DOI: 10.1002/ejoc.200500479

Ion-Pairing Effects in the Self-Assembly of a Fluorescent Pseudorotaxane

Miguel Clemente-León,[a,b] Chiara Pasquini,[c] Virginie Hebbe-Viton,[d] Jerome Lacour,[d] Antonella Dalla Cort,*[c] and Alberto Credi*[a]

Keywords: Ion pairs / Photochemistry / Rotaxanes / Self-assembly / Molecular recognition

Herein we report on the self-assembly, in a low polarity solvent, of a pseudorotaxane species comprising binaphthyl-26-crown-8 (BN26C8) as the macrocyclic host and anthracenyl-benzylammonium as the threadlike positively charged guest (ABH^+). Absorption and luminescence data reveal a very efficient energy transfer process occurring from the binaphthyl to the anthracene singlet excited states. The self-assembly is highly dependent on the nature of the counteranion confirming the crucial role played by it in the competition between the self-assembly process and the formation of ion pairs (ABH^+X^-). This behavior can be readily evidenced in dilute solutions from the analysis of the luminescence properties of the system. The complexation of chloride, sulfate and hexafluorophosphate salts of ABH^+ by racemic BN26C8 as well as the complexation of ABH^+ salts of the chiral anion *tris*[tetrachlorobenzenediolato]phosphate(V) ($TRISPHAT^-$) by (+) BN26C8 are described. The efficiency in complexation follows the trend $PF_6^- > TRISPHAT^- > Cl^-, SO_4^{2-}$. The use of the chiral anion TRISPHAT allowed us to investigate the possibility of inducing stereoselective control on the formation of the interpenetrating assembly. Preliminary ^1H NMR spectroscopic evidence supports the fact that the chiral anion is paired to the supramolecular complex and that its configuration influences the recognition process.

Introduction

Pseudorotaxanes are host–guest systems composed minimally of a threadlike molecule surrounded by a macrocycle.[1] These supermolecules have been attracting considerable attention,[2] not only for their structural features, but also because of the variety of properties and functions that can be engineered within them. For example, pseudorotaxane structures constitute a convenient basis for the design and construction of simple prototypes of artificial nanoscale devices and machines.[3–12]

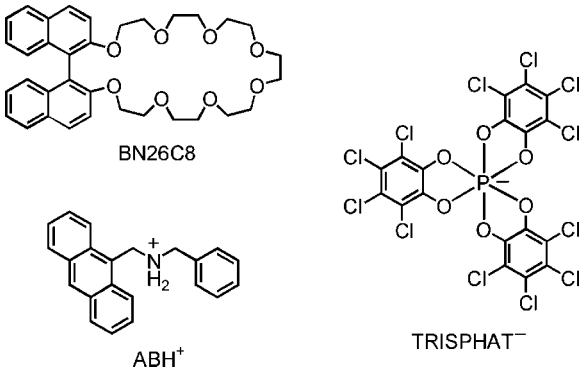
It has long been known[13] that crown ethers give adducts with RNH_3^+ ammonium ions, stabilized by [N^+–H···O] hydrogen bonds.[14] More recently it has been shown[15] that when the crown ether ring is large enough, suitably chosen dialkylammonium ions ($R_2NH_2^+$) can thread through the macrocycle to give pseudorotaxane species in solution by virtue of strong [N^+–H···O] and [C–H···O] hydrogen-bonding interactions. Upon deprotonation of the ammonium ion by addition of a base, the hydrogen bonds are broken and dethreading of the pseudorotaxane takes place. The complex can be re-assembled by adding an acid which regenerates the ammonium ion.[4,16]

Low polarity solvents are frequently used to maximize electrostatic interactions, including hydrogen bonding.[17] In such solvents, ions show a strong tendency to form tight ion pairs.[18] Therefore, when considering the association in apolar solvents between two molecular components where either one of them or both are charged, ion pairing may come into play. Despite the fact that this phenomenon can largely affect the behavior of the host–guest complex,[19] it has been frequently overlooked. The role of ion pairing in the determination of the stability constant of complexes between neutral hosts and positively charged guests has been studied recently by NMR spectroscopic investigations by Gibson and co-workers.[20] It has also been found that the nature of the counteranion influences the kinetics of the self-assembly process of calixarene-based pseudorotaxanes[21] and the ratio of translational isomers in bistable donor/acceptor rotaxanes.[22]

To gain insight into these problems and in view of future applications, we investigated the influence of a number of anions on the formation of the pseudorotaxane system obtained by racemic binaphthyl-26-crown-8, BN26C8, and anthracenyl-benzylammonium cation, ABH^+ in CH_2Cl_2 (see Scheme 1). We recently reported[4] that this system behaves as a molecular level plug/socket device controlled by reversible threading/dethreading of the two components in solu-

[a] Dipartimento di Chimica "G. Ciamician", Università di Bologna,
via Selmi 2, 40126 Bologna, Italy
[b] Present address: Instituto de Ciencia Molecular, Universidad de Valencia,
Dr. Moliner 20, 46100 Burjassot, Spain
[c] Dipartimento di Chimica and IMC-CNR, Università La Sapienza di Roma,
Box 34 Roma 62, piazzale A. Moro 5, 00185 Roma, Italy
E-mail: Antonella.dallacort@uniroma1.it
[d] Université de Genève, Département de Chimie Organique,
Quai Ernest Ansermet 30, 1211 Geneva 4, Switzerland

tion obtained by acid-base stimulation. As previously mentioned, in apolar media the counteranion of ABH^+ should strongly influence the efficiency of the self-assembly process since it competes with the host for the guest. A number of different salts, namely hexafluorophosphate, (Δ)-*tris*[tetrachlorobenzenediolato]phosphate(v) (TRISPHAT),[23] chloride and sulfate, were employed in the experiments as sources of the ABH^+ cation. To study the intercomponent interactions, the photophysical properties of the supramolecular complex were compared with those of the molecular components. The disassembly of the supramolecular species upon addition of a base and the subsequent acid-driven reassembly was investigated. Moreover, the possibility of achieving chiral recognition by interaction of TRISPHAT with the bimolecular adduct intrigued us. The well-dispersed negative charge of this chiral anion should lead in lipophilic media to very strong complexes[24] that hopefully can effect the matching with optically pure (+)-BN26C8. To test this hypothesis, an achiral cation, such as ABH^+, is a perfect choice. Enantiomeric recognition of chiral ammonium ions by crown ethers containing binaphthyl is a well documented property,[25] but until now not much attention has been devoted to the problem of how the configuration of a chiral counteranion can influence the recognition processes.[26] Preliminary NMR spectroscopic measurements on (+)BN26C8 and the two enantiomers of the [ABH][TRISPHAT] salt were performed in $CDCl_3/CD_3CN$, 6:1, and the effect of anion chirality on the enantioselective formation of pseudorotaxane complexes has been considered.



