Successive translocation of the rings in a [3]rotaxane

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Abstract

A [2]rotaxane, a [3]rotaxane and the corresponding thread containing two succinamide (*succ*) binding stations and a central redox-active pyromellitimide (*pmi*) station were studied. Infrared spectroelectrochemical experiments revealed the translocation of the macrocycle between the succinamide station and the electrochemically reduced *pmi* station (radical anion and dianion). Remarkably, in the [3]rotaxane, the rings can be selectively translocated. One-electron reduction leads to the translocation of one of the two macrocycles from the succinamide to the pyromellitimide station, while activation of the shuttle via two-electron reduction results in the translocation of *both* macrocycles: the dianion, due to its higher electron density and hence greater hydrogen bond accepting affinity, is hydrogen-bonded to both macrocycles. Systems with such an on-command contraction are known as molecular muscles. The relative strengths of the binding between the macrocycle and the imide anions could be estimated from the hydrogen bond induced shifts in the C=O stretching frequencies of hydrogen bond accepting amide groups of the macrocycle.

Introduction

The concept of a “molecular machine” has inspired scientists already for several decades. Thanks to the advancement of synthetic methodology, many different types of molecular machines have been realized.^[1-5] Some of these have appealing analogies in the macroscopic world, such as valves^[6-8] and muscles.^[9-11] Others are better viewed as information processors,^[12] or function as single-molecular chemical factories.^[13,14] For the design of molecular muscles different approaches have been explored,^[15-18] but the use of mechanically interlocked building blocks is advantageous because it allows to put constraints on the relative movements of the components.^[19-27] In the present work, we describe the translation of either one or both of the macrocyclic rings in a [3]rotaxane by one-electron or two-electron reduction of a central diimide.

In previous studies in our laboratories, we have investigated the hydrogen bonding interactions between the macrocycle and the binding stations of rotaxanes that are switchable by electron transfer.^[28-33] Infrared spectroscopy has proven to be a powerful tool in these studies, because intercomponent interactions lead to specific spectroscopic signatures.^[29,34-38]

In this paper, the switching in [2] and [3]rotaxanes **2** and **3** (Scheme 1) containing a pyromellitimide (*pmi*) station is investigated by means of IR spectroelectrochemistry. The hydrogen bonding between the macrocycle and the reduced aromatic imide station is evaluated in terms of acceptor strength and spatial arrangement of the hydrogen bond accepting C=O groups. The binding of the macrocycle to the *pmi* station will be compared to the binding to the 1,8-naphthalimide^[28,29,36,37] and naphthalene diimides^[32] in the corresponding rotaxanes studied before.

Scheme 1 Structures of thread **1**, [2]rotaxane **2** and [3]rotaxane **3** equipped with a pyromellitimide (*pmi*) and two succinamide (*succ*) binding stations.

The electrochemical behavior of *N*-substituted pyromellitimides is characterized by two reversible steps (in DMF: -0.7 V and -1.4 V vs. SCE) corresponding to the formation of the radical anion and the dianion, respectively.^[39-41] In the reduced species, the additional electrons in the LUMO are stabilized by delocalization of the charge over the carbonyls through the aromatic ring. Compared to the naphthalimide station, the pyromellitimide contains a smaller aromatic core over which the excess electrons are delocalized. This is expected to result in higher electron densities on the carbonyls in the dianion, and hence a larger hydrogen bond accepting affinity compared to the naphthalimide case. On the other hand, the orientation of the C=O bonds is slightly different, which may affect the geometric complementarity with the amide donors on the benzylic amide macrocycle.

The macrocycle translocation in the pyromellitic rotaxanes **2** and **3** has been studied in our laboratory by means of UV-Vis spectroscopy.^[32,42] The differences between the electronic absorption spectra of electrochemically generated radical anions and dianions of the [2]rotaxane (**2**^{•-} and **2**²⁻), and thread (**1**^{•-} and **1**²⁻) were analyzed. In THF, only a marginal blue-shift (1 nm) and broadening of the D₀ → D₁ transition^[40] at 717 nm of **2**^{•-} relative to **1**^{•-} was observed. The absorption spectrum of the dianion **2**²⁻ showed a more pronounced signature of macrocycle translocation: a blue-shift of 17 nm (570 → 553 nm). Also in this case a band broadening was observed. The changes in the absorption spectra were sufficiently large to allow us to study the dynamics of the shuttling in a time resolved manner with transient absorption spectroscopy. The shifts of the absorption maxima of **2**^{•-} and **3**^{•-} relative to thread **1**, which are caused by hydrogen bonding of the reduced *p**mi* station with the macrocycle, were found to be similar (ca. 4 nm). The observed shuttling rate ($k_{shuttle}$) was larger for the [3]rotaxane ($k_{shuttle} = 3.3 \times 10^{-4} \text{ s}^{-1}$) than for the [2]rotaxane ($k_{shuttle} = 2.3 \times 10^{-4} \text{ s}^{-1}$).^[32,42]

Despite the fact that the change in band shape demonstrates the existence of interactions between the macrocycle and the radical anion of the pyromellitimide chromophore, the small shift could be a sign that the translocation of the macrocyclic ring might not be complete. In other words: a fraction of **2**^{•-} could still exist as the co-conformer in which the macrocycle resides at the succinamide station rather than at the reduced pyromellitimide station. The UV-Vis techniques that were used did not allow us to separately detect the two distinct co-conformers. Alternatively, even if shuttling is complete, the hydrogen bond interactions between the macrocycle and the reduced *p**mi* station might be too weak to substantially modify the electronic properties of the latter.

Infrared spectroscopy offers possibilities to complement the results obtained with the UV-Vis based techniques, because instead of looking at one single chromophore, several IR-active groups involved in the shuttling process can be probed. In particular, the amide groups of the macrocycle and the succinamide station, and the C=O stretching modes of the imide stations are exceptionally good probes for the study of hydrogen-bond stabilized conformers.^[33,36-38] The amide C=O stretching [$\nu(\text{CO})$], often called the Amide I band, and NH stretching [$\nu(\text{NH})$] frequencies are strongly affected by hydrogen bonds.^[43,44] Hydrogen bonding between amide groups decreases the NH and C=O bond orders in both acceptor amide and donor amide.^[34,38,45] Therefore, for amides involved in hydrogen bonding, generally a substantial red-shift of the $\nu(\text{CO})$ and $\nu(\text{NH})$ frequencies is observed.

