DOI: 10.1002/chem.200701531

Infrared Study of Intercomponent Interactions in a Switchable Hydrogen-Bonded Rotaxane

Dhiredj C. Jagesar,[a] **František Hartl,**[b] **Wybren Jan Buma,**[a] **and Albert M. Brouwer***[a]

Abstract: The macrocycle in rotaxane **1** is preferentially hydrogen bonded to the succinamide station in the neutral form, but can be moved to the naphthalimide station by one-electron reduction of the latter. The hydrogen bonding between the amide NH groups of the macrocycle and the C=O groups in the binding stations in the thread was studied with IR spectroscopy in different solvents in both states. In addition, the solvent effect on the vibrational frequencies was analyzed; a correlation with the solvent acceptor number (AN) was observed. The conformational switching upon reduction could be detected by monitoring the hydrogen-bond-induced shifts of the ν(CO) frequencies of the C=O groups of the succinamide and the reduced naphthalimide stations. The macrocycle was found to shield the encapsulated station from the solvent: wavenumbers of ν(CO) bands of the C=O groups residing inside the macrocycle cavity remain unaffected by the solvent polarity.

Keywords: electrochemistry · IR spectroscopy · molecular shuttles · rotaxanes

Introduction

Exploitation of intercomponent mobility in rotaxanes and other interlocked molecular assemblies has emerged as an appealing subject of research during the past decade.[1–5] The key challenge is to control the intercomponent degrees of freedom, which can be accomplished by the modulation of the weak interactions between the components. In the case of rotaxanes, changing the interactions between the macrocyclic ring and binding stations in the thread can result in reversible transitions between structurally well-defined states in which the ring binds to different parts of the thread (co-conformers). If this shuttling is signaled by an observable change in a physical or chemical property of the system, the molecule behaves as a switch. These molecular switches are also referred to as molecular motors, because they are, in principle, capable of converting chemical energy into mechanical work. Molecular switches have also been proposed to be promising candidates for key elements in molecular scale information processing devices. Interlocked systems have been designed in which hydrogen bonding,[6–9] π–π-interactions,[10,11] metal coordination,[12,13] Coulombic forces, and hydrophobic interactions[14,15] are utilized, not only to allow template-directed synthesis, but also to control the intercomponent interactions. To fully exploit the potential of these molecules and for the design of new molecules with improved performance, a detailed understanding of the intercomponent interactions is mandatory.

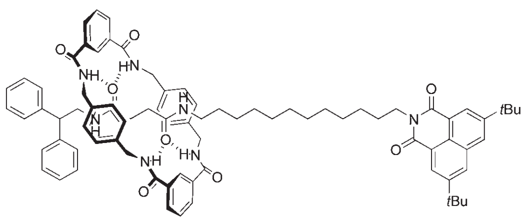
In this report, we describe the infrared study of hydrogen-bond interactions in rotaxane **1** containing two potential binding stations for the macrocycle: a succinamide and a naphthalimide station. The succinamide group is known to be a better hydrogen-bond acceptor than the naphthalimide station. Hence, in the thermodynamically favored conformer the macrocycle resides at the succinamide station.[16,17]

The switching function in rotaxane **1** is based on the shuttling of the macrocycle between the two stations, which is triggered by one-electron reduction of the naphthalimide station, either electrochemically[16] or photochemically[17] (Scheme 1). The thus-formed radical anion has a higher hydrogen-bonding affinity towards the macrocycle, which results in a net translational motion of the macrocycle towards the naphthalimide radical anion to form the energetically more favorable co-conformer ni-$\mathbf{1}^{\bullet-}$.

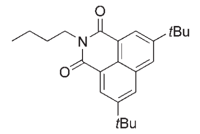
---

[a] D. C. Jagesar, Prof. Dr. W. J. Buma, Prof. Dr. A. M. Brouwer
Van 't Hoff Institute for Molecular Sciences
University of Amsterdam
Nieuwe Achtergracht 129
1018 WS Amsterdam (The Netherlands)
Fax (+31) 205-255-670
E-mail: a.m.brouwer@uva.nl

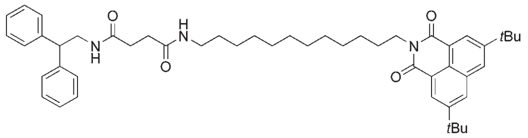
[b] Dr. F. Hartl
Van 't Hoff Institute for Molecular Sciences
University of Amsterdam
Nieuwe Achtergracht 166
1018 WV Amsterdam (The Netherlands)



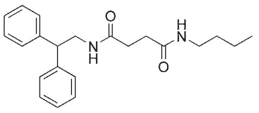
1



3



2



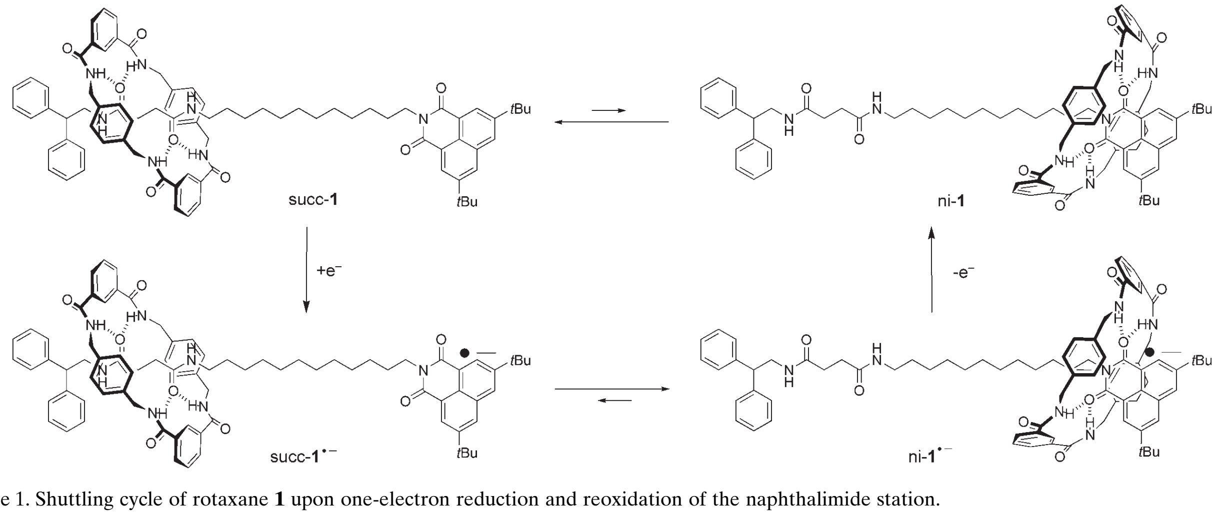
4

The shuttling process was studied in a time-resolved way by using the electronic absorption spectrum of the naphthalimide radical anion as a probe.[17] With this method, the shuttling was revealed by monitoring the precise position of the strong electronic absorption band near 420 nm, which undergoes a blue shift when the macrocycle binds to the radical anion.

An alternative approach to study the structural changes during the shuttling process is by using the macrocycle as a probe, as in contrast to the succinamide and naphthalimide stations, this component is directly involved at every stage of the process. In the course of the shuttling cycle, hydrogen bonds of the macrocycle to the succinamide station are broken, and after the shuttling new hydrogen bonds are formed with the naphthalimide radical anion. Thus, direct monitoring of hydrogen bonds during the shuttling would be an ideal way to study the process.

IR spectroscopy is a promising technique for this purpose. It provides structural information, and can be applied with the submicrosecond time resolution needed to monitor the shuttling process.[18] IR spectroscopy has been widely used in the analysis of secondary structural motifs in proteins and peptides, which are determined to a large extent by hydrogen-bonding interactions.[19–21] These studies, therefore, usually focus on the detection of hydrogen bonds between amide groups. The amide $C{=}O$ stretching (ν(CO), often called the amide I band) and N–H stretching (ν_s(NH)) frequencies are strongly affected by hydrogen bonds,[22–24] making the amide group an exceptionally good probe for the study of hydrogen-bond-stabilized conformers. Hydrogen bonding between amide groups decreases the NH and $C{=}O$ bond orders in both acceptor amide and donor amide.[24,25] Therefore, for amides involved in hydrogen bonding, generally, large red shifts of the ν(CO) and ν(NH) frequencies are observed.

So far, only a few reports on the application of IR spectroscopy in studies of intercomponent interactions in interlocked molecules have been published in the literature.[26–30] The first one was reported for a hydrogen-bonded[2] catenane. In particular, the characterization of amide $C{=}O$ and NH vibrations in a benzylic amide [2]catenane, and the consequences of the interlocked structure for these vibrations have been presented.[26] The studied [2]catenane was an interlocked dimer of the macrocycle contained in **1**. In a later work, IR spectroscopy was used to study external effects on the intercomponent hydrogen bonding in this [2]catenane incorporated in different inorganic salt matrices.[27] The salt matrix was shown to influence the number and geometry of hydrogen bonds between the macrocycle amide groups. The only reported IR study of interlocked molecules in solution was done on a succinamide rotaxane. 2D IR spectroscopy was used to determine the conformations of this rotaxane by means of the dipolar interactions of the $C{=}O$ groups.[29] Hydrogen bonds in rotaxanes and the effect on the vibrational frequencies of the involved donor and acceptor



Scheme 1. Shuttling cycle of rotaxane **1** upon one-electron reduction and reoxidation of the naphthalimide station.

groups have also been analyzed with quantum chemical calculations.[25] Calculation of the vibrational frequencies in rotaxane mimics (hydrogen-bonded complexes of isophtalic amide donor and different acceptors) showed pronounced red shifts of ν(CO) bands of both the acceptor (35–65 cm^{-1}) and donor.

