Constructing Molecular Machinery: A Chemically-Switchable [2]Catenane

Vincenzo Balzani,*,† Alberto Credi,† Steven J. Langford,‡
Françisco M. Raymo,§,¶ J. Fraser Stoddart,*,§ and
Margherita Venturi†

Dipartimento di Chimica "G. Ciamician"
Università di Bologna, via Selmi 2
I-40126 Bologna, Italy
School of Chemistry, University of Birmingham
Edgbaston, Birmingham B15 2TT, UK
Department of Chemistry and Biochemistry
University of California, 405 Hilgard Avenue
Los Angeles, California 90095-1569

Received December 21, 1999

Molecular motors—both rotary and linear ones—are commonplace in biological systems,[1] but the idea of constructing molecular-level machines is a recent one.[2] Artificial molecular machines can be defined[3] as assemblies of discrete numbers of components designed to perform mechanical-like movements (outputs) when subjected to external stimuli (inputs).[4,5]

Under suitable chemical, photochemical, or electrochemical stimulation, mechanically interlocked molecular compounds[6] like rotaxanes and catenanes can undergo co-conformational[7] changes reminiscent of motions associated with some macroscopic machines. In particular, the dynamic behavior of appropriately desymmetrized [2]catenanes makes them ideal candidates for investigating switching phenomena at a molecular level.[8] The co-conformational changes usually occur between two different, well-defined translational isomers[9] and are accompanied by the switching "on" or "off" of some observable property, such as electronic absorption, luminescence, NMR signals, and electrochemical potentials. Control of at least one of these outputs opens up possibilities to be able to process information at the molecular level.[10] Here, we report a rare instance of a desymmetrized [2]-catenane in which (1) reversible switching can be induced between two different species by chemical inputs and where (2) the outputs are optical and electrochemical.

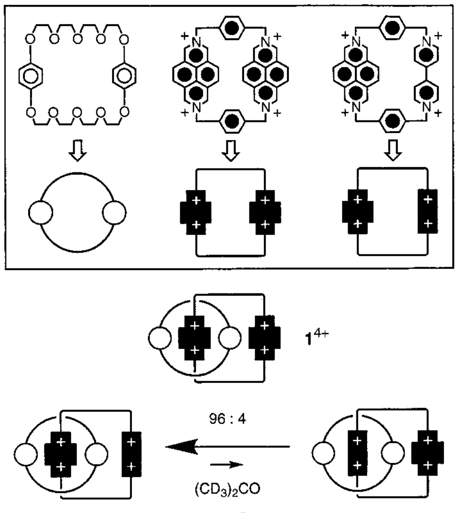

Figure 1. The [2]catenane $\mathbf{1}^{4+}$ and the translational isomers ($\mathbf{2A}^{4+}$ and $\mathbf{2B}^{4+}$) of the [2]catenane $\mathbf{2}^{4+}$.

The syntheses of the [2]catenanes $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$ (Figure 1) have been reported recently.[11] Whereas in $\mathbf{1}^{4+}$, the bis-*p*-phenylene-[34]crown-10 (BPP34C10) macrocycle, with its two π-electron-rich hydroquinone rings, is interlocked with a symmetrical cyclophane containing two π-electron-deficient diazapyrenium (DAP^{2+}) units, in $\mathbf{2}^{4+}$ the symmetrical cyclophane is substituted by a dissymmetrical one in which one of the DAP^{2+} units is replaced by a π-electron-deficient bipyridinium (BPY^{2+}) unit. Since the DAP^{2+} unit interacts more strongly than the BPY^{2+} one with the π-electron-rich 1,5-dinaphtho[38]crown-10,[12] it can be expected that the preferred translational isomer of the [2]-catenane $\mathbf{2}^{4+}$ is the one with the DAP^{2+} unit located inside the BPP34C10 macrocycle (isomer $\mathbf{2A}^{4+}$). This prediction is confirmed by the ratio 96:4 for $\mathbf{2A}^{4+}$:$\mathbf{2B}^{4+}$ obtained from ^{1}H NMR

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[*] Author for correspondence. Fax: 39 051 2099456. E-mail: vbalzani@ciam.unibo.it.