In this work, the macrocycle positioning in **2** and **3** and their radical anions and dianions will be studied with infrared spectroelectrochemistry. The C=O stretching frequencies of the macrocycle [$\nu(\text{CO})_{mac}$], the succinamide station [$\nu(\text{CO})_{suc}$] and the pyromellitimide station [$\nu(\text{CO})_{pmi}$] will be used to identify the co-conformers formed upon electrochemical

reduction of **2** and **3** with one and two electrons. An interesting question is whether in the [3]rotaxane *one* or *both* macrocycles move to the reduced pyromellitimide station (Scheme 2). The infrared experiments can give more insight into this matter.

Scheme 2 Three different possible co-conformers of **3** resulting from translocation of one or both macrocycles.

Results and Discussion

Infrared Spectra

The Amide I regions of the IR spectra of compounds **1**, **2**, **3** and model compound **4** are shown in Figure 1A. The spectra were scaled to the intensity of the isolated band at $\sim 1723\text{ cm}^{-1}$ in order to facilitate comparison. The IR spectrum of **4** contains two bands in the Amide I region: a weak absorption at 1775 cm^{-1} and a strong one at 1724 cm^{-1} . These spectral features are in agreement with those reported in the literature for *N*-substituted pyromellitimides.^[39,46,47] The high frequency band is assigned to the symmetric C=O stretching [$\nu_s(\text{CO})_{pmi}$], while the low frequency band originates from antisymmetric C=O stretching [$\nu_{as}(\text{CO})_{pmi}$] of the imide as shown in Figure 1. The assignment of the bands was supported by B3LYP model calculations: two bands at 1776 cm^{-1} (weak) and 1733 cm^{-1} (strong) are predicted, which agrees nicely with the experimental result.

Figure 1 Amide I region in the IR spectra of model compound **4** and pyromellitimide thread **1**, [2]rotaxane **2** and [3]rotaxane **3** in THF. The spectra were scaled to the intensity of the $\nu_{as}(\text{CO})_{pmi}$ band at $\sim 1723\text{ cm}^{-1}$ in order to facilitate comparison. Vibrational modes and corresponding wavenumbers of the pyromellitimide model compound **4**.

The $\nu(\text{CO})$ bands of the pyromellitimide station in **1**, **2**, **3** are found at 1772 and 1723 cm^{-1} , almost at the same positions as in **4**. The slight band broadening in **1**, **2** and **3** compared to **4** indicates that the model compound **4** does not capture all the essential features of the pyromellitic station in **1**, **2** and **3**.

The bands of the pyromellitimide station are well separated from the $\nu(\text{CO})$ bands of the succinamide station [$\nu(\text{CO})_{succ}$] and the macrocycle [$\nu(\text{CO})_{mac}$]. In the IR spectrum of thread **1**, the characteristic band pattern of the succinamide station appears between 1690 and 1600 cm^{-1} .^[29,37] The strong band at 1677 cm^{-1} can be assigned to the unperturbed $\nu(\text{CO})_{succ}$ mode. The contribution from C=O stretching in intramolecularly hydrogen bonded conformations appears on the red side of the main band. A remarkable difference with the band pattern found in a previously studied succinamide model compound^[29] is the additional band at 1635 cm^{-1} . This band is assigned to $\nu(\text{CO})$ modes in folded conformations stabilized by intramolecular hydrogen bonds between the two succinamide stations (Scheme 3). The proposed structure of *folded-1* is stabilized by a hydrogen bonding motif which is very similar to the ones responsible for the stabilization of antiparallel β -sheets and β -hairpins in many proteins.^[48] The succinamide model compound has conformations with hydrogen bonds between the two amides of the succinamide unit. These hydrogen bonds lead to red shifts of 20 cm^{-1} , but the red-shift of the hydrogen bonded $\nu(\text{CO})_{succ}$ band of *folded-1* (42 cm^{-1}) is significantly larger implying that hydrogen bonding is stronger in *folded-1*. A reasonable explanation for this difference is that the geometries of the hydrogen bonds in *folded-1* are much more favorable than for the intra-

succinamide hydrogen bonds. Despite this, the relative intensities of the free and hydrogen bonded C=O stretching bands suggests that the folded conformations are of minor importance; the extended conformations are predominant.

Scheme 3 Structures of two possible conformations of thread **1**: the predominant extended and the minor folded conformations.

In the IR spectrum of [2]rotaxane **2**, an additional band is present at 1667 cm⁻¹ which originates from the macrocycle C=O stretching [$\nu(\text{CO})_{\text{mac}}$]. The free $\nu(\text{CO})_{\text{succ}}$ band (1677 cm⁻¹) is still present as a shoulder on the $\nu(\text{CO})_{\text{mac}}$ band at 1667 cm⁻¹, but it is less intense than in **1**. This is in agreement with our expectation. In **2**, one succinamide station is expected to be free, giving rise to free $\nu(\text{CO})_{\text{succ}}$ bands (as in **1**), while the other one is occupied by the macrocycle. The hydrogen-bonded $\nu(\text{CO})_{\text{succ}}$ band of the occupied succinamide station is red-shifted by 44 cm⁻¹ and appears at 1633 cm⁻¹.

For the [3]rotaxane **3**, apart from $\nu(\text{CO})_{\text{pmi}}$ bands, only two bands are observed in the 1600 – 1690 cm⁻¹ range of the IR spectrum: the $\nu(\text{CO})_{\text{mac}}$ band at 1667 cm⁻¹ and the hydrogen-bonded $\nu(\text{CO})_{\text{succ}}$ band at 1633 cm⁻¹. The latter is more intense than in **2**, because in **3** both succinamide stations are occupied and hydrogen-bonded to a macrocycle. For the same reason the free $\nu(\text{CO})_{\text{succ}}$ band is absent. Also, the $\nu(\text{CO})_{\text{mac}}$ is more intense because **3** contains two macrocycles.

The infrared spectra of the rotaxanes show that in the neutral molecules the macrocycles are practically exclusively located on the succinamide stations. In the ¹H NMR spectra (see Experimental Section and reference [32]) the free succinamide CH₂-protons give peaks at ~2.3 ppm, while they are shifted to 1.0 ppm when shielded by the macrocycle aromatic rings. The CH₂-protons near the imide station resonate at the same chemical shifts in the thread and in the rotaxanes. All these observations indicate a high positional integrity of the molecular shuttles in the neutral form.^[32,49]

Infrared Spectroelectrochemistry

Model Compound

Upon one-electron reduction of **4** four new red-shifted strong bands from the radical anion (**4**^{•-}) at 1661, 1653, 1642 and 1637 cm⁻¹ grow in at the expense of the bands of the neutral molecule (Figure 2).

