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Photoinduced Electron Transfer in a Triad That Can Be Assembled/Disassembled by Two Different External Inputs. Toward Molecular-Level Electrical Extension Cables

Roberto Ballardini,[†] Vincenzo Balzani,[*,‡] Miguel Clemente-León,[‡,§] Alberto Credi,[‡]
Maria Teresa Gandolfi,[*,‡] Eléna Ishow,[‡,||] Julie Perkins,[⊥] J. Fraser Stoddart,[*,⊥]
Hsian-Rong Tseng,[⊥] and Sabine Wenger[⊥]

Contribution from Istituto FRAE-CNR, via Gobetti 101, 40129 Bologna, Italy, Dipartimento di Chimica "G. Ciamician", Università degli Studi di Bologna, via Selmi 2, 40126 Bologna, Italy, and Department of Chemistry and Biochemistry, University of California Los Angeles, 405 Hilgard Avenue, Los Angeles, California 90095

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Abstract: We have designed, synthesized, and investigated a self-assembling supramolecular system which mimics, at a molecular level, the function performed by a macroscopic electrical extension cable. The system is made up of three components, $\mathbf{1}^{2+}$, $\mathbf{2}\text{-H}^{3+}$, and **3**. Component $\mathbf{1}^{2+}$ consists of two moieties: a $[\mathrm{Ru(bpy)_3}]^{2+}$ unit, which plays the role of an electron donor under light excitation, and a DB24C8 crown ether, which fulfills the function of a socket. The wire-type component $\mathbf{2}\text{-H}^{3+}$ is also composed of two moieties, a secondary dialkylammonium-ion center and a bipyridinium unit, which thread into the DB24C8 crown-ether socket of $\mathbf{1}^{2+}$ and the 1/5DN38C10 crown-ether socket **3**, respectively. The photochemical, photophysical, and electrochemical properties of the three separated components, of the $\mathbf{1}^{2+} \supset \mathbf{2}\text{-H}^{3+}$ and $\mathbf{2}\text{-H}^{3+} \subset \mathbf{3}$ dyads, and of the $\mathbf{1}^{2+} \supset \mathbf{2}\text{-H}^{3+} \subset \mathbf{3}$ triad have been investigated in $\mathrm{CH_2Cl_2}$ solution containing 2% MeCN. Reversible connection/disconnection of the two plug/socket systems can be controlled independently by acid/base and redox stimulation. The behavior of the various different dyads and triad has been monitored by light absorption and emission spectroscopies, as well as by electrochemical techniques. In the fully connected $\mathbf{1}^{2+} \supset \mathbf{2}\text{-H}^{3+} \subset \mathbf{3}$ triad, light excitation of the $[\mathrm{Ru(bpy)_3}]^{2+}$ unit of component $\mathbf{1}^{2+}$ is followed by electron transfer ($k = 2.8 \times 10^8\ \mathrm{s}^{-1}$) to the bipyridinium unit of component $\mathbf{2}\text{-H}^{3+}$, which is plugged into component **3**. Possible schemes to obtain improved molecular-level electrical extension cables are discussed.

Introduction

Miniaturization of the components for the construction of useful devices is currently pursued by the large-downward (top-down) approach. This approach, however, which leads solid-state physicists and electronic engineers to manipulate progressively smaller pieces of matter, has intrinsic limitations.[1] An alternative approach to the construction of nanoscale-sized components and devices is the small-upward (bottom-up) approach. Chemists, by the nature of their discipline, are in an ideal position to develop bottom-up strategies because they are able to manipulate molecules, that is, the smallest entities of matter that have distinct structures, shapes, and properties. The chemical, bottom-up approach to nanotechnology implies passing from molecules to supramolecular species and is driven by the idea that the macroscopic concept of device can be extended to the molecular level.[2,3] A *molecular-level device* can be defined as an assembly of a discrete number of molecules designed to achieve a specific function: each molecular component performs a simple act, while the entire supramolecular structure performs a more complex function, which results from the cooperation of the various molecular components.

Stimulated by this vision, we and others[4,5] have constructed and investigated a number of supramolecular systems *specifically designed* to play the role of molecular-level devices, that is, aggregates able to perform a particular function upon application of an external energy input. In this framework, construction of chemical computers (i.e., of computers based on molecular-level components) has been anticipated.[6] Apart

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[*] To whom correspondence should be addressed. E-mail: vbalzani@ciam.unibo.it (V.B.).

[†] Istituto FRAE-CNR.

[‡] Università di Bologna.

[§] Present address: Instituto de Ciencia Molecular, Universitat de València, Dr Moliner 50, 46100 Burjassot, Spain.

[||] Present address: Department of Chemistry, ENS Cachan, 61 Avenue du President Wilson, 94235 Cachan Cedex, France.

[⊥] University of California, Los Angeles.

