View Article Online / Journal Homepage / Table of Contents for this issue

PAPER

NJC
www.rsc.org/njc

Luminescent host–guest complexes involving molecular clips and tweezers and tetracyanobenzene

Filippo Marchioni,[a] Alberto Juris,*[a] Matthias Lobert,[b] Uta P. Seelbach,[b] Björn Kahlert[b] and Frank-Gerrit Klärner[b]

[a] *Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, I-40126 Bologna, Italy. E-mail: alberto.juris@unibo.it; Fax: +39 051 2099456; Tel: +39 051 2099481*
[b] *Institut für Organische Chemie der Universität Duisburg-Essen, D-45117 Essen, Germany*

Received (in Durham, UK) 4th February 2005, Accepted 18th March 2005
First published as an Advance Article on the web 21st April 2005

Downloaded by University of California - Los Angeles on 01 January 2013
Published on 21 April 2005 on http://pubs.rsc.org | doi:10.1039/B501880C

The molecular tweezer **1** and the clips **2** and **3**, containing naphthalene or anthracene in the sidewalls, form host–guest complexes in $CHCl_3$ solution with the guest **TCNB** (1,2,4,5-tetracyanobenzene). The interaction leading to formation of the adduct is essentially of CT (charge-transfer) nature. A luminescence emission of CT origin is observed from the host–guest complexes both in fluid solution at 298 K and in rigid matrix at 77 K; to our knowledge, this is the first case of CT luminescence from a host–guest complex. At room temperature, the luminescence maxima are observed at 570, 614, and 668 nm, respectively, for the complexes based on the hosts **1**, **2**, and **3**. Spectrophotometric and spectrofluorimetric titrations were performed to investigate the association processes. In all cases 1 : 1 complexes are formed, with association constants 7.3×10^5, 5.4×10^6, and 1.24×10^4 L mol^{-1}, respectively, for the receptors **1**, **2**, and **3**. In the case of **2**, a species with a 2 : 1 host : guest ratio is also formed. The system **1**+**TCNB** was further investigated by cyclic and differential pulse voltammetry, giving the rate constants for adduct formation (1.9×10^8 L mol^{-1} s^{-1}) and disassembling (2.0×10^2 s^{-1}). The association/dissociation dynamics between the receptors **1** and **2** and the guest **TCNB** is discussed in relation to the receptor topology.

Introduction

Molecular recognition and self-assembly are key concepts in the realm of supramolecular chemistry.[1,2] These processes are based on weak but specific intermolecular interactions, such as hydrogen bonding,[3] ion pairing,[4] arene–arene interactions,[5] and hydrophobic effects in aqueous media.[5,6] The design of an efficient synthetic receptor requires a precise control of its topological and electronic properties. The hydrocarbons **1–3** (Fig. 1) are members of an interesting family of receptors, developed by Klärner *et al.*,[7–10] featuring an "inside" cavity whose shape depends both on the number of the methylene bridges (which are four in **1**, three in **2** and two in **3**) and on the components used to build the sidewalls (benzene, naphthalene, or anthracene). On the basis of their shape, these receptors have been named "molecular tweezer" (**1**) and "molecular clips" (**2** and **3**).

Semi-empirical calculations[11,12] have shown that the concave side of such molecules is surprisingly negative for a hydrocarbon; this feature explains why molecular tweezers and clips can selectively bind a variety of electron-deficient aromatic and aliphatic substrates. The interaction between the electron-donating receptor and the electron-accepting guest is essentially of charge-transfer (CT) nature, and is thus strongly influenced by the solvent used. For example, the adducts form efficiently in chloroform but not in acetonitrile, which is a much more polar solvent. Experimentally, NMR techniques have been most often employed to measure the association constant K_a of the host–guest adduct. For some guest species, such as **TCNB** (1,2,4,5-tetracyanobenzene, Fig. 1) or **TCNQ** (7,7,8,8-tetracyanoquinodimethane), however, the K_a values for the formation of the complexes **TCNB@1**, **TCNQ@1**, and **TCNB@2** are too high to be reliably measured in this way.[7,9,12]

