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Radical-Pairing Interactions in a Molecular Switch Evidenced by Ion Mobility Spectrometry and Infrared Ion Spectroscopy

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Abstract: The digital revolution sets a milestone in the progressive miniaturization of working devices and in the underlying advent of molecular machines. Foldamers involving mechanically entangled components with modular secondary structures are among the most promising designs for molecular switch-based applications. Characterizing the nature and dynamics of their intramolecular network following the application of a stimulus is the key to their performance. Here, we use non-dissociative electron transfer as a reductive stimulus in the gas phase and probe the consecutive co-conformational transitions of a donor-acceptor oligorotaxane foldamer using electrospray mass spectrometry interfaced with ion mobility and infrared ion spectroscopy. A comparison of collision cross section distributions for analogous closed-shell and radical molecular ions sheds light on their respective formation energetics, while variations in their respective infrared absorption bands evidence changes in intramolecular organization as the foldamer becomes more compact. These differences are compatible with the advent of radical-pairing interactions

Introduction

[*]

At the interface between isolated entities and supramolecular assemblies lies a distinctive class of compounds referred to as mechanically interlocked molecules^[1,2] (MIMs). Exploiting the non-trivial topologies of rotaxanes and cate-

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nanes,^[3] MIMs are patterned around entangled molecular parts whose relative positioning may be purposely controlled.^[4] This unique structural property results in discreet co-conformational arrangements^[5] that may interconvert through the application of external stimuli, thereby generating a defined directional motion.^[6,7] Such features have been largely exploited in artificial molecular machines^[8-11] (AMMs), from the pioneering shuttle design^[12] to "smart" stimuli-responsive materials.^[13,14] When used as components of MIMs, donor-acceptor oligorotaxane foldamers rely on intramolecular charge-transfer complexes built around π - π stacking interactions and multiple [C-H-O] hydrogen bonds^[15,16] to oscillate between differentially folded and stretched co-conformations.^[17] [4]5NPR is a prototypical example of such systems^[18] and consists of a flexible poly(ethylene oxide) (PEO) dumbbell functionalized by 1,5dioxynaphthalene (DNP) donors, onto which are threaded three cyclobis(paraquat-*p*-phenylene) tetracationic



Figure 1. Structure and example of co-conformation for [4]5NPR¹²⁺ (PF₆⁻ counterions are not shown).

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(CBPQT⁴⁺) rings, each of them incorporating two 4,4'bipyridinium (BIPY²⁺) acceptor units (Figure 1). The structure is coordinated to a maximum of 12 intercalating $PF_6^$ counterions. Co-conformational transitions are triggered by tailoring the system's electrostatic balance consecutive to a change in the oxidation state of the viologen motifs, thus resulting in a redox-sensitive switching motion.^[19]

While oligorotaxane foldamers stand as a case study for investigating folding dynamics,^[20,21] they are also envisioned as ideal candidates for the development of conducting molecular wires^[22] in the framework of single molecule electronics^[23] (SME). Such a practical application would benefit from the emergence of conductive radical-pairing interactions between neighbouring viologen motifs as the acceptor units shift from their fully oxidized dicationic form BIPY²⁺ to their radical cationic form BIPY⁺⁺ following a redox stimulus.^[24] Although cyclic voltammetry experiments have demonstrated the capability of each viologen motif to accommodate one electron^[25,26] to possibly interact with each other,^[27] little is known about the structure of these radical species and how their interactions compete with donoracceptor interactions to affect foldamers' co-conformational landscape.

The present study exploits the option of electron-transfer dissociation (ETD)^[28] offered by mass spectrometry (MS) platforms to selectively generate and isolate intermediate oxidation states. While ETD has been previously used to characterize supramolecular complexes,^[29-32] we aim here to benefit from the energy-tempering properties of the buffer gas as a way to perform electron transfers without dissociation^[33,34] and induce successive charge reductions of viologen motifs^[35] embedded within [4]5NPR. The gas-phase equilibrium geometries of the consecutive products are subsequently interrogated structurally using MS interfaced with complementary structure-sensitive techniques, that is, ion mobility^[36] (IM) and infrared ion spectroscopy^[37] (IRIS).