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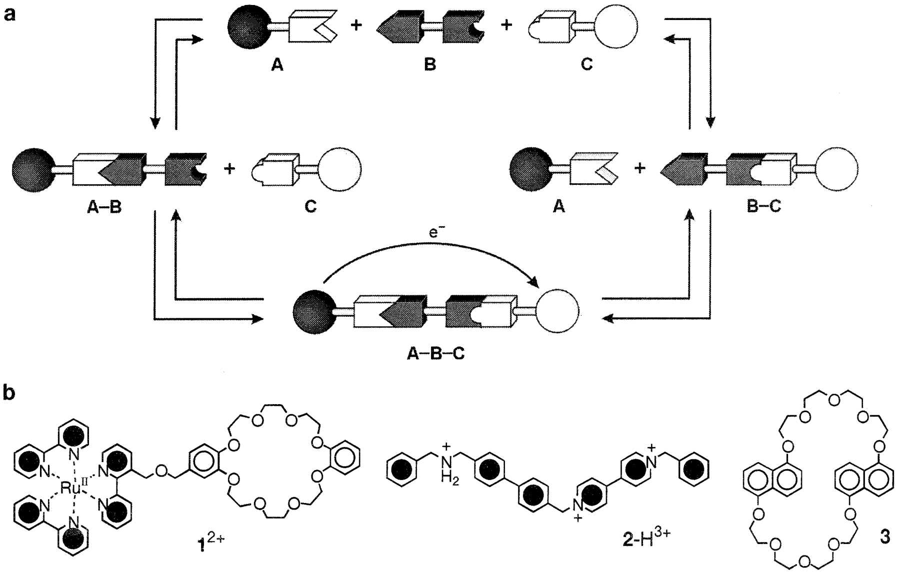

Figure 1. (a) Schematic representation of an extension. (b) The three components of the investigated self-assembling system.

from such a futuristic application, the design and realization of a *molecular-level electronic set* (i.e., a set of molecular-level systems capable of performing functions that mimic those executed by the components of macroscopic electronic devices) is of great scientific interest because it introduces new concepts into the field of chemistry and stimulates the ingenuity of research workers.

In the past few years, many systems that could prove useful for information processing at the molecular level[7] (e.g., wires,[8] antennas,[9] switches,[10,11] rectifiers,[12] plug/socket devices,[13] memories,[10,14] logic gates[10,15]) have been constructed and studied. In this paper, we report the results of a detailed investigation on photoinduced electron transfer in a supramolecular triad that can be assembled/disassembled in a *controlled* manner by two *different* external inputs, namely, (i) acid/base and (ii) redox stimuli. The investigated system mimics, at the molecular level, the function performed by a macroscopic electrical extension cable.

Design

A macroscopic electrical extension cable is a wire with two connecting ends used to transfer electrons from a power supply (source) to a remote load (drain). A supramolecular system capable of mimicking the function performed by a macroscopic extension must consist of three molecular components (A, B,

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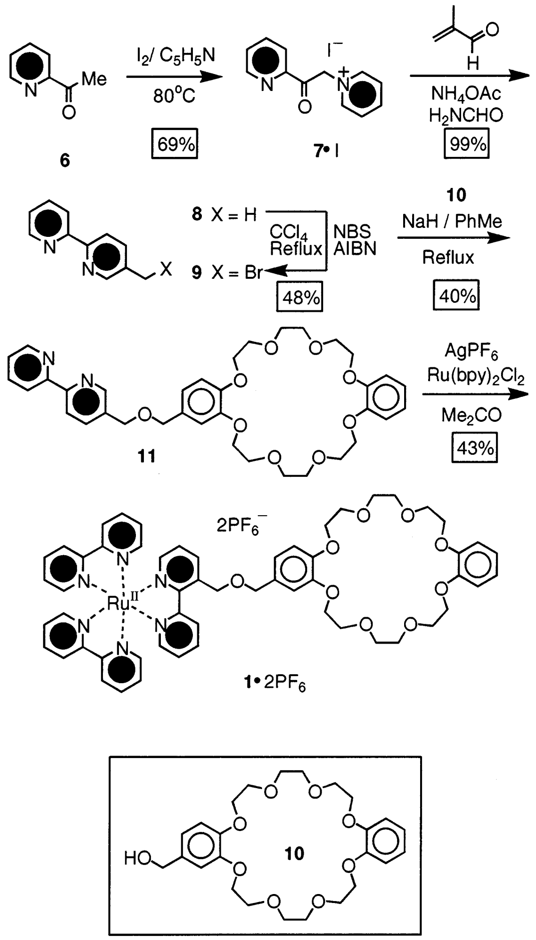
and C in Figure 1a) programmed to operate as an electron source (A), a wire (B), and an electron drain (C), in turn. The three components must also be programmed so that one end of the wire can be plugged in/out of the source and the other end can be plugged in/out of the drain. Furthermore, each plug in/out function has to be reversible, controllable by an external input, and monitorable. It is, of course, very difficult to design, and even more so to prepare, molecular components that will self-assemble spontaneously into a supramolecular system capable of satisfying all the described requirements. We shall demonstrate, however, that, by using the molecular components **1**$^{2+}$, **2**-H^{3+}, and **3**, shown in Figure 1b, we have succeeded in meeting most of the essential requirements and that we are now in the position to design more satisfactory, second-generation molecular-level electrical extension cables. Compound **1**$^{2+}$, which fulfills the role of an electron-source component, is composed of two moieties: (i) a $[Ru(bpy)_3]^{2+}$ unit, which is known[16] to be a strong electron donor in the excited state, and (ii) a dibenzo[24]crown-8 (hereafter indicated by DB24C8), which is capable of playing the role of a socket.[17] Compound **2**-H^{3+}, which fulfills the role of a connecting wire-type component, contains two moieties, a secondary dialkylammonium center, which is known[17c,d,f] to thread as a plug into the DB24C8 socket, and a bipyridinium moiety which can insert itself in a plug-like manner[18] into compound **3**, namely 1,5-dinaphtho[38]crown-10 (hereafter indicated by 1/5DN38C10), which fulfills the role of an electron drain (socket) component. Because the wire-type component **2**$^{3+}$ is short and relatively rigid, the problem of folding, which is often encountered in pseudorotaxane chemistry, is not expected to be important. In this system, (i) the two plug/socket functions can be controlled *reversibly* and *independently* by external acid/base and redox stimuli, respectively, and (ii) the occurrence of the connections can be monitored by changes in the absorption spectra, emission spectra, and electrochemical potentials. In the fully connected system, light excitation of the $[Ru(bpy)_3]^{2+}$ unit of compound **1**$^{2+}$ is followed by electron transfer to the bipyridinium unit of compound **2**-H^{3+}, which is plugged into compound **3**. The electron-transfer process can be monitored by changes in the emission spectra, and its rate can be determined from lifetime measurements.