The goal of the present work is to study the nature and strength of the intercomponent hydrogen bonds in the neutral and reduced forms of rotaxane **1** and thread **2** and to investigate how these interactions are modified by medium polarity. Furthermore, we want to correlate these interactions with properties, such as shuttling rate and co-conformer distribution. In addition, the solvent effect on the vibrational frequencies will be analyzed. For a detailed understanding of the relationship between spectral features and molecular conformations, the C=O stretching modes of **1** and **2** will be characterized. Additional information is obtained from an analysis of the N−H stretching vibrations. The structures and energies of the co-conformers of rotaxane **1** are to a large extent determined by the formation of hydrogen bonds. Hydrogen bonding is strongly affected by the solvent polarity, being more favored in solvents of lower polarity. To study the effect of the solvent polarity on the hydrogen bonding in **1**, IR spectra were recorded in structurally similar non-hydrogen bonding chlorinated solvents with different dielectric constants (ε): chloroform ($CHCl_3$, $\varepsilon = 4.70$), dichloromethane (CH_2Cl_2, $\varepsilon = 8.93$) and 1,2-dichloroethane ($ClCH_2CH_2Cl$, $\varepsilon = 10.36$). Also weakly hydrogen-bond-accepting solvents, THF ($\varepsilon = 7.58$) and butyronitrile (PrCN, $\varepsilon = 27.2$) were used.

Examination of the molecular structures of **1** and **2** leads us to predict the appearance of a complex combination of IR bands originating from different ν(CO) modes of C=O groups of the succinamide (succ-CO) and naphthalimide (ni-CO) stations and the macrocycle (macro-CO). In the IR spectra of the radical anions, drastic changes of the ν(CO) bands of the naphthalimide C=O groups (ni$^{\bullet-}$-CO) are to be expected. To facilitate the assignment of the bands, model compounds for the succinamide (**4**) and naphthalimide (**3**) stations were synthesized and studied. Unfortunately, the macrocycle itself could not be used in this study because of its very poor solubility in non-hydrogen bonding solvents.[31] Model compounds **3** (neutral molecule and radical anion) and **4** will be shown to allow separate assignment of the ν(CO) bands in the IR spectra to different C=O groups present in the succinamide and naphthalimide moieties of **1**, $\mathbf{1}^{\bullet-}$, **2** and $\mathbf{2}^{\bullet-}$. Also, B3LYP/6–31G(d) calculations have been performed to predict the nature and frequencies of the vibrational modes and further support the spectral analysis.

Results and Discussion

An overview of the different ν(CO) bands expected in the IR spectra of **1**–**4** is given in Figure 1.

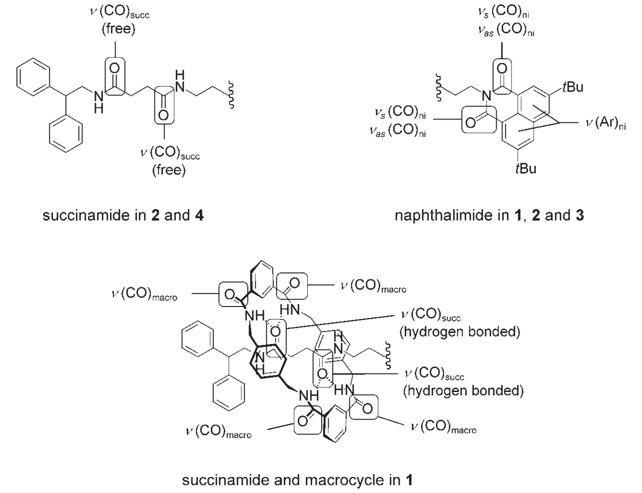


Figure 1. The different ν(CO) bands of C=O groups in the succinamide and naphthalimide units and the macrocycle. The intramolecularly hydrogen-bonded conformations of the succinamide station (**4a** and **4b**, Scheme 2) are not included in this overview.

To allow comparison of the IR bands in the different compounds, all spectra were scaled to the intensity of naphthalimide symmetric C=O stretching ($\nu_s(\mathrm{CO})_{ni}$) band at ≈ 1700 cm^{-1}. This ν(CO) band was chosen as a standard for two reasons: this C=O group was found to be free of interactions with other parts of the molecule and the corresponding ν(CO) band is well separated from the other bands. The absorption coefficient of the $\nu_s(\mathrm{CO})_{ni}$ band at ≈ 1700 cm^{-1} is $(6 \pm 2) \times 10^2$ L mol^{-1} cm^{-1}. Due to the procedure for sample preparation, the concentration of each solution, and, therefore, the molar absorption coefficients, were known only approximately.

Model compounds: The IR spectra of compounds **1**–**4** in CH_2Cl_2 are depicted in Figure 2A. The IR spectrum of **3** shows the characteristic features of naphthalimides:[32] four bands are observed in the C=O region. The bands at 1698 and 1660 cm^{-1} are assigned to the symmetric ($\nu_s(\mathrm{CO})_{ni}$) and antisymmetric ($\nu_{as}(\mathrm{CO})_{ni}$) C=O stretching modes, respectively, while the other two bands at 1630 and 1603 cm^{-1} originate from aromatic ring vibrations ($\nu(\mathrm{Ar})_{ni}$). The B3LYP calculation predicts a similar band pattern: four bands in the spectral range of interest, at 1707 ($\nu_s(\mathrm{CO})_{ni}$), 1673 ($\nu_{as}(\mathrm{CO})_{ni}$), 1618 ($\nu(\mathrm{Ar})_{ni}$), and 1565 cm^{-1} ($\nu(\mathrm{Ar})_{ni}$).

In the C=O stretching range of the IR spectrum of **4** in CH_2Cl_2, a broad band at 1672 cm^{-1} with a tail on the low frequency side is observed. This band was analyzed by fitting it to a sum of Lorentzian profiles, and it was found to be composed of three contributions (Figure 3D). The two components at 1676 and 1669 cm^{-1} arise from unperturbed C=O stretching. The red-shifted broad band at 1657 cm^{-1} is attributed to C=O stretching in the intramolecular hydrogen-bonded seven-membered ring conformations **4a** and **4b** (Scheme 2).[33] Assuming that hydrogen bonding does not change the absorption coefficient of the C=O stretching mode, we can estimate from the relative contributions of the three Lorentzians to the absorption band that approximately

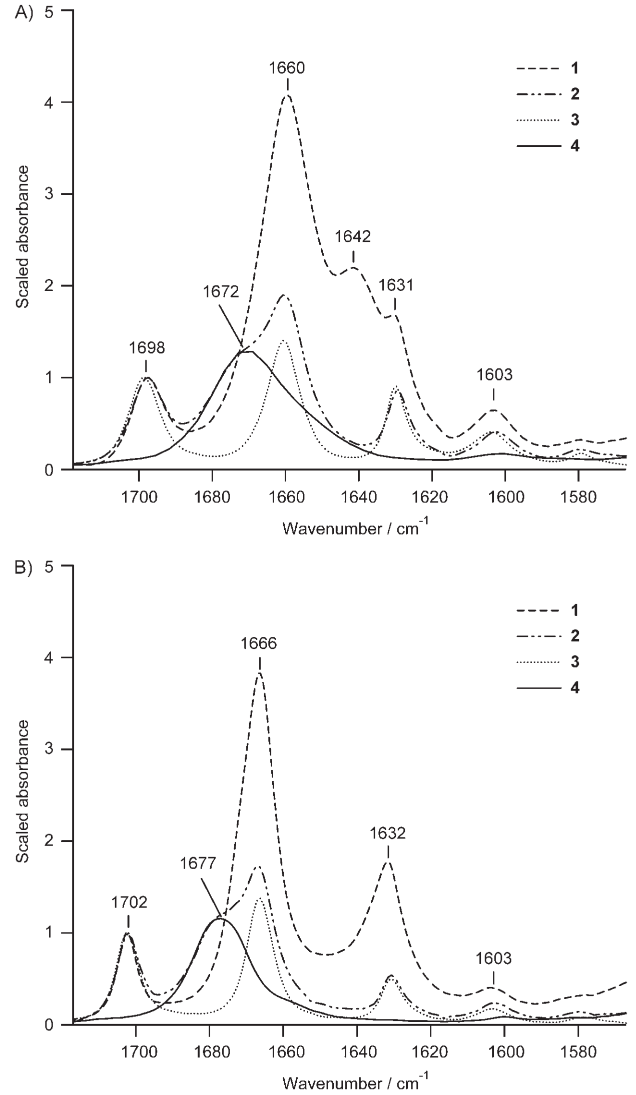


Figure 2. Amide I region of the IR absorbance spectra of **1**–**4** in A) CH_2Cl_2 and B) THF. The spectra were scaled to the intensity of the $\nu_s(CO)_{ni}$ band at ≈1700 cm^{-1}.

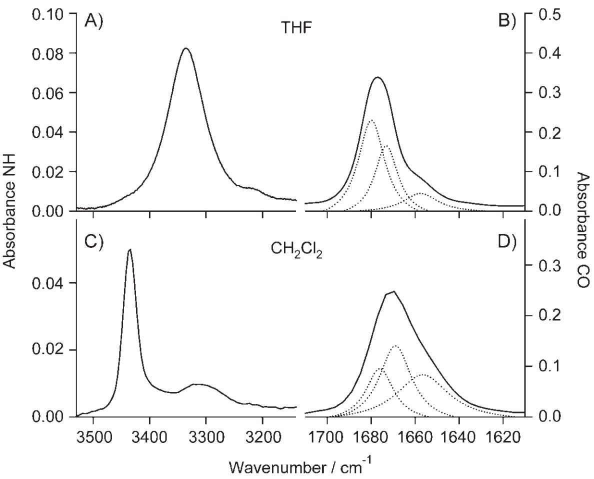
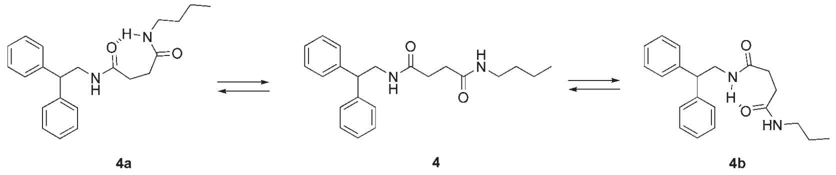


Figure 3. IR spectra of **4** in THF (NH region (A) and amide I region (B)) and CH_2Cl_2 (NH region (C) and amide I region (D)). The bands in B and D were fitted to a sum of three Lorentzian profiles.

one third of **4** exists in these hydrogen-bonded conformations.