Results and Discussion

Our strategy consists of promoting the co-conformational switching motion of [4]5NPR by tailoring its global charge state z using two different approaches (Figure 2). The first approach capitalizes on the distribution of multiply-charged ions inherently produced by electrospray ionization^[38] (ESI). Such ions carry different numbers of PF₆⁻ counterions but maintain all acceptor units in their oxidized dicationic form BIPY²⁺, therefore allowing the production of closed-shell ions ranging from [[4]5NPR⁺¹²(PF₆⁻)]¹¹⁺ to [[4]5NPR⁺¹²- $(PF_6^{-})_7]^{5+}$ (Supplementary Figure S1). The second approach relies on a reductive stimulus achieved through gas-phase non-dissociative electron transfers (ETnoD) performed inside the trapping region of the mass spectrometer through ion-ion reactions with an electron donor carrier.^[39] This process results in a gradual reduction of the acceptor units to their radical cationic form BIPY $\ensuremath{^{+}}$ with a fixed PF_6^- content, thus allowing the production of radical ions ranging from $[[4]5NPR^{+12}(PF_6^{-})]^{11+}$ to $[[4]5NPR^{+12}(PF_6^{-})]^{----5+}$ with a maximum of six transferred electrons (Supplementary Figure S2). Exploring both transitions permits portraying the co-conformational switching motion of an oligorotaxane foldamer in the gas phase, while comparing them helps in establishing the presence and structural effect of radical-pairing interactions.

Ion mobility relies on the transport properties of ions dragged by an electric field through a buffer gas.^[36] Drift time measurements allow retrieving an ion's collision cross section (CCS) Ω which gathers information related to its size and shape.^[40] While monitoring the relative fluctuations in the CCS along a reaction pathway is particularly appropriate for probing conformational rearrangements, absolute CCS quantities also constitute benchmarks that permit selecting representative structures within a pool of in silico generated candidates. These strategies are used here to unravel the co-conformational switching motion of [4]5NPR following a variation of its charge state z (Figure 3).

The ESI trend starts with a plateau associated with a single co-conformation at high charge states $z \ge 9 +$ before showing



Figure 2. Instrumental workflow used to characterize the co-conformational dynamics and intramolecular network of [4]SNPR. Ions are first of all generated using ESI. A precursor of interest is selected (here illustrated for z = 11 +), its charge state is possibly reduced using ETnoD (red) and the resulting products are analysed by a) IM and b) IRIS, both interfaced with MS.

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Figure 3. Ion mobility and computational results relating to the coconformational switching of [4]5NPR, following a variation of its charge state *z*. a) Variation of the CCS with *z* for ESI-generated closedshell species [[4]5NPR⁺¹²(PF₆⁻)_n]⁽¹²⁻ⁿ⁾⁺ and ETnoD-generated radical species [[4]5NPR⁺¹²(PF₆⁻)_n]^{x(11-x)+} starting from the *z*=11+ precursor. b) Equilibrium geometries of the most-abundant closed-shell co-conformations computed in vacuo at the PM6 level of theory. c) Detailed CCS distributions for *z*=7+ (ESI) and *z*=7+^{••••} (ETnoD).

a progressive decrease in the CCS from z = 9 + to z = 5 + withcoexisting stable co-conformations (Figure 3a). Using the semiempirical parametrized PM6 in silico approach,^[41] we correlated these observations with a stepwise folding of the foldamer. The process starts from elongated rod structures driven by electrostatic repulsions between the unscreened CBPQT⁴⁺ rings at high charge states and reaches a folded globular structure favoring π - π stacking interactions and [C– H…O] hydrogen bonding after progressive screening from the PF_6^- at low charge states (Figure 3b). In between lies a transition zone where the foldamer backbone progressively shrinks, first on one side (z = 8 +) and then on both sides (z =7+) to achieve a helical pattern (z=6+). The presence of coexisting co-conformations for a single charge state involves slight differences in the backbone folding and/or in the location of the coordinated PF₆⁻ counterions (Supplementary Figure S3).