In this paper, the interaction between the three receptors **1–3** and the guest **TCNB** is investigated in detail at room temperature by photophysical techniques. The adducts formed between **TCNB** and the receptors **1–3** are luminescent. Although luminescence from CT complexes involving **TCNB** is well known,[13,14] this appears to be the first case of CT luminescence from host–guest complexes. Spectrophotometric and spectrofluorimetric titrations have been exploited to obtain an accurate measure of the association constant with the guest **TCNB** in $CHCl_3$ solution. The system **1**+**TCNB** has been further characterized by cyclic and differential pulse voltammetry in CH_2Cl_2 solution, and the obtained K_a value has been compared with that derived from photophysical techniques. On the basis of the results obtained, the association/dissociation dynamics between host and guest are discussed in relation with the receptor topology.

Experimental section

The receptors **1–3** were available from previous investigations. All solvents were of the best commercial quality and were used as received.

All measurements were performed on freshly prepared air-equilibrated solutions. The absorption and emission spectra of the solutions remained stable for at least two days. Absorption spectra were recorded with a Perkin-Elmer λ16 or a Perkin-Elmer λ40 spectrophotometer. Luminescence experiments were performed in $CHCl_3$ solutions at room temperature and in a 1 : 1 *v*/*v* CH_2Cl_2–$CHCl_3$ rigid matrix at 77 K, by using a Perkin-Elmer LS-50 spectrofluorimeter equipped with a red-sensitive Hamamatsu R928 photomultiplier. Luminescence maxima tabulated are uncorrected for detector response. Luminescence lifetimes were measured with an Edinburgh 199 single-photon counting apparatus (D_2 lamp, 310 nm, time resolution 0.5 ns).

DOI: 10.1039/b501880c

This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2005

View Article Online

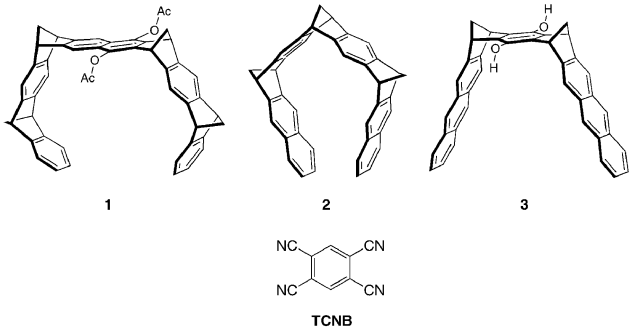

Fig. 1 Structural formulae of compounds **1**, **2**, **3** and **TCNB**.

Analysis of the decay traces was performed with software provided with the instrument.

Electrochemical measurements were carried out in argon-purged CH_2Cl_2 (Romil Hi-Dry™) solutions at room temperature with a EcoChemie Autolab 30 multipurpose instrument interfaced to a personal computer. The working electrode was a glassy carbon electrode (0.09 cm^2, Amel). The counter electrode was a Pt spiral and a silver wire was employed as a quasi-reference electrode (AgQRE). The concentration of the compounds was 2×10^{-3} M and tetrabutylammonium hexafluorophosphate ($TBAPF_6$) 0.05 M was used as supporting electrolyte. All the potentials reported are referred to SCE by measuring the AgQRE potential with respect to ferrocene (+0.460 V *vs.* SCE). Cyclic voltammograms (CV) were obtained with scan rates in the range 0.02–1 V s^{-1}; differential pulse voltammetry experiments (DPV) were performed with a scan rate of 20 mV s^{-1}, a pulse height of 75 mV, and a duration of 40 ms. For reversible processes the half-wave potential values are reported; the same values are obtained from the DPV peaks and from an average of the cathodic and anodic cyclic voltammetric peaks. For irreversible processes the reported values are those evaluated from the peak potentials in the DPV experiments. To establish the reversibility of a process, we used the criteria of (i) separation close to 60 mV between cathodic and anodic peaks, (ii) close to unity ratio of the intensities of the cathodic and anodic currents, and (iii) constancy of the peak potential on changing sweep rate in the cyclic voltammograms.