Scheme 1. Structural formulae of the compounds examined.

Results and Discussion

Photophysical Properties of the Molecular Components

All photophysical experiments have been performed in an air-equilibrated CH_2Cl_2 solution at room temperature, unless otherwise specified. The absorption and fluorescence spectra of the crown ether BN26C8 and of the examined salts of ABH^+ are reported in Figure 1. The relevant photophysical data are gathered in Table 1.

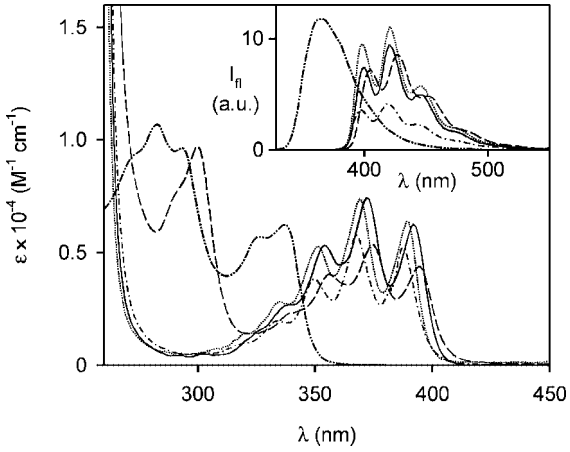


Figure 1. Absorption and fluorescence (inset) spectra of BN26C8 (–••–••), and of ABH^+ as hexafluorophosphate (——), TRISPHAT (– – –), chloride (·····) and sulfate (–·–·) salts in CH_2Cl_2 at room temperature. For the ABH^+ salts, all the molar absorption coefficients refer to the ABH^+ species; λ_{exc} = 290 nm for BN26C8 and 372 nm for ABH^+.

The absorption and fluorescence spectra of BN26C8 (Figure 1) show the typical bands of its binaphthyl chromophoric unit.[27] The fluorescence emission is very intense (Φ = 0.49) and its lifetime is 5.2 ns. All the different ABH^+ salts exhibit the characteristic[27] absorption and fluorescence bands of their anthracene chromophore (Figure 1). In addition, [ABH][(Δ)-TRISPHAT] displays an absorption

Table 1. Absorption and luminescence data for the binaphthocrown ether BN26C8 and the examined salts of the anthraceneammonium ion ABH^+ (air-equilibrated CH_2Cl_2 solution, room temperature).

Compound[a]	Absorption		Fluorescence		
	λ_{max} [nm]	ε [L·mol^{-1}·cm^{-1}]	λ_{max} [nm]	Φ	τ [ns]
BN26C8	282 (336)	10800 (6500)	370	0.49	5.2
[ABH][PF_6]	372	7400	421	0.30	10
[ABH][(Δ)-TRISPHAT]	300 (375)	9700 (5300)	435	0.32	11
[ABH][Cl]	369	7400	421	0.36	7.9
[ABH]$_2$[SO_4]	368	5800[b]	418	0.15	2.5[c]
[nBu$_4$N][(Δ)-TRISPHAT]	300	11000	—	—	—
AB[d]	367	11000	415	0.13	3.2

[a] Concentration of the compounds: 8.0×10^{-6} mol·L^{-1}. [b] Molar absorption coefficient refers to the ABH^+ species. [c] Double exponential decay with τ_1 = 2.5 ns (94%) and τ_2 = 9.3 ns (6%). [d] Obtained by deprotonation of [ABH][TRISPHAT] with 1.4 equiv. of nBu$_3$N.

band with λ_{max} = 300 nm. The comparison with the absorption spectrum of [nBu$_4$N][TRISPHAT] indicates that such a band is due to the TRISPHAT$^-$ anion.

It can be noted that the absorption and fluorescence features of the anthracene unit depend on the counteranion of the ABH$^+$ cation (Figure 1 and Table 1). Other relevant observations are: (i) the absorption and fluorescence spectra of the various salts of ABH$^+$, recorded in acetonitrile solution, are very similar to each other; (ii) the absorption spectrum of [ABH][PF$_6$] does not change appreciably on going from CH_2Cl_2 to CH_3CN solution; (iii) the absorption spectral shapes of the PF_6^-, Cl^- and SO_4^{2-} salts of ABH$^+$ do not depend on concentration in the range examined (8.0×10^{-6} to 1.3×10^{-4} mol·L^{-1}); (iv) the shape of the absorption spectrum of [ABH][TRISPHAT] in CH_2Cl_2 changes slightly on varying the concentration; particularly, in the anthracene $S_0\rightarrow S_1$ absorption region (350–420 nm), it approaches that of [ABH][PF$_6$] upon dilution. These results are in agreement with the presence of compact ion pairs[18] between the ABH$^+$ cation and some of the examined anions in the apolar CH_2Cl_2 solvent. Such ion pairs exhibit photophysical properties that are slightly different from those of the solvated ABH$^+$ ion, which is most likely the dominant species in the relatively polar CH_3CN solvent. It should be noted that the spectroscopic properties of the anthracene unit are very sensitive to the nature of the substituent in the 9-position,[27] and that electronic interactions between the anions and anthracene can take place.[19b,19f] Our observations suggest that hexafluorophosphate anions do not associate with ABH$^+$ under these conditions, whilst chloride and sulfate anions do, in line with the ion-pairing abilities of these anions.[28] The TRISPHAT anion shows an intermediate behavior that will be discussed in detail later on.