The ETnoD trend achieved by a gradual reduction of the z = 11 + precursor to lower charge state radical species follows the same overall pattern as the ESI trend, suggesting that both processes qualitatively induce analogous folding pathways (Figure 3 a). The correlation between the two trends is especially good for high charge states, when the content in BIPY⁺⁺ units is low. As the number of transferred radicals increases, expressly starting from $z = 7 + \cdots$, variations regarding the absolute CCS quantities and co-conformational multiplicity appear (Figure 3 c). The first discrepancy here concerns the loss of the two satellite co-conformations at

 $^{\rm TW}{\rm CCS}_{N2\rightarrow {\rm He}}\,{=}\,870\pm37$ Å 2 and 969 ± 33 Å 2 in the ESI distribution and the appearance of a supplemental co-conformation at a higher ${\rm \widetilde{TW}CCS}_{N2 \rightarrow He}\,{=}\,1002\,{\pm}\,34$ ${\rm \mathring{A}}^2$ in the ETnoD distribution. This loss is likely attributable to drastically dissimilar mechanisms of ion formation for the two processes. Indeed, ESI involves the desolvation and ionization of analytes as they are transferred from the solution into the gas phase. The gradual solvent evaporation engenders a cooling effect that results in the release of "cold" gaseous molecular ions from internal energy perspectives.^[42] This situation limits the crossing of isomerisation barriers so that the subsequent gas-phase conformations may be kinetically trapped in local energy minima.^[43] The validity of this scenario was confirmed by performing collisional activation experiments which yielded a unique conformer under harsh energetic conditions (Supplementary Figure S4). On the other hand, ETnoD is associated with the transfer of electron(s) to a pre-formed gaseous molecular ion and thus corresponds to a transition from the gas-phase potential energy surface of the electrosprayed ionic precursor to that of the corresponding reduced radical product. This highly exothermic process involves the dissipation of the electronic recombination energy into accessible vibrational states of the product ion, resulting in "hot" gaseous radical ions.[44] Isomerisation to distant energy minima, with a memory of the precursor geometry (Supplementary Figure S5), may then become possible. The second discrepancy lies in a shift in the CCS of the principal co-conformation from $^{TW}CCS_{N2\rightarrow He} =$ 915 ± 34 Å² using ESI to 931 ± 30 A² after ETnoD. Although barely statistically significant, this gap may reflect minor differences in the foldamer folding possibly related to variations in its intramolecular interaction network.

Infrared (IR) spectral properties such as frequency, intensity and peak width are sensitive to local folding details and can be used to diagnose even minor variations in the strength and angle of resonant chemical bonds as well as in intramolecular interactions.^[45] In this context, IR spectroscopy appears as the ideal technique when it comes to identifying possible radical-pairing interactions along the co-conformational switching motion, thereby confirming hypotheses derived from IM datasets. IR Measurements were performed here using infrared ion spectroscopy^[37] (IRIS), and the corresponding action spectra were obtained by reporting the fragmentation yield of the selected precursor ion as a function of the irradiating photons' wavenumber $\tilde{\nu}$. Figure 4 illustrates the IR spectra of [4]5NPR acquired in the mid-infrared region as a function of its charge state z generated by ESI (Figure 4a) and after ETnoD on the z = 11 + precursor (Figure 4b). The typical MS/MS spectrum resulting from IR irradiation is shown in Supplementary Figure S6, irrespective of the charge and multiplicity of the precursor.^[46]

The ESI species display seven major absorption bands (Table 1), which were initially assigned based on in silico IR spectra generated for compact and elongated closed-shell configurations of [4]5NPR modelled at the PM6 level of theory (Supplementary Figure S7). The assignment of the four bands associated with CBPQT⁴⁺ was further validated after optimization of its isolated structure at the density functional theory (DFT) level (Figure 5a). The respective