Experimental errors in the reported data are as follows: absorption maxima, 2 nm; molar absorption coefficients, 10%; excited state lifetimes, 10%; redox potentials, 10 and 20 mV for reversible and irreversible processes, respectively.

Results and discussion

System 1+TCNB—absorption and emission properties

The separate components **1** and **TCNB** are colorless in chloroform solution. When both species are present in equimolar concentration (1.85×10^{-4} M) the solution becomes yellow, due to the formation of a new broad, low intensity band with maximum at 417 nm. Table 1 lists the lowest-energy features of the observed absorption spectra. This behaviour had already been observed[7] and related to the formation of a CT adduct between the two species, indicated as **TCNB@1**. Moreover, in the region at $\lambda < 340$ nm the absorption spectrum of the solution containing **TCNB@1** is different from the sum of the spectra of the separate components, again as a consequence of the CT interaction between the two species.

Fig. 2 illustrates the emission bands featured by the separate components **1** and **TCNB** and by the solution containing the two species together. The separate components **1** and **TCNB** show, both at room temperature in fluid solution and in rigid matrix at 77 K, the typical π–π* fluorescence emission expected for such aromatic species. Indeed, for both compounds the emission band is structured and shows only a small blue shift on lowering temperature, while the lifetime values remain in the ns range. The relevant data are collected in Table 1. The phosphorescence emissions of both **1** and **TCNB** can also be observed at 77 K as structured bands: the 0–0 energy is at 450 and 440 nm, and the lifetime is 3.4 and 1.3 seconds, respectively, for **1** and **TCNB**.

Table 1 Photophysical properties[a]

		Luminescence			
		298 K		77 K[b]	
Compound	Absorption λ_{max} (nm) [ε (M^{-1} cm^{-1})]	λ (nm)[c]	τ (ns)	λ (nm)[c]	τ (ns)
1	295 [26100] 320 [2490] 335 [2660]	344	6.6	340	11.3
2	279 [16500] 310 [4370] 324 [3670]	342	1.5	330	12.4
3	337 [10400] 353 [13400] 373 [9710]	377	1.0	379	5.1
TCNB	304 [2530] 316 [3400]	332	1.1	322	5.8
TCNB@1	417	570	920	560	460
TCNB@2	413	614	28	586	1000
TCNB@3	525	668	4.2	670	12.1

[a] $CHCl_3$ solution, unless otherwise noted. [b] In CH_2Cl_2–$CHCl_3$ 1 : 1 *v*/*v*. [c] Uncorrected for detector response.

In the solution containing both **1** and **TCNB** the intensity of luminescence emissions of the two separate components is much weaker, whereas a new broader and structureless emission band is observed at 570 nm, with lifetime 920 ns. Shape, lifetime, and band shift on lowering temperature, of this new emission band are very different from those observed for the separate components, and are characteristics of a CT emission. The excitation spectrum of this emission band matches the absorption spectrum of the mixture, including the band at 417 nm, indicating that the emission band at 570 nm originates from the adduct **TCNB@1**.

The photophysical properties observed can be discussed on the basis of the schematic energy level diagram shown in Fig. 3. In the separate components **1** and **TCNB**, luminescence is observed from their respective singlet excited states. In the adduct **TCNB@1** a new charge-transfer state is present, which quenches by energy transfer the higher energy states characteristic of the separate components; as a result, the adduct luminesces only from the CT state. It should be noted that such adducts represent the first example of CT luminescence from host–guest complexes,[15] although CT luminescence

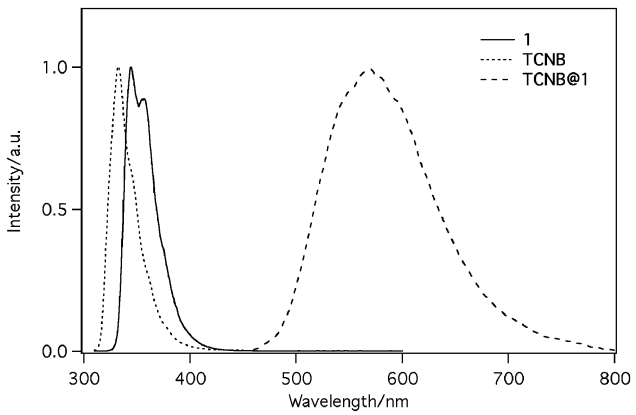

Fig. 2 Emission spectra of the isolated species **1** and **TCNB**, and of the adduct **TCNB@1** (room temperature, solutions in chloroform).