[†] University of Bologna.

[‡] University of Birmingham.

[§] University of California - Los Angeles.

[¶] Current address: Center for Supramolecular Science, Department of Chemistry, University of Miami, 1301 Memorial Drive, Coral Gables, FL 33124-0431.

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10.1021/ja994454b CCC: $19.00

spectroscopy in $(CD_3)_2CO$ at −80 °C.[11] Previously, we have found[12,13] that the DAP^{2+} unit forms very stable adducts with aliphatic amines, whereas the BPY^{2+} unit does not show this kind of interaction.[12] We thought that this contrasting behavior of DAP^{2+} and BPY^{2+} units toward the aliphatic amines might be exploited to switch (Figure 1) the [2]catenane $\mathbf{2}^{4+}$ between its two $\mathbf{2A}^{4+}$ and $\mathbf{2B}^{4+}$ translational isomers.[14]

On addition of 5.0×10^{-3} M $Me(CH_2)_5NH_2$ to a 5.0×10^{-4} M MeCN solution of $\mathbf{2A}^{4+}$, the absorption bands, characteristic of the DAP^{2+} unit, are substantially depressed, and two broad and intense bands appear in the visible region ($\lambda_{max} = 460$ nm, $\epsilon = 17000$ M^{-1} cm^{-1}; $\lambda_{max} = 610$ nm, $\epsilon = 8400$ M^{-1} cm^{-1}).[15] These changes are similar to those observed on addition of $Me(CH_2)_5NH_2$ to dibenzyldiazapyrenium,[13] its pseudorotaxanes,[10b,12,13] and also the [2]catenane $\mathbf{1}^{4+}$. They indicate that an adduct is formed between the DAP^{2+} unit of $\mathbf{2}^{4+}$ and $Me(CH_2)_5NH_2$. The emission band around 700 nm, characteristic of the amine adduct of the DAP^{2+} unit,[10b,13] is not observed in the case of $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$ since it is quenched by low-lying charge-transfer excited states.

The differential pulse voltammogram[15] of $\mathbf{2}^{4+}$ shows (Figure 2 top, curve a) monoelectronic peaks at −0.31 and −0.57 V vs SCE that can be assigned to the first reduction of the alongside BPY^{2+} unit and the first reduction of the inside DAP^{2+} unit. After addition of $Me(CH_2)_5NH_2$, the two reduction peaks are displaced toward more negative potentials by 60 and 20 mV, respectively (Figure 2 top, curve b). The value of the first potential is consistent with the reduction of an inside BPY^{2+} unit, as observed in the previously studied[8b] symmetrical catenane where the BPP34C10 macrocycle is interlocked with cyclophane containing two BPY^{2+} units. The second peak can be assigned to the first reduction of the DAP^{2+} unit engaged with amine. The latter assignment is supported by experiments carried out on the symmetrical catenane $\mathbf{1}^{4+}$ containing only DAP^{2+} units. The differential pulse voltammogram of this compound (Figure 2 bottom, curve a) shows two peaks at −0.37 and −0.52 V vs SCE that can be assigned to the first reduction of the alongside and inside DAP^{2+} unit, respectively. After addition of $Me(CH_2)_5NH_2$, only one peak is observed at −0.55 V vs SCE (Figure 2 bottom, curve b). The area of this peak is almost equal to the sum of the area of the two peaks observed before the addition of amine. This result indicates that the DAP^{2+} unit engaged with amine and the DAP^{2+} unit located in the inside position are reduced at almost the same potential. It follows that, after the addition of $Me(CH_2)_5NH_2$ to $\mathbf{2}^{4+}$, the DAP^{2+} unit engages itself with the amine, while the BPY^{2+} unit locates itself inside the BPP34C10 macrocycle.