Variations in the IR spectra when switching from ESI to ETnoD species concern i) the absence of the band at 840 cm⁻¹ (orange), which is awaited as the counterion content remains unchanged and fixed to a single PF_6^- throughout the complete reduction process, as well as ii) the retention of the

bands at 1150 cm^{-1} (cyan) and 1620 cm^{-1} (purple), and iii) the ap-



Figure 4. IR action spectra of [4]5NPR in different charge states z for a) ESI-generated species [[4]5NPR⁺¹²(PF₆⁻),₁]⁽¹²⁻ⁿ⁾⁺ and b) ETnoD-generated species [[4]5NPR⁺¹²(PF₆⁻)]^{x,(11-x)+} starting from the z = 11 + precursor. Major bands are coloured according to Table 1.

Table 1: Positions and assignments of IR bands for [4]5NPR.

Color	Apex	Assignment ^[a]	Localization
Red	750 cm ⁻¹	ρ (dithiolane)	End groups
Orange	840 cm ⁻¹	υ (P-F) _{op}	PF_6^-
Cyan	1150 cm^{-1}	$\upsilon (H_2 C \cdot N)_{op}$	CBPQT ⁴⁺ /CBPQT ²⁽⁺⁾
Yellow	1410 cm^{-1}	δ (C-H _{2,corner}) _{in}	CBPQT ⁴⁺
Green	1440 cm^{-1}	v (C=C _{ring semicircular}) _{ip}	CBPQT ⁴⁺
Blue	1510 cm ⁻¹	γ (C=C _{ring})	DNP
Purple	1620 cm^{-1}	υ (C=C _{ring,BIPY}) _{op}	CBPQT ⁴⁺ /CBPQT ²⁽⁺⁺⁾

[a] $\rho = rocking$, v = stretching, $\delta = in$ -plane scissoring, $\gamma = bending$, op = out of phase, ip = in phase.

intensities of the IR bands vary when decreasing the charge state z to result in i) a progressive appearance of the orange band and ii) a progressive extinction of the six other spectral bands. The former observation is explained by the increasing content in PF_6^- counterions when going from [[4]5NPR⁺¹²- $(PF_{6}^{-})^{1+}$ to $[[4]5NPR^{+12}(PF_{6}^{-})_{7}]^{5+}$. The second observation finds its roots in the orientation of the individual transition dipoles belonging to the resonant oscillators within the foldamer. For the elongated co-conformations, the three CBPQT⁴⁺ rings and the encapsulated DNP units are, respectively, parallel. The individual transition dipoles of the corresponding oscillators are then all aligned and add up constructively, thereby generating a large dipole moment and strong absorption bands.^[47] As the foldamer becomes more compact, the parallelism between the CBPQT⁴⁺ rings breaks down, leading to unaligned individual transition dipoles and to a progressive extinction of the associated spectral bands (Supplementary Figure S8).

pearance of two additional bands (gray), at 1250 and 1410 cm^{-1} as the charge state decreases. The comparison of in silico IR spectra computed for the isolated CBPQT⁴⁺ (Figure 5a) and CBPQT²⁽⁻⁺⁾ (Figure 5b) shows that the cyan and purple bands associated with out-ofphase vibrational motions are in common, while the yellow and green bands associated with in-phase vibrational motions are extinguished in the radical form. This observation results from differences in the geometry of both contenders: the two pyridinium rings constitutive of a closed-shell BIPY²⁺ unit are twisted by $\approx 45^{\circ}$ with respect to each other, whereas they are planar after the addition of one electron. CBPQT²⁽⁺⁾ consequently belongs to the symmetric D_{2h} point group and the in-phase vibrational motions are forbidden by IR selection rules. While these features rationalize the differences observed in the modulation of intensity between the yellow/green bands and the cyan/purple bands as the number of transferred radicals increases, the retention of the latter at low charge states is still to be explained. Indeed, IM data