Downloaded by University of California - Los Angeles on 01 January 2013
Published on 21 April 2005 on http://pubs.rsc.org | doi:10.1039/B501880C

View Article Online

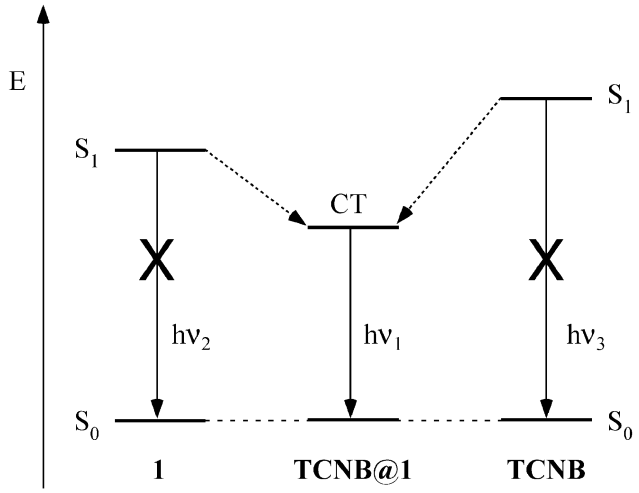

Fig. 3 Schematic energy level diagram for the system **1**+**TCNB**.

involving **TCNB** in other donor–acceptor complexes and exciplexes is a well-documented phenomenon.[13,14]

The distinctive luminescence of the adduct **TCNB@1** was exploited to measure the association constant between **1** and **TCNB**. A titration experiment was performed by adding **TCNB** to a solution of **1**, while exciting the sample at 417 nm and monitoring the luminescence at 570 nm. The data obtained by plotting the luminescence intensity *versus* the number of equivalents of **1** added (Fig. 4) were fitted using standard methods, yielding a value of 7.3×10^5 L mol^{-1} for the association constant K_a. It is worth underlining that using a luminescence titration it has been possible to measure accurately this association constant, whereas with an NMR measurement only a rough estimate ($K_a > 10^5$ L mol^{-1}) was previously obtained.[7,12] Although the value of the association constant is rather high, complete formation of the adduct **TCNB@1** does not occur in a 1.85×10^{-4} M solution of **1** and **TCNB**. Indeed, simple arithmetic worked on the equilibrium **1** + **TCNB** ⇌ **TCNB@1** shows that about 9% of **1** and **TCNB** remains unassociated, thus accounting for the residual luminescence emissions observed from the separate species.

System 1+TCNB—electrochemical behaviour

Electrochemical experiments were performed to better characterize the donor–acceptor interaction within the **TCNB@1** adduct. As only a narrow potential window is accessible in $CHCl_3$, for electrochemical measurements the solvent used was

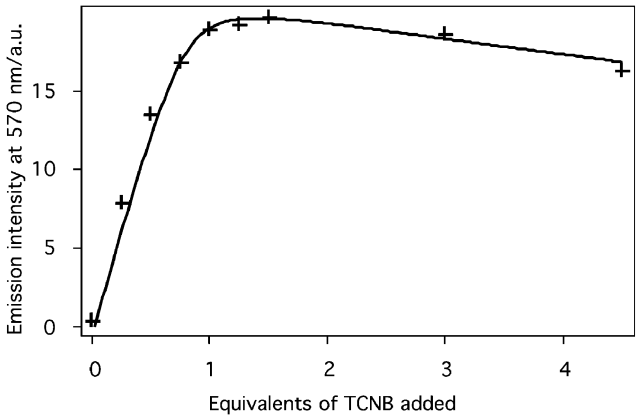

Fig. 4 Spectrofluorimetric titration of a 4×10^{-5} M solution of the receptor **1** with **TCNB**, monitoring the luminescence emission of the adduct **TCNB@1** at 570 nm (chloroform solution, room temperature). The points are the experimental data, and the curve shows the fitting result.