Results and Discussion

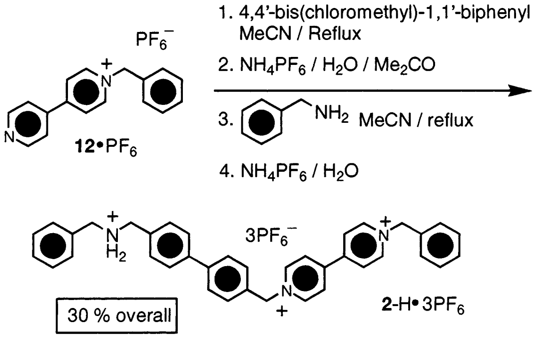
Syntheses. 1/5DN38C10 (**3**) was synthesized according to a literature procedure.[18a] The syntheses of **1**$^{2+}$ and **2**-H^{3+} are summarized in Schemes 1 and 2.

Synthesis of Component 1^{2+}**.** The synthesis of **1**$^{2+}$ is outlined in Scheme 1. 2-Acetylpyridine (**6**) was transferred into (2-pyridacyl)pyridium iodide (**7**·I) in 69% yield by its treatment with I_2 in C_5H_5N. The synthesis of 5-methyl-2,2′-bipyridine (**8**) was accomplished almost quantitatively by pyridine ring annulation of (2-pyridacyl)pyridium iodide (**7**·I) in formamide solution in the presence of methacrolein and ammonium acetate. The bipyridine derivative **8** underwent AIBN-catalyzed bromination with NBS in CCl_4, giving 5-bromomethyl-2,2′-bipyridine (**9**) in 48% yield. Alkylation (NaH/PhMe) of the hydroxymethylated dibenzo[24]crown-8 derivative[19] **10** with **9** afforded (40%) the bipyridine-tagged crown ether **11**. The ruthenium complex **1**$^{2+}$ was obtained as its bis(hexafluorophosphate) salt in 43% overall yield, after treating *cis*-bis(2,2′-bipyridine)-dichloro-ruthenium(II)[20] with the ligand **10** in aqueous EtOH, followed by counterion exchange ($NH_4PF_6/H_2O/Me_2CO$).

Scheme 1



Scheme 2



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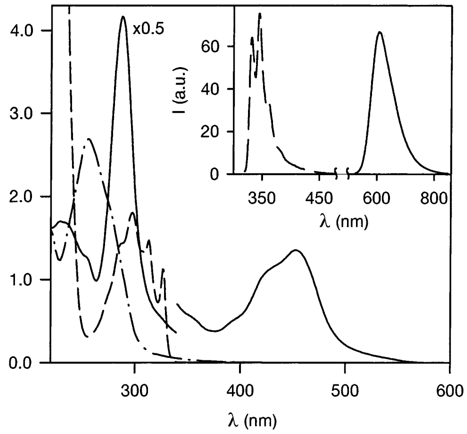

Figure 2. Absorption and (inset) emission spectra of components $\mathbf{1}^{2+}$ (—), $\mathbf{2}$-H^{3+} (— • —), and **3** (— —) (CH_2Cl_2/MeCN, 98:2, v/v, room temperature; λ_{exc} = 450 and 295 nm for $\mathbf{1}^{2+}$ and **3**, respectively).

Table 1. Electrochemical Data[a]

cmpd	E_{ox}[b] (V)			E_{red}[b] (V)		
$\mathbf{1}^{2+}$	+1.31[c,d]	+1.41[d]	+1.58[d]			−1.25
$\mathbf{2}$-H^{3+}				−0.24	−0.67	
3	+1.11[d]	+1.25[d]				
$\mathbf{1}^{2+} \supset \mathbf{2}$-$H^{3+}$	+1.29[c,d]	+1.41[d]	+1.54[d]	−0.24	−0.67	−1.27
$\mathbf{2}$-$H^{3+} \subset \mathbf{3}$	+1.15[d]	+1.24[d]		−0.31	−0.67	

[a] Argon purged CH_2Cl_2/MeCN 90:10 (v/v) solution, room temperature. [b] Halfwave potential values in V vs SCE; reversible and monoelectronic processes, unless otherwise indicated. [c] Shoulder. [d] Not fully reversible process; potential value estimated from DPV peaks.