Of the four anions used as counterions for ABH$^+$, only TRISPHAT exhibits an absorption band in the examined UV/Visible range (see Figure 1). Emission spectra recorded on [nBu$_4$N][TRISPHAT] upon excitation at 300 nm show that the anion is not luminescent. Fluorescence excitation spectra (not shown here) indicate that the anthracene emission is sensitized by light absorption from TRISPHAT$^-$, which means that energy transfer from TRISPHAT$^-$ to the anthracene unit takes place. Since excitation spectra recorded for [ABH][TRISPHAT] in CH_3CN show no TRISPHAT sensitization of the anthracene fluorescence, we conclude that energy transfer can only take place within the ion pairs. In 8.0×10^{-6} and 1.3×10^{-4} mol·L^{-1} CH_2Cl_2 solutions, the efficiency of this process is 11% and 24%, respectively. However, the actual efficiency for the energy transfer process cannot be estimated because we do not know the fraction of ion-paired species in our experimental conditions.

Formation of the Host–Guest Pseudorotaxane Complex

The formation of a pseudorotaxane complex between the host BN26C8 and the guest ABH$^+$ has been investigated by absorption and fluorescence titrations. The titration experiments have been carried out both by adding increasing amounts of the host to the guest in solution, and vice versa.

Typical titration experiments are those performed on [ABH][PF$_6$] and reported in a previous paper.[4] The addition of increasing amounts of [ABH][PF$_6$] to a CH_2Cl_2 solution of BN26C8 causes a progressive quenching[29] of the binaphthyl fluorescence (λ_{max} = 370 nm) and a concomitant sensitization of the anthracene fluorescence (λ_{max} = 421 nm) upon binaphthyl excitation at 292 nm. After addition of an excess of [ABH][PF$_6$], the binaphthyl-type fluorescence of BN26C8 is completely quenched and the excited-state lifetime can no longer be measured. These observations are consistent with the formation of a pseudorotaxane-type complex [BN26C8⊃ABH]$^+$ wherein an efficient energy transfer process from the first singlet excited state of the binaphthyl moiety of BN26C8 to that of the anthracene unit of ABH$^+$ takes place, as can be expected from the photophysical properties of such chromophoric units.[27] The energy-transfer rate constant is estimated to be larger than 4×10^9 s^{-1}.[4] The titration curve obtained by monitoring the decrease of the fluorescence of BN26C8 suggests[30] the formation of a 1:1 complex with a stability constant of the order of 10^6 L·mol^{-1}.

In the reverse titration experiment, that is the addition of BN26C8 to a solution of [ABH][PF$_6$], it is convenient to look at changes in the anthracene $S_0\rightarrow S_1$ absorption bands (350–420 nm region), where the added crown ether does not contribute to the absorption spectrum. Significant changes in the absorption spectrum are indeed observed, with the presence of clean isosbestic points. Such changes are consistent with the formation of a 1:1 complex with a stability constant exceeding 10^6 L·mol^{-1}, in full agreement with the fluorescence titration experiments.

Titration of 2.0×10^{-5} mol·L^{-1} BN26C8 with either [ABH][Cl] or [ABH]$_2$[SO$_4$], up to the addition of a fivefold excess of ABH$^+$, results in a modest (<20%) decrease[29] of the luminescence of BN26C8, and no sensitization of the anthracene fluorescence upon excitation of the binaphthyl unit. Similarly, titration of either [ABH][Cl] or [ABH]$_2$[SO$_4$] with the host does not cause changes in the absorption spectra in the 350–420 nm region. Hence, in our experimental conditions there is no evidence of formation of a complex between BN26C8 and ABH$^+$ as chloride or sulfate salts.

The addition of increasing amounts of BN26C8 to a dilute solution of [ABH][TRISPHAT] leads to absorption spectral changes in the 350–420 nm region (Figure 2) similar to those observed for the PF_6^- salt of ABH$^+$. The inset of Figure 2 shows the absorbance values at 392 nm as a function of added host, which are consistent with a stability constant for the 1:1 complex of 5×10^6 L·mol^{-1}. Note that the decrease in absorbance observed after addition of an excess of crown ether is only due to the volume increase of the solution. It can also be observed that the BN26C8 fluorescence is strongly quenched until the host–guest ratio is ≤1; for addition of more than one equivalent of the host, the fluorescence intensity increases with host concentration

as for a solution of pure BN26C8 under the same conditions.

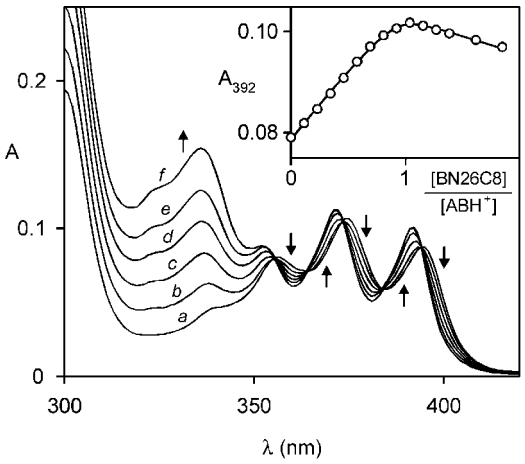


Figure 2. Absorption spectral changes observed for the $S_0 \rightarrow S_1$ anthracene bands on titration of 2.1×10^{-5} mol·L^{-1} [ABH][TRISPHAT] with BN26C8 (CH_2Cl_2, room temperature). Curves from *a* to *f* correspond to the addition of 0, 0.2, 0.4, 0.6, 0.8, and 1.0 equiv., respectively, of BN26C8. The inset shows the titration plot obtained from the absorbance values at 392 nm; the full line is the fitted curve relative to the formation of a 1:1 complex with $K = 5 \times 10^6$ L·mol^{-1}.

In the reverse titration experiment, i.e., the addition of [ABH][TRISPHAT] to BN26C8, a quenching of the host luminescence is indeed observed (Figure 3). A typical titration curve is shown in the inset of Figure 3. Interestingly, the fluorescence intensity of the host decreases smoothly on addition of the guest and is not completely quenched even after addition of four equivalents of [ABH][TRISPHAT]. The lifetime of such residual fluorescence is identical to that of free BN26C8. These results are in qualitative agreement with the formation of a complex between BN26C8 and ABH^+, but the fluorescence titration curve shown in Figure 3 is not consistent with the results of the absorption experiments in which BN26C8 is used as a titrating agent (Figure 2). The most satisfactory data fit is obtained by assuming the formation of a 1:1 complex with a stability constant of 8×10^5 L·mol^{-1}. However, this model implies that such a supramolecular species exhibits a binaphthyl-type fluorescence with a quantum yield equal to 15% of that of free BN26C8, and a correspondingly reduced lifetime (ca. 0.8 ns). The fluorescence lifetime measurements, however, suggest that the residual binaphthyl-type fluorescence has to be assigned to the uncomplexed crown ether. Moreover, the lack of complete quenching of the binaphthyl fluorescence in the $[BN26C8 \supset ABH]^+$ complex would indicate a poor efficiency of the energy transfer process to the anthracene unit, in contrast with the results obtained for the PF_6^- salt of ABH^+.