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Figure 5. In silico IR spectra of a) CBPQT⁴⁺ and b) CBPQT²⁽⁺⁾ computed at the M06-2X/6-31 + G(d,p) level.^[53] Major bands are coloured according to Table 1.

agree with a trend of increasingly compact structures as zdecreases and, following the same reasoning as for ESI species, we would expect a progressive disruption in the alignment of the individual transition dipoles and a consecutive extinction of the spectral bands. Reciprocally, their preservation indicates that dipole alignment is conserved, suggesting a preferential orientation of the $CBPQT^{2(+)}$ rings. As such an alignment is not observed for compact folds bearing CBPQT⁴⁺, this orientation is likely driven by the formation of radical-pairing interactions between adjacent CBPQT²⁽⁺⁾ as they come into closer proximity during compaction of the foldamer.^[48] This hypothesis is further supported by the two grey bands appearing at low charge states and which show remarkable agreement with the totally symmetric (a,) vibrational modes probed by Raman spectroscopy on methyl viologen radical cations.^[49,50] The activation of these modes in IR results from a vibronic coupling as a consequence of enhanced charge transfer between dimerized species during the vibrational motion.^[51] Rationalized by the Ferguson-Person model,^[52] these IR absorption bands are related to an out-of-phase vibration of two paired radical cations which, when translated to [4]5NPR, implies radicalpairing interactions between CBPQT²⁽⁺⁺⁾ rings.

Conclusion

With the objective of unraveling the structural features of an oligorotaxane foldamer, the present study involves the hybrid utilization of a mass spectrometer both as a reactor, through gas-phase electron-transfer reduction, and as an analyzer, through interfacing with ion mobility and gas-phase infrared ion spectroscopy. By manipulating the charge state of the foldamer, we were able to induce co-conformational transitions as part of a switching motion. By selectively controlling the oxidation state of the CBPQT acceptor units, we were able to investigate the structural implications linked with the presence of radicals. Ion mobility data indicate similar folding trends for closed-shell and radical species. The major differences in their respective collision cross section distributions are related to the energetics of product formation: softer for ESI, which leads to kinetically trapped coconformations, and harsher for ETnoD, which makes it possible to populate distant local minima. IR action spectra are composed of seven major absorption bands whose respective intensities are deeply modulated according to the foldamer's charge state. Except for the band related to PF₆⁻ counterions, a compaction of the foldamer structure leads to progressive extinction of the vibrational bands for closedshell species, which was correlated to a randomization in the orientations of individual transition dipoles. For radical species derived from ETnoD, the vibrational bands related to CBPQT²⁽⁺⁺⁾ remain active throughout the complete folding pathway, an observation which, when considered along with the appearance of supplemental bands linked to vibronic coupling in dimerized radicals, demonstrate the advent of radical-pairing interactions.

We foresee that the combined methodology here applied could serve as a proof-of-concept when it comes to the structural interrogation of isolated electrochemically-sensitive molecular systems. It could efficiently complement existing protocols performed in solution that typically involve reductive agents^[54] or electrodes with varying potential, as in cyclic voltammetry^[55] and spectroelectrochemistry,^[56] in view of providing relevant structural data. This aspect is even more important since theoretical modelling of open-shell systems has proven non-trivial: the unrestricted Kohn-Sham formalism, at the basis of the density functional theory (DFT), is subjective to spin contamination,^[57] while more accurate alternatives, such as multireference methods, are still currently restricted to small systems.^[58] In this context, our method could be favourably used to monitor the conformational dynamics of redox-active systems such as switching rotaxanes,[59,60] transition-metal coordination complexes or enzymatic biomolecules.[61,62]

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Conflict of interest

The authors declare no conflict of interest.

Keywords: donor-acceptor foldamer · electron transfer · infrared spectroscopy · ion mobility · mass spectrometry

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