For the *trans* conformation of **4**, the B3LYP calculations predict the vibrational bands of the ν(CO) modes at 1713 and 1699 cm^{-1}, with similar intensities. Experimentally, a band is found at 1672 cm^{-1}, which can be modeled as a sum of two Lorentzian peaks at 1676 and 1669 cm^{-1}. The agreement between experimental and calculated frequencies is not perfect, but the calculation supports the notion that there are two modes with distinctly different frequencies. A similar conclusion was drawn from 2D IR experiments on a related succinamide rotaxane.[29] The presence of two distinct bands implies that the C=O transition moments are not antiparallel to each other but almost perpendicular. This is in nice agreement with the B3LYP calculation, which predicts a dihedral angle of 122°. In the case of **1**, the bifurcated sets of hydrogen bonds with the macrocycle NH groups require an antiparallel configuration of the C=O groups,[34] and indeed, for rotaxane **1**, only one $\nu(CO)_{succ}$ band is observed (Figure 5B). In the internally hydrogen-bonded *gauche* conformation (corresponding to **4a**), one band is calculated at essentially the same wavenumber as that of the *trans* form (1716 cm^{-1}), the other one at a lower frequency (1680 cm^{-1}). In the experimental spectrum, the latter band is found at 1657 cm^{-1}. A comparison of the calculated energies indicates that the hydrogen-bonded form has a lower energy for the isolated molecules (−2.3 kcal mol^{-1}), but in CH_2Cl_2, the extended form is predicted to be more stable by 1.2 kcal mol^{-1}. This is in good agreement with our interpretation of the IR spectra of **4**, which concludes that the extended form is the predominant species.

In the amide I range of the IR spectrum of **4** in THF, the bands are slightly blue-shifted with respect to the corresponding peaks in CH_2Cl_2, and are narrower. The NH stretching in **4**, on the other hand, reveals the opposite changes, the bands being red-shifted and broadened in THF (Figure 3A and B). Hydrogen bonding between THF and the NH groups of **4** is most likely to be the reason for these effects. THF is a hydrogen-bond acceptor, hence, only a strong direct effect on the NH stretching mode is present, and a weaker indirect effect on the



Scheme 2. Intramolecularly hydrogen-bonded conformations **4a** and **4b**.

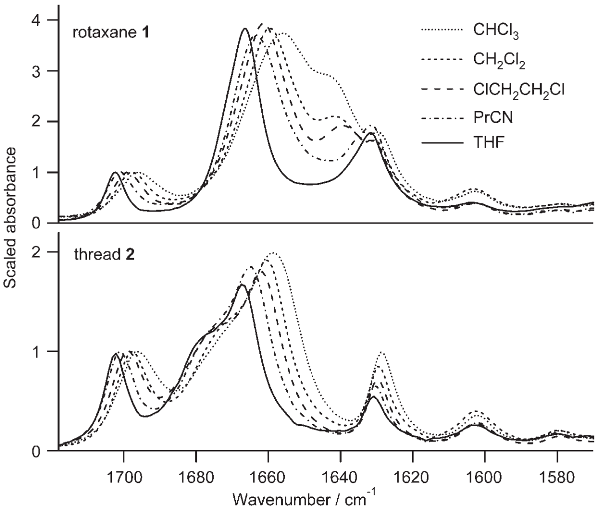
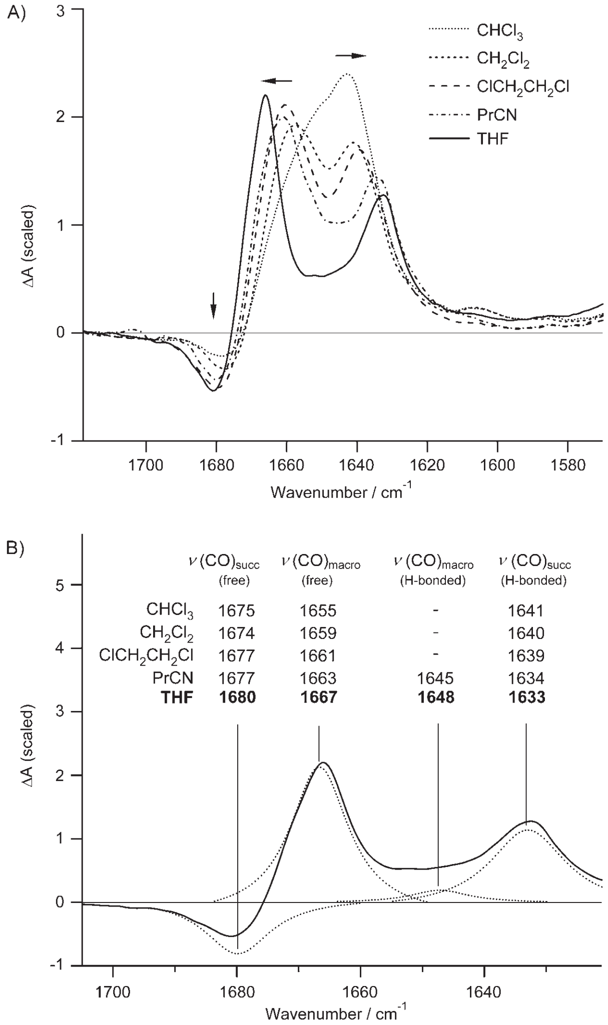


Figure 4. Amide I region of IR absorbance spectra of rotaxane **1** and thread **2** in CHCl$_3$, CH$_2$Cl$_2$, ClCH$_2$CH$_2$Cl, PrCN, and THF. All spectra have been scaled to the intensity of the $\nu_s(CO)_{ni}$ band at ≈1700 cm^{-1}.



	$\nu(CO)_{succ}$ (free)	$\nu(CO)_{macro}$ (free)	$\nu(CO)_{macro}$ (H-bonded)	$\nu(CO)_{succ}$ (H-bonded)
CHCl$_3$	1675	1655	-	1641
CH$_2$Cl$_2$	1674	1659	-	1640
ClCH$_2$CH$_2$Cl	1677	1661	-	1639
PrCN	1677	1663	1645	1634
THF	**1680**	**1667**	**1648**	**1633**

Figure 5. A) Difference absorbance IR spectra (**1** minus **2**) in CHCl$_3$, CH$_2$Cl$_2$, ClCH$_2$CH$_2$Cl, PrCN, and THF. The spectra were obtained by subtracting the thread spectrum from the rotaxane spectrum after scaling at the $\nu_s(CO)_{ni}$ band. The arrows indicate the changes in this range of solvents. B) Fitting result of the difference absorbance spectra. —— is the absorbance difference spectrum in THF. The spectra were fitted to a sum of three or four Lorentzians (•••••). The peak positions in all solvents are given as numbers.

C=O stretching. The smaller contribution of the low-frequency Lorentzian to the band indicates that the intramolecular hydrogen bonding leading to **4a** and **4b** is disrupted to a large extent.

Apart from the free NH-stretching band, a broad red-shifted band belonging to NH stretching in **4a** and **4b** is observed in CH$_2$Cl$_2$. This band pattern is characteristic for molecules in which intramolecular hydrogen bonding between amide groups is possible.[34]

Rotaxane and thread: The IR spectra of **2** in CHCl$_3$, CH$_2$Cl$_2$, ClCH$_2$CH$_2$Cl, PrCN, and THF are similar (Figure 4). In the spectral range of interest, the IR spectrum of **2** is equal to the sum of the spectra of **3** and **4**, indicating the absence of significant interactions between the naphthalimide and succinamide stations. In the chlorinated solvents, all ν(CO) modes are affected by the changes in solvent polarity, showing a blue shift of the corresponding bands with increasing dielectric constant. Only the aromatic ring vibration at 1603 cm^{-1} remains unaffected.

The IR spectrum of **1** displays a more complicated combination of bands (Figure 4). An important observation is that the IR spectrum does not show any indication of the existence of co-conformer ni-**1**, the $\nu_s(CO)_{ni}$ band at 1698 cm^{-1} in THF remains completely unaffected compared to **2**. This is in agreement with NMR spectroscopic studies on co-conformer distribution in **1** in different solvents; the predominant co-conformer (>95%) is succ-**1**.[16] Crystal structures of succinamide-based rotaxanes show that two sets of bifurcated hydrogen bonds can exist between the macrocycle NH groups and the C=O groups of the succinamide station.[16]

To obtain a clearer picture of the additional bands in **1**, difference absorbance spectra were constructed by subtracting the scaled IR spectra of **2** from those of **1** (Figure 5A). As stated above, the ν(CO) modes localized on the naphthalimide station remain unaffected in **1**, so corresponding bands are expected to vanish in the difference spectrum. The positive peaks in the difference spectra are contributions from the C=O stretching vibrations of the macrocycle amide groups ($\nu(CO)_{macro}$). Shifts of bands of the succinamide station due to interactions with the macrocycle may give rise to negative or positive bands in the difference spectrum.

The difference spectra were fitted to a sum of Lorentzian peaks; the results are displayed in Figure 5B. In THF, the $\nu(CO)_{macro}$ band is found at 1667 cm^{-1}. This band gradually shifts to 1655 cm^{-1} in CHCl$_3$. In THF and PrCN, a weak band is observed at 1645 and 1648 cm^{-1}, respectively, which may be attributed to hydrogen-bonded C=O groups of the macrocycle. Hydrogen bonding between the succ-NH groups and the macro-CO groups is possible due to the flexibility of the macrocycle: the macro-CO groups can point inward to from hydrogen bonds with the succ-NH groups. Molecular modeling and crystal structures of related rotaxanes[35–37] show that this binding motif can exist, but it probably plays a minor role. In the chlorinated solvents, this band was not found, probably because it is obscured by the strong $\nu(\mathrm{CO})_{\mathrm{macro}}$ and $\nu(\mathrm{CO})_{\mathrm{succ}}$ bands. Due to the red shift of the $\nu(\mathrm{CO})_{\mathrm{macro}}$ band towards the $\nu(\mathrm{CO})_{\mathrm{succ}}$ band, the overlap is larger in the chlorinated solvents.