Synthesis of Component 2-H^{3+}. The synthesis of $\mathbf{2}$-H^{3+} is outlined in Scheme 2. The known compound,[21] *N*-benzyl-4-pyridium-4′-pyridine ($\mathbf{12}$·PF_6), was treated with 5 equiv of 4,4′-bis(chloromethyl)-1,1′-biphenyl in MeCN to afford, after counterion exchange (NH_4PF_6/H_2O/Me_2CO), a reactive benzyl chloride which was not isolated, but rather treated directly with $PhCH_2NH_2$, to give the trication $\mathbf{2}$-H^{3+} as its tris(hexafluorophosphate) salt following counterion exchange (NH_4PF_6/H_2O). The overall yield for the four reactions was 30%.

Properties of Components 1^{2+}, 2-H^{3+}, and 3. All the experiments have been performed at room temperature in CH_2Cl_2 solution containing a fraction of MeCN (2% and 10% for the photophysical and electrochemical experiments, respectively) because trication $\mathbf{2}$-H^{3+} is insoluble in neat CH_2Cl_2. Component $\mathbf{1}^{2+}$ (Figure 1b) is composed of a DB24C8 unit appended to a $[Ru(bpy)_3]^{2+}$ moiety. The absorption spectrum of this component (Figure 2) is dominated by the bands of the $[Ru(bpy)_3]^{2+}$ moiety, which extend into the visible region, and the emission spectrum shows (Figure 2, inset) only the well-known[16] $[Ru(bpy)_3]^{2+}$ band with λ_{max} = 608 nm (τ = 420 ns). Clearly, the emission of the DB24C8 ring is quenched by the appended $[Ru(bpy)_3]^{2+}$ moiety. The redox behavior of $\mathbf{1}^{2+}$ (Table 1) is that expected from the behavior of the two separated moieties.[16,22] In particular, it does not show any redox process in the potential range 0/−1 V versus SCE, a feature which is important for selective connection/disconnection in our supramolecular system.

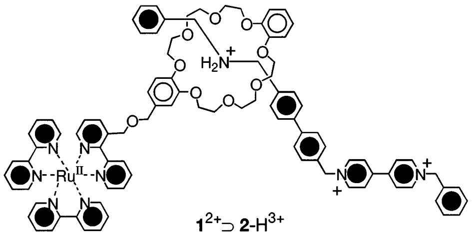

Figure 3. Schematic representation of the threading of the NH_2^+ center in component $\mathbf{2}$-H^{3+} into the cavity of the DB24C8 moiety of component $\mathbf{1}^{2+}$.

Component $\mathbf{2}$-H^{3+} shows an absorption spectrum (Figure 2) dominated by the strong band for the bipyridinium unit in the near UV spectral region,[23] and no emission. In electrochemical experiments, compound $\mathbf{2}$-H^{3+} shows (Table 1) the two characteristic[23] reversible, one-electron reduction peaks for the bipyridinium unit.

Component **3** shows (Figure 2) absorption bands in the UV region, a strong fluorescence band with λ_{max} = 346 nm[24] (τ = 8 ns) and two irreversible, one-electron oxidation peaks which can be assigned (Table 1)[24b] to its dioxynaphthalene ring systems.

Two-Component Supramolecular System 1^{2+} ⊃ 2-H^{3+}. It is well-known[17] that secondary dialkylammonium centers can thread DB24C8 by virtue of strong $N^+-H\cdots O$ and $C-H\cdots O$ hydrogen-bonding interactions. In principle, although the bipyridinium units can penetrate a DB24C8 ring partially, the interaction (stabilized by charge transfer and weak $C-H\cdots O$ hydrogen bonding) is orders of magnitude weaker.[5b,25] It can therefore be expected that, on mixing components $\mathbf{1}^{2+}$ and $\mathbf{2}$-H^{3+}, a supramolecular entity $\mathbf{1}^{2+} \supset \mathbf{2}$-$H^{3+}$ is obtained,[26] with the NH_2^+ center of the wire-type component $\mathbf{2}$-H^{3+} threaded (Figure 3) into the cavity of DB24C8. In this threaded superstructure, one might expect[27,28] that the luminescent excited

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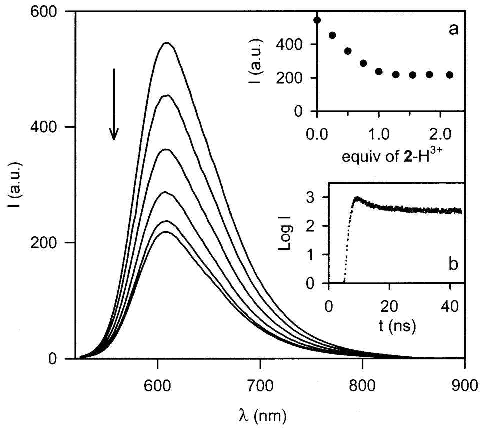

