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Nadia Dozova, Rajesh Kumar, Tuhin Pradhan, Fabien Lacombat, Bernard Valeur, et al.. Photo-induced cation translocation in a molecular shuttle based on a calix[4]-biscrown including DCM and DMABN chromophores. *Chemical Communications*, 2015, 51 (80), pp.14859-14861. 10.1039/C5CC06054K . hal-01198902

HAL Id: hal-01198902

<https://hal.sorbonne-universite.fr/hal-01198902>

Submitted on 14 Sep 2015

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Photo-induced cation translocation in a molecular shuttle based on a calix[4]-biscrown including DCM and DMABN chromophores†

Received 20th July 2015,
Accepted 18th August 2015

Nadia Dozova,^{a,‡} Rajesh Kumar,^{b,‡} Tuhin Pradhan,^b Fabien Lacombat,^a Bernard Valeur,^{*c} Jong Seung Kim,^{*b} and Pascal Plaza^{*a}

DOI: 10.1039/c5cc06054k
www.rsc.org/chemcomm

We present a new molecular shuttle, consisting of a calixarene core attached to two different photoactive centers, DCM and DMABN. We show that a K^+ ion bound to the DCM-grafted crown is translocated towards the other site of the molecule upon photoexcitation, but not released to the bulk.

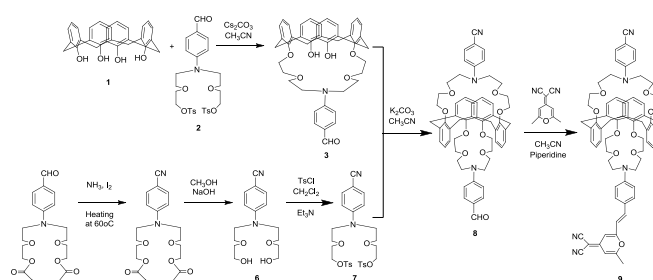
The movement of a subpart under the influence of an external stimulus¹ in bistable supramolecular systems is highly interesting in the fields of binary logic computing, molecular memories, and machines.² Molecular shuttles have been demonstrated by the, pH or redox-driven, movement of a subpart in mechanically interlocked molecules³ or translocation of a metal ion in a ditopic receptor.⁴

Light-induced switching in addition offers the advantage of working rapidly and precisely, both in space and time. In a previous paper,⁵ we reported a symmetric ditopic receptor of potassium ion, Calix-DCM2, consisting of a 1,3-alternate calix[4]biscrown core with the merocyanine dye DCM (4-dicyanomethylene-2-methyl-6-p-diethylaminostyryl-4H-pyran) inserted into each crown. We showed that upon excitation of DCM at 470 nm, a positive charge was created on the nitrogen atom of the crown within the chromophore due to intramolecular charge transfer, which repels the K^+ ion towards the opposite crown in the picosecond timescale, without photoejection to the bulk.⁵ Let us note that spontaneous tunneling of K^+ across the calix[4]arene cavity was not detected by NMR spectroscopy of the core compound at temperatures lower than 105 °C.⁶

In the present paper, we report a dissymmetric ditopic receptor of potassium ion (compound **9**) whose core is identical to that of Calix-DCM2 but which includes two different photoactive centers. One of the chromophores is still

DCM while the other one is DMABN⁷ (*p*-dimethylaminobenzonitrile), also known to undergo a photoinduced intramolecular charge transfer. In such a dissymmetric shuttle the back and forth translocation of potassium ion is expected to be controlled by irradiation at 470 nm (excitation of DCM) and 290 nm (excitation of DMABN).

The synthesis of **9** is shown in Scheme 1 (and detailed in ESI†, §1). The reaction of **2** with the calix[4]arene in the presence of Cs_2CO_3 afforded calix[4]arene aldehyde **3** with 24 % yield. **5** was synthesized by heating a mixture of aldehyde **4**, ammonia solution and iodine for 14 hr. The hydrolysis of **5** with NaOH (aq.) followed by tosylation gave **7** with 78% yield. The reaction of calix[4]arene aldehyde **3** with tosylated **7** in the presence of K_2CO_3 furnished **8** which on reaction with 2-(2,6-dimethyl-4*H*-pyran-4-ylidene)malononitrile afforded **9** as red solid (26%). All compounds have been characterized by ¹H and ¹³C NMR spectroscopy, as well as ESI-MS (see ESI†, §1). NMR spectra of **9** in the presence of K^+ ions, proving that complexation is effective, are given in ESI† (§2).