Table 2 Electrochemical results in deaerated CH_2Cl_2 solution, from CV and DPV measurements

Compound	E_{ox}, (V) *vs.* SCE	E_{red}, (V) *vs.* SCE
1	+1.52 irr.	(<−1.8)
TCNB	(>+1.8)	−0.62
1+TCNB	+1.65 irr.	−0.62, −0.91

CH_2Cl_2, which is similar to $CHCl_3$ for polarity and hydrophobicity. Other solvents typically used in electrochemical work, like acetonitrile, could not be used because the adduct **TCNB@1** does not form in such media. Table 2 lists the potential values obtained by cyclic voltammetry (CV) for the reversible processes; for irreversible processes data were obtained from differential pulse voltammetry (DPV) scans.

In the examined potential window the two separate components feature distinct redox processes: the tweezer **1** shows only a single irreversible oxidation wave at +1.52 V, while **TCNB** can only be reduced reversibly at −0.62 V. When the two species are present in equimolar concentration, two processes are present in the cathodic CV scan (Fig. 5). The first process is clearly due to free **TCNB**, while the second is attributed to **TCNB** present within the adduct, where the charge-transfer interaction makes **TCNB** more difficult to reduce. On the anodic side, the wave corresponding to oxidation of the tweezer **1** shifts to more positive values, as the presence of the guest **TCNB** makes **1** more difficult to oxidize. However, owing to the irreversibility of the process, it is not possible to resolve the two potential values corresponding to free and hosting **1**.

Digital simulation[16] of cyclic voltammetry experiments performed at different scan rates (Fig. 5) allowed us to estimate the rate constants of adduct formation/disassembling. The following two processes were considered:

$$\text{Process 1} \quad \mathbf{TCNB} + \mathbf{1} \rightleftharpoons \mathbf{TCNB@1}$$

$$\text{Process 2} \quad \mathbf{TCNB}^- + \mathbf{1} \rightleftharpoons \mathbf{TCNB}^-\mathbf{@1}$$

In the first process, the rate of formation of the adduct (forward direction) was calculated to be $k_1(f) = 1.9 \times 10^8$ L mol^{-1} s^{-1} and the reverse (back) reaction $k_1(b) = 2.0 \times 10^2$ s^{-1}. From these data the equilibrium constant of process 1 can be evaluated as $k_1(f)/k_1(b) = 9.5 \times 10^5$ L mol^{-1}, in good agree-

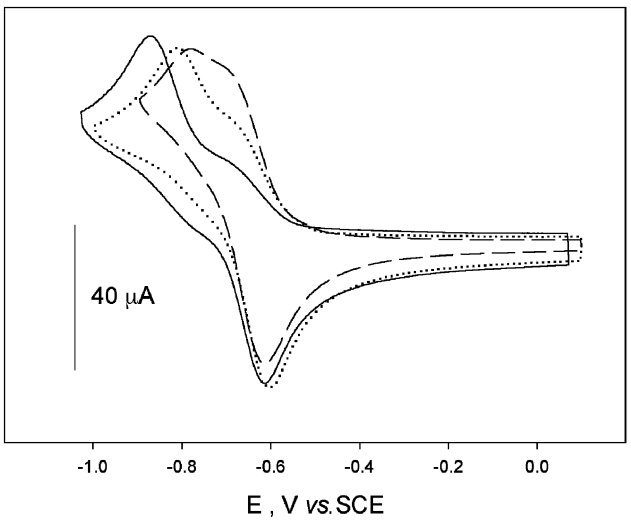

Fig. 5 Cyclic voltammograms of room temperature dichloromethane solutions containing **1** and **TCNB** 2×10^{-3} M recorded at different scan rates (500 mV s^{-1}, continuous line; 100 mV s^{-1}, dotted line; 20 mV s^{-1}, dashed line).