Figure 4. Quenching of the $[Ru(bpy)_3]^{2+}$ luminescence intensity (λ_{exc} = 450 nm) upon titration of a 5.0×10^{-5} M solution of $\mathbf{1}^{2+}$ with $\mathbf{2}\text{-H}^{3+}$ (CH_2Cl_2/MeCN, 98:2, v/v, room temperature). Inset a shows the titration based on the luminescence intensity at 608 nm; inset b shows the biexponential decay observed for an equimolar solution of $\mathbf{1}^{2+}$ and $\mathbf{2}\text{-H}^{3+}$. For more details, see the text.

state of the $[Ru(bpy)_3]^{2+}$ moiety of $\mathbf{1}^{2+}$ is quenched by electron transfer to the bipyridinium unit of $\mathbf{2}\text{-H}^{3+}$. Upon titration of a 5.0×10^{-5} M solution of $\mathbf{1}^{2+}$ with $\mathbf{2}\text{-H}^{3+}$, a decrease in intensity of the $[Ru(bpy)_3]^{2+}$ luminescence is indeed observed (Figure 4) until a plateau is reached. Before addition of $\mathbf{2}\text{-H}^{3+}$, the luminescent signal exhibits a monoexponential decay with τ = 420 ns. On addition of $\mathbf{2}\text{-H}^{3+}$, a double exponential decay is observed (Figure 4, inset b) with lifetimes of about 3.5 and 400 ns. The two lifetimes are maintained throughout the titration, with an increase in the relative weight of the short lifetime on increasing concentration of $\mathbf{2}\text{-H}^{3+}$, until the plateau is reached. In the plateau region, the two lifetimes are still present. Addition of tributylamine restores the original luminescence intensity and causes the disappearance of the short lifetime.

The results can be interpreted as follows. The decrease of the $[Ru(bpy)_3]^{2+}$ luminescence intensity of component $\mathbf{1}^{2+}$ on addition of $\mathbf{2}\text{-H}^{3+}$, and the presence of only one short lifetime that remains constant throughout the titration, show that the quenching process is static in nature and takes place inside a well-defined adduct.[29] Most likely, such an adduct has a pseudorotaxane-type superstructure (Figure 3) in keeping with those observed in very similar systems.[17,25] In the adduct, the luminescent excited state of the $[Ru(bpy)_3]^{2+}$ moiety of component $\mathbf{1}^{2+}$ is quenched[27,28] by electron transfer to the bipyridinium unit of $\mathbf{2}\text{-H}^{3+}$ (Figure 5). The rate constant of the electron-transfer quenching process, obtained from the equation $k = 1/\tau - 1/\tau°$, where τ and $\tau°$ are the short and long (unquenched) emission lifetimes, respectively, was found to be 2.8×10^8 s^{-1}. The lack of complete quenching of the $[Ru(bpy)_3]^{2+}$ luminescence on increasing the amount of added $\mathbf{2}\text{-H}^{3+}$ (Figure 4, inset a) shows that only a fraction of the $\mathbf{1}^{2+}$ species is engaged in adduct formation with $\mathbf{2}\text{-H}^{3+}$. This result can be attributed to the fact that addition of $\mathbf{2}\text{-H}^{3+}$ implies the simultaneous addition of 3 equiv of PF_6^- counterions. Therefore, on increasing the amount of added $\mathbf{2}\text{-H}^{3+}$, the concentration of PF_6^- counterions becomes large, and considering the low polarity of the solvent used, the NH_2^+ center of $\mathbf{2}\text{-H}^{3+}$ becomes more and more engaged in tight ion pairs with the PF_6^- counterions. Such ion pairs between $\mathbf{2}\text{-H}^{3+}$ and PF_6^- cannot associate with $\mathbf{1}^{2+}$ on account of steric reasons and because of the decrease in the hydrogen-bonding acceptor properties of the NH_2^+ centers. The role played by the presence of ion pairs in preventing the inclusion of ammonium ions into neutral receptors in low polarity solvents has been emphasized recently.[30] A confirmation of the role played by ion pairing on preventing the association between $\mathbf{1}^{2+}$ and $\mathbf{2}\text{-H}^{3+}$ was obtained by experiments carried out in the presence of Cl^- ions, which are known[31] to exhibit a strong tendency to form ion pairs. For example, addition of 2 equiv of Bu_4NCl to a solution containing 1.0×10^{-4} M $\mathbf{1}^{2+}$ and $\mathbf{2}\text{-H}^{3+}$ caused a 2-fold increase of the luminescence intensity in the $[Ru(bpy)_3]^{2+}$ moiety and a corresponding decrease in the relative weight of the short lifetime. From the initial part of the titration curve (insert in Figure 4), where the formation of the adduct predominates with respect to ion pairing, a value of about 10^5 M^{-1} was obtained for the stability constant of $\mathbf{1}^{2+} \supset \mathbf{2}\text{-H}^{3+}$. This value is in agreement[17c,32] with the stability constants obtained for pseudorotaxanes formed between DB24C8 and dibenzylammonium derivatives in CH_2Cl_2. The restoration of the original luminescence intensity and the disappearance of the short lifetime upon addition of tributylamine is caused by the deprotonation of the NH_2^+ center in $\mathbf{2}\text{-H}^{3+}$ and the consequent dethreading of $\mathbf{1}^{2+} \supset \mathbf{2}\text{-H}^{3+}$ (Figure 5). In conclusion, the NH_2^+ center in component $\mathbf{2}\text{-H}^{3+}$ threads the DB24C8 ring in component $\mathbf{1}^{2+}$ (with a complexation efficiency around 60% for a 5.0×10^{-5} M equimolar solution of the components), the threading/dethreading process is reversible and acid/base controllable, and in the threaded structure, a photoinduced electron-transfer process takes place from the $[Ru(bpy)_3]^{2+}$ moiety of component $\mathbf{1}^{2+}$ to the bipyridinium unit of $\mathbf{2}\text{-H}^{3+}$.

