pubs.acs.org/joc

Folding and Unfolding Movements in a [2]Pseudorotaxane

Moorthy Suresh,[†] Amal Kumar Mandal,[†] Manoj K. Kesharwani,[†] N. N. Adarsh,[§] Bishwajit Ganguly,^{*,†} Ravi Kumar Kanaparthi,[‡] Anunay Samanta,^{*,‡} and Amitava Das^{*,†}

[†]Central Salt and Marine Chemicals Research Institute (CSIR), Bhavnagar, Gujarat, India, [‡]University of Hyderabad, Hyderabad, India, and [§]Indian Association for the Cultivation of Science, Kolkata, India

ganguly@csmcri.org; assc@uohyd.ernet.in; amitava@csmcri.org

Received September 10, 2010



A new dibenzo[24]crown-8 derivative (1) was synthesized and functionalized with aromatic moieties such as naphthalene and coumarin units. These two fluorophores are known to form an effective FRET (Forster resonance energy transfer) pair, and this formed the basis for the design of this host crown ether derivative. Results of the steady-state and time-resolved fluorescence studies confirmed the resonance energy transfer between the donor naphthalene moiety and acceptor coumarin fragment, while NMR spectra and computational studies support a folded conformation for the uncomplexed crown ether 1. This was found to form an inclusion complex, a [2]pseudorotaxane type with imidazolium ion derivatives as the guest molecules with varying alkyl chain lengths ($[C_4min]^+$ or $[C_{10}mim]^+$). The host crown ether (1) tends to adopt an open conformation on formation of the intervoven inclusion complex $(1 \cdot [C_4 \text{mim}]^+ \text{ or } 1 \cdot [C_{10} \text{mim}]^+)$. This change in conformation, from the folded to a open one, was predicted by computational as well as ¹H NMR studies and was confirmed by single crystal X-ray structure for one $(1 \cdot [C_4 \text{mim}]^+)$ of the two inclusion complexes. The increase in the effective distance between the naphthalene and coumarin moieties in the open conformation of these inclusion complexes was also supported by the decrease in the effective FRET process that was operational between naphthalene and coumarin moieties in the free molecule (1). Importantly, this inclusion complex formation was found to be reversible, and in the presence of a stronger base/polar solvent, such as triethyl amine/DMSO, the deprotonation/effective solvation of the cationic imidizolium ions ($[C_4min]^+$ or $[C_{10}min]^+$) resulted in decomplexation or dethreading with restoration of the original emission spectra for 1, which signifies the subsequent increase in the FRET process. Thus we could demonstrate that a molecular folding-unfolding type of movement in the crown ether derivative could be induced by chemical input as an imidazolium ion.

Introduction

The development of inclusion complexes such as pseudorotaxanes,¹ rotaxanes,² and catenanes,³ where the host–guest assembly together can perform some desired function, is of current research interest in supramolecular chemistry.⁴ Forces that are generally operational for the generation of these host– guest assemblies are various nonbonding interactions such as $\pi-\pi$ interaction, ^{5a-j} hydrogen bonding, ^{5k-m} hydrophobic, ^{5n,o} and van der Waals^{5p,q} interactions. Change(s) in any or a combination of these interactions may lead to different conformations of the host or orientation of the host and the guest in the assembly with respect to each other. This opens up the possibility of achieving desired mechanical movements such as molecular motion with an appropriate external stimulation. Achieving such molecular motion with an ionic input could lead to the design of a supramolecular assembly that is capable of mimicking the function of biological motors at the molecular level.⁶ Recently Rebek et al. have shown that intermolecular resonance energy transfer (RET) between pyrene and perylene moieties occurs when monofunctionalized pyragallol or resorcinol arene moieties form self-assembled hexameric capsule-like architecture. It is shown that formation of such self-assembled structures is a random process and one out of many conformers, and assemblies could show the RET process.⁷ In our attempt to develop such a system where the RET process can be achieved with more control and as a result of some ionic input, we have designed a simple bisbenzocrown derivative, as this class of compounds is known to adopt different conformations in the presence and absence of the guest molecule. To the best of our knowledge there is only one reference available in the literature that describes the RET

(2) (a) Cordova, R. A.; Kaifer, A. E.; Stoddart, J. F. Nature (London)
1994, 369, 133–137. (b) Solladie, N.; Chambron, J.-C.; Dietrich-Buchecker,
C. O.; Sauvage, J.-P. Angew. Chem., Int. Ed. Engl. 1996, 35, 906–909.
(c) Vogtle, F.; Dunnwald, T.; Handel, M.; Jager, R.; Meier, S.; Harder, G.
Chem.—Eur. J. 1996, 2, 640–643. (d) Leigh, D. A.; Murphy, A.; Smart, J. P.;
Slawin, A. M. Z. Angew. Chem., Int. Ed. Engl. 1997, 36, 728–732. (e) Jiang,
W.; Winkler, H. D. F.; Schalley, C. A. J. Am. Chem. Soc. 2008, 130, 13852–13883. (f) Li, L.; Clarkson, G. J. Org. Lett. 2007, 9, 497–500.