Scheme 1. Synthesis of compound **9**.

Fig. 1A shows the absorption spectrum of **9** during a titration by KSCN. The main changes occur near the DCM absorption band, which decreases and shifts from 486 to 398 nm. These spectral changes are similar to those reported for the complexation of Calix-DCM2⁵ or DCM-crown,⁸ a DCM-based monotopic fluoroionophore. Only a small decrease and no shift is observed in the DMABN absorption band (297 nm), contrary to the related case of DMABN-crown5 complexed to Ca^{2+} or Ba^{2+} ,⁹ which suggests that binding of K^+ on the DMABN side is weaker than that on the DCM side. By globally fitting the spectra of Fig. 1A with a complexation model that

^aDr. N. Dozova, Fabien Lacombat, Dr. P. Plaza, Ecole Normale Supérieure-PSL Research University, Département de Chimie, Sorbonne Universités - UPMC Univ Paris 06, CNRS UMR 8640 PASTEUR, 24, rue Lhomond, 75005 Paris, France. E-mail: pascal.plaza@ens.fr

^bDr. R. Kumar, Dr. T. Pradhan, Prof. J.S.Kim, Department of Chemistry, Korea University, Seoul 136-701, Korea Fax: +82-2-3290-312. E-mail: jongskim@korea.ac.kr

^cPr. B. Valeur, Département CASER, Conservatoire National des Arts et Métiers, Paris, France. E-mail: bernard.valeur@cnam.fr

‡Equally contributed to this work.

†Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See

DOI: 10.1039/c5cc06054k

distinguishes the two binding sites (see ESI[†], §3), we calculated the equilibrium constants for the successive binding of two K⁺ ions. We note L, ML_{DCM}, ML_{DMABN} and M₂L the free ligand, the two 1:1 complexes on the DCM and DMABN sides and the 2:1 complex, respectively. Fig. 1B shows the absorption spectra of L, M₂L and a weighted average of those of ML_{DCM} and ML_{DMABN}, labeled ML, with coefficients 1/(1+K_e) and K_e/(1+K_e), respectively; K_e is the equilibrium constant of exchange between ML_{DCM} and ML_{DMABN}. By detailed analysis of the ML spectrum we found that in 95% of the 1:1 complexes the cation is located on the DCM side (K_e=0.05).

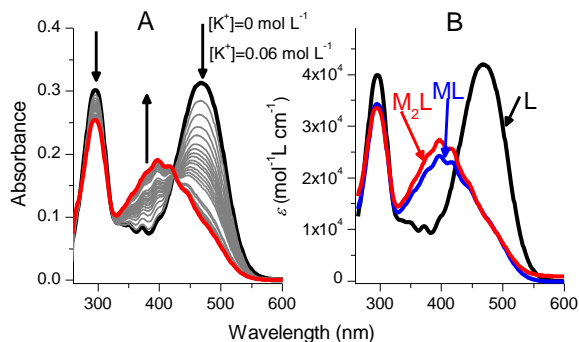


Fig. 1. A: absorption spectra of a solution of **9** in acetonitrile for different K⁺ concentrations ([**9**]=7.5 × 10⁻⁶ mol L⁻¹). B: spectra of the L, ML and M₂L species. The composite ML spectrum is defined as: $\epsilon_{ML} = (\epsilon_{MLDCM} + K_e \epsilon_{MLDMABN}) / (1 + K_e)$, where K_e=0.05 is the equilibrium constant of exchange between ML_{DCM} and ML_{DMABN} (cf. ESI[†], §3).

The transient absorption spectra of the free ligand (L) and of a sample containing 86% ML_{DCM} complex (noted ML90 because 90% of the initially excited molecules are ML_{DCM} complexes) in acetonitrile were then recorded after sub-100-fs excitation at 387.5 nm. The raw data are shown in ESI[†] (§4, Figs. S22 and S23). Both sets of time-resolved spectra were globally fitted to a sum of five exponentials, convoluted by the instrument response function (~120 fs). We show in Fig. 2 the so-called evolution-associated difference spectra (EADS), which provide a dynamically-labeled summary of the evolution of the transient absorption data. They correspond to the states of a formal cascading model (see ESI[†], §5.1) and benefit from noise-filtering and deconvolution.

