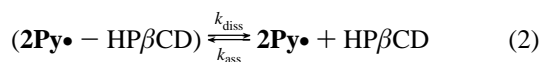


Figure 6. Variation of the second-order rate decay of 2Py^\bullet with the cyclodextrin concentration measured as the ratio between the value in water k_{water} and the value in the presence of $\text{HP}\beta\text{CD}$ k_{CD} as function of the cyclodextrin concentration in $\text{mol}\cdot\text{L}^{-1}$. The line is the parabolic fitting for $K = 11 \text{ mol}\cdot\text{L}^{-1}$ (see text).

on the $\text{HP}\beta\text{CD}$ concentration, showing a protective effect of the $\text{HP}\beta\text{CD}$ toward the bimolecular reaction. As displayed in Figure 6, the relative variation of the rate constant, $k_{\text{water}}/k_{\text{CD}}$, with the $\text{HP}\beta\text{CD}$ concentration (k_{CD} is the apparent second-order rate constant measured in the presence of $\text{HP}\beta\text{CD}$, k_{water} is the second-order rate constant in the absence of $\text{HP}\beta\text{CD}$) clearly demonstrates that the neutral radical is included inside the cyclodextrin. The next question is to determine whether the coupling reaction occurs between two complexed radicals (reaction 3') or if one or both radicals have to leave the host to react (reactions 2 + 3).

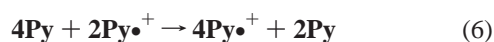
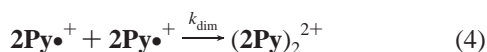


If the equilibrium (2) is fast, (i.e., equilibrium (2) acts as a pre-equilibrium prior the reaction step (3), or $k_{\text{ass}}[\text{HP}\beta\text{CD}] \gg k_{\text{water}}[2\text{Py}^\bullet]_0$), the ratio $k_{\text{water}}/k_{\text{CD}}$ follows a parabolic law: $k_{\text{water}}/k_{\text{CD}} = 1 + 2K[\text{CD}] + K^2[\text{CD}]^2$ where $[\text{CD}]$ is the concentration of $\text{HP}\beta\text{CD}$ and K is the thermodynamic association constant ($K = k_{\text{ass}}/k_{\text{diss}}$).³⁴ A good agreement was found between our experimental data and the parabolic variation leading to a value $K = 11 \text{ L}\cdot\text{mol}^{-1}$. At this point, we can discuss on the validity of the assumption that (2) is a fast equilibrium and on its influence on the determination of K . Indeed, a kinetics limitation due to a slow dissociation of the complex would give an apparent higher K value. However in such a case, a first-order decay should also be observed when the dissociation reaction becomes rate-limiting. As explained before, a second-order law for the kinetics decay of 2Py^\bullet was found for all the cyclodextrin concentrations, which confirms the assumption of a fast equilibrium. This value $K = 11 \text{ L}\cdot\text{mol}^{-1}$ is much lower than the thermodynamic association constant measured between the bipyrrrole and $\text{HP}\beta\text{CD}$ ($1300 \text{ L}\cdot\text{mol}^{-1}$) but higher than the value for 2Py^+ since our flash photolysis experiments shows that the cation radical is rapidly expelled outside the cyclodextrin cavity before the dimerization. It can be deduced the relative order for the complexation constants by $\text{HP}\beta\text{CD}$: K (for 2Py) $\gg K$ (for 2Py^\bullet) $\gg K$ (for 2Py^+). This result is consistent with

previously published investigations on the electrochemical behavior of β CD complexes where the association constants are reported to be higher for the reduced guest than for its oxidized form.³⁵ From the weak value for K (for **2Py•**) and the parabolic variation of $k_{\text{CD}}/k_{\text{water}}$, we concluded that the second-order decay reaction for **2Py•** and **2Py•⁺** involves the free radical species (not complexed).