(3) (a) Schill, G. Catenanes, Rotaxanes, Knots; Academic Press: New York,
(b) Nierengarten, J.-F.; Dietrich-Buchecker, C. O.; Sauvage, J.-P.
J. Am. Chem. Soc. 1994, 116, 375–376. (c) Armaroli, N.; Balzani, V.;
Barigelletti, F.; De Cola, L.; Flamigni, L.; Sauvage, J.-P.; Hemmert, C.
J. Am. Chem. Soc. 1994, 116, 5211–5217. (d) Amabilino, D. B.; Dietrich-Buchecker, C. O.; Livoreil, A.; Perez-Garcia, L.; Sauvage, J.-P.; Stoddart,
J. F. J. Am. Chem. Soc. 1996, 118, 3905–3913. (e) Peinador, C.; Blanco, V.;
Quintela, J. M. J. Am. Chem. Soc. 2009, 131, 920–921.
(4) (a) Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Venturi, M.

(4) (a) Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Venturi, M. Acc. Chem. Res. 2001, 34, 445–455. and references therein. (b) Hernandez, J. V.; kay, E. R.; Leigh, D. A. Science 2004, 306, 1532. (c) Chatterjee, M. N.; Kay, E. R.; Leigh, D. A. J. Am. Chem. Soc. 2006, 128, 4058–4073. (d) Serreli, V.; Lee, C.-F.; Kay, E. R.; Leigh, D. A. Nature 2007, 445, 523–527. (e) Sauvage, J. P. Acc. Chem. Res. 1998, 31, 611–619. (f) Raymo, F. M.; Stoddart, J. F. Chem. Rev. 1999, 99, 1643–1963. (g) Onagi, H.; Rebek, J., Jr. Chem. Commun. 2005, 4604–4606.

(5) (a) Cantrill, S. J.; Pease, A. R.; Stoddart, J. F. J. Chem. Soc., Dalton Trans. 2000, 3715-3734. (b) Rebek, J.; Nemeth, D. J. Am. Chem. Soc. 1986, 108, 5637-5638. (c) Burley, S. K.; Petsko, G. A. J. Am. Chem. Soc. 1986, 108, 7995–8001. (d) Hamilton, A. D.; Engen, D. V. J. Am. Chem. Soc. 1987, 109, 5035–5036. (e) Zimmerman, S. C.; Vanzyl, C. M. J. Am. Chem. Soc. **1987**, 109, 7894–7896. (f) Nelson, J. C.; Saven, J. G.; Moore, J. S.; Wolynes, P. G. Science 1997, 277, 1793–1796. (g) Hunter, C. A. Angew. Chem., Int. Ed. Engl. 1993, 32, 1584-1586. (h) Hunter, C. A. Chem. Soc. Rev. 1994, 23, 101. (i) Ferguson, S. B.; Diederich, F. Angew. Chem., Int. Ed. Engl. 1986, 25, 1127-1129. (j) Nishio, M.; Hirota, M. Tetrahedron 1989, 45, 7201. (k) Kotera, M.; Lehn, J.-M.; Vigneron, J.-P. J. Chem. Soc., Chem. Commun. 1994, 197-199. (1) Sijbesma, R. P.; Meijer, E. W. Curr. Opin. Colloid Interface Sci. 1999, 4, 24-32. (m) Jeffrey, G. A. An Introduction to Hydrogen Bonding; Oxford University Press: New York, 1997. (n) Ben-Naim, A. Hydrophobic Interactions; Plenum Press: New York & London, 1980. (o) Bhasikuttan, A. C.; Mohanty, J.; Nau, W. M.; Pal, H. Angew. Chem., Int. Ed. Engl. 2007, 46, 4120-4122. (p) Street, A. G.; Mayo, S. L. Proc. Natl. Acad. Sci. U.S.A. 1999, 96, 9074-9076. (q) Ohta, K.; Ikejima, M.; Moriya, M.; Hasebe, H.; Yamamoto, I. J. Mater. Chem. 1998, 8, 1971-1977

(6) (a) Fletcher, S. P.; Dumur, F.; Pollard, M. M.; Feringa, B. L. Science 2005, 310, 80-82. (b) Badjic, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. Science 2004, 303, 1845. (c) Ballardini, R.; Balzani, V.; Clemente Leon, M.; Credi, A.; Gandolfi, M. T.; Ishlow, E.; Perkins, J.; Stoddart, J. F.; Tseng, H.-R.; Wenger, S. J. Am. Chem. Soc. 2002, 124, 12786–12795.