The negative band at 1680 $\mathrm{cm^{-1}}$ (in $CHCl_3$ 1675 $\mathrm{cm^{-1}}$) represents the decrease of free succ-CO groups in **1** compared to **2**. The positive band near 1640 $\mathrm{cm^{-1}}$ can be assigned to stretching of the hydrogen-bonded C=O groups in the succinamide station. The red shift of the hydrogen-bonded relative to free $\nu(\mathrm{CO})_{\mathrm{succ}}$ in, for example, CH_2Cl_2 is 34 $\mathrm{cm^{-1}}$. This is 14 $\mathrm{cm^{-1}}$ larger than in the case of conformers **4a** and **4b** relative to **4** and is caused by strong hydrogen bonding with NH groups in the macrocycle. The hydrogen bonding is stronger in **1** because two bifurcated hydrogen bonds with each succ-CO are possible, while intramolecular hydrogen bonds in **4a** and **4b** do not have optimal geometries. The calculated red shifts of the $\nu(\mathrm{CO})$ band in analogous hydrogen-bonded complexes of isophtalic amide and different acceptors obtained by Reckien and co-workers (35–40 $\mathrm{cm^{-1}}$), agree well with our experimentally observed red shift.[25]

Remarkably, the hydrogen-bonded $\nu(\mathrm{CO})_{\mathrm{succ}}$ band lies within 2 $\mathrm{cm^{-1}}$ in the chlorinated solvents (1639–1641 $\mathrm{cm^{-1}}$), while all other bands related to the amide or imide groups in **1** and **2** are solvatochromic (see below). The absence of a solvent effect implies shielding of the C=O groups from the solvent by the macrocycle. In PrCN, this band appears at 1634 $\mathrm{cm^{-1}}$, which is almost the same as in THF. The difference in behavior compared with the chlorinated solvents is probably caused by the hydrogen-bond accepting properties of PrCN and THF. Hydrogen bonding of the solvents with the NH groups of the amides in the succinamide moiety reduces the corresponding C=O stretching frequency.

Solvent effects: The IR frequencies in **1** and **2** undergo substantial red shifts in the solvent range THF, PrCN, $ClCH_2CH_2Cl$, CH_2Cl_2, and $CHCl_3$. The shifts are not systematic with the dielectric constant of the solvent; hence evaluation of specific solvent effects, such as hydrogen bonding and donor–acceptor interactions is required. The evaluation of specific and nonspecific solvent effects is often conducted by using linear solvation energy relationships (LSER).[38] The effect of a solvent on a given vibrational mode can be described by Equation (1).[39]

$$\nu = \nu_0 + \sum_i \alpha_i P_i \tag{1}$$

In this equation, ν is the wavenumber of the absorption band in the particular solvent, P_i is one of the solvent parameters: acceptor number[40] (AN), donor number (DN), polarity (Y; derived from the static dielectric constant as: $Y = (\varepsilon_s - 1)/(\varepsilon_s + 2)$),[38] and polarizability (π; derived from the solvent refractive index by using: $\pi = (n^{2-} - 1)/(n^2 + 2)$).[38] The response of the observed effect to the respective solvent parameter is described by α_i and ν_0 is the wavenumber for the case in which all values for P_i are zero.

The solvent-induced shifts of the IR frequencies of **1** and **2** were evaluated with this LSER method. The wavenumbers of the $\nu_s(\mathrm{CO})_{\mathrm{ni}}$ and $\nu_s(\mathrm{Ar})_{\mathrm{ni}}$ bands of **2** were taken directly from the IR spectra. Because of band overlap, the $\nu(\mathrm{CO})_{\mathrm{succ}}$ band of **2** and $\nu(\mathrm{CO})_{\mathrm{macro}}$ band of **1** were obtained from peak fitting (Figure 5B). The strongest correlation was found with the solvent acceptor number. The results of this analysis are presented in Figure 6 and Table 1.

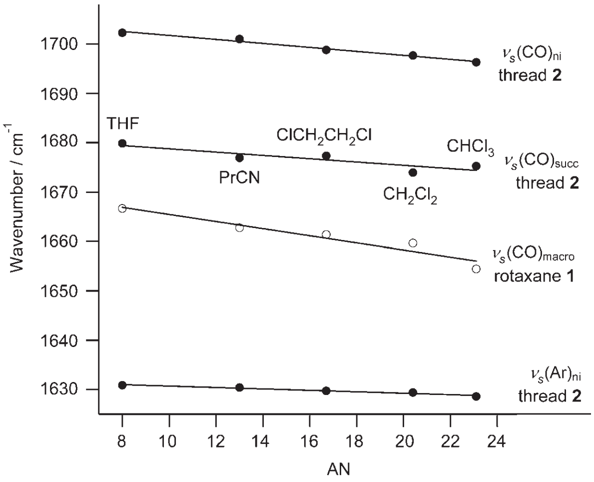


Figure 6. Plot of $\nu_s(\mathrm{CO})_{\mathrm{ni}}$, $\nu(\mathrm{Ar})_{\mathrm{ni}}$, and $\nu(\mathrm{CO})_{\mathrm{succ}}$ in **2** (●) and $\nu(\mathrm{CO})_{\mathrm{macro}}$ in **1** (○) wavenumbers versus solvent acceptor number (AN). The obtained values of ν_0, and α are listed in Table 1.

Table 1. Coefficients ν_0 and α, and standard deviations were obtained by using the LSER [Eq. (1)] analysis with the solvent acceptor number.

Mode	Compound	ν_0	α
$\nu_s(\mathrm{CO})_{\mathrm{ni}}$	2	1705.8 ± 0.5	−0.40 ± 0.03
$\nu(\mathrm{CO})_{\mathrm{succ}}$	2	1682 ± 2	−0.33 ± 0.10
$\nu(\mathrm{CO})_{\mathrm{macro}}$	1	1673 ± 2	−0.72 ± 0.12
$\nu(\mathrm{Ar})_{\mathrm{ni}}$	2	1632.2 ± 0.3	−0.15 ± 0.02

The solvent acceptor number is a measure of the solvent electrophilicity.[40] The negative value for α demonstrates a red shift of the corresponding vibrational mode, which in turn is a result of bond weakening. So, in the more electrophilic solvents, electron density is withdrawn from the bonds associated with the vibrational mode. The absolute values of α reveal that the C=O stretching frequencies, in particular, those of the exposed C=O groups in the macrocycle, are more sensitive to the solvent acceptor number than the C=C stretching in the aromatic ring of the naphthalimide ($\nu(\mathrm{Ar})_{\mathrm{ni}}$).

NH stretching of 1 and 2: The NH region in the IR spectra of **1** and **2** is depicted in Figure 7. Despite the poor signal-

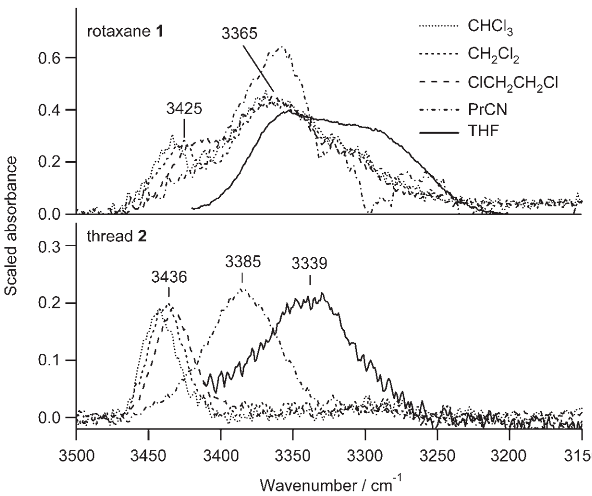


Figure 7. NH-stretching region of IR absorbance spectra of rotaxane **1** and thread **2** in $CHCl_3$, CH_2Cl_2, $ClCH_2CH_2Cl$, PrCN, and THF. All spectra were scaled to the intensity of the $\nu_s(CO)_{ni}$ band at $\approx 1700\,cm^{-1}$.

to-noise ratio, clear bands can be distinguished. The NH-stretching band of free NH groups in thread **2** in $CHCl_3$ appears at $3443\,cm^{-1}$ and shifts to 3436 and $3432\,cm^{-1}$ in CH_2Cl_2 and $ClCH_2CH_2Cl$, respectively. The contribution of the hydrogen-bonded NH stretching due to conformers with an intrasuccinamide hydrogen bond is present as a broad band centered around $3300\,cm^{-1}$. Although it is impossible to make a good estimate of the integrated intensity of this band, it appears that only a small fraction of the NH groups are hydrogen bonded. In PrCN and THF, the NH-stretching bands are significantly broadened and red-shifted to 3385 and $3339\,cm^{-1}$, respectively, due to hydrogen bonds between the solvent molecules and the succinamide NH groups.

In the NH-stretching region of the IR spectrum of rotaxane **1**, bands that can be assigned to the succinamide station and the macrocycle can be distinguished. In the chlorinated solvents, the NH stretching of the succinamide station is centered near $3425\,cm^{-1}$, which is at a slightly lower frequency (shift $\approx 10\,cm^{-1}$) than in thread **2**. The macrocycle NH stretching appears as a broad band with a maximum at $3365\,cm^{-1}$. While the amide I band shows a substantial solvent effect in the chlorinated solvents, the macrocycle NH stretching is unaffected by the solvent polarity. These NH groups are situated in the interior of the macrocycle and are shielded from the solvent. In PrCN and THF, this band is red-shifted, indicating that the solvent also forms hydrogen bonds with the macrocycle when its NH groups are not involved in hydrogen bonds with the thread.