Such a complicated behavior, and particularly the different results obtained in the two titration experiments, can be rationalized on the basis of the formation of tight ion pairs between the ABH^+ cation and the $TRISPHAT^-$ anion, which prevent the threading of the guest into the macrocyclic cavity of the host. An alternative explanation

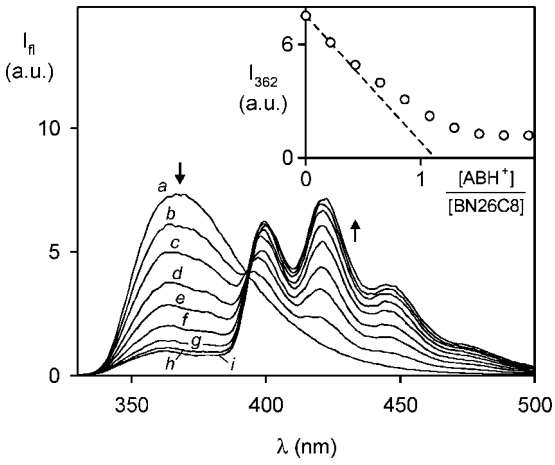


Figure 3. Changes in the fluorescence spectra (λ_{exc} = 320 nm) observed on titration of 2.0×10^{-5} mol·L^{-1} **1** with [ABH][TRISPHAT] (CH_2Cl_2, room temperature). Curves from *a* to *i* correspond to the addition of 0, 0.21, 0.43, 0.65, 0.86, 1.08, 1.29, 1.51, and 1.94 equiv., respectively, of [ABH][TRISPHAT]. The inset shows the titration plot obtained from the fluorescence intensity values at 362 nm; the dashed line represents the tangent to the first part of the curve.

involves the presence of two different types of conformations for the $[BN26C8 \supset ABH]^+$ pseudorotaxane. In one type the fluorescence of BN26C8 would be completely quenched, whereas it would not be quenched at all in the other type. In the assumption that the different conformations cannot equilibrate within the excited-state lifetime of BN26C8 (5.2 ns), this picture gives an interpretation for the residual fluorescence intensity of the complex. However, it does not account for the different shape of the absorption and fluorescence titration curves. Moreover, the existence of conformations where the energy transfer process is inefficient appears unlikely since molecular models show that the maximum distance between binaphthyl and anthracene units in the $[BN26C8 \supset ABH]^+$ complex (≈15 Å) is much shorter than their Förster radius (26 Å).[31] It has been frequently observed[19,20] that in apolar solvents the association between an uncharged host and a positively charged guest is in competition with ion pairing of the latter species [Equation (1)], unless specific stabilization of the guest counteranions can be provided by the host itself.[32,33]

$$ABH^+ + X^- \rightleftharpoons ABH^+ \cdot X^- \quad (1)$$

Two limiting cases can be identified for these systems, that is, the active species for the formation of the complex is either the solvated guest species [Equation (2)] or the guest-anion pair [Equation (3)]. When Equation (2) is the one that holds, ion pairing is in competition with the self-assembly equilibrium and occurs at the expense of complex formation. This behavior was observed and reported for the complex formed by dibenzo-24-crown-8 and the dibenzylammonium cation.[20a] Anions with a high tendency to form ion pairs, such as chloride and sulfate, are able to completely prevent the self-assembly, at least under our conditions. The soft hexafluorophosphate anion is the most innocent in this regard.[34] According to this idea, the different results ob-

tained in the absorption and fluorescence titrations for the TRISPHAT salt fall in between the two mentioned cases. When a dilute solution of [ABH][TRISPHAT] is titrated with BN26C8, the amount of anion remains constant and small throughout the experiment, whereas in the reverse titration not only ABH^+, but also $TRISPHAT^-$, are added to the crown ether. In fact, the tangent to the first part of the fluorescence titration curve (Figure 3), i.e. when BN26C8 is in large excess compared to [ABH][TRISPHAT], point to the formation of a non-fluorescent 1:1 complex, in line with the behavior of the [ABH][PF_6] salt. Finally, additions of [nBu$_4$N][TRISPHAT] to a solution containing 3.5×10^{-5} mol·L^{-1} BN26C8 and [ABH][TRISPHAT] cause a progressive recovery of the binaphthyl-type fluorescence intensity, clearly indicating that an increase in the concentration of $TRISPHAT^-$ ion leads to the disassembly of the pseudorotaxane complex [Equations (1) and (2)]. So we have to conclude that [ABH][TRISPHAT] salt is predominantly ion-paired in CH_2Cl_2 solution. This, together with the steric hindrance of this anion, decreases the efficiency of the threading process evidencing the fact that $TRISPHAT^-$ behaves as a less discreet partner than the PF_6^- anion. The trend observed in the association ability, that is $PF_6^- > TRISPHAT^- > Cl^-$, SO_4^{2-}, can be attributed to the effect of the anion that clearly controls the formation of the pseudorotaxane system.

$$ABH^+ + BN26C8 \rightleftharpoons [BN26C8\supset ABH]^+ \quad (2)$$

$$ABH^+\cdot X^- + BN26C8 \rightleftharpoons [BN26C8\supset ABH]^+\cdot X^- \quad (3)$$

Base-Induced Disassembly of the Pseudorotaxane

Since the self-assembly of the examined pseudorotaxane is mainly driven by [N^+–H···O] interactions, it can be anticipated that deprotonation of the ammonium center of the guest will lead to a substantial destabilization of the complex.