(7) (a) Barrett, E.; Dale, T. J.; Rebek, J., Jr. J. Am. Chem. Soc. 2008, 130, 2344–2350. (b) Barrett, E. S.; Dale, T. J.; Rebek, J., Jr. Chem. Commun. 2007, 4224–4226.

response of the fluorescence output signal as a consequence of the formation of a host-guest inclusion complex.^{8a} However, neither change in conformation nor any molecular movement was reported as a result of such inclusion complex formation. To demonstrate how RET can further be used to probe the folding-unfolding movement in a definite selfassembled system, we have synthesized a new crown ether derivative (1) substituted with naphthalene (nap) and coumarin (cou) functionality as the donor and acceptor component, respectively (Scheme 1), as these are known to form a RET pair^{8b} and allow us to study any conformational change of the crown moiety on forming the inclusion complex. We have used imidazolium (1-butyl-3-methylimidazolium $([C_4 mim]^+)$ and 1-decyl-3-methylimidazolium $([C_{10} mim]^+))^9$ ions, as these are known to form a [2]pseudorotaxane type of inclusion complex with bisbenzo crown ether derivatives.^{2f} In this paper, we have described how the formation of a simple [2]pseudorotaxane adduct, between 1 and $[C_4 mim]^+$ or $[C_{10}mim]^+$, could induce conformational change of the crown ether based host fragment and RET process operational between nap and cum fragments. Ratiometric changes in the fluorescence readout signal as a consequence of the RET process enabled us to read the conformational changes or the molecular movements. Such an example is rare in the literature.

Results and Discussion

A database search on the structural aspects of various derivatives of dibenzo[24]crown-8 reveals both open and folded conformations. In order to establish the actual conformation for the 1, its ¹H NMR spectra was compared with that of 2,3-dihydroxy naphthalene (N), 6,7-dihydroxy coumarin (C), and a physical equimolar mixture of N and C of comparable concentrations clearly revealed an upfield shift for H_3 atom (6.20-6.18), H_4 (7.65-7.55 ppm), and H_5 , H_8 (6.9–6.8 ppm) of coumarin moiety (Supporting Information). These upfield shifts owing to the shielding effect for the part of the naphthalene moiety support a proximate distance between coumarin and naphthalene moiety in 1 and thus confirm the folded conformation. 2D-NOESY spectrum was also recorded, which revealed the NOE effect between two chromophores (Supporting Information). The observed cross peaks for $H_4/H_{a,f}$ at $\delta = 7.3$ ppm and for $H_4/H_{c,d}$ at $\delta = 7.1$ ppm confirm the NOE effect between nearby H-atoms of two different aromatic moieties and thus the folded conformation.

Any possibility of intermolecular interaction as a probable reason for these upfield shifts was ignored; as no further shift was observed when ¹H NMR and 2D-NOESY spectra for **1** were recorded using an even higher concentration of **1**.

Complexation Studies of Host 1 with $[C_4mim]^+/[C_{10}mim]^+$. In order to examine the possibility of formation of the interwoven complex between 1 and imidazolium ion, we recorded ¹H NMR spectra for 1 in the absence and presence of varying concentration of $[C_4mim]^+$ in CD₂Cl₂ (Figure 1). A downfield shift of H_I proton from $\delta = 8.47$ ppm to $\delta = 8.54$ ppm indicates $[C-H\cdots O]$ interaction of the acidic H_I

 ^{(1) (}a) Ashton, P. R.; Philp, D.; Spencer, N.; Stoddart, J. F. J. Chem. Soc., Chem. Commun. 1991, 1677–167. (b) Fyfe, M. C. T.; Glink, P. T.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. Angew. Chem., Int. Ed. Engl.
 1997, 36, 2068–2070. (c) Ashton, P. R.; Langford, J.; Spencer, S. N.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. Chem. Commun. 1996, 1387–1388. (d) Mirzoian, A.; Kaifer, A. E. Chem.—Eur. J. 1997, 3, 1052– 1058. (e) Baxter, P. N. W.; Lehn, J.- M.; Sleiman, H.; Rissanen, K. Angew. Chem., Int. Ed. Engl. 1997, 36, 1294–1296.

^{(8) (}a) Ishow, E.; Credi, A.; Balzani, V.; Spadola, F.; Mandolini, L. *Chem.*—*Eur. J.* **1999**, *5*, 984–989. (b) Lee, M. H.; Quang, D. T.; Jung, H. S.; Yoon, J.; Lee, C.-H.; Kim, J. S. *J. Org. Chem.* **2007**, *72*, 4242–4245.
(9) Park, S.; Kazlauskas, R. J. *J. Org. Chem.* **2001**, *66*, 8395–8401.



FIGURE 1. ¹H NMR spectra (500 MHz, CD₂Cl₂, 298 K) of (A) 1, (B) [C₄mim]⁺, and (C) 1 · [C₄mim]⁺ in CD₂Cl₂.





(i) K₂CO₃, Kl, 2-(2-(2-chloroethoxy) ethoxy) ethanol, Dry DMF, (ii) Ts-Cl, NaOH, THF/H₂O, (iii) 6,7-dihydroxy coumarin, Cs₂CO₃, Dry DMF, (iv) 1,2-dihydroxy benzene, Cs₂CO₃, Dry DMF, Yield: **1** (58%); **1D** (62%).