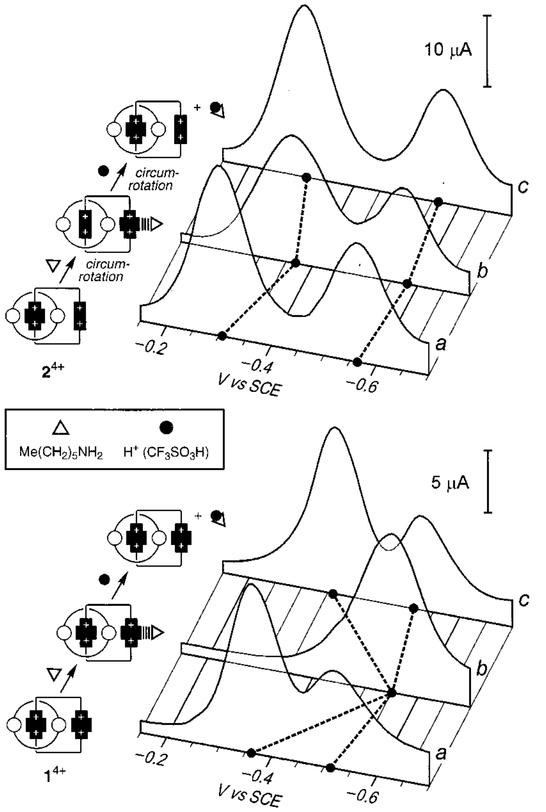

Figure 2. Differential pulse voltammetry reduction pattern (MeCN, 5.0×10^{-4} M, 298 K, scan rate 20 mV s^{-1}, pulse height 75 mV) of $\mathbf{1}^{4+}$ (bottom) and $\mathbf{2}^{4+}$ (top). Curves a: starting solutions. Curves b: after addition of 10 equiv of $Me(CH_2)_5NH_2$. Curves c: after subsequent addition of 10 equiv of CF_3SO_3H.

The amine-driven isomerization (Figure 1) of $\mathbf{2A}^{4+}$ to $\mathbf{2B}^{4+}$ can be reversed quantitatively by addition of CF_3SO_3H in a stoichiometric amount with respect to the previously added amine. Protonation of the amine disrupts the adduct with DAP^{2+}, thereby restoring the interactions between the electron-donating hydroquinone rings of the BPP34C10 macrocycle and the electron-accepting DAP^{2+} unit of the cyclophane. As a consequence, another circumrotation of the tetracationic cyclophane occurs, giving back the original translational isomer $\mathbf{2A}^{4+}$ in which the DAP^{2+} unit occupies the inside position. This outcome is demonstrated by the full recovery of the original absorption spectrum and by the fact that the differential pulse voltammogram of $\mathbf{2}^{4+}$, recorded after acid addition (Figure 2 top, curve c), is identical to that obtained before the addition of amine (Figure 2 top, curve a). The full reversibility of the interaction of DAP^{2+} with the amine is confirmed by the fact that, even in the case of $\mathbf{1}^{4+}$, the initial and final spectra and voltammetric patterns (Figure 2 bottom, curves a and c) are identical.

It should be noted that the two stable states of the $\mathbf{2}^{4+}$ system are characterized not only by different electrochemical properties but also by different colors. In principle, both outputs can be useful to process information at the molecular level.[10]

Acknowledgment. This research was supported by the Ramsay Memorial Fellowship Trust (S.J.L.), the EU (TMR Grant FMRX-CT96-0076), the University of Bologna (Funds for Selected Research Topics), and MURST (Supramolecular Devices Project).

Supporting Information Available: UV/vis absorption changes for catenane $\mathbf{2}^{4+}$ upon addition of $Me(CH_2)_5NH_2$ and subsequent addition of CF_3SO_3H (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The equipment and experimental procedures have been described previously [see ref 8b]. When 1 equiv of $Me(CH_2)_5NH_2$ was added to $\mathbf{2}\cdot 4PF_6$ dissolved in $(CD_3)_2CO$, the ^1H NMR spectrum of the [2]catenane “underwent” profound changes. Subsequent addition of 1 equiv of CH_3CO_2H to the sample, “regenerated” a ^1H NMR spectrum which was essentially identical with that recorded initially for $\mathbf{2}\cdot 4PF_6$. Although this experiment confirmed the reversibility of the chemically induced process, more experiments need to be performed to be able to assign the signals in the ^1H NMR spectrum of the complex(es) formed between $\mathbf{2}\cdot 4PF_6$ and $Me(CH_2)_5NH_2$.