IR spectroelectrochemistry: The electrochemistry of **1** and **2** was already studied in detail.[17] The CV response of **2** in THF exhibits a reversible, one-electron wave corresponding to reduction and reoxidation of the naphthalimide group (−1.41 V versus Fc/Fc^+). Rotaxane **1**, on the other hand, displays an irreversible behavior. This irreversibility is due to shuttling: the species formed after reduction is ni-$\mathbf{1}^{\bullet-}$, which has a more positive oxidation potential than the bare radical anion $\mathbf{2}^{\bullet-}$.

Amide I: Upon one-electron reduction of model compound **3**, three new bands of $\mathbf{3}^{\bullet-}$ appear at 1616, 1565, and $1534\,cm^{-1}$ at the expense of the $\nu(CO)_{ni}$ bands at 1703 and $1667\,cm^{-1}$ and the $\nu(Ar)_{ni}$ band at $1631\,cm^{-1}$ in **3** (Figure 8).

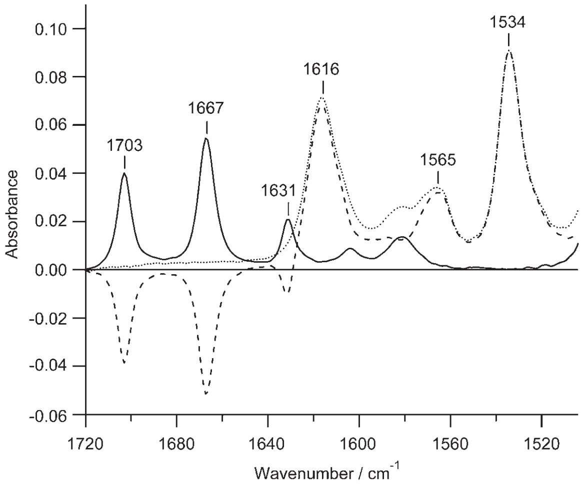


Figure 8. Amide I region of the IR spectra of the naphthalimide model compound **3** (——), $\mathbf{3}^{\bullet-}$ (•••••), and difference spectrum ($\mathbf{3}^{\bullet-}$ minus **3**) (-----) in THF.

Calculation of the vibrational frequencies of $\mathbf{3}^{\bullet-}$ predicts the three bands to be stronger than for the neutral molecule, and shifted to 1633 ($\nu_s(CO)_{ni}$), 1589 ($\nu_{as}(CO)_{ni}$) and $1532\,cm^{-1}$ ($\nu(Ar)_{ni}$), which agrees well with the experimental result. An additional aromatic ring vibration at $1558\,cm^{-1}$ is predicted, but with a very low intensity. The calculation shows that the normal modes associated with the three bands are similar in the radical anion and in the neutral molecule, and also that the order of the frequencies is the same. The C=O stretching modes have a larger shift than the aromatic ring vibration, but the latter is substantial as well. Because the singly occupied molecular orbital in $\mathbf{3}^{\bullet-}$ is strongly delocalized over the whole π-system, not only the C=O, but also the C=C bonds are weakened compared to those in **3**.

A similar picture emerges for $\mathbf{2}^{\bullet-}$ (Figure 9). In this case, the characteristic band pattern of the succinamide station between 1700 and $1640\,cm^{-1}$, in **2** obscured by the $\nu_{as}(CO)_{ni}$ band, is clearly visible in the radical anion. The tail on the red side of the $\nu_s(CO)_{ni}$ band of $\mathbf{2}^{\bullet-}$ at $1616\,cm^{-1}$ (not present in the spectrum of $\mathbf{3}^{\bullet-}$), supports the existence of a small fraction of $\mathbf{2}^{\bullet-}$ in which hydrogen bonds exist between the succinamide station and naphthalimide radical anion (folded conformations, see Scheme 3).

In the course of the reduction of rotaxane **1**, the three naphthalimide bands at 1702, 1667 and $1631\,cm^{-1}$ gradually disappeared and new bands at 1591, 1546 and $1518\,cm^{-1}$ grew in. The initially obscured $\nu(CO)_{succ}$ and $\nu(CO)_{macro}$

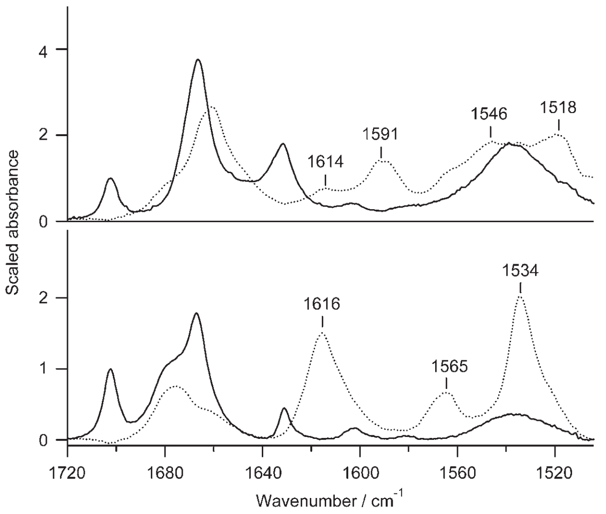


Figure 9. IR spectra of neutral (——) and reduced (•••••) top: rotaxane **1** (**1**$^{\bullet-}$ reduced) and bottom: thread **2** (**2**$^{\bullet-}$ reduced) in THF.

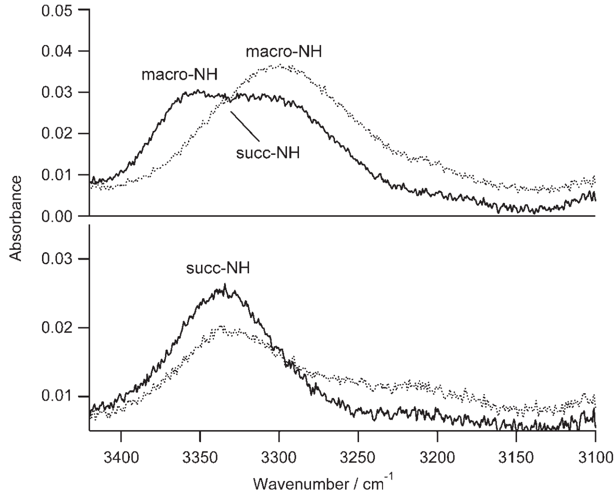


Figure 10. NH-stretching region of the IR spectra of neutral (——) and reduced (•••••) thread **1** (**1**$^{\bullet-}$ reduced) and rotaxane **2** (**2**$^{\bullet-}$ reduced) in THF.

bands in **1** are visible in **1**$^{\bullet-}$. The $\nu(\mathrm{CO})_{\mathrm{macro}}$ band has shifted to a lower wavenumber and appears at 1658 cm^{-1} (Figure 9).

NH stretching: The NH stretching region in the IR spectrum of the neutral molecule and radical anion of the rotaxane (**1** and **1**$^{\bullet-}$) and the thread (**2** and **2**$^{\bullet-}$) in THF are depicted in Figure 10. In the spectrum of **2**$^{\bullet-}$, an intensity decrease of the NH-stretching band at 3340 cm^{-1} is observed, while the red-shifted band of more strongly hydrogen-bonded NH stretching increases. This supports the presence of hydrogen bonds between the NH groups of the succinamide station and the C=O groups of the naphthalimide radical anion in the folded conformation (folded-**2**$^{\bullet-}$, Scheme 3). The relative intensities of the free and hydrogen-bonded NH-stretching bands indicate that the extended-**2**$^{\bullet-}$ conformation is the predominant species.

The NH-stretching region of reduced rotaxane **1**$^{\bullet-}$ reveals some interesting features. The NH-stretching band of the less-strongly bound NH groups in the macrocycle (3365 cm^{-1}) has almost disappeared. The band of the NH stretching at $\approx$3300 cm^{-1} is more intense than in neutral **1**. The stronger hydrogen-bonding interactions in **1**$^{\bullet-}$ compared to **1** support the notion that the macrocycle is indeed hydrogen bonded to the naphthalimide radical anion.

Different spectra: A convenient way to analyze the processes accompanying the reduction is by comparing the difference absorbance spectra between radical anion and neutral molecule for rotaxane **1** and thread **2** (Figure 11). In both the rotaxane and thread, three negative bands are present. For **2**$^{\bullet-}$, three prominent new bands appear in the IR spectrum at 1616, 1565 and 1534 cm^{-1}. These bands are shifted to lower wavenumbers in **1**$^{\bullet-}$ and appear at 1591, 1551 and

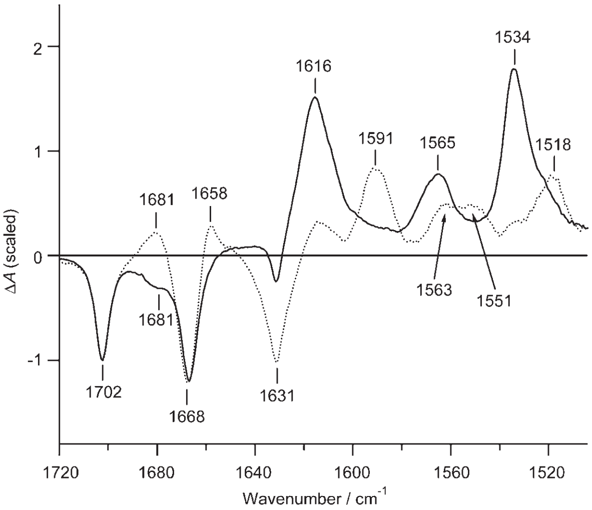
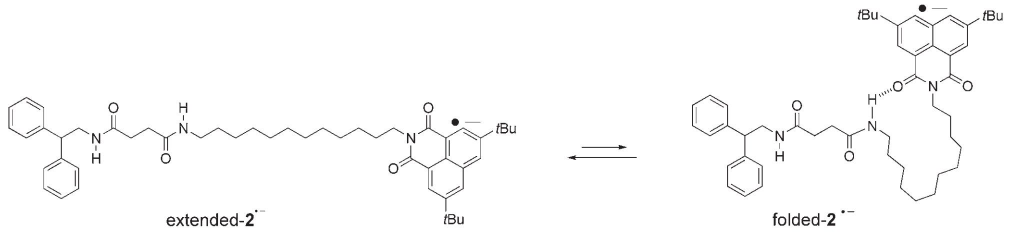


Figure 11. Difference absorbance spectra (radical anion minus neutral) of rotaxane **1** (•••••) and thread **2** (——) in THF.