(i) K₂CO₃, KI, 2-(2-(2-chloroethoxy) ethoxy) ethanol, Dry DMF, (ii) Ts-Cl, NaOH, THF/H₂O, (iii) 6,7-dihydroxy coumarin, Cs₂CO₃, Dry DMF; Yield: **1A** (54%).

atom of $[C_4mim]^+$ with the lone pair of electrons residing on the oxygen atom of the macrocyclic crown ether backbone. For $H_{II}(\delta_{HII} = 7.29 \text{ ppm to } 7.20 \text{ ppm})$ and $H_{IV}(\delta_{HIV} = 4.15 \text{ ppm to } 4.10 \text{ ppm})$ atoms, upfield shifts were observed. This could be explained on the basis of the polarization or shift of electron density upon complexation through formation of $[(C-H)_{Imidazolium} \cdots O_{Crown}]$ hydrogen bonding. One would expect that stabilization of partial positive charge of the N₁ atom of $[C_4mim]^+$ by ion—dipole interaction involving the nearby crown oxygen atoms shifts the electron density of the

imidazolium ring toward positive N_3 atom. Thus, the protons $(H_{III} \text{ and } H_{IV})$ that are nearer to the N_3 atom are influenced by the increased electron density on the N_3 atom of $[C_4 \text{mim}]^+$ moiety. Thus, as a consequence of this polarization of aromatic electrons, signals for H_V at 3.91 ppm in $[C_4 \text{mim}]^+$ is found to be downfield shifted to $\delta = 3.94$ ppm in the hydrogen-bonded adduct; the positive inductive effect of -CH₃ partially stabilizes the positive charge on the N_3 atom.

More interestingly, downfield shift ($\Delta \delta H_3 = 0.24$ ppm and $\Delta \delta H_4 = 0.11$ ppm) for H₄ and H₃, with respect to that of 1, was observed for the [2]pseudorotaxane, which suggested that the two arene fragments move away from each other when $[C_4 mim]^+$ was included in the host crown moiety. Little downfield shifts were also observed for H₈, H_c, and H_d. Further, the NOEs observed between H_4/H_c and H_4/H_f in 1 were absent in the interwoven complex, $1 \cdot [C_4 \text{mim}]^+$. All of these observations suggest that the complex adopts a different conformation compared to that in 1 with lesser (if any) $\pi - \pi$ stack interaction. This indicates an unfolding of the crown moiety of 1 in the [2]pseudorotaxane complex, $[1 \cdot C_4 \text{mim}]^+$. Thus, the inclusion complex formation makes the crown moiety change its conformation from a folded one to an unfolded one. Associated shifts were also observed for aliphatic hydrogen atoms of 1 and $[C_4 mim]^+$; however, due to the complicated nature of the overlapping spectra it was difficult to assign the extent of the shift for individual hydrogen atoms. Similar studies were repeated using $[C_{10}mim]^+$ instead of $[C_4 mim]^+$, and analogous unfolding of the crown conformation was also observed (Supporting Information).

The formation of the [2]pseudorotaxane was also confirmed by the ESI mass spectra: a strong m/z signal at 705.72 (100%) for $1 \cdot [C_4 mim]^+$ and 789.75 (100%) for $1 \cdot [C_4 mim]^+$ confirms the 1:1 stoichiometry (Supporting Information). Further, evidence for the proposed [2]pseudorotaxane formation was obtained from the single crystal X-ray structure for $1 \cdot [C_4 mim]PF_6$, though the R-factor (gt) was high (18%) (Figure 2). Despite our best efforts, we could not develop a better quality single crystal with a lower R-factor (gt), and we have provided details about the structure in the Supporting



FIGURE 2. Molecular structure of $1 \cdot [C_4 \text{mim}]^+$.

Information. However, the structure¹⁰ is good enough to confirm the proposed interwoven complex formation in the case of $1 \cdot [C_4 \text{mim}]^+$ and validate the optimized structure for the interwoven complex (*vide infra*, Figure 3b).

Computational Studies

The intervoven complex formation $(1 \cdot [C_4 \text{mim}]^+)$ observed through NMR and fluorescence spectral data was also examined by molecular modeling studies. The conformational study of 1 and its interwoven complexes $1 \cdot [C_4 \text{mim}]^+$ and $1 \cdot [C_{10}mim]^+$ was evaluated with molecular mechanics and DFT calculations. Initially, the conformational search was performed for 1, $1 \cdot [C_4 \text{mim}]^+$, and $1 \cdot [C_{10} \text{mim}]^+$ with the MM2 force field¹¹ in CH₂Cl₂ medium. The selected conformers were taken for further optimization using the DFT (GGA/BLYP/DNP) method¹² in CH_2Cl_2 employing a COSMO solvation model.¹³ The lowest energy conformer at the GGA/BLYP/DNP level of 1 was found to be the folded structure having naphthalene and coumarin moieties close to each other (6.77 Å), which corroborates the feasibility of FRET (Figure 3a). However, in the interwoven complex between 1 and $[C_4mim]^+/[C_{10}mim]^+$, the crown ether conformation changes from a folded to an unfolded situation, where the naphthalene and coumarin moieties move apart (15.09 Å/15.88 Å), and reduces the possibility of energy transfer between these two moieties (Figure 3b/3c). The calculated interwoven complex was found to be similar to that of the X-ray crystal structure obtained for $1 \cdot [C_4 \text{mim}]^+$ (Figure 2). These results further corroborate the reduction in the FRET process, when the interwoven complex is formed.