Downloaded by University of California - Los Angeles on 01 January 2013
Published on 21 April 2005 on http://pubs.rsc.org | doi:10.1039/B501880C

View Article Online

Downloaded by University of California - Los Angeles on 01 January 2013
Published on 21 April 2005 on http://pubs.rsc.org | doi:10.1039/B501880C

ment with the K_a value (7.3×10^5 L mol^{-1}) obtained from the titration experiment.

The second process is analogous to the first one, but involves **TCNB**$^-$, that is the reduced **TCNB** species. The rate constants obtained for the forward and back reactions were $k_2(f) = 1.5 \times 10^3$ L mol^{-1} s^{-1} and $k_2(b) = 1.6 \times 10^2$ s^{-1}, and the associated equilibrium constant is thus $k_2(f)/k_2(b) = 9.4$ L mol^{-1}. These calculated constants indicate that the **TCNB** guest is released from the tweezer host with approximately the same rate (2.0×10^2 *vs.* 1.6×10^2 s^{-1}) independently from the net charge carried.[17] In contrast, the rate for entering into the receptor is very sensitive to the charge of the guest, decreasing by five orders of magnitude on passing from **TCNB** to **TCNB**$^-$.

System 2+TCNB

The photophysical properties of the host species **2** are very similar to those featured by **1** (Table 1), owing to the fact that the relevant chromophore (naphthalene) is essentially the same in both receptors. On mixing together **2** and **TCNB** the behaviour is at first sight similar to that previously described for the **1**+**TCNB** system: the resulting solution becomes yellow, and a new emission band is observed at 614 nm (Table 1), indicating the formation of adduct species.

Differently from the previous **1**+**TCNB** system, however, a luminescence titration failed to give a reliable value for the association constant of the simple adduct **TCNB@2**. However, it is known from microcalorimetric titration experiments that the **2**+**TCNB** system is complicated by the formation of different adducts.[9] Thus, a global analysis fit[18,19] was performed on both the absorption and luminescence spectra recorded in the titration experiment. A good fit was obtained only taking into consideration the simultaneous presence of adducts in 1 : 1 (**TCNB@2**) and 1 : 2 (**TCNB@**$2 \cdot$**2**) guest : host ratios. Inclusion of the 2 : 1 species, $2 \cdot$**TCNB@2**, produced a worse fitting. The two partial formation constants were evaluated as $K_{1:1} = 5.4 \times 10^6$ L mol^{-1} and $K_{1:2} = 1.1 \times 10^4$ L mol^{-1}, corresponding to the two processes:

$$\mathbf{TCNB} + \mathbf{2} \rightleftharpoons \mathbf{TCNB@2}$$

$$\mathbf{TCNB@2} + \mathbf{2} \rightleftharpoons \mathbf{TCNB@}2 \cdot \mathbf{2}$$

By considering that our data were obtained at 20 °C, there is a fair agreement with the values previously obtained by microcalorimetric titration at 25 °C,[9] which resulted 1.43×10^7 and 4.35×10^4 L mol^{-1} for $K_{1:1}$ and $K_{1:2}$, respectively.

System 3+TCNB

Preliminary data on this system have already been published.[15] The photophysical properties of the clip **3** are essentially controlled by the presence of anthracene units, differently from **1** and **2** where the relevant chromophoric unit is naphthalene. As a consequence, the emission band of the clip **3** is at lower energy compared to the other receptors **1** and **2** (Table 1). On mixing together **3** and **TCNB** the solution becomes purple, due to a new absorption band at 525 nm, and a new very weak emission band is observed at 668 nm (Table 1), indicating the formation of adduct species. The red shift of the absorption and emission bands in **TCNB@3** with respect to the previous systems is consistent with the CT character of the adduct, as the anthracene unit features a lower potential for oxidation with respect to the naphthalene unit contained in **1** and **2**.

Analogously to the previous systems, titration experiments were performed by adding **TCNB** to **3** in chloroform solution. The changes in absorption spectra were recorded, and the data fitted by global analysis.[18,19] The presence of the sole 1 : 1 adduct **TCNB@3** was required for a good fit, and the association constant of the adduct was found to be 1.24×10^4 L mol^{-1}. Consideration of other adducts with 2 : 1 or 1 : 2 component ratios resulted in a worse fit; their presence appears thus negligible.