Figure 2 Partial IR spectra of the neutral pyromellitimide model compound **4** (—), radical anion **4**^{•-} (····) and dianion **4**²⁻ (- - -) in THF.

An isobestic point is detected at 1690 cm⁻¹. This result is in agreement with spectra reported in the literature for an *N*-butyl substituted pyromellitimide.^[39] The fact that the spectrum of **4**^{•-} contains four bands is surprising, because the B3LYP calculation predicts the presence of only two bands, originating from the $\nu_s(\text{CO})_{\text{pmi}}$ mode at 1655 cm⁻¹ and the $\nu_{\text{as}}(\text{CO})_{\text{pmi}}$ mode at 1649 cm⁻¹. The presence of four bands in the experimental spectrum can be explained by Fermi resonance. The phenomenon of Fermi resonance may arise when two vibrational transitions (usually a fundamental and an overtone) possess the same transition energy and symmetry. In such cases of accidental degeneracy, the two modes can mix causing the

bands to shift apart in energy and share intensity. The weak overtone will gain considerable intensity due to mixing with the strong fundamental and can appear nearly as strong as the fundamental. Instead of observing only one strong band of the fundamental mode and a weak band from the overtone, two nearly equally intense bands may be observed. In the literature, some cases of Fermi resonances with the C=O stretching modes in neutral imides have been reported.^[50-54] For example, in *N*-substituted phthalimides, both the symmetric and antisymmetric C=O stretching vibrations are in resonance with an overtone of an Ar-CO mode, resulting in the splitting of each corresponding C=O stretching band into two equally intense bands.^[51] So far, examples of Fermi coupling of C=O stretching modes of mono- and dianions of aromatic imides have not been reported in literature.

In the case of **4^{•-}**, splitting of the $\nu(\text{CO})_{\text{pmi}}$ bands by Fermi resonance with an overtone can only occur if the fundamental of this overtone is at half the wavenumber of the fundamental $\nu(\text{CO})_{\text{pmi}}$ mode. The wavenumbers of the $\nu(\text{CO})_{\text{pmi}}$ modes are calculated at 1655 and 1649 cm^{-1} , so the fundamental of the interacting overtone must be at approximately 826 cm^{-1} . The B3LYP calculation indeed predicts a weak band at 827 cm^{-1} , corresponding to a deformation of the pyromellitimide skeleton. In the harmonic approximation, the overtone of this mode will have a wavenumber of 1654 cm^{-1} , which is at almost the same wavenumber as the $\nu(\text{CO})_{\text{pmi}}$ vibrations. Unfortunately, the presence of this band could not be confirmed with the experimental spectra, because of strong absorptions of the electrolyte (NBu₄PF₆) and solvent (THF) below 1000 cm^{-1} .

The four bands in the spectrum of **4^{•-}** can now be assigned, based on the conclusion that the observed band pattern result from splitting of the unperturbed $\nu_s(\text{CO})_{\text{pmi}}$ and $\nu_{as}(\text{CO})_{\text{pmi}}$ due to Fermi resonance. The first doublet of almost equally intense bands at 1661 and 1653 cm^{-1} is assigned to the $\nu_s(\text{CO})_{\text{pmi}}$ vibration in Fermi resonance with the overtone of the pyromellitimide skeleton deformation. In analogy, the doublet consisting of bands at 1642 and 1637 cm^{-1} is assigned to the $\nu_{as}(\text{CO})_{\text{pmi}}$ vibration.

For the dianion **4²⁻**, B3LYP calculations predict the presence of three bands: the $\nu_s(\text{CO})_{\text{pmi}}$, the $\nu_{as}(\text{CO})_{\text{pmi}}$ and an aromatic ring vibration [$\nu(\text{Ar})_{\text{pmi}}$]. Surprisingly, also for the dianion **4²⁻**, the experimental spectrum contains more bands. Six new bands are observed: two weak bands at 1713 and 1546 cm^{-1} , and reasonably strong bands at 1669, 1607, 1569 and 1517 cm^{-1} (Figure 2). Based on the result of the B3LYP calculation, three of these six bands can be assigned: the $\nu_s(\text{CO})_{\text{pmi}}$ at 1607 cm^{-1} (predicted: 1600 cm^{-1}) the $\nu_{as}(\text{CO})_{\text{pmi}}$ at 1569 cm^{-1} (1570 cm^{-1}) and the $\nu(\text{Ar})_{\text{pmi}}$ at 1517 cm^{-1} (1521 cm^{-1}). The other three bands (1713, 1669 and 1546 cm^{-1}) were not predicted by the B3LYP calculation. Therefore, we presume that these bands are due to overtones or Fermi resonance.

Macrocycle Translocation in the Radical Anions

The IR spectrum of the radical anion of the thread (**1^{•-}**, Figure 3A) contains two doublets due to Fermi resonance, belonging to the $\nu_s(\text{CO})_{\text{pmi}}$ (1659 and 1647 cm^{-1}) and the $\nu_{as}(\text{CO})_{\text{pmi}}$ mode (1641 and 1631 cm^{-1}). The wavenumbers were obtained after fitting the cluster of four bands to a sum of four Lorentzian peaks. The bands were assigned in analogy to **4^{•-}**. The average wavenumber of the bands of each doublet, which is an approximation of the wavenumber of the unperturbed vibration, is 1653 cm^{-1} for the $\nu_s(\text{CO})_{\text{pmi}}$ and 1636 cm^{-1} for the $\nu_{as}(\text{CO})_{\text{pmi}}$ mode. As was the case in the spectra of the neutral molecules, band broadening in **1^{•-}** compared to **4^{•-}** is also observed. The band patterns, however, are similar for **1^{•-}** and **4^{•-}**.

Figure 3 Parts of the IR spectra of neutral (—) and radical anion (····) of (A) pyromellitimide thread **1**, (B) [2]rotaxane **2** and (C) [3]rotaxane **3** in THF. The spectra of the neutral species were scaled to the intensity of the $\nu_{as}(CO)_{pmi}$ band at $\sim 1723\text{ cm}^{-1}$.

In order to highlight the changes caused by reduction of the *pmi* unit, the difference spectra of the threads and the rotaxanes, in which the spectra of the neutral forms are subtracted from the spectra of the corresponding radical anions, are displayed in Figure 4. The bands characteristic of the radical anion thus appear as positive, those of the neutral form as negative. When bands are not changed, they cancel, but small shifts are easily seen as narrow features, both positive and negative.

Figure 4 Difference IR spectra (radical anion minus neutral) of thread **1** (—), [2]rotaxane **2** (····) and [3]rotaxane **3** (- - -) in THF. The spectra were scaled to the intensity of the $\nu_{as}(CO)_{pmi}$ band at $\sim 1723\text{ cm}^{-1}$ before subtraction.