Thus, it may appear from the above discussion that there is an apparent disagreement between the optimized structure for the lowest energy uncomplexed crown in which both chromophores are positioned with a larger distance of ~6.7 Å and the observed NMR spectral shifts due to $\pi - \pi$ interactions. Other low energy conformers for the uncomplexed crown showed the smaller distances between the chromophores, which might be attributed to the observed NMR signals in the experimental studies (Supporting Information). Further, note that the $\pi - \pi$ interaction between substituted aromatic moieties can be observed within ~7 Å as reported in the literature.¹⁴

UV-vis, Fluorescence, and TCSPC Studies. The absorption spectrum of 1 in dichloromethane shows maxima at 280 nm ($\pi \rightarrow \pi^*$; log $\varepsilon = 3.14$, S₀ \rightarrow S₁), a typical band pattern for naphthalene moiety, and at 340 nm ($\pi \rightarrow \pi^*$; log $\varepsilon = 3.28$, S₀ \rightarrow S₁) for the coumarin moiety. Further, the absorption spectra of 1 in different solvents of varying polarity did not show any new features indicative of ground state interaction between the naphthalene and coumarin subunits of 1

When excited at 280 nm, where naphthalene absorbs predominantly (Figure 4), the fluorescence spectrum of 1



FIGURE 3. GGA/BLYP/DNP optimized lowest energy conformer of (a) 1, (b) $1 \cdot [C_4 \text{mim}]^+$, and (c) $1 \cdot [C_{10} \text{mim}]^+$.



FIGURE 4. Fluorescence spectra of 1 (1.0×10^{-7} M) in dichloromethane upon addition of increasing concentration of (a) [C₄mim]⁺ and (b) [C₁₀mim]⁺; λ_{exc} was 280 nm. Inset: overlap spectra for the emission spectrum of 1D and absorption spectrum of 1A.

consisted of emission predominantly from the coumarin moiety ($\lambda_{max} = 420$ nm) in addition to the typical weak naphthalene emission at 340 nm. In order to understand the process better, emission spectra of two model compounds, (donor crown) **1D** and (acceptor crown) **1A**, in CH₂Cl₂ solution were recorded (Supporting Information). Emission maximum for **1D** was observed at 320 nm ($\lambda_{exc} = 280$ nm, $\phi =$ 0.35 with respect to naphthalene in cylcohexane, $\tau_1 = 9.61$ ns), whereas that for **1A** was at 420 nm ($\lambda_{exc} = 340$ nm, $\phi =$ 0.1 with respect to quinine sulfate in 0.1 M H₂SO₄, $\tau = 0.9$ ns). The quantum yields were calculated using eq 1.

$$\phi_f = \phi_f'(I_{\text{sample}}/I_{\text{std}})(A_{\text{std}}/A_{\text{sample}})(\eta^2_{\text{sample}}/\eta^2_{\text{std}}) \qquad (1)$$

where ϕ_f^{\prime} is the absolute quantum yield of the reference compound, I_{sample} and I_{std} are the integrated emission intensities, A_{sample} and A_{std} are the absorbance at the excitation wavelength, and η^2_{sample} and η^2_{std} are the respective refractive indices. Further, examination of the emission spectra of **1D** and the absorption spectra of **1A** suggests a significant spectral overlap and thus supports the possibility of resonance energy transfer from the photoexcited naphthalene moiety to the coumarin fragment in **1**, following the Forster theory by weak dipole–dipole induced interaction. To ascertain that such a process is operational in **1**, we have carried out time-resolved emission studies using the time correlated single photon counting (TCSPC) technique (Supporting Information).

Fluorescence decay traces ($\lambda_{exc} = 280$ nm) monitored at 320 nm could be best fitted to a biexponential function with time constants of $\tau_1 = 0.32 \pm 0.002$ ns (95.65%) and $\tau_2 = 8.68 \pm 0.02$ ns (4.35%), and the decay trace monitored at 470 nm was best fitted to the biexponential function with a negative pre-exponential factor, $I(t) = 1.61\exp(-t/\tau_1) - 0.61\exp(-t/\tau_2)$

with τ_1 and τ_2 given as 0.85 ± 0.01 ns and 0.32 ± 0.005 ns. The decay parameters and in particular the presence of 0.32 ns component with both the 320 and 470 nm emission bands and negative pre-exponential factor associated with the later emission provide convincing evidence of the energy transfer process in 1. Comparison of the decay constants for 1 and 1D clearly reveals that the short lifetime ($\tau_1 = 0.32 \pm 0.002$ ns (95.65%) of the naphthalene moiety in 1 is the consequence of fluorescence quenching due to the RET process. Based on the steady-state and time-resolved emission data, the Forster distance (R_o) was evaluated using the standard equation and found to be 26.9 Å with the energy transfer efficiency (Φ) of 96%. Thus, the energy transfer from photoexcited naphthalene to nearby coumarin confirms the proximity of two chromophores, which is favorable for high energy transfer efficiency.