The addition of base (nBu$_3$N) does not cause changes in the absorption and fluorescence spectra of BN26C8. In the case of the ABH^+ salts, the addition of tributylamine causes a blue shift in the anthracene absorption (Figure 4) and fluorescence bands, and a decrease in the fluorescence intensity and lifetime (Table 1). Isosbestic points are observed in the absorption spectra. These changes stop after the addition of one equivalent of base, indicating that the deprotonated species AB is obtained. The quenching of the fluorescence of amine AB compared to the ammonium compound ABH^+ can be attributed to the occurrence, in the amine species, of a charge-transfer interaction involving the nitrogen lone pair.[35]

The addition of nBu$_3$N to a solution containing 1.3×10^{-5} mol·L^{-1} BN26C8 and 9.1×10^{-5} mol·L^{-1} [ABH][TRISPHAT] leads to absorption changes that are consistent with the formation of the deprotonated compound AB, and to the increase of the fluorescence emission

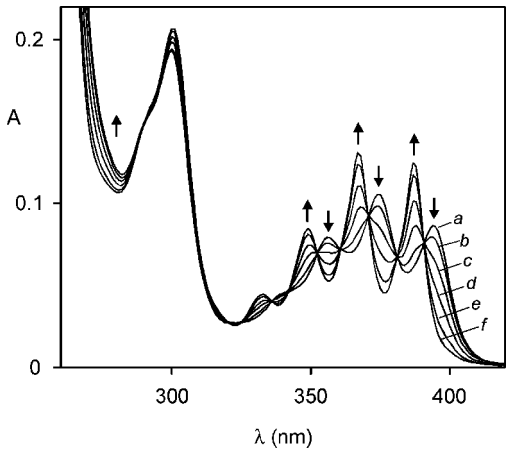


Figure 4. Absorption spectral changes observed on titration of 2.1×10^{-5} mol·L^{-1} [ABH][TRISPHAT] with nBu$_3$N (CH_2Cl_2, room temperature). Curves from a to f correspond to the addition of 0, 0.2, 0.4, 0.6, 0.8 and 1.0 equiv., respectively, of nBu$_3$N.

characteristic of free BN26C8 (Figure 5). After addition of one equivalent of tributylamine with respect to ABH^+ the fluorescence intensity reaches, within experimental errors, the value expected for the free host at the concentration employed. This observation indicates that nBu$_3$N causes the deprotonation of the ammonium center of ABH^+ and the subsequent disassembly of the pseudorotaxane, in line with the results obtained in a previous investigation[4] for [ABH][PF_6].

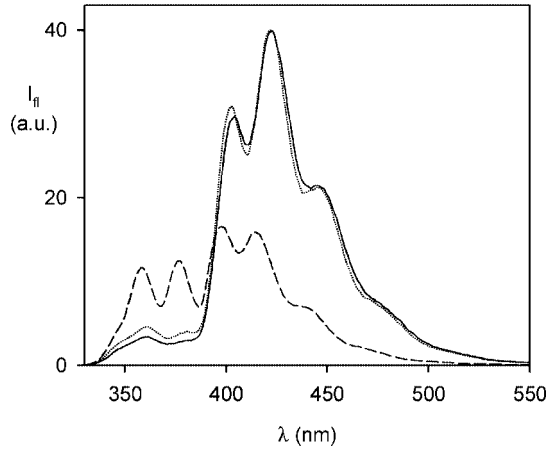


Figure 5. Fluorescence spectra (λ_{exc} = 292 nm) of a solution containing 1.3×10^{-5} mol·L^{-1} BN26C8 and 9.1×10^{-5} mol·L^{-1} [ABH][TRISPHAT] (——), of the same mixture after addition of 1.0 equiv. of nBu$_3$N with respect to ABH^+ (– – –), and after subsequent addition of 1.4 equiv. of CF_3SO_3H (·····). The features that are present in the region of the binaphthyl fluorescence (330–390 nm) are due to reabsorption by the anthracene unit.

The re-assembly of the pseudorotaxane species can be obtained by addition of an acid, e.g. CF_3SO_3H, that protonates the amine unit of AB once again. This is supported by the changes in the absorption and fluorescence spectra observed upon addition of a slight excess (1.4 equiv.) of CF_3SO_3H, which are opposite to those obtained after the initial treatment with nBu$_3$N. However, the fluorescence of

BN26C8 is less quenched than in the starting solution, indicating that the re-assembly process is not quantitative (Figure 5). This lack of reversibility can be explained by the formation of ion pairs between the $CF_3SO_3^-$ anions and the ABH^+ cations, which occur after addition of acid. Acid-base reactions, owing to their reversibility, are convenient processes to control the switching of chemical systems.[3] It is clear that in the present case the repeated addition of base and acid leads to the accumulation of "waste products", i.e., cations and anions, that compromises the operation of the molecular switch, unless they are removed from the system.

Preliminary ^{1}H NMR Spectroscopic Measurements of Chiral Recognition

As previously mentioned, we included the TRISPHAT anion in our study to investigate the possibility of inducing stereoselective control on the formation of the interpenetrating assembly through host–anion interactions. Obviously to obtain such a result the counteranion should interact tightly with the ABH^+ species threaded in the host BN26C8. From the results obtained in the absorption and fluorescence titrations for the TRISPHAT salt we learnt that this anion can partially prevent an efficient threading process. Nevertheless, we ran a number of ^{1}H NMR spectroscopic experiments on the [BN26C8 ⊃ ABH]$^+$X$^-$ complexes. To this purpose we first recorded the ^{1}H NMR spectra of the salts [ABH][PF_6], [ABH][(Δ)-TRISPHAT] and

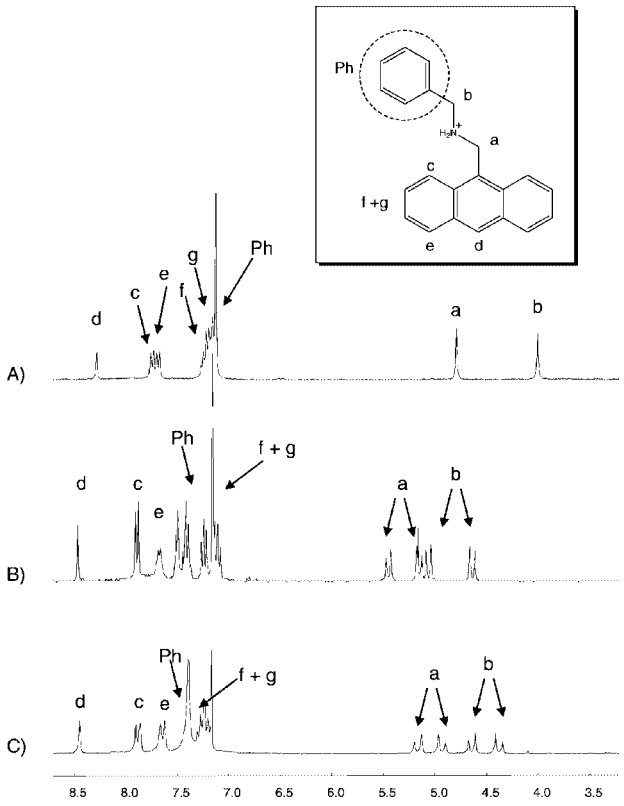


Figure 6. ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$, 1:6) of A) 9.64×10^{-3} mol·L^{-1} [ABH][PF_6], B) 9.12×10^{-3} mol·L^{-1} [ABH][(Δ)-TRISPHAT] and C) 2.88×10^{-2} mol·L^{-1} [ABH][(Λ)-TRISPHAT]. Differences between spectra B and C are due to concentration effects.