Association/dissociation dynamics

The K_a values for formation of the 1 : 1 adducts between **TCNB** and the various hosts are clearly related to the topology of the receptor. The highest K_a value (5.4×10^6 L mol^{-1}) is observed for the host **2**, indicating that **TCNB** fits very well into this clip. It is known[9] that in this adduct the **TCNB** guest is included with the molecular plane almost parallel with respect to the naphthalene units, as depicted in Fig. 6b. The clip **3**, on the other hand, has a much more "open" structure and is not flexible enough to enclose efficiently the guest **TCNB**; as a consequence, a much smaller K_a value is observed (1.24×10^4 L mol^{-1}). An intermediate K_a value is obtained for the tweezer **1** (7.3×10^5 L mol^{-1}); in this case it is known[12] that **TCNB** is parallel to the upper (central) naphthalene unit, as shown in Fig. 6a.

The reaction between **TCNB** and the receptors **1** and **2** has been further characterized to evaluate the association/dissociation barriers for the host–guest complex formation. Fig. 6 shows Gibbs energy diagrams for the association/dissociation processes of these species. The ΔG values (−7.9 and −9.0 kcal mol^{-1}) have been obtained from the measured K_a values (see above). The $\Delta G^{\#}$ values for dissociation of the host–guest complex (15.7 and 12.4 kcal mol^{-1}) have been derived by NMR measurements, from line shape analysis of the temperature-dependent spectra.[10] From these diagrams it becomes evident that the association between **1** and **TCNB** has a substantial activation barrier whereas the activation barrier for the association between **2** and **TCNB** is small (not far from

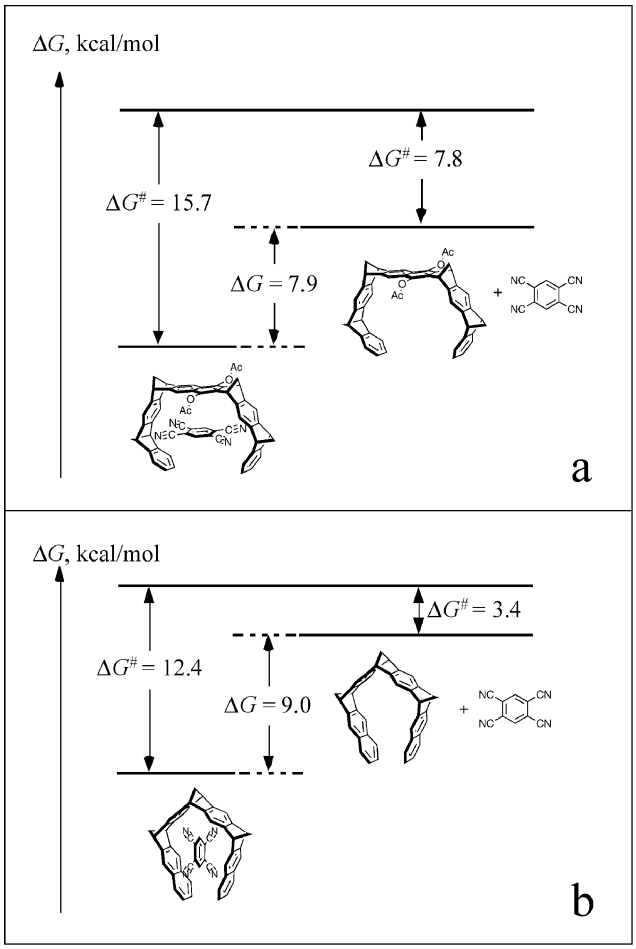

Fig. 6 Gibbs energy profiles of the reaction of inclusion of **TCNB** by the receptors **1** (a) and **2** (b). For details, see text.

a diffusion-controlled process). These findings can be explained by the different topology of the tweezer **1** and clip **2**. The tweezer **1** has the topology of an almost closed wheel, which makes the inclusion of the guest molecule inside the cavity a kinetically rather difficult process whereas the clip **2** has a much more open topology, which makes the inclusion of the guest molecules easier and hence the activation barrier for this process smaller. The same arguments can be applied to the activation barrier for adduct dissociation, which is higher in the case of the more closed receptor **1**.