On addition of an increasing amount of $[C_4 mim]^+$ or $[C_{10}mim]^+$ to a solution of 1 in CH₂Cl₂, a gradual decrease in the fluorescence emission at 420 nm ($\lambda_{exc} = 280$ nm) with concomitant enhancement at 340 nm was registered (Figure 4). The ratiometric emission response of 1 with the revival of naphthalene emission at 340 nm at the expense of coumarin emission with the increase in concentration of $[C_4 mim]^+$ or $[C_{10} mim]^+$ suggests the formation of the interwoven [2]pseudorotaxane complex. This causes a change in conformation of the crown ring in 1 from a folded to an unfolded one. Thus, this conformational change partially interrupts the interaction of coumarin and naphthalene moieties that existed in the folded conformation and reduces the RET. Fluorescence decay traces recorded for $1 \cdot [C_4 \text{mim}]^+$ and $1 \cdot [C_{10} \text{mim}]^+$ following excitation with a 280 nm source are shown in Supporting Information Figures 25 and 26. The decay traces, monitored at (acceptor emission), could be best fitted to a biexponential model with decay time constants with $\tau_1 = 0.33 \pm 0.03$ ns (42.5%) and $\tau_2 = 1.1 \pm$ 0.01 ns (57.5%) for the complex $1 \cdot [C_4 \text{mim}]^+$ and $\tau_1 = 0.25 \pm$ 0.01 ns (70%) and $\tau_2 = 1.05 \pm 0.01$ ns (30%) for complex $1 \cdot [C_{10} \text{mim}]^+$. Comparison of these decay parameters with those for 1 suggests that the component for the coumarin moiety has gone down from 100% to 30% with an associated increase in the naphthalene component for $1 \cdot [C_{10}mim]^+$. The extent of these changes is a little less for $1 \cdot [C_4 \text{mim}]^+$. Thus, TCSPC studies support the unfolding of the crown conformation of 1 on formation of a [2]pseudorotaxane complex. Residual emission for the coumarin moiety ($\lambda_{exc} = 280$ and $\lambda_{emi} = 420$ nm) suggests the both folded and unfolded conformation exist in equilibrium in the solution. This is also indicative of a modest affinity constant value for the interwoven complex formation.

⁽¹⁰⁾ Crystal dimension: $0.14 \times 0.04 \times 0.02 \text{ mm}^3$; T = 100(2) K; monoclinic, space group C2/m; a = 32.186(4), b = 11.5459(13), c = 12.7286(15)Å; $\beta = 104.996(3)^\circ$; V = 4569.1(9) Å³; Z = 4, $\rho_{\text{calcd}} = 1.229$ g cm⁻³; $\mu = 0.136 \text{ mm}^{-1}$; F(000) = 1764; $\theta_{\text{min/max}} = 1.31^\circ/25.00^\circ$; $R_{\text{int}} = 0.0852$; range of h, k, l = -30/38, -13/13, -14/15; 11,533 reflections collected of which 4223 were unique, 2412 observed $[I > 2\alpha(I)]$ reflections, 266 parameters were refined; $R_1 = 0.1827$, wR2 = 0.4524; goodness of fit on $F^2 = 1.492$; CCDC 775359 contains the supplementary crystallographic data for this paper.

^{(11) (}a) Allinger, N. L. J. Am. Chem. Soc. 1977, 99, 8127–8134. (b) Burkert, U.; Allinger, N. L. Molecular Mechanics; ACS Monograph 177; American Chemical Society: Washington, DC, 1982.

^{(12) (}a) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.;
Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* 1992, *46*, 6671–6687.
(b) Becke, A. D. *J. Chem. Phys.* 1997, *107*, 8554–8560. (c) Lee, C. L.; Yang, W.; Parr, R. G. *Phys. Rev. B* 1988, *37*, 785–789.

^{(13) (}a) Neese, F. J. Chem. Phys. 2003, 119, 9428. (b) Neese, F. Curr. Opin. Cell Biol. 2003, 7, 125–135.

^{(14) (}a) Hunter, C. A.; Lawson, K. R.; Perkins, J.; Ursh, C. J. Chem. Soc., Perkin Trans. 2 2001, 651–669. (b) Burley, S. K.; Petsko, G. A. Science 1985, 229, 23–28.