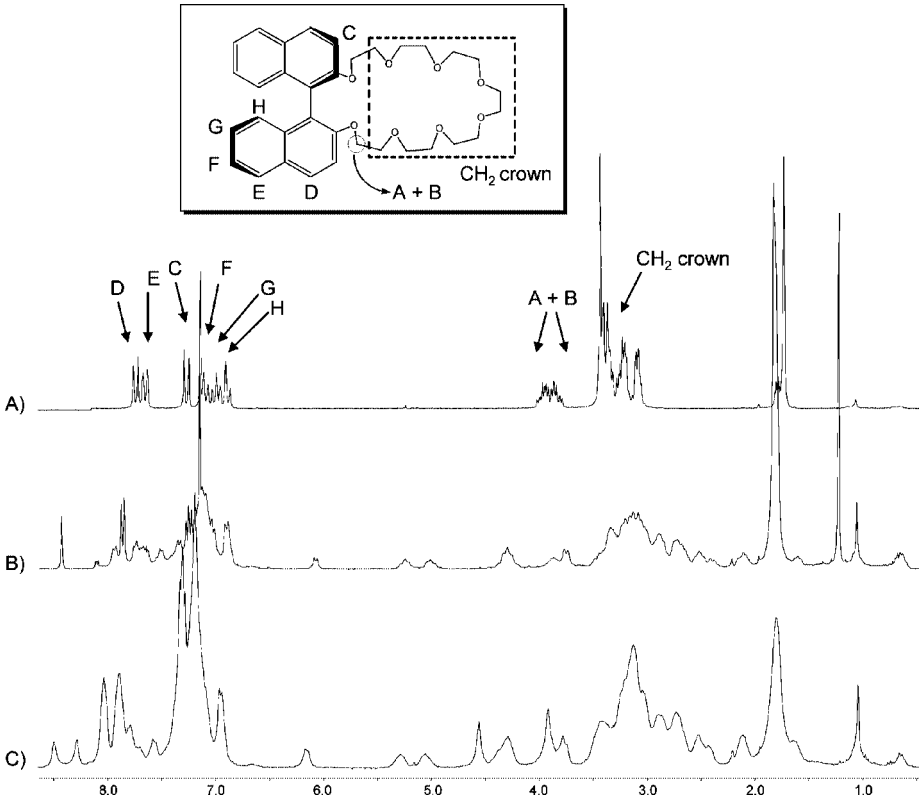


Figure 7. ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$, 1:6, 9.64×10^{-3} mol·L^{-1}) of A) (+)-BN26C8, B) [(+)-BN26C8⊃[ABH][(Δ)-TRISPHAT]] and C) [(+)-BN26C8⊃[ABH][(Λ)-TRISPHAT]].

[ABH][(Λ)-TRISPHAT] in $CDCl_3/CD_3CN$, 6:1 solutions, Figure 6. As expected, effective NMR enantiodifferentiation is achieved, meaning that the system is anion sensitive. Then we recorded the ^1H NMR spectra of the 1:1 mixture of (+)BN26C8 and optically active (Δ)- and (Λ)-TRISPHAT salts of ABH, respectively, in the same medium and with a concentration of 9.64×10^{-3} mol·L^{-1} (Figure 7, b and c). The comparison of the two spectra shows several differences and suggests the formation of different adducts corresponding to the two diastereomeric ternary complexes. Unfortunately, because of the broadening of signals, no precise peak assignment can be done. Moreover, the present observations are not sufficient to establish how the configuration of the chiral counteranion influences the recognition process. However, these preliminary results seem to be consistent with a picture in which the anion is placed in close proximity with the [BN26C8⊃ABH]$^+$ complex and in principle support the feasibility of using ion-pairing control on the stereoselective formation of interpenetrating assemblies.

Conclusions

We have studied the photophysical properties of a binaphthocrown ether macrocycle and an anthraceneammonium ion, and their self-assembly in a low-polarity solvent to give a hydrogen-bonded pseudorotaxane species. We investigated the influence of a number of anions on the formation of the pseudorotaxane species in dilute solutions in CH_2Cl_2. UV/Visible spectroscopic techniques are a valuable tool for investigating such processes in dilute solutions. In particular, the association can be easily evidenced by the analysis of the steady-state and time-resolved fluorescence properties of the system. The luminescence properties of the examined systems point out that the crown ether host and the anion actually compete for the cation. The self-assembly process is thus dramatically dependent on the nature of the counteranion of the ammonium guest because of this competition between the formation of the pseudorotaxane and the ion pairing of the guest. We clearly envisioned the trend in complexation, $PF_6^- >$ TRISPHAT$^-$ > Cl^-, SO_4^{2-}. Surprisingly, we found that, despite its well-dispersed negative charge, the TRISPHAT counteranion forms contact ion pairs with the positively charged guest. This decreases the efficiency of the self-assembly process to give the pseudorotaxane and confirms the important role played by the anion in the formation of the complexes. Furthermore, the chirality of the anion results in a potential tool for addressing the question of how close is the anion to the supramolecular cationic complex. Preliminary NMR spectroscopic experiments, carried out with a 1:1 mixture of (+)BN26C8 and optically active (Δ)- and (Λ)-TRISPHAT ABH salts, respectively, support the idea that the anion is located very close to the [BN26C8⊃ABH]$^+$ complex and can in principle influence the stereoselectivity of the pseudorotaxane system. Chiral anions of suitable geometry and symmetry, capable of maximizing the interactions with the chiral host and also of reducing the competition toward the guest that prevents high efficiency of the interpenetrating process, are currently under investigation.