The difference spectrum of the thread **1** reveals the changes in the vibrations of the *pmi* unit upon reduction. The major bands are the characteristic ones of the pyromellitimide C=O stretching: negative $\nu(CO)_{pmi}$ bands of the neutral molecule and the positive $\nu(CO)_{pmi}$ bands of the radical anion. Some red-shifted broad bands are observed in the $1500\text{--}1610\text{ cm}^{-1}$ range. These can be ascribed to $\nu(CO)_{pmi}$ modes of folded conformations stabilized by hydrogen bonds between the succinamide stations and the reduced pyromellitimide station. Such folded conformations were also detected for the previously studied thread which contained succinamide and naphthalimide stations.^[29] The relative intensities of the unperturbed bands and the red-shifted bands show that the extended conformations are predominant.

The radical anions of the rotaxanes, **2**^{•−} and **3**^{•−}, exhibit a different band pattern compared to that of the thread **1**^{•−}. The difference spectra of both rotaxanes are strikingly different from that of **1**, but very similar to each other. Already two important conclusions can be drawn from this observation. First of all, it indicates that *a structural change has occurred in both rotaxanes*, and secondly: *this structural change is the same for both rotaxanes*. The only explanation for the difference between the difference spectra of thread and rotaxanes is that macrocycle translocation takes place.

The change of band pattern of the imide C=O vibrations is in part due to the absence of the Fermi resonance that splits some bands in **1**^{•−}, but not in the rotaxanes **2**^{•−} and **3**^{•−}. The red-shifted bands at 1632 and 1599 cm^{-1} are attributed to $\nu_s(CO)_{pmi}$ and $\nu_{as}(CO)_{pmi}$ modes of the pyromellitimide radical anion which is hydrogen bonded to the macrocycle. This red-shift causes a mismatch between the wavenumbers of the $\nu(CO)_{pmi}$ modes and the resonant overtone. Consequently, Fermi resonance is no longer possible in **2**^{•−} and **3**^{•−}. The red-shifts of the $\nu_s(CO)_{pmi}$ and $\nu_{as}(CO)_{pmi}$ bands (21 and 37 cm^{-1} respectively) compared to the corresponding bands (average of the band wavenumbers of each Fermi doublet) in **1**^{•−} reflect the bond weakening of the *pmi* carbonyls, caused by hydrogen bonding with the macrocycle.

Macrocycle translocation might be expected to lead to changes in the band pattern as a result of distortion of the symmetry of the reduced station. Upon binding of the macrocycle to one imide group, a redistribution of the electron density of the radical anion is likely to take place that will result in an increase of electron density on the imide group involved in hydrogen bonding. Consequently, the C=O bond strengths may change, and the two imide

groups can be expected to exhibit different $\nu(\text{CO})_{\text{pmi}}$ frequencies. The hydrogen bonded imide will give rise to red-shifted frequencies compared to the bare radical anion, while blue-shifted frequencies are expected from the free imide. Following this reasoning, additional bands are expected in the spectra of $\mathbf{2}^{\bullet-}$ and $\mathbf{3}^{\bullet-}$. Such blue-shifted bands, however, could not be resolved in the spectra of $\mathbf{2}^{\bullet-}$ and $\mathbf{3}^{\bullet-}$.

A possible hypothesis to explain this unexpected result is that the macrocycle binds to C=O groups of opposite sides (chair conformation in Figure 5) rather than the same side (boat conformation) of the diimide. In the chair-type hydrogen bonded complex, the two imide groups are equivalent. The preference of the macrocycle for binding to two imides can be made plausible with the following arguments. By placing the radical anion in the cavity of the macrocycle, the polar radical anion is shielded from the relatively non-polar solvent. Also, apart from stabilization by hydrogen bonds, π - π interactions between the benzene rings of the radical anion and macrocycle might lead to additional energy minimization. Definitive proof for this hypothesis can however not be provided by our IR method. Theoretical calculations can give more insight into the existence of the different proposed binding modes and the relative energies of the corresponding complexes.

Figure 5 Possible binding modes of the macrocycle to the *pmi* radical anion in $\mathbf{2}^{\bullet-}$.

Further evidence for translocation of the macrocycle is found in the changes of the C=O stretching frequencies of the succinamide station and the macrocycle. In the difference spectra of both $\mathbf{2}^{\bullet-}$ and $\mathbf{3}^{\bullet-}$, a positive free $\nu(\text{CO})_{\text{succ}}$ band at 1678 cm^{-1} is visible. So, the succinamide station is no longer hydrogen bonded to the macrocycle, which is clear evidence that the ring has moved: in the radical anion, the succinamide station is liberated. Remarkably, the intensities of the free $\nu(\text{CO})_{\text{succ}}$ bands of $\mathbf{3}^{\bullet-}$ and $\mathbf{2}^{\bullet-}$ are very similar. This means that in $\mathbf{3}^{\bullet-}$ only one succinamide station is liberated i.e. only one macrocycle has moved to the reduced pyromellitimide station, the other macrocycle stays at the succinamide station. So, *pmi-succ-3* $^{\bullet-}$ is the predominant co-conformer of $\mathbf{3}^{\bullet-}$ (Scheme 2). If both macrocycles of $\mathbf{3}^{\bullet-}$ would move to the pyromellitimide station, the intensity of the free $\nu(\text{CO})_{\text{succ}}$ band of $\mathbf{3}^{\bullet-}$ would be twice as high than for $\mathbf{2}^{\bullet-}$, because of the presence of two free succinamide stations.

The position switching of only one macrocycle in $\mathbf{3}^{\bullet-}$ indicates that simultaneous binding of both macrocycles to the *pmi* station does not lead to further energy minimization of the shuttle. In other words, the energy gain by formation of an additional set of hydrogen bonds with the *pmi* station does not compensate for the loss associated with breaking hydrogen bonds with the succinamide station. So, the affinity of the macrocycle for the singly occupied *pmi* station in *pmi-succ-3* $^{\bullet-}$ is lower than for the succinamide station. Apparently, hydrogen bonding on one imide polarizes the *pmi* radical anion, taking away the driving force for binding on the other side. In the chair binding mode (Figure 5) the *pmi* radical anion can obviously bind only one ring.