Two-Component Supramolecular System $\mathbf{2}\text{-H}^{3+} \subset \mathbf{3}$. Contrary to what happens for DB24C8, 1/5DN38C10 has a larger affinity for the bipyridinium unit than it has for the NH_2^+ center in component $\mathbf{2}\text{-H}^{3+}$. The reason for this different behavior is twofold: (i) 1/5DN38C10 is much larger than DB24C8 and lacks a contiguous ring of appropriately spaced oxygen atoms; hence, its interaction with NH_2^+ center in $\mathbf{2}\text{-H}^{3+}$ is disfavored,[25] and (ii) the more extended aromatic ring system and the stronger electron-donor power of the 1,5-dioxynaphthalene units favor[18,33] the formation of $\pi-\pi$ stacking and CT interactions with the electron-acceptor bipyridinium unit of $\mathbf{2}\text{-H}^{3+}$. Formation of pseudorotaxanes by self-threading of a bipyridinium unit into 1/5DN38C10 has been demonstrated previously.[18a,25] It is, therefore, to be expected that, on mixing components $\mathbf{2}\text{-H}^{3+}$ and $\mathbf{3}$, a supramolecular $\mathbf{2}\text{-H}^{3+} \subset \mathbf{3}$ entity is obtained in which the bipyridinium unit of the wire-type component $\mathbf{2}\text{-H}^{3+}$ is threaded (Figure 6) into the cavity of 1/5DN38C10.

Upon titration of a 1.0×10^{-4} M solution of $\mathbf{2}\text{-H}^{3+}$ with $\mathbf{3}$, a new absorption band with λ_{max} = 527 nm develops (Figure

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[29] Dynamic quenching becomes appreciable only in the experiments with higher concentrations of $\mathbf{2}\text{-H}^{3+}$, as shown by the observed small decrease of the long lifetime during titration.

[30] Böhmer, V.; Dalla Cort, A.; Mandolini, L. *J. Org. Chem.* **2001**, *66*, 1900−1902.

[31] The ability of Cl^- ions to form ion pairs with ammonium ions in nonpolar solvents has been exploited to drive the dethreading of a pseudorotaxane formed between DB24C8 and an anthracenylammonium ion. See: Montalti, M.; Prodi, L. *Chem. Commun.* **1998**, 1461−1462.

[32] Ashton, P. R.; Ballardini, R.; Balzani, V.; Gómez-López, M.; Lawrence, S. E.; Martínez-Díaz, M. V.; Montalti, M.; Piersanti, A.; Prodi, L.; Stoddart, J. F.; Williams, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 10641−10651.

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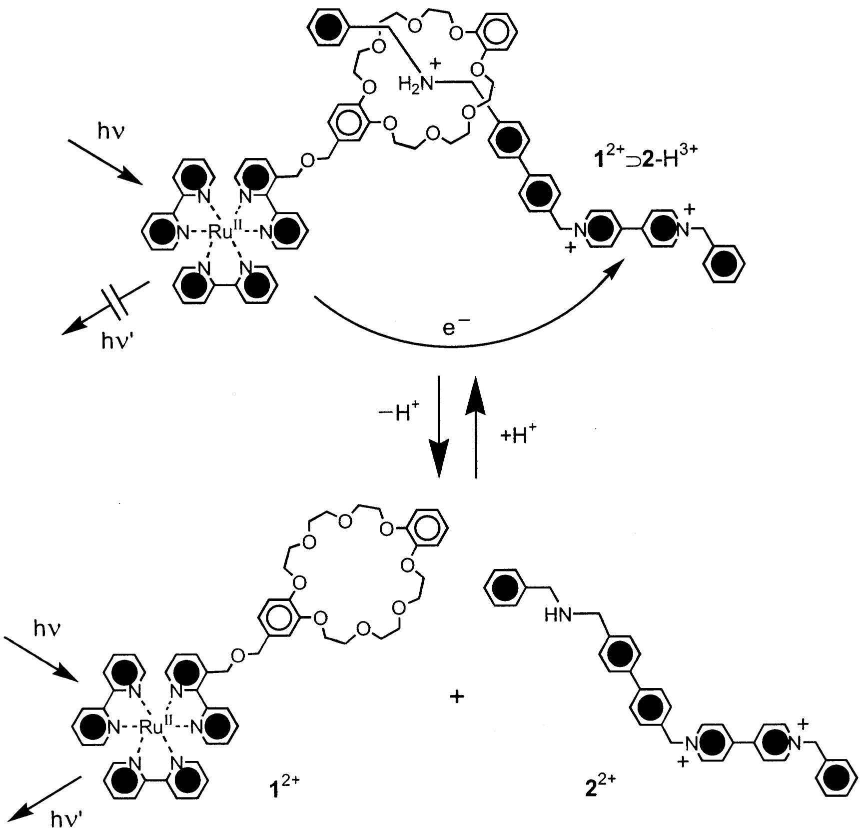

Figure 5. Acid/base-controlled connection/disconnection of the $\mathbf{1}^{2+}$ and $\mathbf{2}\text{-H}^{3+}/\mathbf{2}^{2+}$ components. In the connected structure, the luminescence of the $[\mathrm{Ru(bpy)_3}]^{2+}$ moiety of component $\mathbf{1}^{2+}$ is quenched by electron transfer to the bipyridinium unit of $\mathbf{2}\text{-H}^{3+}$.