Experimental Section

Synthesis: Racemic BN26C8 and optically pure (+)BN26C8,[4] ABH$^+$ hexafluorophosphate and chloride,[16] [ABH][(Λ)TRISPHAT] and [ABH][(Δ)TRISPHAT][36] were synthesized according to the procedures described in the literature. The sulfate salt of ABH$^+$ was prepared from ABH$^+$ chloride through precipitation of silver chloride after treatment with silver sulfate.

Absorption and Luminescence Measurements: Experiments were carried out at room temperature (ca. 295 K) on air-equilibrated CH_2Cl_2 or CH_3CN (Merck Uvasol) solutions in the concentration range from 8.0×10^{-6} to 1.3×10^{-4} mol·L^{-1}. UV/Visible absorption and luminescence spectra were recorded with a Perkin–Elmer λ40 spectrophotometer and a LS50 spectrofluorimeter, respectively. Luminescence quantum yields were determined by the optically dilute method using anthracene in degassed ethanol as a standard.[37] Luminescence lifetimes were measured by time-correlated single-photon counting with Edinburgh Instruments DS199 apparatus equipped with a cooled Hamamatsu R928 photomultiplier. The exciting light was produced by a gas arc lamp (model nF900, filled with D_2) that delivered pulses of about 1 ns (fwmh). The excitation wavelength was selected by means of a monochromator, and the light emitted from the sample was filtered by using a cut-off filter. The estimated experimental errors are: 2 nm on band maxima, ±5% on the molar absorption coefficients, fluorescence intensities and fluorescence lifetimes, and ±7% on the fluorescence quantum yield values.

Titration Experiments: In a typical titration experiment, small aliquots (10 μL) of a concentrated solution of one component were added with a calibrated microsyringe to a known volume (2 mL) of a dilute (2×10^{-5} mol·L^{-1}) solution of the other component contained in a quartz cuvette. The fluorescence intensity values detected throughout the experiments were corrected[38] for the nonlinear intensity vs. absorbance response of the instrument and for inner filter effects, particularly the reabsorption of the binaphthyl fluorescence by the anthracene chromophore. In all cases, efforts were made to adjust the experimental conditions in order to minimize the corrections. The dilution of the solution during the titration was also taken into account. The errors on such corrected fluorescence intensity values depend largely on the amount of light reabsorption; under the conditions employed the errors were estimated to be not larger than ±15%. The absorption and fluorescence titration curves were fitted according to the equation $K = C_{complex}/C_{host} \times C_{guest}$, using $C_{host} = C°_{host} - C_{complex}$ and $C_{guest} = C°_{guest} - C_{complex}$. For the absorption titrations performed in the 360–420 nm region, where the added host does not contribute to the absorption spectrum, $C_{complex}$ was derived from the following equation: $A(\lambda) = \varepsilon(\lambda)_{guest} \times C_{guest} + \varepsilon(\lambda)_{complex} \times C_{complex} = \varepsilon(\lambda)_{guest} \times (C°_{guest} - C_{complex}) + \varepsilon(\lambda)_{complex} \times C_{complex}$. Similarly, the binaphthyl-type corrected luminescence intensity of the host was derived from the equation: $I(\lambda) = F(\lambda)_{host} \times C_{host} + F(\lambda)_{complex} \times C_{complex} = F(\lambda)_{host} \times (C°_{host} - C_{complex}) + F(\lambda)_{complex} \times C_{complex}$, where $F(\lambda)_{host}$ and $F(\lambda)_{complex}$ are proportionality factors between the concentration of the compound and its corrected luminescence intensity at the observed wavelength. Hence, $C_{complex}$ can be expressed as a function of $F(\lambda)_{host}$, $F(\lambda)_{complex}$ and $C°_{host}$. For more details, see ref.[38]

^1H NMR Spectroscopic Experiments: ^1H NMR spectra were recorded with a Bruker AC300 spectrometer, at room temperature

(ca. 295 K). For solubility reasons, a mixture of $CDCl_3/CD_3CN$, 6:1 was employed. The concentration of the examined solutions was 9.64×10^{-3} mol·L^{-1}.

Acknowledgments

This research was supported by MIUR, COFIN 2003 (Supramolecular Devices project). The European Union is gratefully acknowledged for a Marie Curie Fellowship (to M.C.-L.) and for support under the auspices of the Molecular-Level Devices and Machines network (HPRN-CT-2000-00029). C.P. thanks COST D11 Supramolecular Chemistry WG 003/98 for financing a stay at the University of Geneva.