The C=O stretching of the macrocycle which is hydrogen-bonded to the *pmi* radical anion appears at 1664 cm^{-1} (Figure 3). In the case of the naphthalimide rotaxane, the corresponding band was observed at a lower frequency of 1660 cm^{-1} .^[29] Since shuttling takes place, one expects a negative peak at 1667 cm^{-1} from the C=O stretching in the macrocycle which was originally hydrogen bonded to the succinamide station. The dip between the bands at 1678 and 1659 cm^{-1} in the difference spectrum in Figure 4 is due to this contribution. The subtraction of the initial $\nu(\text{CO})_{\text{mac}}$ is also the reason for the distortion of

the $\nu(\text{CO})_{\text{succ}}$ (1678 cm^{-1}) band and the red-shifted new $\nu(\text{CO})_{\text{mac}}$ band.

The absorption between the peaks at 1664 cm^{-1} [$\nu(\text{CO})_{\text{mac}}$] and 1632 cm^{-1} [$\nu_s(\text{CO})_{\text{pmi}}$] in the spectra of $2^{\bullet-}$ and $3^{\bullet-}$ is attributed to hydrogen-bonded $\nu(\text{CO})_{\text{succ}}$ modes. In $\text{pmi-}2^{\bullet-}$, additional hydrogen bonding between the free succinamide stations is possible. These inter-succinamide hydrogen bonds are inhibited in $3^{\bullet-}$ because one succinamide station remains occupied by a macrocycle. This is clearly evident from the difference spectrum of $3^{\bullet-}$: the contribution of hydrogen-bonded $\nu(\text{CO})_{\text{succ}}$ modes between 1676 and 1659 cm^{-1} is smaller than in $2^{\bullet-}$. This is the only difference in the difference spectra of the radical anion and neutral forms of **2** and **3**. The assignments of the most important peaks in the spectra of neutral compounds and radical anions are summarized in Table 1.

Table 1 Wavenumbers (cm^{-1}) of IR modes in the amide I region of the neutral and radical anions of model compound **4**, thread **1**, and rotaxanes **2** and **3** in THF.

Macrocycle Translocation in the Dianion

A band pattern similar to that obtained for the dianion of model compound **4** can be recognized in the spectrum of 1^{2-} (Figure 6A). Five relatively red-shifted absorption bands from the pmi station are found at 1709 , 1659 , 1602 , 1573 and 1513 cm^{-1} . A counterpart of the weak band of 4^{2-} at 1546 cm^{-1} is not found in the spectrum of 1^{2-} , but it might be shifted and obscured by the broad band at 1573 cm^{-1} or the Amide II band at 1540 cm^{-1} . The $\nu(\text{CO})_{\text{succ}}$ band overlaps with the pmi band at 1659 cm^{-1} . The difference spectrum (dianion vs. neutral, Figure 7), contains the expected negative peaks from $\nu(\text{CO})_{\text{pmi}}$ modes of the neutral molecule. The negative $\nu(\text{CO})_{\text{succ}}$ peak at 1669 cm^{-1} represents a decrease of free succ-CO groups in the dianion. This means that compared to **1**, in 1^{2-} a larger fraction of the succinamide stations is involved in hydrogen bonding, presumably with the two-electron reduced pyromellitimide station in a folded conformation.

Figure 6 Partial IR spectra of the neutral (—) and dianion (---) of (A) pyromellitimide thread **1**, (B) [2]rotaxane **2** and (C) [3]rotaxane **3** in THF. The spectra were scaled to the intensity of the $\nu_{\text{as}}(\text{CO})_{\text{pmi}}$ band of the neutral species at $\sim 1723\text{ cm}^{-1}$. The band near 1580 cm^{-1} is due to the electrolyte.

The IR spectra of 2^{2-} and 3^{2-} display more complicated band patterns (Figure 6B and C). In contrast to the case of the radical anions $2^{\bullet-}$ and $3^{\bullet-}$ the difference spectra of the dianions 2^{2-} and 3^{2-} (dianion vs. neutral, Figure 7) are clearly different from each other. Apart from the negative $\nu(\text{CO})_{\text{pmi}}$ bands, two additional negative peaks at 1669 and 1633 cm^{-1} are found in the difference spectra. These negative bands are attributed to the $\nu(\text{CO})_{\text{mac}}$ and hydrogen bonded $\nu(\text{CO})_{\text{succ}}$ modes, respectively, as in the neutral rotaxane. The decrease of these absorptions clearly indicates that the macrocycle in 2^{2-} and 3^{2-} is no longer hydrogen bonded to the succinamide station. The increase of the free $\nu(\text{CO})_{\text{succ}}$ band intensity at 1679 cm^{-1} supports this conclusion. The $\nu(\text{CO})_{\text{mac}}$ appears at 1660 and 1661 cm^{-1} for 2^{2-} and 3^{2-} respectively. In the radical anion, this band was positioned at 1664 cm^{-1} . The additional red-shift nicely agrees with stronger hydrogen bonding between macrocycle and the dianion of the pmi station.

Figure 7 Difference IR spectra (dianion minus neutral) of thread **1** (—), [2]rotaxane **2** (····) and [3]rotaxane **3** (- - -) in THF. The spectra were scaled to the intensity of the $\nu_{as}(\text{CO})_{\text{pmi}}$ band at $\sim 1723\text{ cm}^{-1}$ before subtraction.

Interestingly, the negative and positive $\nu(\text{CO})_{\text{succ}}$ (1633 and 1679 cm^{-1}) and $\nu(\text{CO})_{\text{mac}}$ bands (1669 and 1658 cm^{-1}) are roughly twice as intense in **3**²⁻ than in **2**²⁻. This is clear evidence for the existence of co-conformer *pmi-pmi-3*²⁻ (see Scheme 2): *in the dianion of the [3]rotaxane both macrocycles are hydrogen-bonded to the reduced pyromellitimide station*. As a result, the difference spectra of the dianions **3**²⁻ and **2**²⁻ are different.

Bands arising from modes located on the reduced pyromellitic station in **2**²⁻ are observed at 1709 , ~ 1648 (shoulder on the $\nu(\text{CO})_{\text{mac}}$ band at 1660 cm^{-1}), 1609 , 1546 and 1508 cm^{-1} (Figure 6 and Figure 7). Remarkably, the band at 1609 cm^{-1} is blue-shifted 7 cm^{-1} compared to the corresponding band in **1**²⁻. The reason for this unexpected blue-shift is uncertain. As was discussed for the radical anion **2**^{•-}, ring translocation might lead to changes in the band pattern as a result of distortion of the symmetry of the reduced *pmi* station. This is also the case if the chair binding mode prevails (Figure 5).