Acknowledgements

This work has been supported MIUR (PNA-based nanotechnologies and microsystems for food diagnostics), University of Bologna (Funds for selected topics), and Deutsche Forschungsgemeinschaft (SFB452).

References

1 J. M. Lehn, *Supramolecular Chemistry. Concepts and Perspectives*, Wiley-VCH, Weinheim, 1995.
2 J. L. Atwood and J. W. Steed, *Supramolecular Chemistry*, Wiley-VCH, Weinheim, 2000.
3 L. J. Prins, D. N. Reinhoudt and P. Timmerman, *Angew. Chem. Int. Ed.*, 2001, **40**, 2383.
4 J. P. Gallivan and D. A. Dougherty, *J. Am. Chem. Soc.*, 2000, **122**, 870.
5 E. A. Meyer, R. K. Castellano and F. Diederich, *Angew. Chem. Int. Ed.*, 2003, **42**, 1210.
6 L. F. Newcomb, T. S. Haque and S. H. Gellman, *J. Am. Chem. Soc.*, 1995, **117**, 6509.
7 F. G. Klärner, U. Burkert, M. Kamieth and R. Boese, *J. Phys. Org. Chem.*, 2000, **13**, 604.
8 F. G. Klärner, J. Panitzky, D. Bläser and R. Boese, *Tetrahedron*, 2001, **57**, 3673.
9 F. G. Klärner, M. Lobert, U. Naatz, H. Bandmann and R. Boese, *Chem. Eur. J.*, 2003, **9**, 5036.
10 F. G. Klärner and B. Kahlert, *Acc. Chem. Res.*, 2003, **36**, 919.
11 F. G. Klärner, J. Panitzky, D. Preda and L. T. Scott, *J. Mol. Model.*, 2000, **6**, 318.
12 F. G. Klärner, U. Burkert, M. Kamieth, R. Boese and J. Benet-Buchholz, *Chem. Eur. J.*, 1999, **5**, 1700.
13 G. Jones II, in *Photoinduced Electron Transfer, Part A*, ed. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1998.
14 I. Deperasinska, J. Prochorow and J. Dresner, *J. Lumin.*, 1998, **79**, 65.
15 F. G. Klärner, B. Kahlert, R. Boese, D. Bläser, A. Juris and F. Marchioni, *Chem. Eur. J.*, 2005, DOI: 10.1002/chem.200401257.
16 *DigiSim 3.05*, BioAnalytical Systems, West Lafayette, IN; http://www.bioanalytical.com/.
17 The value of the rate constant $k_1(b) = 200\ s^{-1}$ agrees very well with the rate constant determined for the dissociation of complex **TCNB@1** by the line-shape analysis of the temperature-dependent ^1H NMR spectrum of a (2 : 1) mixture of **1** and **TCNB** in $C_2D_2Cl_4$ (coalescence temperature 60 °C, $k = 313\ s^{-1}$, $\Delta G^{\neq} = 15.7$ kcal mol^{-1}). In toluene-d_8 the dissociation is slightly faster. From a temperature-dependent ^1H NMR spectrum of a (1 : 2) mixture of **1** and **TCNB** the coalescence between free and complexed **TCNB** was observed at 60 °C, $k = 1000\ s^{-1}$, $\Delta G^{\neq} = 15.0$ kcal mol^{-1}; U. Burkert, Dissertation, University of Essen, Essen, 1999 and U. Seelbach, Dissertation, University of Essen, Essen, 2002.
18 H. Gampp, M. Maeder, C. J. Meyer and A. D. Zuberbühler, *Talanta*, 1985, **32**, 257.
19 R. A. Binstead, *SPECFIT*, Spectrum Software Associates, Chapel Hill, NC, 1996.

Downloaded by University of California - Los Angeles on 01 January 2013
Published on 21 April 2005 on http://pubs.rsc.org | doi:10.1039/B501880C