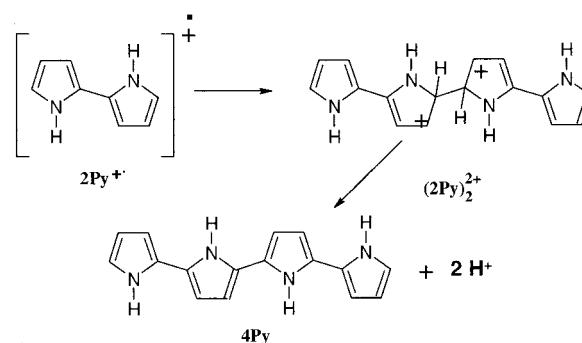
Deprotonation Reaction in Pyrrole Series. After the carbon–carbon bond formation reaction, the next chemical step to produce the final quaterpyrrole is a deprotonation reaction (rearomatization). This reaction is an important step in the polymerization reaction, where the dication must eliminate two protons to permit the polymer to grow (see Scheme 3, same reactions occur during bithiophene polymerization). Pyrrole and oligopyrroles are weak bases that undergo protonation at the 2- and 3-positions, which under acid conditions can react with another pyrrole to form a nonconjugated dimer (2,2'-(1'-pyrrolinyl)pyrrole) and other nonconducting polymers.³⁶ It has been suggested that the defects observed in polypyrrole can be related to the formation of such nonconjugated oligomers (see references 5–10, 37, and references therein). In a previous work,¹⁰ we noticed that quaterpyrrole was not stable in acetonitrile at pH below 7–8, and it is likely that protonated quaterpyrrole may undergo the same type of condensation reactions. To limit the influence of these side reactions and the formation of defects in the polymer, the generated protonated dication (**(2Py)₂²⁺**) has to be deprotonated as fast as possible and the released protons have to be trapped to avoid protonations of the other pyrrole species (the starting bipyrrrole, for example).

Experimentally, it is difficult to study the kinetics of the deprotonation reaction or the formation of **4Py** as their expected absorption bands are in the same wavelengths ranges as those of **2Py** or **2Py•⁺** (or even below).¹⁰ However, the oxidation potential of the oligopyrrole decreases with increasing size of the oligomer. For example, the quaterpyrrole is more readily oxidized than bipyrrrole, which is more readily oxidized than pyrrole.¹⁶ Consequently, the quaterpyrrole **4Py** formed after the deprotonation reaction will be immediately oxidized to its cation radical **4Py•⁺** by **2Py•⁺** if the deprotonation step is faster than the lifetime of **2Py•⁺**. In electrochemical investigations,¹⁰ this phenomenon was clearly observed in acetonitrile and allowed to estimate that the deprotonation rate constant k_{H} , in acetonitrile, is in the range of 0.1 s⁻¹.



In our experiments performed in water, a remaining absorbance recorded a long time after the laser pulse (after 10 ms) is seen in the 370-nm range similar to the known spectra of the neutral quaterpyrrole **4Py**. However, no absorbance around 518 and 980 nm¹⁰ that could be ascribed to the radical cation **4Py•⁺** was visible. It means that reaction 6 does not occur because **2Py•⁺** has disappeared before **4Py** is produced because of the slower deprotonation of **(2Py)₂²⁺** arising a long time after the carbon–carbon bond formation. Since neutral **4Py** is observed on absorption spectra recorded 1 ms after the pulse, a large increase of the deprotonation rate occurs, comparing with the behavior observed in dry acetonitrile (reaction time of several seconds).¹⁰

SCHEME 3



2T•⁺ Decay and Consecutive Deprotonation Reactions of 2T Dihydrodimer Dication. The decay of **2T•⁺** observed at 580 nm has been studied for different HP β CD concentrations. In all cases, it fits a second-order law (Figure 7) with a derived rate constant³⁸ $2k_{\text{dim}} = 6.8 \times 10^8 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ ($\lambda = 580 \text{ nm}$) which was found to be independent with the laser intensity. Experiments have also been performed after addition of K₂S₂O₈, to avoid interference with the absorption of the triplet state, and give similar results ($2k_{\text{dim}} = 6.4 \times 10^8 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$). The value of $2k_{\text{dim}}$ is not sensitive to the presence of HP β CD: for a HP β CD concentration of $3 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $2k_{\text{dim}} = 6.8 \times 10^8 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ while $2k_{\text{dim}} = 8.4 \times 10^8 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ in a $10^{-1} \text{ mol}\cdot\text{L}^{-1}$ HP β CD solution.³⁹ Therefore, similarly to what we obtained about the dimerization of **2Py•⁺**, it can be deduced that (i) **2T•⁺** is not included inside the cyclodextrin cavity, (ii) the dimerization occurs between two radical cations in water, outside the cyclodextrin host, and (iii) the cation radical of bithiophene does not react with water or cyclodextrin. The reactivity observed for **2T•⁺** in aqueous solution appears to be very similar to the one known in organic media.^{28,40}

Differential spectra recorded a long time (>0.5 ms) after the pulse show an absorbance located at 640 nm (Figure 8). This absorption maximum is ascribed to the absorption of the

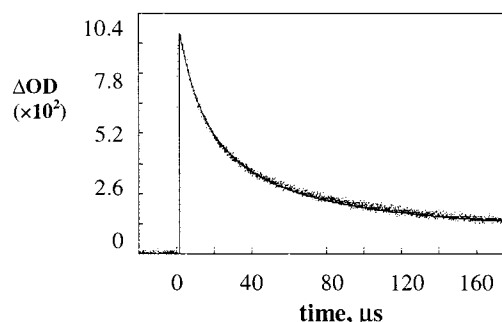


Figure 7. Decay of **2T•⁺** monitored at 580 nm in N₂O-saturated aqueous solution containing $10^{-1} \text{ mol}\cdot\text{L}^{-1}$ KBr, $10^{-4} \text{ mol}\cdot\text{L}^{-1}$ **2T**, and $3 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ HP β CD. The line is the second-order fit.