Scheme 3. Structures of extended (predominant) and the folded conformations of **2**$^{\bullet-}$.

1518 cm^{-1}. The larger shift to lower wavenumbers of the naphthalimide radical anion bands in $\mathbf{1}^{\bullet-}$ with respect to those of $\mathbf{2}^{\bullet-}$ provides clear evidence that translational movement of the macrocycle from the succinamide station to the naphthalimide radical anion has taken place in $\mathbf{1}^{\bullet-}$. This spectral red shift in $\mathbf{1}^{\bullet-}$ is induced by hydrogen bonding between the NH groups of the macrocycle and the carbonyls of the radical anion. A red shift in $\mathbf{2}^{\bullet-}$ (compared to $\mathbf{3}^{\bullet-}$) appears only as a shoulder on the main band (1616 cm^{-1}), and hydrogen bonding of the imide anion with the succinamide NH groups (folded-$\mathbf{2}^{\bullet-}$) is of minor importance. In analogy with the situation in $\mathbf{2}^{\bullet-}$, the extended conformation of $\mathbf{1}^{\bullet-}$ is expected to be the predominant species.

In the difference absorbance spectrum of the rotaxane, two additional positive bands at 1658 and 1681 cm^{-1} are present. The first band (1681 cm^{-1}) has the same position as the $\nu(\mathrm{CO})_{\mathrm{succ}}$ band in **4**, and belongs to $\nu(\mathrm{CO})_{\mathrm{succ}}$, which has been liberated after shuttling. The second band at 1658 cm^{-1} is from the macrocycle C=O stretching. This is red-shifted by 9 cm^{-1} due to an indirect effect of hydrogen bonding to the NH groups of the amides. The computational study of Reckien et al. reports shifts of −5 to −16 cm^{-1} for similar cases.[25] In the predominant co-conformer ni-$\mathbf{1}^{\bullet-}$ (Scheme 1), the hydrogen bonds from the macrocycle NH groups to the radical anion are stronger than those in co-conformer succ-$\mathbf{1}^{\bullet-}$, which causes further weakening of the macrocycle C=O bond and, as a consequence, a more red-shifted C=O stretching is observed. Another consequence is that also the amide II band ($\approx$1520 cm^{-1} in **1**) of the macrocycle amide groups is expected to change. A shift to higher frequency is predicted by computation.[25] The precise changes in the amide II band could not be resolved due to the overlap with the $\nu_{as}(\mathrm{CO})_{\mathrm{ni}}$ and $\nu(\mathrm{Ar})_{\mathrm{ni}}$ bands of the naphthalimide radical anion. Conversely, the apparent changes in the latter bands can also be influenced by changes in the amide II bands. The (unexpected) shift of the $\nu(\mathrm{Ar})_{\mathrm{ni}}$ peak from 1534 cm^{-1} in thread **2** to 1518 cm^{-1} in the rotaxane **1** is, therefore, uncertain. The most important bands present in the IR spectra of neutral and reduced **1** and **2** are listed in Figure 12 and Table 2.

To analyze the solvent effect on the switching, IR spectroelectrochemical experiments of **1** and **2** were also carried out in PrCN (Figure 13). For $\mathbf{2}^{\bullet-}$ in PrCN, the $\nu_s(\mathrm{CO})_{\mathrm{ni}}$ band shows a solvatochromic red shift (relative to THF) and appears at 1612 cm^{-1}. For ni-$\mathbf{1}^{\bullet-}$ in PrCN, however, the $\nu_s(\mathrm{CO})_{\mathrm{ni}}$ band remains at almost the same position (1592 cm^{-1}) as in THF. This, again, is clear evidence that the macrocycle shields the carbonyl groups of the station to which it is hydrogen bonded from the solvent. This was also previously concluded from the electronic absorption spectra of the radical anion in ni-$\mathbf{1}^{\bullet-}$: the absorption maximum of ni-$\mathbf{2}^{\bullet-}$ shifts to the blue in more polar solvents, but in ni-$\mathbf{1}^{\bullet-}$, it does not depend on the medium polarity because the effect of the hydrogen bonds made with the macrocycle is stronger than that of solvation.[17]

Table 2. Wavenumbers of IR modes of neutral and reduced **1**, **2**, and **3** in THF.

Mode	Neutral [cm^{-1}]			Radical anion [cm^{-1}]		
	3	**2**	**1**	$\mathbf{3}^{\bullet-}$	$\mathbf{2}^{\bullet-}$	$\mathbf{1}^{\bullet-}$
$\nu_s(\mathrm{CO})_{\mathrm{ni}}$	1703	1702	1702	1616	1616	1591
$\nu(\mathrm{CO})_{\mathrm{macro}}$	–	–	1667[a]	–	–	1658
$\nu(\mathrm{CO})_{\mathrm{macro}}$	–	–	1648[b]	–	–	-
$\nu(\mathrm{CO})_{\mathrm{succ}}$	–	1680[a]		–	–	1681
$\nu(\mathrm{CO})_{\mathrm{succ}}$	–	1658[b]	1633[b]	–	–	–
$\nu_{as}(\mathrm{CO})_{\mathrm{ni}}$	1667	1667	1667	1565	1565	1551
$\nu(\mathrm{Ar})_{\mathrm{ni}}$	1631	1631	1631	1534	1534	1518

[a] Free C=O. [b] Hydrogen bonded C=O.

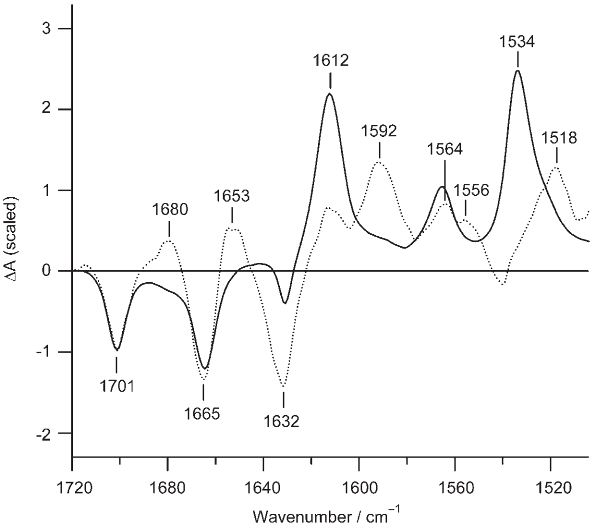


Figure 13. Difference absorbance spectra (radical anion minus neutral) of rotaxane **1** (•••••) and thread **2** (——) in butyronitrile.

The difference absorbance spectrum (radical anion versus neutral molecule) of the rotaxane in THF and PrCN suggest that a small fraction of the radical anion is not hydrogen bonded: absorbance from free radical anion is observed at 1616, 1563 and 1534 cm^{-1}(in THF), suggesting that a small fraction of $\mathbf{1}^{\bullet-}$ exists as the succ-$\mathbf{1}^{\bullet-}$ co-conformer. This seems to conflict with previous studies on the co-conformer distribution of $\mathbf{1}^{\bullet-}$.[16,17] However, the presence of bands at-

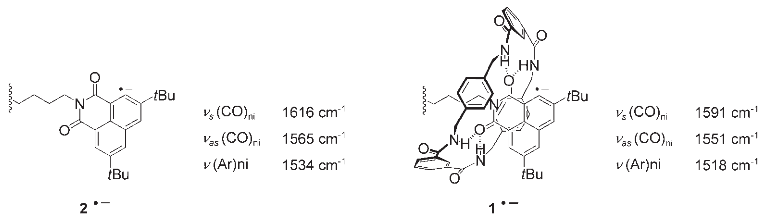


Figure 12. Structures of the naphthalimide radical anion in rotaxane ($\mathbf{1}^{\bullet-}$) and thread ($\mathbf{2}^{\bullet-}$), with wavenumbers of the most important IR modes characteristic for the binding of the macrocycle to the naphthalimide radical anion.

tributable to the imide radical anion in a non-hydrogen-bonded form does not necessarily mean that the molecules exist in the succ-$\mathbf{1}^{\bullet -}$ co-conformer. Cyclic voltammetry, UV/Vis spectroelectrochemistry and transient absorption spectroscopy experiments with **1**, reveal almost quantitative conversion of succ-$\mathbf{1}^{\bullet -}$ to ni-$\mathbf{1}^{\bullet -}$ (ratio ni-$\mathbf{1}^{\bullet -}$/succ-$\mathbf{1}^{\bullet -}$ >1500).[17] Assuming full conversion to ni-$\mathbf{1}^{\bullet -}$ in the present IR experiments, we can conclude that in this co-conformer not all the C=O groups of the naphthalimide anion are involved in hydrogen bonding, and also that more than one type of hydrogen bond with different geometry and strength is present. An additional indication for this is the fact that the $\nu_s(\mathrm{CO})_{\mathrm{ni}}$ band of ni-$\mathbf{1}^{\bullet -}$ (1591 $\mathrm{cm^{-1}}$) is broad, probably composed of bands from C=O stretching of differently hydrogen bonded C=O groups.

The switching is driven by the fact that hydrogen bonding between a macrocycle and naphthalimide radical anion is energetically favored over hydrogen bonding between the macrocycle and succinamide station, that is, the hydrogen bonds between macro-NH and $\mathrm{ni}^{\bullet -}$-CO are stronger than between macro-NH and succ-CO. This is confirmed by the fact that the $\nu(\mathrm{CO})_{\mathrm{macro}}$ band exhibits a red shift of 9 $\mathrm{cm^{-1}}$ in ni-$\mathbf{1}^{\bullet -}$ compared to succ-**1**. The red shift is obviously caused by stronger hydrogen bonds in ni-$\mathbf{1}^{\bullet -}$ compared to succ-**1**.