Despite the fact that the hydrogen-bond induced shifts of the bands in **2**²⁻ and **3**²⁻ compared to **1**²⁻ are difficult to resolve, comparison between **2**²⁻ and **3**²⁻ is possible because of clear differences in the spectra, specifically in the bands at 1609 and 1549 cm^{-1} . These bands are also present in the spectrum of **3**²⁻ but less intense than in that of **2**²⁻. And also, additional red-shifted shoulders are observed for **3**²⁻ at 1595 and 1538 cm^{-1} . For the *pmi-pmi-3*²⁻ co-conformer with the structure as sketched in Scheme 2, we would expect two clear bands which are red-shifted compared to the corresponding bands for **2**²⁻. The observed band pattern of *pmi-pmi-3*²⁻ could mean that the binding mode of the two macrocycles is somewhat different from the one proposed in Scheme 2. It could well be that due to steric hindrance between the two macrocycles, not all eight N-H groups of the macrocycles can simultaneously hydrogen-bond to the pyromellitimide radical anion. The assignments and band positions of the major bands of the dianions are listed in Table 2.

Table 2 Wavenumbers (cm^{-1}) of IR bands in the amide I region of dianions **4**²⁻, **1**²⁻, **2**²⁻ and **3**²⁻ in THF. The wavenumbers were determined from the spectra in Figure 6. Numbers for the neutral systems are the same as in Table 1, and are included to facilitate comparison.

Hydrogen Bond Acceptor Strength of the *pmi* Station

The co-conformer distribution in the reduced states of aromatic imide based rotaxanes is determined by the driving force for the translation of the ring. This driving force can be related to the reduction potential of the aromatic imides based on the following arguments. The electron affinity and thus reduction potential of aromatic monoimides and diimides depends on the size of the aromatic core and the number of imide groups over which the excess electron can be delocalized.^[39] In our aromatic monoimide and diimide rotaxanes, this delocalization determines the electron density on the hydrogen bond accepting carbonyl groups. The larger hydrogen bond affinity of the reduced aromatic imide station compared to that of the succinamide station provides the driving force for the shuttling process in the rotaxanes that we have studied. We may expect that the reduction potential is a good measure for the driving force responsible for the shuttling process because the more delocalized the charge is in the radical anion, the easier it will be to reduce the compound and the lower will be the charge density on the carbonyl groups that accept hydrogen bonds

from the macrocycle. For aromatic imide compounds, the potential for the first electron reduction shifts to more positive values in the following order: 1,8-naphthalimide < pyromellitimide < naphthalene diimide < perylene diimide.^[39-41,55] Consequently, in this series the driving force for macrocycle translocation is expected to decrease. In the case of the naphthalimide(*ni*)-based shuttle it was concluded that activation by one-electron reduction, either electrochemically or photochemically, results in a quantitative conversion to the shuttled co-conformer.^[28,29,49] Also in the naphthalene diimide system (*ndi*), which has a smaller driving force than the mono-imide system, the shuttling in the radical anion was found to be close to complete (>80%).^[32] These results suggest that macrocycle translocation in the pyromellitimide based rotaxanes will be close to quantitative as well, because the driving force will be larger than for the naphthalene diimide system. The results for **2**^{•-} and **3**^{•-} are in agreement with this expectation.

The red-shifts of the $\nu(\text{CO})_{\text{pmi}}$ (21 cm⁻¹, 1653 cm⁻¹ → 1632 cm⁻¹) and $\nu_{\text{as}}(\text{CO})_{\text{pmi}}$ (37 cm⁻¹, 1636 cm⁻¹ → 1599 cm⁻¹) frequencies of **2**^{•-} and **3**^{•-} are larger on average than was observed for the naphthalimide rotaxane (1616 cm⁻¹ → 1591 cm⁻¹ and 1565 cm⁻¹ → 1551 cm⁻¹)^[29]. This suggests that hydrogen bonding with the radical anion of the imide station is stronger in the pyromellitimide rotaxanes. However, the difference in geometry and thus electron distributions of the pyromellitic and naphthalimide station makes this conclusion premature. A more reliable observable for the comparison of hydrogen bond accepting affinities of different imide stations, is the red-shift of the macrocycle C=O stretching upon binding to the imide anion. In the radical anion of the naphthalimide rotaxane, a red-shift of 7 cm⁻¹ was observed (1667 cm⁻¹ → 1660 cm⁻¹). For **2**^{•-} and **3**^{•-}, this red-shift is significantly smaller: 3 cm⁻¹ (1667 cm⁻¹ → 1664 cm⁻¹). This difference shows that hydrogen bonding of the macrocycle with the pyromellitimide radical anion is weaker than with the naphthalimide radical anion, as anticipated above.

For the dianions **2**²⁻ and **3**²⁻ on the other hand, the red-shifts of the $\nu(\text{CO})_{\text{mac}}$ are similar to the one observed for the radical anion of the *ni*-shuttle. This result demonstrates that hydrogen bonding with the macrocycle is comparably strong in **2**²⁻, **3**²⁻ and the radical anion of the *ni*-shuttle.

As we noted earlier, the rate of the macrocycle translation in the photochemically generated radical anions of the *pmi* rotaxanes is smaller than that in the corresponding naphthalimide and naphthalene diimide rotaxanes: $k_{\text{shuttle}}(\text{pmi}) < k_{\text{shuttle}}(\text{ndi}) \leq k_{\text{shuttle}}(\text{ni})$. This shows that the strengths of binding to the final station are not decisive for the rate of the shuttling process. This is understandable if the transition structures for the *pmi*^{•-} system are different from those for the *ni*^{•-} and *ndi*^{•-} stations, which is likely to be the case for the “chair”-type binding suggested in Figure 5.

Conclusion

Infrared spectroelectrochemical experiments with [2]rotaxane **2** and [3]rotaxane **3** containing two succinamide (*succ*) stations and a redox-active pyromellitimide (*pmi*) binding station revealed the shuttling of the macrocycle between the *succ* station and the one-electron and two-electron reduced *pmi* station (that is, in the radical anion and dianion states, respectively).

The evidence for ring translocation was found in the signatures of hydrogen bonding between amides: hydrogen bonds of the macrocycle NH groups with the carbonyls of the *succ* station are broken, which leads to C=O stretching frequencies characteristic for unperturbed carbonyls. Complementary to this, formation of hydrogen bonds with the carbonyls of the electrochemically activated pyromellitimide station leads to hydrogen-bond

induced shifts of the corresponding carbonyl stretching frequencies.

Splitting of the $\nu(\text{CO})_{\text{pmi}}$ bands of the radical anions of thread **1** and model compound **4** could be traced back to Fermi resonance with an overtone vibration. In the radical anions of the rotaxanes **2** and **3**, red-shifts of the $\nu(\text{CO})_{\text{pmi}}$ frequencies induced by hydrogen bonding with the macrocycle, resulted in disruption of the Fermi resonance.