[1] J.-P. Sauvage, C. O. Dietrich-Buchecker (Eds.), *Molecular Catenanes, Rotaxanes and Knots*, Wiley-VCH, Weinheim, **1999**.
[2] J. L. Atwood, J. W. Steed (Eds.), *Encyclopedia of Supramolecular Chemistry*, Dekker, New York, **2004**.
[3] V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines – A Journey into the Nano World*, Wiley-VCH: Weinheim, **2003**.
[4] E. Ishow, A. Credi, V. Balzani, F. Spadola, L. Mandolini, *Chem. Eur. J.* **1999**, *5*, 984–989.
[5] R. Ballardini, V. Balzani, M. Clemente-Léon, A. Credi, M. T. Gandolfi, E. Ishow, J. Perkins, J. F. Stoddart, H.-R. Tseng, S. Wenger, *J. Am. Chem. Soc.* **2002**, *124*, 12786–12795.
[6] F. Cacialli, J. S. Wilson, J. J. Michels, C. Daniel, C. Silva, R. H. Friend, N. Severin, P. Samorì, J. P. Rabe, M. J. O'Connell, P. N. Taylor, H. L. Anderson, *Nature Materials* **2002**, *1*, 160–164.
[7] A. Credi, V. Balzani, S. J. Langford, J. F. Stoddart, *J. Am. Chem. Soc.* **1997**, *119*, 2679–2681.
[8] R. Hernandez, H. R. Tseng, J. W. Wong, J. F. Stoddart, J. I. Zink, *J. Am. Chem. Soc.* **2004**, *123*, 1248–1249.
[9] P. Thordarson, E. J. A. Bijsterveld, A. E. Rowan, R. J. M. Nolte, *Nature* **2003**, *424*, 915–918.
[10] W. S. Jeon, A. Y. Ziganshina, J. W. Lee, Y. H. Ko, J. K. Kang, C. Lee, K. Kim, *Angew. Chem. Int. Ed.* **2003**, *42*, 4097–4100.
[11] For a recent example, see: C. M. Keaveney, D. A. Leigh, *Angew. Chem. Int. Ed.* **2004**, *43*, 1222–1224.
[12] J. D. Badjić, V. Balzani, A. Credi, S. Silvi, J. F. Stoddart, *Science* **2004**, *303*, 1845–1849.
[13] a) L. F. Lindoy, *The Chemistry of Macrocyclic Ligands*, Cambridge University Press, Cambridge, **1989**; b) E. P. Kyba, R. C. Hegelson, K. Madan, G. W. Gokel, T. L. Tarnoswki, S. S. Moore, D. J. Cram, *J. Am. Chem. Soc.* **1977**, *99*, 2564–2571; c) C. J. Pedersen, *J. Am. Chem. Soc.* **1967**, *89*, 7017–7036.
[14] M. Meot-Ner (Mautner), *Chem. Rev.* **2005**, *105*, 213–284.
[15] a) A. G. Kolchinski, D. H. Busch, N. W. Alcock, *J. Chem. Soc., Chem. Commun.* **1995**, 1289–1291; b) P. R. Ashton, E. J. T. Chrystal, P. T. Glink, S. Menzer, N. Spencer, C. Schiavo, J. F. Stoddart, P. A. Tasker, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1996**, *2*, 709–728; c) D. Philp, J. F. Stoddart, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1155–1196; d) P. R. Ashton, P. T. Glink, M.-V. Martínez-Díaz, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1930–1933; e) M. Montalti, R. Ballardini, L. Prodi, V. Balzani, *Chem. Commun.* **1996**, 2011–2012.
[16] P. R. Ashton, R. Ballardini, V. Balzani, M. Gómez-López, S. E. Lawrence, M.-V. Martínez-Díaz, M. Montalti, A. Piersanti, L. Prodi, J. F. Stoddart, D. J. Williams, *J. Am. Chem. Soc.* **1997**, *119*, 10641–10651.
[17] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, **1988**.
[18] N. Isaacs, *Physical Organic Chemistry*, Longman, Essex, **1987**, pp. 49–55.
[19] Representative examples: a) R. Arnecke, V. Böhmer, R. Cacciapaglia, A. Dalla Cort, L. Mandolini, *Tetrahedron* **1997**, *53*, 4901–4908; b) M. Montalti, L. Prodi, *Chem. Commun.* **1998**, 1461–1462; c) S. Bartoli, S. Roelens, *J. Am. Chem. Soc.* **1999**, *121*, 11908–11909; d) V. Böhmer, A. Dalla Cort, L. Mandolini, *J. Org. Chem.* **2001**, *66*, 1900–1902; e) S. Bartoli, S. Roelens, *J. Am. Chem. Soc.* **2002**, *124*, 8307–8315; f) C. A. Hunter, C. M. R. Low, C. Rotger, J. G. Vinter, C. Zonta, *Chem. Commun.* **2003**, 834–835; g) G. Heinrichs, L. Vial, J. Lacour, S. Kubik, *Chem. Commun.* **2003**, 1252–1253.
[20] a) J. W. Jones, H. W. Gibson, *J. Am. Chem. Soc.* **2003**, *125*, 7001–7004; b) F. Huang, J. W. Jones, C. Slebodnik, H. W. Gibson, *J. Am. Chem. Soc.* **2003**, *125*, 14458–14464.
[21] A. Credi, S. Dumas, S. Silvi, M. Venturi, A. Arduini, A. Pochini, A. Secchi, *J. Org. Chem.* **2004**, *69*, 5881–5887.
[22] B. W. Laursen, S. Nygaard, J. O. Jeppesen, J. F. Stoddart, *Org. Lett.* **2004**, *6*, 4167–4170.
[23] J. Lacour, V. Hebbe-Viton, *Chem. Soc. Rev.* **2003**, *32*, 373–382.
[24] E. Martinez-Viviente, P. S. Pregosin, C. Herse, J. Lacour, *Chem. Eur. J.* **2004**, *10*, 2912–2918.
[25] X. X. Zhang, J. S. Bradshaw, R. M. Izatt, *Chem. Rev.* **1997**, *97*, 3313–3361.
[26] a) D. B. Llewellyn, D. Adamson, B. A. Arndtsen, *Org. Lett.* **2000**, *2*, 4165–4168; b) G. Heinrichs, S. Kubik, J. Lacour, L. Vial, *J. Org. Chem.* **2005**, *70*, 4498–4501.
[27] I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Compounds*, Academic Press, London, **1965**.
[28] A. Bianchi, K. Bowman-James, E. Garcia-España (Eds.), *Supramolecular Chemistry of Anions*, Wiley-VCH, New York, **1997**.
[29] Dynamic quenching can be ruled out in our conditions because of the short excited-state lifetime of the energy donor and the low concentration of the energy acceptor.
[30] The experimental errors in the fluorescence titration experiments are large because the fluorescence intensity values of the binaphthyl unit have to be corrected for the absorption of the anthracene moiety. See the experimental section.
[31] See: J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 2nd ed., Plenum, New York, **1999**, p. 368.
[32] For reviews on ion-pair recognition, see: a) M. T. Reetz, in: *Comprehensive Supramolecular Chemistry* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. Macnicol, F. Vögtle), Pergamon Press, Oxford, **1996**, vol. 2, p. 553; b) P. A. Gale, *Coord. Chem. Rev.* **2003**, *240*, 191–221.
[33] For a recent example, see ref. 21.
[34] R. Schmidt, K. Kirchner, F. L. Dickert, *Inorg. Chem.* **1988**, *27*, 1530–1536.
[35] A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515–1566.
[36] C. Pasquini, V. Desvergnes-Breuil, J. J. Jodry, A. Dalla Cort, J. Lacour, *Tetrahedron Lett.* **2002**, *43*, 423–426.
[37] A. Credi, M. T. Gandolfi, M. Montalti, L. Prodi (Eds.), *Handbook of Photochemistry*, 3rd ed., CRC Press, Boca Raton, **2005**.
[38] A. Credi, L. Prodi, *Spectrochim. Acta A* **1998**, *54*, 159–170.

Received: June 28, 2005
Published Online: November 3, 2005