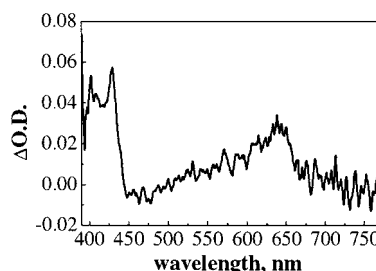


Figure 8. Flash photolysis of N₂O-saturated aqueous $10^{-4} \text{ mol}\cdot\text{L}^{-1}$ **2T**, $3 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ HP β CD, and $10^{-1} \text{ mol}\cdot\text{L}^{-1}$ KBr showing differential absorption spectra recorded 500 μs after the LASER pulse.

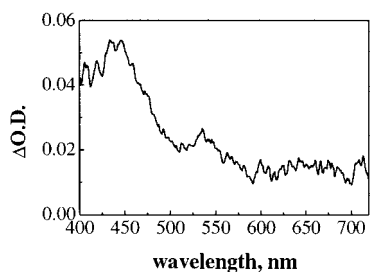


Figure 9. Flash photolysis of N_2O -saturated aqueous $2 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ **3T**, $7 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ HP β CD, and $10^{-1} \text{ mol}\cdot\text{L}^{-1}$ KBr showing differential absorption spectra recorded 1 ms after the LASER pulse.

quaterthiophene cation radical, **4T** $^{\bullet+}$.²⁶ Contrarily to what we observed for the bipyrrrole, the produced dimer appears clearly as its oxidized cation radicals. Thus, it can be deduced that the deprotonation reaction of the dication dihydrodimer (**2T**) $_2^{2+}$ involved during bithiophene polymerization is much faster than that of (**2Py**) $_2^{2+}$. It is consistent with the fact that the aromaticity energy is higher for thiophenes (29 kcal/mol) than for pyrroles (23 kcal/mol),⁴¹ resulting probably in a lower tendency to rearomatize for the pyrroles cation radicals than the corresponding thiophenes cation radicals. From simulation of the polymerization mechanism,²⁴ taking into account the values measured for k_{dim} and assuming that the homogeneous electron-transfer rate constant is closed to diffusion limit k_{diff} , we estimated a value of $k_{\text{H}} = 500 \text{ s}^{-1}$ for the deprotonation rate constant of (**2T**) $_2^{2+}$ in water. This value has to be compared with that obtained in organic solvent for similar dihydrodimers. For example, the deprotonation rate constants of (**2T**) $_2^{2+}$ for some substituted oligothiophenes were lower than 10 s^{-1} in acetonitrile.⁴²

3T $^{\bullet+}$ Decay. The very weak water solubility of **3T** requires a minimum HP β CD concentration of $7 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ to perform the experiments. The association constant was $K = 5800 \text{ L}\cdot\text{mol}^{-1}$,²⁸ meaning that, under our experimental conditions, most of the **3T** molecules are bound to HP β CD molecules. Another experimental difficulty with **3T** is the strong absorbance of the triplet state **3T**, which makes impossible the kinetics study during the first 100 μs . Addition of persulfate decreases considerably the lifetime of the triplet state allowing the study of the kinetics decay. However, the use of such a strong oxidant may also be a problem because the homogeneous oxidation of **3T** is likely to occur. An apparent second-order law ($2k = 5\text{--}6 \times 10^9 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) was found for the decay of the cation radical **3T** $^{\bullet+}$. This value has to be considered as overestimated⁴³ because of the possible presence of sexithiophene **6T** traces formed by oxidation of **3T** by persulfate and, consequently, the apparent rate constant may be found higher because of a possible reaction between **3T** $^{\bullet+}$ and **6T**. At longer time, it was possible to record spectra without using potassium persulfate (Figure 9). In these conditions, a maximum absorbance is observed around 440 nm, which can be ascribed to the formation of **6T**.⁴⁴ From this experiment, it can be deduced that the dimerization of **3T** $^{\bullet+}$ leads to the formation of the dimer, in accordance with the second-order nature of the decay, and that the cation radical undergoes no (or little) reaction with water molecules. There is no trace of any absorbance that can correspond to the formation of the cation radical **6T** $^{\bullet+}$ (expected in the 680–800 nm range), indicating that the deprotonation reaction of the (**3T**) $_2^{2+}$ dihydrodimer is much lower than that of the (**2T**) $_2^{2+}$ dihydrodimer. Such results suggest that the deprotonation rate constant tends to decrease with the chain length.