In the [3]rotaxane **3**, the macrocycle position can be switched selectively. The radical anion of the *pmi* station is occupied by only one of the two available macrocycles. Activation of the shuttle with two electrons on the other hand, results in the translocation of both macrocycles: the dianion, due to its higher electron density and hence greater hydrogen bond accepting affinity, is hydrogen-bonded to both macrocycles.

The controlled switching of the position of the two rings is demonstrated here for the first time in a hydrogen-bond based rotaxane. “Molecular muscles” based on rotaxane architectures based on different types of interactions have been described in the literature.^[19,21,22,56,57] In these reported systems, the contraction is achieved by switching of the rings. Rotaxane **3** can be used as the starting point for the design of systems with molecular muscle functionality, for example similar to the one described by Liu et al.^[21] By the translocation of the rings, the distance between the rings is reduced. In addition, the possibility of selective translocation of the rings in **3** might function as the basic principle for delivering two consecutive contractions, simply by activation with one or two electrons.

The strengths of the hydrogen bonding interactions between the reduced imide stations and the macrocycle could be estimated from the red-shifts of the $\nu(\text{CO})_{\text{mac}}$ band. It was concluded that compared to the naphthalimide radical anion, the radical anion of the *pmi* station exhibits lower hydrogen bond affinity towards the macrocycle. The *pmi* dianion on the other hand, binds to the macrocycle with a similar strength as the naphthalimide radical anion.

Experimental Details

Synthesis

The synthesis and characterization of the thread **1** and the five-component clipping reaction to obtain rotaxanes **2** and **3** was described before.^[32] In the present work we report the characterization of **3**, which was not used in the previous study. The pyromellitimide model compound **4** was synthesized through condensation of pyromellitic anhydride and neopentylamine in DMF with 58% isolated yield using the procedure described below.

2,6-dineopentylpyrrolo[3,4-*f*]isoindole-1,3,5,7(2*H*,6*H*)-tetraone

A solution of pyromellitic anhydride (0.72 g, 2.56 mmol) and neopentylamine (2.8 g, 32.2 mmol) in DMF (20 mL) was refluxed for 3 days. A white precipitate was formed. The reaction mixture was poured into H₂O (50 mL) and the white powder was separated through filtration. The powder was dissolved in CH₂Cl₂ (20 mL) and washed with 1M HCl (3 × 10 mL), H₂O (3 × 10 mL) and brine (3 × 10 mL). The organic layer was dried over MgSO₄ and the solvent was evaporated, affording the crude **4**. The crude product was crystallized from ethyl acetate as white platelets. Yield: 0.53 g (58%). ¹H NMR (400 MHz, CDCl₃): δ = 8.31 (s, 2H, aromatic H), 3.59 (s, 4H, N-CH₂-C), 1.01 (s, 18H, C-CH₃).

[2]-(1,7,14,20-Tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetrabenzocyclohexacosane)-[*N,N'*-bis(12-{[4-(2,2-diphenylethylamino)-4-

oxobutanoyl]amino}dodecyl)-pyromellitic diimide]-rotaxane (**2**) and
 [3]-Bis(1,7,14,20-tetraaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-
 tetrabenzocyclohexacosane)-[*N,N'*-bis(12-{[4-(2,2-diphenylethylamino)-4-
 oxobutanoyl]amino}dodecyl)-pyromellitic diimide]-rotaxane (**3**)

Solutions of isophthaloyl dichloride (271 mg, 1.34 mmol) in chloroform (10 mL) and *p*-xylylenediamine (182 mg, 1.34 mmol) with triethylamine (375 μ L, 2.67 mmol) in chloroform (10 mL) were simultaneously added using motor-driven syringe pumps over 4 h to a solution of thread **1** (190 mg, 0.167 mmol) in chloroform (25 mL). Following addition, the mixture was allowed to stir for a further 16 h before removal of the off-white precipitate by filtration. The resulting filtrate was concentrated under reduced pressure and the crude product purified by repeated flash chromatography (SiO_2 ; 2:45:50 methanol/ethyl acetate/dichloromethane) to afford, in order of elution:

[3]rotaxane **3** as a colourless solid (15.0 mg, 4.1%); mp > 140 $^{\circ}\text{C}$ (decomp.); ^1H NMR (400 MHz, CDCl_3): δ = 8.25 (s, 4H, H_C), 8.11 (s, 2H, H_E), 8.08 (d, J = 7.6 Hz, 8H, H_B), 7.63 (br s, 8H, H_D), 7.54 (t, J = 7.6 Hz, 4H, H_A), 7.30-7.15 (m, 20H, H_{Ph}), 7.07 (s, 16H, H_F), 6.70 (br t, 2H, H_J), 6.55 (br t, 2H, H_I), 4.51-4.43 (m, 16H, H_E), 4.11 (br t, 2H, H_A), 3.74-3.71 (m, 8H, H_B & H_J), 3.01 (br s, 4H, H_G), 1.68 (br s, 4H, H_I), 1.39 (br s, 4H, H_J), 1.28-1.16 (m, 32H, alkyl CH_2), 1.01-0.99 (m, 8H, H_A & H_J); ^{13}C NMR (100 MHz, CDCl_3): δ = 173.1 (succinamide $\text{C}=\text{O}$), 172.9 (succinamide $\text{C}=\text{O}$), 166.42 (macrocycle or imide $\text{C}=\text{O}$), 166.40 (macrocycle or imide $\text{C}=\text{O}$), 141.5 (phenyl ArC_q), 137.5 (xylyl C_q), 137.1 (pyromellitic ArC_q), 133.7 (isophthaloyl ArC_q), 131.5 (ArCH_B), 129.2 (ArCH_F), 129.0 (ArCH_A), 128.9 (phenyl ArCH), 127.8 (phenyl ArCH), 127.1 (phenyl ArCH), 124.0 (ArCH_C), 117.8 (ArCH_E), 50.5 (CH_A), 44.8 ($\text{CH}_{2(B)}$), 44.0 ($\text{CH}_{2(E)}$), 39.8 ($\text{CH}_{2(G)}$), 38.9 ($\text{CH}_{2(I)}$), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.22 (CH_2), 29.19 (CH_2), 29.1 (CH_2), 28.8 (CH_2), 28.1 (CH_2), 27.3 (CH_2), 26.9 (CH_2), 26.4 (CH_2); HRMS (FAB, THIOG matrix): m/z = 2207.1038 [$(\text{M}+\text{H})^+$] (anal. calcd for $^{12}\text{C}_{133}^{13}\text{CH}_{145}\text{N}_{14}\text{O}_{16}^+$: m/z = 2207.0997);

[2]rotaxane **2** as a colourless solid (114 mg, 41%). The spectroscopic characterization of **2** was reported in ref.^[32].