The time constants for L were found to be: $\tau_1 = 0.19 \pm 0.01$ ps, $\tau_2 = 0.7 \pm 0.2$ ps, $\tau_3 = 7.5 \pm 0.5$ ps, $\tau_4 = 350 \pm 20$ ps and $\tau_5 = 2130 \pm 30$ ps. A detailed description of the EADS (Fig. 2-left) is provided in ESI[†] (§5.2). The main features are as follows. The initially excited state (associated to EADS1) evolves very quickly (190 fs) to produce a new state, featuring an excited-state absorption (ESA) maximum at 530 nm and a stimulated emission (SE) band at 610 nm (EADS2). From previous studies on DCM and DCM-crown,¹⁰ this product can be assigned to an intramolecular charge transfer (ICT) state within the excited DCM moiety, which brings a positive charge on the nitrogen atom imbedded in the crown. The next kinetic phase (evolution from EADS2 to EADS3 in 0.72 ps), essentially characterized by a red shift of the SE band (610 to 630 nm), is interpreted as the dynamic solvation of the ICT state in acetonitrile. During the third kinetic step (7.5 ps) the SE band only slightly shifts to the blue, by ~2 nm. From a similar report in the case of DCM,^{10a} we assign this effect to a cooling of the ICT state. A subsequent larger red shift of the SE emission band (9 nm) in 350 ps, not previously observed for DCM or free DCM-crown, is proposed to be due to a structural relaxation of the molecule, possibly involving the central

calix[4]bis-crown scaffold. Finally EADS5, the spectrum of the long-lived excited state, decays to the ground state in 2.13 ns.

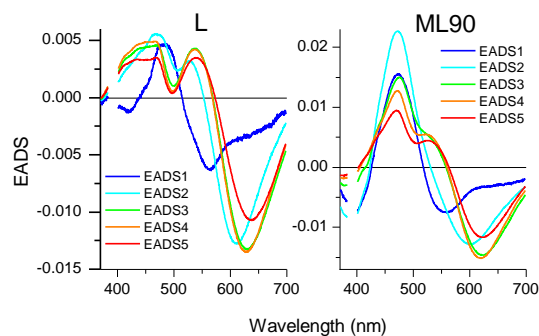


Fig. 2. Global analysis of the transient absorption spectra of compound **9**. Left: EADS of the free ligand L. Right: EADS of the ML90 sample.

Turning to ML90, global analysis provided the following time constants: $\tau_1 = 0.20 \pm 0.01$ ps, $\tau_2 = 0.94 \pm 0.2$ ps, $\tau_3 = 8.0 \pm 0.3$ ps, $\tau_4 = 280 \pm 30$ ps and $\tau_5 = 1620 \pm 20$ ps. The EADS (Fig. 2-right) are commented in details in ESI[†] (§5.3). In brief, it appears that immediately upon excitation of ML_{DCM}, a state similar to the initially excited state of L is produced. This means that the metal-ligand interaction is extremely quickly disrupted upon excitation of ML_{DCM} and already complete in EADS1 (of ML90). Subsequently we observe that the transient spectra of ML_{DCM} evolve similarly as those of L but more slowly. The formation of the ICT state extends over a longer time, mostly occurring in 0.94 ps. We conclude that the presence of the K⁺ ion in the vicinity of the N atom of the DCM anilino group substantially reduces the rate of the formation of the ICT state. The same observation was repeatedly made in the case of DCM-crown complexed to several metal ions (Li⁺, Ca²⁺, Sr²⁺)^{10c,11} and it was proposed that the formation of the ICT is coupled to a movement of the cation away from the N atom of the crown, which lowers the potential energy barrier between LE and ICT states. Solvation dynamics of acetonitrile, causing a red shift of the SE band, also contribute to the first two kinetic steps (0.20 and 0.94 ps). As for L, a slight blue shift of the SE band is observed in the third phase (8.0 ps) and attributed to a cooling of the newly formed ICT state. A subsequent red shift (~3 nm) of the SE band is observed during the fourth phase (280 ps), of smaller amplitude than for L, and is assigned to a structural relaxation involving the calixarene tube. The excited state characterized by EADS5 finally decays to the ground state with a time constant of 1.62 ns.