The energy transfer efficiencies (Φ) between naphthalene and coumarin moiety in $1 \cdot [C_4 mim]^+$ and $1 \cdot [C_{10} mim]^+$ were evaluated. For $1 \cdot [C_4 mim]^+$, Φ is 85.2%, whereas for $1 \cdot [C_{10} mim]^+$, Φ is 76%. The association constants (K_a) of 1:1 complex for $1 \cdot [C_4 mim]^+$ and $1 \cdot [C_{10} mim]^+$ are found to be 162.92 M⁻¹ ($\Delta G^\circ = -3.22$ kcal mol⁻¹) and 232.27 M⁻¹ ($\Delta G^\circ = -3.01$ kcal mol⁻¹), respectively. Higher binding affinity for $1 \cdot [C_{10} mim]^+$ explains the relatively lower residual emission for the folded conformation ($\lambda_{exc} = 280$ nm, $\lambda_{emi} = 420$ nm). Addition of polar solvents such as DMSO to the inclusion complex resulted in retrieval of emission of 1 due to the effective solvation of imidazolium cations by polar solvent. Thus, addition of DMSO to the pseudorotaxane complex dethreads the imidazolium ion from the crown and makes the system reversible (Supporting Information).

Conclusion

In brief, we have shown that inclusion of imidazolium ions, having a C_{10} or C_4 -alkyl chain, in nonpolar media forms respective [2]pseudorotaxane complexes with a polyether macrocycle, which in the absence of any inclusion adopts a folded conformation. The inclusion process induces the macrocyclic moiety to unfold to a different extent based on the alkyl chain length. Appropriate choice of the two chromophores belonging to a FRET pair allowed us to probe different degrees of mechanical movement on formation of [2]pseudorotaxane complexes. Thus, the controlled movement of molecular components by selective chemical stimuli can be exploited in designing nanomolecular devices.

Experimental Section

Synthesis of 1. Esculetin (6,7-dihydroxy coumarin) (0.49 g, 2.7 mmol) was dissolved in 100 mL of freshly dried DMF in a two-neck round-bottom flask. To this solution was added Cs₂CO₃ powder (1.8 g, 5.4 mmol). This mixture was allowed to stir for 15 min, and the compound **B** (ditosylate of oligo-(ethylene glycol) derivative of naphthalene) (2.0 g, 2.7 mmol) dissolved in 75 mL of dry DMF was added dropwise for 2 h at 60 °C. Then temperature was raised to 80 °C, and the mixture was allowed to stir for 5 days. The solvent was removed under reduced pressure and extracted three times with CHCl₃ and water. Organic layers were combined and dried over anhydrous sodium sulfate. Solvent was removed under reduced pressure to give crude product that was purified on a silica gel column, using chloroform/methanol (98:2 v/v) as an eluent to yield 1 (0.87 g, 58%), as a white powder. ¹H NMR (500 MHz, CD_2Cl_2 , δ ppm) 7.654 - 7.635 (2H, dd, J = 3.5), 7.561 - 7.542 (1H, d, J = 9.5), 7.311-7.292 (2H, dd, 3.5), 7.103-7.096 (2H, d, J = 3.5), 6.833 (1H, s), 6.795 (1H, s), 6.181-6.162 (2H, d, 9.5), 4.228-4.201 (4H, q, J=4.5), 4.172 (2H, t, J=4.5), 4.128 (2H, t, J=4.5), 3.938 (4H, t, 4.5), 3.893 (4H, t, J = 4.5), 3.810–3.804 (8H, m). ¹³C NMR: 161.8, 152.8, 150.2, 149.0, 145.9, 143.3, 129.4, 126.4, 124.4, 113.5, 111.74, 110.7, 107. 9, 101.1, 71.6, 70.2, 69.9, 69.5, 69.2. Elemental analysis calcd for C₃₁H₃₄O₁₀: C, 65.71; H, 6.05. Found: C, 65.23; H, 5.96. (ESI-MS) calcd for C₃₁H₃₄O₁₀ 566.60, found 589.52 [M + Na]⁺. Mp: 160 °C. HRMS: calcd 589.2050 for $[1 + Na]^+$; found 589.2023 (Supporting Information).

Synthesis of 1D. Catechol (2,3-dihydroxy benzene) (0.3 g, 2.7 mmol) was dissolved in 100 mL of freshly dried DMF in a two-neck round-bottom flask. To this solution was added Cs_2CO_3 powder (1.8 g, 5.4 mmol). This mixture was allowed to stir for 15 min, and compound B (ditosylate of oligo(ethylene glycol) derivative of naphthalene) (2.0 g, 27.32 mmol) dissolved

in 75 mL of dry DMF was added dropwise for 2 h at 60 °C. Then the temperature was raised to 80 °C, and the mixture was allowed to stir for 5 days. The solvent was removed under reduced pressure and extracted three times with CHCl₃ and water. Organic layers were combined and dried over anhydrous sodium sulfate. Solvent was removed under reduced pressure to give crude product that was purified on a silica gel column, using chloroform/methanol (98:2 v/v) as an eluent to yield 1D (0.85 g, 62%), as a white powder. ¹H NMR (500 MHz, CD_2Cl_2 , δ ppm) 7.680-7.634 (2H, dd, J=3.2), 7.344-7.297 (2H, dd, J=3.2); 7.1 (2H, s), 6.878 (4H, s), 4.267 (4H, t, J=4.4), 4.162 (4H, t, J=4.4), 4.003 (4H, t, J = 4.4), 3.934 (4H, t, J = 4.6), 3.882 (8H, s). ¹³C NMR: 150.9, 131.1, 128.0, 125.9, 123.2, 116.1, 109.7, 73.1, 71.9, 71.1. Elemental analysis calcd for C₂₈H₃₄O₈: C, 67.45; H, 6.87. Found: C, 67.2; H, 6.8. ESI-MS: calcd for C₂₈H₃₄O₈ 498.56, found 521.58 [M + Na]⁺. Mp: 90 °C.