The IR spectra were recorded on a Bruker Vertex 70 FTIR spectrometer. For further details of sample preparation and spectroelectrochemical experiments, see reference ^[29]. For the

B3LYP calculations of the C=O vibrations in **4**, the neopentyl group was replaced by an ethyl group. In the present work, the 6-31G+(d) basis set was used. The harmonic frequencies were scaled by a factor 0.9738.^[58]

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Scheme 1 Structures of thread **1**, [2]rotaxane **2** and [3]rotaxane **3** equipped with a pyromellitimide (*pmi*) and two succinamide (*succ*) binding stations.

Scheme 2 Three different possible co-conformers of **3** resulting from translocation of one or both macrocycles.

Figure 1 Amide I region in the IR spectra of model compound **4** and pyromellitimide thread **1**, [2]rotaxane **2** and [3]rotaxane **3** in THF. The spectra were scaled to the intensity of the $\nu_{as}(\text{CO})_{pmi}$ band at $\sim 1723 \text{ cm}^{-1}$ in order to facilitate comparison. Vibrational modes and corresponding wavenumbers of the pyromellitimide model compound **4**.

Scheme 3 Structures of two possible conformations of thread **1**: the predominant extended and the minor folded conformations.

Figure 2 Partial IR spectra of the neutral pyromellitimide model compound **4** (—), radical anion **4^{•-}** (····) and dianion **4²⁻** (---) in THF.

Figure 3 Parts of the IR spectra of neutral (—) and radical anion (····) of (A) pyromellitimide thread **1**, (B) [2]rotaxane **2** and (C) [3]rotaxane **3** in THF. The spectra of the neutral species were scaled to the intensity of the $\nu_{as}(\text{CO})_{pmi}$ band at $\sim 1723\text{ cm}^{-1}$.

Figure 4 Difference IR spectra (radical anion minus neutral) of thread **1** (—), [2]rotaxane **2** (····) and [3]rotaxane **3** (---) in THF. The spectra were scaled to the intensity of the $\nu_{as}(CO)_{pmi}$ band at $\sim 1723\text{ cm}^{-1}$ before subtraction.

Figure 5 Possible binding modes of the macrocycle to the *pmi* radical anion in **2**^{•-}.

Figure 6 Partial IR spectra of the neutral (—) and dianion (---) of (A) pyromellitimide thread **1**, (B) [2]rotaxane **2** and (C) [3]rotaxane **3** in THF. The spectra were scaled to the intensity of the $\nu_{as}(CO)_{pmi}$ band of the neutral species at $\sim 1723\text{ cm}^{-1}$. The band near 1580 cm^{-1} is due to the electrolyte.

Figure 7 Difference IR spectra (dianion minus neutral) of thread **1** (—), [2]rotaxane **2** (····) and [3]rotaxane **3** (- - -) in THF. The spectra were scaled to the intensity of the $\nu_{as}(CO)_{pmi}$ band at $\sim 1723\text{ cm}^{-1}$ before subtraction.

Table 1 Wavenumbers (cm⁻¹) of IR modes in the amide I region of the neutral and radical anions of model compound **4**, thread **1**, and rotaxanes **2** and **3** in THF.

Mode	Neutral				Radical anion			
	4	1	2	3	4^{•-}	1^{•-}	2^{•-}	3^{•-}
$\nu(\text{CO})_{\text{mac}}$	-	-	1667	1667	-	-	1664	1664
$\nu(\text{CO})_{\text{succ}}$ (free)	-	1677	1677 ^[a]	-	-	1677 ^[a]	1677 ^[a]	1677 ^[a]
$\nu(\text{CO})_{\text{succ}}$ (H-bonded)	-	1635	1633	1633	-	-	-	-
$\nu_s(\text{CO})_{\text{pmi}}$	-	-	-	-	1661 ^[b]	1659 ^[b]	-	-
$\nu_s(\text{CO})_{\text{pmi}}$	1775	1772	1772	1772	1653 ^[b]	1647 ^[b]	1632	1632
$\nu_{\text{as}}(\text{CO})_{\text{pmi}}$	1724	1723	1723	1723	1642 ^[b]	1641 ^[b]	1599	1599
$\nu_{\text{as}}(\text{CO})_{\text{pmi}}$	-	-	-	-	1637 ^[b]	1631 ^[b]	-	-

[a] Shoulder on the $\nu(\text{CO})_{\text{mac}}$ band.

[b] Band splitting due to Fermi resonance (see the text for details).

Table 2 Wavenumbers (cm⁻¹) of IR bands in the amide I region of dianions **4²⁻**, **1²⁻**, **2²⁻** and **3²⁻** in THF. The wavenumbers were determined from the spectra in Figure 6. Numbers for the neutral systems are the same as in Table 1, and are included to facilitate comparison.

Mode	Neutral				Dianion			
	4	1	2	3	4²⁻	1²⁻	2²⁻	3²⁻
$\nu(\text{CO})_{\text{mac}}$	-	-	1667	1667	-	-	1660	1661
$\nu(\text{CO})_{\text{succ}}$ (free)	-	1677	1677 ^[a]	-	-	1677 ^[a]	1677 ^[a]	1677 ^[a]
$\nu(\text{CO})_{\text{succ}}$ (H-bonded)	-	1635	1633	1633	-	-	-	-
n.a. ^[b]	-	-	-	-	1713	1709	1709	1709
n.a. ^[b]	-	-	-	-	1669	1659	~1648	~1648
$\nu_s(\text{CO})_{\text{pmi}}$	1775	1772	1772	1772	1607	1602	1609 ^[c]	1609 ^[c]
	-	-	-	-	-	-	-	1595 ^[c]
$\nu_{\text{as}}(\text{CO})_{\text{pmi}}$	1724	1723	1723	1723	1569	1573	1546 ^[c]	1546 ^[c]
	-	-	-	-	-	-	-	1538 ^[c]
n.a. ^[b]	-	-	-	-	1546	-	-	-
$\nu(\text{Ar})_{\text{pmi}}$	-	-	-	-	1517	1513	1508 ^[c]	1508 ^[c]

[a] Shoulder on the $\nu(\text{CO})_{\text{mac}}$ band.

[b] Band could not be assigned as a fundamental.

[c] Hydrogen bonded C=O.

For TOC