From the fact that hydrogen bonds in ni-$\mathbf{1}^{\bullet -}$ are stronger than in succ-**1**, one would expect a larger hydrogen-bond-induced red shift of the $\nu_s(\mathrm{CO})_{\mathrm{ni}}$ band relative to the $\nu(\mathrm{CO})_{\mathrm{succ}}$ band. However, the red shift of the $\nu(\mathrm{CO})_{\mathrm{succ}}$ band of **1** in THF is 47 $\mathrm{cm^{-1}}$ (1680–1633 $\mathrm{cm^{-1}}$), while the largest shift observed in the spectrum of ni-$\mathbf{1}^{\bullet -}$ is for the $\nu_s(\mathrm{CO})_{\mathrm{ni}}$ band (25 $\mathrm{cm^{-1}}$). The observation that the $\nu_s(\mathrm{CO})_{\mathrm{ni}}$ band in the radical anion exhibits a smaller red shift than the $\nu(\mathrm{CO})_{\mathrm{succ}}$ band in the neutral molecule, means that the former is less sensitive to hydrogen bonding, but the reason for this is not obvious.

To understand in more detail the influence of the strength of the H-bonding interactions on the equilibrium between succ-$\mathbf{1}^{\bullet -}$ and ni-$\mathbf{1}^{\bullet -}$, experiments with structurally modified rotaxanes are in progress. In these new molecular shuttles, the naphthalimide station was replaced by other aromatic imides. Due to the different size of the aromatic core, the electron density on the carbonyl groups in the radical anion will be different. An important result of the study with a naphthalene bisimide system is that despite the smaller driving force than in the naphthalene monoimide system, shuttling still occurs to a large extent ($>80\,\%$).[41] This supports the idea that in $\mathbf{1}^{\bullet -}$, the conversion to the ni-$\mathbf{1}^{\bullet -}$ co-conformer is close to quantitative. Therefore, the minor fraction of apparently free C=O groups in ni-$\mathbf{1}^{\bullet -}$, represented by the bands at 1614 and 1563 $\mathrm{cm^{-1}}$ (in THF), must represent a fraction of species in which not all $\mathrm{ni}^{\bullet -}$-CO's are hydrogen bonded to the macrocycle NH groups.

Conclusion

The amide I region in the IR spectra of **1** and **2** in solvents of different polarity ($\mathrm{CHCl_3}$, $\mathrm{CH_2Cl_2}$, $\mathrm{ClCH_2CH_2Cl}$, PrCN, and THF) was analyzed. In the major co-conformer of **1**, the macrocycle is situated at the succinamide station. Both **1** and **2** show bands due to the naphthalimide station, originating from symmetric and antisymmetric C=O stretching and aromatic ring vibrations. All these modes are solvatochromic and exhibit a red shift with increasing solvent acceptor number. In the IR spectrum of **2**, $\nu(\mathrm{CO})_{\mathrm{succ}}$ bands of both free and hydrogen-bonded C=O groups were observed. In rotaxane **1**, a major part of the succinamide C=O groups was found to be hydrogen bonded to the NH groups of the macrocycle. The shift with respect to the free $\nu(\mathrm{CO})_{\mathrm{succ}}$ in **2** is large (47 $\mathrm{cm^{-1}}$) because two bifurcated hydrogen bonds can be formed with each carbonyl.[16]

The IR spectroelectrochemical experiments unambiguously show that the macrocycle undergoes translational movement from the succinamide to the one-electron-reduced naphthalimide station. Upon reduction of thread **2**, three new bands of the radical anion appear in the spectrum, while the bands from the neutral naphthalimide disappear. In rotaxane **1**, the same bands show up, but shifted to lower frequencies. This red shift of the C=O stretching modes (25 $\mathrm{cm^{-1}}$) is a result of bond weakening caused by hydrogen bonding with the NH groups of the macrocycle. The $\nu(\mathrm{CO})_{\mathrm{macro}}$ band also shows a shift to lower frequency (9 $\mathrm{cm^{-1}}$ in THF) because the amide N−H groups are involved in hydrogen bonds (indirect effect). Also, after shuttling a band from the liberated succinamide station appears in the spectrum.

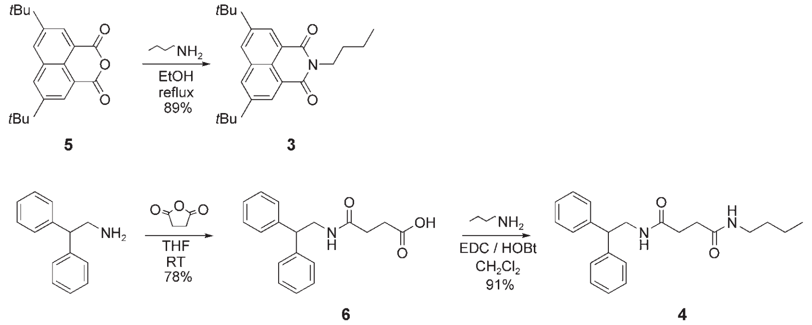
A remarkable observation is the shielding effect of the macrocycle. The succ-CO and $\mathrm{ni}^{\bullet -}$-CO groups encapsulated by the macrocycle are isolated from the solvent. The corresponding $\nu(\mathrm{CO})$ bands do not show any dependence on the solvent polarity.

Experimental Section

Syntheses: Compounds **1** and **2** were prepared as described in previous work.[17] The syntheses of compounds **3** and **4** are depicted in Scheme 4. Compound **3** was synthesized from precursor **5** in 89 % yield. Compound **5** was prepared by using a literature procedure.[17] Compound **4** was synthesized in two steps from commercially available 2,2-diphenylethylamine and succinic anhydride in 71 % yield.

***N*-Butyl-2,5-di-*tert*-butylnaphthalimide (3)**: A solution of **5** (205 mg, 0.66 mmol) and *N*-butyl amine (481 mg, 6.6 mmol) in ethanol (25 mL) was refluxed overnight and stirred at room temperature for 3 d. After this time, the white precipitate was filtered off and washed with ethanol and dried in air. Product **3** was obtained as a white powder. Yield: 215 mg (89 %); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 8.64$ (d, 2H; arom. H), 8.12 (d, 2H; arom. H), 4.20 (t, 2H; $\mathrm{N{-}CH_2{-}C}$), 1.72 (quin., 2H; $\mathrm{N{-}CH_2{-}}\mathit{CH_2}\mathrm{{-}CH_2}$), 1.47 (m, 20H; *t*Bu + $\mathrm{{-}CH_2{-}}\mathit{CH_2}\mathrm{{-}CH_3}$), 0.98 ppm (t, 3H; $\mathrm{CH_2{-}}\mathit{CH_3}$); elemental analysis calcd (%) for $\mathrm{C_{24}H_{31}NO_2}$: C 78.86, H 8.55, N 3.83, O, 8.75; found: C 78.20, H 8.50, N 3.98, O 9.24.

***N*-(2,2-Diphenylethyl)succinamic acid (6)**: A mixture of 2,2-diphenylethylamine (5.79 g, 29.3 mmol) and succinic anhydride (4.41 g, 44.0 mmol, 1.5 equiv) in THF was stirred overnight. The solvent was evaporated



Scheme 4. Syntheses of naphthalimide and succinamide model compounds **3** and **4**.

under reduced pressure and the white solid obtained was triturated with water to remove excess succinic anhydride and polar byproducts. After drying, **6** was obtained as a light-brown powder. Yield: 6.78 g (78%); ^{1}H NMR (400 MHz, CD_3OD): $\delta = 7.38$–7.16 (m, 10H; arom. H), 4.24 (t, $J = 8.1$ Hz, 1H; $(Ph)_2CH{-}C$), 3.81 (d, $J = 8.1$ Hz, 2H; $C{-}CH_2{-}N$), 2.47 (t, $J = 7.0$ Hz, 2H; $C{-}\mathit{CH_2}{-}COOH$), 2.34 ppm (t, 2H, $J = 7.0$ Hz, 2H; $HNOC{-}\mathit{CH_2}{-}C$).

***N*-Butyl-*N'*-(2,2-diphenylethyl)succinamide (4)**: A solution of **6** (168 mg, 0.566 mmol) in CH_2Cl_2 (10 mL) was added to a mixture of *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC) (297 mg, 1.55 mmol) and 1-hydroxybenzotriazole (HOBt) (123 mg, 0.913 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 10 min. A solution of butyl amine (41.4 mg, 0.566 mmol) in CH_2Cl_2 (5 mL) was added, and the reaction mixture was stirred overnight. The solvent was evaporated and the residue was dissolved in EtOAc. The solution was washed subsequently with 1 M HCl (3×), saturated $NaHCO_3$ (3×), and water (3×). The organic layer was dried over $MgSO_4$ and the solvent was evaporated, affording **4** as a white powder. Yield 182 mg (91%); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.39$–7.18 (m, 10H; arom. H), 5.85 (brs, 2H; NHs), 4.16 (t, 1H; $(Ph)_2CH{-}C$), 3.88 (dd, 2H; $(Ph)_2CH{-}\mathit{CH_2}{-}N$), 3.19 (m, 2H; $N{-}\mathit{CH_2}{-}CH_2$), 2.40 (s, 4H; $OC{-}\mathit{CH_2}{-}\mathit{CH_2}{-}CO$), 1.46 (quin., 2H; $N{-}CH_2{-}\mathit{CH_2}{-}CH_2$), 1.34 (quin., 2H; $CH_2{-}\mathit{CH_2}{-}CH_3$), 0.92 (t, 3H; $CH_2{-}CH_2{-}\mathit{CH_3}$); elemental analysis calcd (%) for $C_{22}H_{28}N_2O_2$: C 74.97, H 8.01, N 7.95, O 9.08; found: C 74.83; H 8.56; N 7.88; O 8.67.