Synthesis of 1A. Esculetin (6,7-dihydroxy coumarin) (0.52 g, 2.9 mmol) was dissolved in 100 mL of freshly dried DMF in a two-neck round-bottom flask. To this solution was added Cs₂CO₃ powder (1.9 g, 5.8 mmol). Then the reaction mixture turned from yellow to pale green color. This mixture was allowed to stir for 15 min, and compound D (ditosylate of oligo(ethylene glycol) derivative of benzene) (2.0 g, 2.9 mmol) dissolved in 75 mL of dry DMF was added dropwise for 2 h at 40 °C. Then temperature was raised to 80 °C, and the mixture was allowed to stir for 5 day. The solvent was removed under reduced pressure and extracted three times with CHCl₃ and water. Organic layers were combined and dried over anhydrous sodium sulfate. Solvent was removed under reduced pressure to give crude product that was purified on a silica gel column, using chloroform/methanol (98:4 v/v) as an eluent to yield 1A (0.8 g, 54%), as a pale yellow powder. ¹H NMR (500 MHz, CD₂Cl₂, δ ppm) 7.611-7.592 (1H, d, J=9.5), 6.909 (1H, s,), 6.883 (4H, s), 6.822 (1H, s), 6.223-6.204 (1H, d, J=9.5), 4.182 (2H, t, J=4.5), 4.143 (2H, t, J=4.5), 4.108 (4H, s), 3.909 (2H, t, J=4.5), 3.879 (2H, t, J = 4.5), 3.855 - 3.843 (4H, q), 3.764 (8H, s). ¹³C NMR: 162.9, 154.6, 152.1, 150.8, 147.7, 145.2, 123.3, 116.1, 115.3, 112.9, 103.0, 73.0, 71.7, 71.2, 31.6. Elemental analysis calcd for C₂₇H₃₂O₁₀: C, 62.78; H, 6.24. Found: C, 62.43; H, 6.18. ESI-MS: calcd for $C_{27}H_{32}O_{10}$ 516.54, found 517.24 [M + 1]⁺. Mp: 180 °C.

Computational Methods

An exhaustive conformational search was performed in CH_2Cl_2 as solvent (dielectric constant = 8.9) with the molecular modeling program Macromodel¹⁵ using MM2 force field¹¹ for 5000 Monte Carlo steps. Conformations whose molecular mechanics energy is within 50 kJ/mol compared to calculated global energy minimum (GEM) of a compound were stored. Energy minimizations were performed with the Polak-Ribiere conjugate gradient (PRCG) method, which involves the use of first derivatives with convergence criterion set to 0.05 kJ/Å-mol.¹⁶ Conformational search of crown 1 produced total 2564 unique conformers, which includes 397 conformers with good convergence. However, conformational search of $1 \cdot [C_4 \text{mim}]^+$ and $1 \cdot [C_{10}mim]^+$ produced totals of 1993 and 2428 unique conformers, and only 30 and 91 conformers were of good convergence, respectively. Unique conformers with good convergence, including lowest energy conformer, were stored for further higher level DFT calculations.

The selected conformers were optimized with generalized gradient approximation (GGA) using the BLYP functional¹² integrated in density functional program DMol3 (version 4.1.2)

⁽¹⁵⁾ Mohamdi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440–467.

⁽¹⁶⁾ Polak, E.; Ribiere, G. Rev. Fr. Inf. Rech. Oper. 1969, 16-R1, 35-43.

by Accelrys Inc.¹⁷ The physical wave functions are expanded in terms of numerical basis sets. We used a DNP (double numerical polarized) basis set, which is comparable to the $6-31G^{**}$ basis set. The conductor-like screening model (COSMO) was employed for solvent calculations, and CH₂Cl₂ were used as solvent.¹³

Acknowledgment. DST (Grant No. SR/S1/IC-07/2009) and CSIR India have supported this work. M.S. and

A.K.M. thank CSIR, and M.K.K. and R.K.K. thank UGC, New Delhi for a Senior Research Fellowship.

Supporting Information Available: Synthetic details for reaction intermediates, characterization data (¹H NMR, ¹³C, ESI-MS, 2D-NOESY spectra), and spectroscopic results (UV–vis, fluorescence, and time correlated single photon counting data). This material is available free of charge via the Internet at http://pubs.acs.org.

Suresh et al.

⁽¹⁷⁾ Delley, B. J. Chem. Phys. 2000, 113, 7756-7763.