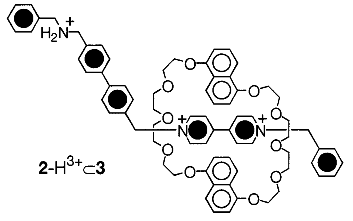

Figure 6. Schematic representation of the threading of the bipyridinium unit of component $\mathbf{2}\text{-H}^{3+}$ into the cavity of 1/5DN38C10 (component **3**).

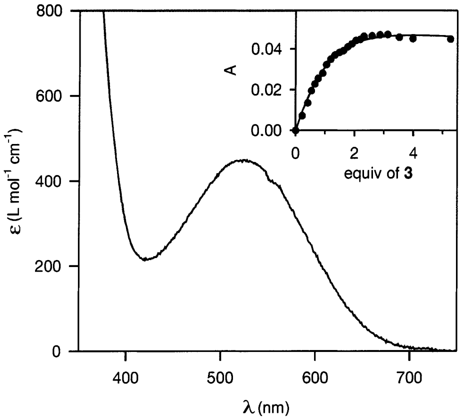

Figure 7. Charge-transfer absorption band exhibited by the $\mathbf{2}\text{-H}^{3+} \supset \mathbf{3}$ adduct. The inset shows the increase of the absorbance at 527 nm observed upon titration of a 1.0×10^{-4} M solution of $\mathbf{2}\text{-H}^{3+}$ with component **3** ($\mathrm{CH_2Cl_2}$/MeCN, 98:2, v/v, room temperature).

7), while quenching of the intensity of the fluorescence band of 1/5DN38C10 ($\lambda_{max} = 346$ nm in Figure 2) is observed. These results can be assigned straightforwardly to the CT interaction in the threaded species.[18a,25,34] The constant fluorescence lifetime observed throughout the titration experiment ($\tau = 8$ ns) can be assigned to uncomplexed 1/5DN38C10 molecules. From the fitting of the absorption titration curve (Figure 7, inset), a stability constant of $(3 \pm 1) \times 10^4$ $\mathrm{M^{-1}}$ can be obtained for the $\mathbf{2}\text{-H}^{3+} \subset \mathbf{3}$ adduct, with an ϵ_{max} value for the CT band of 450 $\mathrm{M^{-1}\ cm^{-1}}$. Since the interaction stabilizing the $\mathbf{2}\text{-H}^{3+} \subset \mathbf{3}$ connection is mainly CT in nature, it was anticipated that the threading/dethreading process could be controlled by redox stimulation.[35] We have found that addition of an excess of Zn powder to a deaerated solution containing 3.5×10^{-5} M $\mathbf{2}\text{-H}^{3+}$ and **3** causes a recovery of the 1/5DN38C10 fluorescence intensity and the appearance (Figure 8) of the strong absorption bands of monoreduced bipyridinium units in the near UV−vis spectral region. The absorbance values[23] indicate a quantitative one-electron reduction of the bipyridinium unit of $\mathbf{2}\text{-H}^{3+}$. Since a reduced bipyridinium unit, if connected to component **3**, would have quenched its fluorescence,[36] we must conclude that one-electron reduction of the bipyridinium units causes (Figure 9) dethreading of the $\mathbf{2}\text{-H}^{3+} \subset \mathbf{3}$ pseudorotaxane. Upon subsequent addition of an excess of the oxidant $\mathrm{NOBF_4}$, the absorption bands of the monoreduced bipyridinium units disappear, and the fluorescence intensity of component **3** is again

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(34) Ashton, P. R.; Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Menzer, S.; Pérez-García, L.; Prodi, L.; Stoddart, J. F.; Venturi, M.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 11171−11197.

(35) Ashton, P. R.; Ballardini, R.; Balzani, V.; Boyd, S. E.; Credi, A.; Gandolfi, M. T.; Gómez-López, M.; Iqbal, S.; Philp, D.; Preece, J. A.; Prodi, L.; Ricketts, H. G.; Stoddart, J. F.; Tolley, M. S.; Venturi, M.; White, A. J. P.; Williams, D. J. *Chem.—Eur. J.* **1997**, *3*, 152−170.

(36) Analysis of the photophysical and redox properties of $\mathbf{2}\text{-H}^{2+}$ and **3** ($E°°(\mathbf{3}) \sim 3.8$ eV, $E°°(\mathbf{2}\text{-H}^{2+}) < 2$ eV, $E(\mathbf{2}\text{-H}^{3+/2+}) = -0.31$ V, $E(\mathbf{3}^{0/-}) = -2.8$ V) reveals that both electron- and energy-transfer quenchings of the fluorescent excited state of **3** by $\mathbf{2}\text{-H}^{2+}$ are thermodynamically allowed processes.