Infrared spectra

Sample preparation: All IR spectra were measured with 2–4 mM solutions. All solutions were prepared in Schlenk flasks by dissolving weighed amounts of compound under dry N_2 in freshly distilled dry solvent to avoid the presence of water in the samples. The solvent was added with a syringe (the volume of the obtained solution was known only approximately). The sample solutions were then transferred to the IR cell with a syringe.

Infrared spectroelectrochemistry: IR spectroelectrochemical measurements were performed in an optically transparent thin-layer electrochemical (OTTLE) cell[42] equipped with CaF_2 optical windows and a minigrid platinum working electrode. The optical beam can pass directly through the working electrode, allowing the redox processes taking place in the thin solution layer surrounding the working electrode to be studied spectroscopically. The controlled-potential electrochemical conversions were carried out with a PA4 potentiostat (EKOM, Polná, Czech Republic). A slow scan rate of $2\ mVs^{-1}$ was used to allow quantitative electrochemical conversion. The spectra were recorded at different points on the thin-layer voltammograms; the scanning of the potential was paused during the recording. Dry tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), crystallized twice from methanol, was used as supporting electrolyte. IR spectra were recorded on Nicolet 6700 FTIR or Bruker Vertex 70 FTIR spectrometers.

Calculations: Calculations of the IR frequencies in the amide I region of the model compounds were carried out at the B3LYP/6–31G(d) level.[43] For the calculations of the C=O vibrations in **4**, the butyl group was replaced by a methyl group, while for **3** and $\mathbf{3}^{\bullet-}$, the butyl group was replaced by an ethyl group, and the *tert*-butyl groups by methyl groups. For the calculation of IR frequencies in a solvent medium, the polarisable continuum model (PCM)[44,45] was used. The computed wavenumbers were scaled by a standard scaling factor of 0.9614.[46]

Acknowledgements

We thank C. Mahabiersing for technical support and Prof. D.A. Leigh (Edinburgh, UK) for providing us with a synthetic building block for thread **2**. This research was supported by The Netherlands Organization for the Advancement of Research (NWO).

---

[1] V. Balzani, A. Credi, S. Silvi, M. Venturi, *Chem. Soc. Rev.* **2006**, *35*, 1135–1149.
[2] H. Tian, Q. C. Wang, *Chem. Soc. Rev.* **2006**, *35*, 361–374.
[3] I. Willner, B. Basnar, B. Willner, *Adv. Funct. Mater.* **2007**, *17*, 702–717.
[4] S. Saha, J. F. Stoddart, *Chem. Soc. Rev.* **2007**, *36*, 77–92.
[5] E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem.* **2007**, *119*, 72–196; *Angew. Chem. Int. Ed.* **2007**, *46*, 72–191.
[6] C. M. Keaveney, D. A. Leigh, *Angew. Chem.* **2004**, *116*, 1242–1244; *Angew. Chem. Int. Ed.* **2004**, *43*, 1222–1224.
[7] V. Serreli, C. F. Lee, E. R. Kay, D. A. Leigh, *Nature* **2007**, *445*, 523–527.
[8] A. M. Brouwer, S. M. Fazio, N. Haraszkiewicz, D. A. Leigh, C. M. Lennon, *Photochem. Photobiol. Sci.* **2007**, *6*, 480–486.
[9] J. Berna, D. A. Leigh, M. Lubomska, S. M. Mendoza, E. M. Perez, P. Rudolf, G. Teobaldi, F. Zerbetto, *Nat. Mater.* **2005**, *4*, 704–710.
[10] J. D. Badjic, C. M. Ronconi, J. F. Stoddart, V. Balzani, S. Silvi, A. Credi, *J. Am. Chem. Soc.* **2006**, *128*, 1489–1499.
[11] V. Balzani, M. Clemente-Leon, A. Credi, B. Ferrer, M. Venturi, A. H. Flood, J. F. Stoddart, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 1178–1183.
[12] J. P. Collin, D. Jouvenot, M. Koizumi, J. P. Sauvage, *Eur. J. Inorg. Chem.* **2005**, 1850–1855.
[13] M. C. Jimenez-Molero, C. Dietrich-Buchecker, J. P. Sauvage, *Chem. Eur. J.* **2002**, *8*, 1456–1466.
[14] E. J. F. Klotz, T. D. W. Claridge, H. L. Anderson, *J. Am. Chem. Soc.* **2006**, *128*, 15374–15375.
[15] H. Isobe, S. Sato, E. Nakamura, *Org. Lett.* **2002**, *4*, 1287–1289.
[16] A. Alteri, F. G. Gatti, E. R. Kay, D. A. Leigh, D. Martel, F. Paolucci, A. M. Z. Slawin, J. K. Y. Wong, *J. Am. Chem. Soc.* **2003**, *125*, 8644–8654.
[17] A. M. Brouwer, C. Frochot, F. G. Gatti, D. A. Leigh, L. Mottier, F. Paolucci, S. Roffia, G. W. H. Wurpel, *Science* **2001**, *291*, 2124–2128.
[18] L. Hviid, J. W. Verhoeven, A. M. Brouwer, M. N. Paddon-Row, J. X. Yang, *Photochem. Photobiol. Sci.* **2004**, *3*, 246–251.
[19] B. Ishimoto, K. Tonan, S. Ikawa, *Spectrochim. Acta A* **1999**, *55*, 2321–2327.
[20] R. A. Shaw, A. Perczel, H. H. Mantsch, G. D. Fasman, *J. Mol. Struct.* **1994**, *324*, 143–150.
[21] G. P. Dado, S. H. Gellman, *J. Am. Chem. Soc.* **1993**, *115*, 4228–4245.
[22] P. Bruni, E. Giorgini, E. Maurelli, G. Tosi, *Vib. Spectrosc.* **1996**, *12*, 249–255.
[23] G. P. Dado, S. H. Gellman, *J. Am. Chem. Soc.* **1992**, *114*, 3138–3139.
[24] W. Herrebout, K. Clou, H. O. Desseyn, N. Blaton, *Spectrochim. Acta A* **2003**, *59*, 47–59.
[25] W. Reckien, B. Kirchner, S. D. Peyerimhoff, *J. Phys. Chem. A* **2006**, *110*, 12963–12970.
[26] M. Fanti, C. A. Fustin, D. A. Leigh, A. Murphy, P. Rudolf, R. Caudano, R. Zamboni, F. Zerbetto, *J. Phys. Chem. A* **1998**, *102*, 5782–5788.

[27] C. A. Fustin, D. A. Leigh, P. Rudolf, D. Timpel, F. Zerbetto, *ChemPhysChem* **2000**, *1*, 97–100.
[28] T. J. Huang, A. Flood, C. W. Chu, S. Kang, T. F. Guo, T. Yamamoto, H. R. Tseng, B. D. Yu, Y. Yang, J. F. Stoddart, *Third IEEE Conference on Nanotechnology (San Francisco)*, **2003**, *2*, 698–701.
[29] O. F. A. Larsen, P. Bodis, W. J. Buma, J. S. Hannam, D. A. Leigh, S. Woutersen, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 13378–13382.
[30] E. DeIonno, H. R. Tseng, D. D. Harvey, J. F. Stoddart, J. R. Heath, *J. Phys. Chem. B* **2006**, *110*, 7609–7612.
[31] A. G. Johnston, D. A. Leigh, A. Murphy, J. P. Smart, M. D. Deegan, *J. Am. Chem. Soc.* **1996**, *118*, 10662–10663.
[32] I. Grabchev, C. Petkov, V. Bojinov, *Dyes Pigm.* **2004**, *62*, 229–234.
[33] S. H. Gellman, G. P. Dado, G. B. Liang, B. R. Adams, *J. Am. Chem. Soc.* **1991**, *113*, 1164–1173.
[34] D. T. McQuade, S. L. McKay, D. R. Powell, S. H. Gellman, *J. Am. Chem. Soc.* **1997**, *119*, 8528–8532.
[35] D. S. Marlin, D. G. Cabrera, D. A. Leigh, A. M. Z. Slawin, *Angew. Chem.* **2006**, *118*, 1413–1418; *Angew. Chem. Int. Ed.* **2006**, *45*, 1385–1390.
[36] D. A. Leigh, M. A. F. Morales, E. M. Perez, J. K. Y. Wong, C. G. Saiz, A. M. Z. Slawin, A. J. Carmichael, D. M. Haddleton, A. M. Brouwer, W. J. Buma, G. W. H. Wurpel, S. Leon, F. Zerbetto, *Angew. Chem.* **2005**, *117*, 3122–3127; *Angew. Chem. Int. Ed.* **2005**, *44*, 3062–3067.
[37] F. Biscarini, M. Cavallini, D. A. Leigh, S. Leon, S. J. Teat, J. K. Y. Wong, F. Zerbetto, *J. Am. Chem. Soc.* **2002**, *124*, 225–233.
[38] W. R. Fawcett, P. Politzer, J. S. Murray, *Theoretical and Computational Chemistry: Quantitative Treatments of Solvent/Solute Interactions*, Elsevier, Amsterdam, **1994**, pp. 183–212.
[39] W. R. Fawcett, A. A. Kloss, *J. Phys. Chem.* **1996**, *100*, 2019–2024.
[40] U. Mayer, V. Gutman, W. Greger, *Monatsh. Chem.* **1975**, *106*, 1235.
[41] J. Baggerman, PhD Thesis, University of Amsterdam, Amsterdam, **2006**.
[42] M. Krejčik, M. Daněk, F. Hartl, *J. Electroanal. Chem.* **1991**, *317*, 179–187.
[43] Gaussian 03 (Revision B.3), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Pittsburgh PA, USA, **2003**.
[44] S. Miertus, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117–129.
[45] M. Cossi, V. Barone, R. Cammi, J. Tomasi, *Chem. Phys. Lett.* **1996**, *255*, 327–335.
[46] A. P. Scott, L. Radom, *J. Phys. Chem.* **1996**, *100*, 16502–16513.

Received: September 27, 2007