Let us note that independent measurements performed on two different L and ML90 samples yielded the same values of τ_5 within 0.05 ns. The difference between L (2.13 ns) and ML_{DCM} (1.62 ns) must therefore be considered significant. The same type of shortening of the excited-state lifetime upon complexation had already been reported for DCM-crown, although with a much smaller amplitude (e.g. 1.94 ns for the complex with Ca²⁺ vs. 2.20 ns for free ligand).^{8,10c} We attribute it to the proximity of K⁺ to the excited DCM, possibly enhancing intersystem crossing or internal conversion. The above descriptions reveal the importance of the time-dependent shift of the SE band. As previously argued for DCM-crown and Calix-DCM2,^{5,11} the position of the SE band may be considered an indication of the distance between the metal ion and the excited DCM: the closer the ion, the stronger its

influence and the more blue-shifted the SE band. Fig. 3 displays this dynamics as precisely measured from the raw data (details in ESI[†], §6.1). The obtained shift trace was in turn fitted by the sum of four exponentials, the parameters of which are gathered in Table S2 (ESI[†], §6.1).

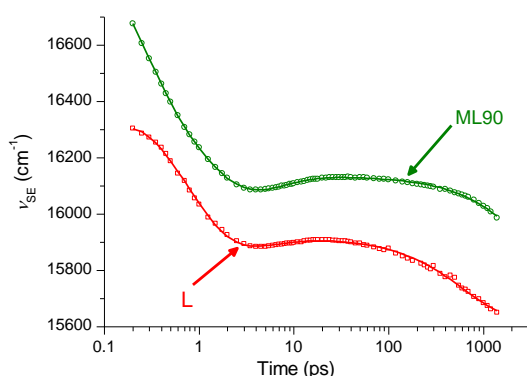


Fig. 3. Frequency of the SE band minimum of L and ML90 as a function of time. The trace is fitted by the sum of four exponentials (see parameters in Table S2).

Detailed analyses of the shift dynamics are provided in ESI[†], (§6.2 and §6.3); the most salient feature is that the last time constant of ML90 ($\tau_{4s} = 4$ ns) is much longer than the corresponding time of L (630 ps). This suggests that, for ML90, the K^+ ion is not very quickly photoreleased to the bulk. Had this occurred, the 630-ps shift component of L would have been observed. On the other hand it is important to recall that for DCM-crown complexes the drift of the cation away from the molecule during photorelease is characterized by a large red shift of the SE band, occurring on a sub-ns timescale: 400 ps for Sr^{2+} and 670 ps for Ca^{2+} , in acetonitrile.¹¹ It should then be asked if photorelease of K^+ from ML_{DCM} could be much slower than photorelease of Sr^{2+} or Ca^{2+} from DCM-crown, and explain the 4-ns shift.

Here we compare more specifically the diffusion kinetics of K^+ and Ca^{2+} , which bind to their respective ligands with similar association constants ($\log K_1 = 3.54$ for ML_{DCM} (ESI[†], §3) and $\log K_3 = 3.79$ for the DCM-crown: Ca^{2+} complex⁸). Although the ionic radius of K^+ is larger than that of Ca^{2+} (1.37 Å vs. 1.00 Å¹²), charge density is the controlling factor and the translational diffusion constant of K^+ is in fact larger: 1.957×10^5 cm² s⁻¹ for K^+ vs. 0.792×10^5 cm² s⁻¹ for Ca^{2+} , in water¹² (to the best of our knowledge, values in acetonitrile are not available). This demonstrates that K^+ is expected to diffuse faster than Ca^{2+} and finally allows us to deduce that the slow shift dynamics observed for ML_{DCM} is incompatible with a photorelease mechanism of K^+ such as the one reported for DCM-crown complexes.

The conclusion we therefore reach is that upon excitation of the DCM chromophore the interaction of the potassium ion with the chromophore is very rapidly broken and that the ion progressively leaves the DCM binding site. Indirect evidence shows that it is not released to the bulk but gets translocated towards the DMABN binding site. Compound **9** thus exemplifies the potentialities of calix[4]arene ditopic receptors including appropriate chromophores as light-driven molecular shuttles.

This work was supported by CRI project (No. 2009-0081566, JSK) from the National Research Foundation of Korea.

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