Conclusion. The use of cyclodextrin gives a unique way to study the reactivity of cation radicals of small oligothiophenes

and oligopyrroles in aqueous media, especially in the case of bithiophene and terthiophene for which the lack of water solubility does not allow such a study. After photochemical oxidation, the cation radical leaves the cyclodextrin host to undergo a coupling with another cation radical, similarly to the reaction occurring in organic media, with no considerable change in the reactivity. In particular, no reaction between cation radicals **2Py** $^{\bullet+}$, **2T** $^{\bullet+}$, or **3T** $^{\bullet+}$ and water or HP β CD molecules was observed. The dimerization rate constants **2Py** $^{\bullet+}$ and **2T** $^{\bullet+}$ are very close (near $10^9 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) both in acetonitrile and water as we may expect a higher reactivity for oligothiophene cation radicals than for the corresponding oligopyrroles. These high values are very close to the diffusion rate limit, k_{diff} , expected value for two positively charged species.⁴⁵ This behavior indicates that the bimolecular reaction is kinetically controlled by the diffusion of the reactants and does not reflect the exact intrinsic reactivity of the cation radicals. In basic media, the cation radical **2Py** $^{\bullet+}$ becomes a neutral radical **2Py** $^{\bullet}$, for which the reactivity is strongly sensitive to the presence of cyclodextrin. However, an association constant $K = 11 \text{ L}\cdot\text{mol}^{-1}$ between HP β CD and **2Py** $^{\bullet}$ was found, indicating that most neutral radicals leave the cyclodextrin cavity before reacting.

The deprotonation reaction consecutive to the dimerization of two cation radicals is much faster for bithiophene than for bipyrrrole, in agreement with the higher aromaticity of thiophenes derivatives. However, the deprotonation rate constant of bipyrrrole dihydrodimers appears to be higher in water than that in acetonitrile. This is an important point because the dihydrodimers resulting from the dimerization are very reactive species, which may generate defects in the polymer and even impede the polymerization itself, by reacting with nucleophilic species that are present in the electrosynthesis medium. To limit these side reactions, the rearomatization process has to be achieved as fast as possible. Our results, showing that a fast deprotonation reaction occurs for bithiophene and for bipyrrrole, indicate that HP β CD aqueous medium is a favorable medium to achieve the electrochemical polymerization of bipyrrrole and of bithiophene. We found this result especially interesting in the case of bithiophene for which it is commonly admitted in literature that water present in the synthesis medium causes inhibition of the electropolymerization process.

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- (32) Experimental error = $\pm 15\%$.
- (33) Such effects have been reported in several instances in the protection of excited states from reacting with quenchers.^{25,28,30} In particular, this protective effect was described for the quenching of **3T** triplet by methyl viologens or Cu(II)SO_4 in the presence of βCD .²⁵
- (34) In this treatment, we assume that the free and complexed radicals have a similar absorbance at the examined wavelength which is generally the case for most host complexes between organic molecules and cyclodextrins.
- (35) For instance, Mirzoian and Kaifer (b) have shown for water soluble viologens (**V**) that the oxidized form (V^{2+}) is weakly bound with βCD while the first reduced species ($\text{V}^{\bullet+}$) is more strongly bound with βCD , and the complexation of the neutral reduced species (**V**) is even stronger ($K = 20000 \text{ L} \cdot \text{mol}^{-1}$). Similar results have been established for nitroxide radicals (c), cobaltocenes (d), ferrocene derivatives (e, f). (b) Mirzoian, A.; Kaifer, A. E. *Chem. Eur. J.* **1997**, *3*, 1052. (c) Saint-Aman, E.; Serve, D. *New J. Chem.* **1989**, *13*, 121. (d) Wang, Y.; Mendoza, S.; Kaifer, A. E. *Inorg. Chem.* **1998**, *37*, 317. (e) McCormack, S.; Russel, N. R.; Cassidy, J. F. *Electrochem. Acta* **1992**, *37*, 1939. (f) Matsue, T.; Evans, D. H.; Osa, T.; Kobayashi, N. *J. Am. Chem. Soc.* **1985**, *107*, 3411.
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- (39) Because of the weak solubility of **2T**, it was not possible to measure its dimerization kinetics rate constant in pure water (i.e., without HP βCD). However, for a HP βCD concentration of $3 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, the ratio of the concentration of complexed **2T** to that of free **2T** is about 1, according to the association constant $K = 3600 \text{ L} \cdot \text{mol}^{-1}$ between **2T** and HP βCD .²⁰
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