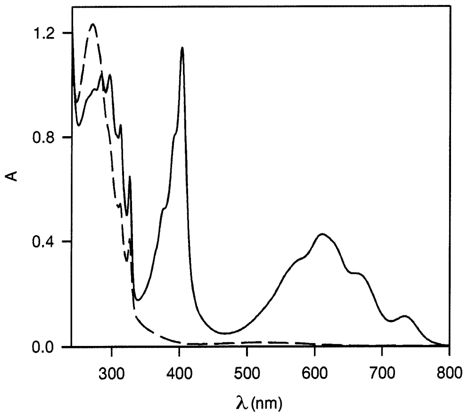

Figure 8. Absorption bands of a solution containing 3.5×10^{-5} M of **2**-H^{3+} and **3** before (— —) and after (—) the addition of an excess of Zn powder. Successive addition of an excess of $NOBF_4$ causes the complete recovery of the original spectrum (CH_2Cl_2/MeCN, 98:2, v/v, room temperature).

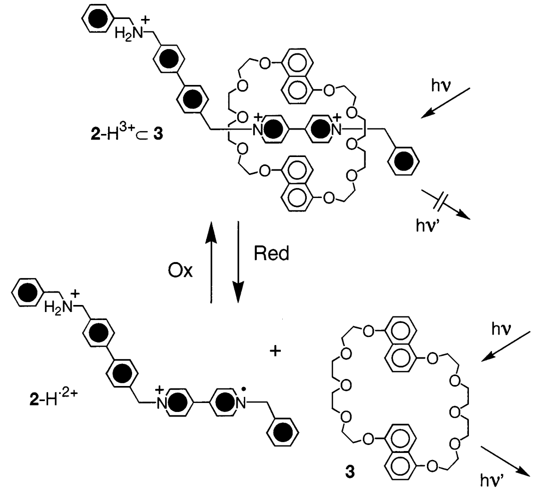

Figure 9. Connection of **2**-H^{3+} and **3** is controlled by reduction/oxidation (chemical or electrochemical) of the bipyridinium unit of component **2**-H^{3+}. The luminescence of crown ether **3** is quenched by the presence of the CT excited state. For more details, see the text.

quenched to the same extent as before addition of Zn, showing that oxidation of the reduced bipyridinium units is followed by a rethreading process of **2**-H^{3+} into **3**.

A more elegant means to disrupt/restore the CT interaction, and therefore to control the connection between **2**-H^{3+} and **3**, is by employing electrochemistry.[35] The trication **2**-H^{3+} undergoes (Table 1) two reversible one-electron reduction processes at −0.24 and −0.67 V while the crown ether **3** undergoes two irreversible one-electron oxidation processes at +1.11 and +1.25 V. After addition of an excess of **3** to a solution of **2**-H^{3+}, in order to ensure complete complexation of the bipyridinium units, the first reduction process of **2**-H^{3+} moves from −0.24 to −0.31 V, as expected for bipyridinium units engaged in CT interactions with dioxynaphthalene units,[34] whereas the second reduction process is not affected. This behavior, which has been observed previously for other pseudorotaxanes of the same family,[35] establishes (Figure 9) that the threaded bipyridinium units dethread after one-electron reduction. After addition of an excess of **2**-H^{3+} to a 2.5×10^{-4} M solution of **3**, its first oxidation peak is shifted toward a more positive potential (+1.15 V), whereas the second one is practically unaffected (+1.24 V). Addition of an excess of 1,1′-dibenzyl-4,4′-bipyridinium (taken as a model compound for the electron-acceptor unit of **2**-H^{3+}) to component **3** gives the same results. The shift of the first oxidation peak is in agreement with the occurrence of CT interactions between the dioxynaphthalene units of **3** and the bipyridinium unit of the thread **2**-H^{3+}. The lack of displacement of the second oxidation peak compared to that of free **3** suggests that, after the first one-electron oxidation, dethreading occurs and hence the second oxidation takes place on the free crown ether. Therefore, dethreading can also be obtained by one-electron oxidation. However, because of their irreversible nature, the redox processes involving **3** are less suitable than the redox processes associated with **2**-H^{3+} to switch on/off the CT interaction and so to control the connection between components **2**-H^{3+} and **3**. In conclusion, the bipyridinium moiety of component **2**-H^{3+} threads through component **3** with a complexation efficiency of around 45% for a 5.0×10^{-5} M equimolar solution of the components. The dethreading/rethreading process is reversible and can be easily controlled (Figure 9) by reduction/oxidation of the bipyridinium moiety of **2**-H^{3+}.

Three-Component Supramolecular System $1^{2+} \supset 2\text{-}H^{3+} \subset 3$. Following the verification, in separated experiments, that the $\mathbf{1}^{2+} \supset \mathbf{2}$-$H^{3+}$ and **2**-$H^{3+} \subset$ **3** connections are robust and can be acid/base (Figure 5) and redox (Figure 9) controlled, respectively, we have examined the behavior of solutions containing all the three components. From the results we obtained with the $\mathbf{1}^{2+} \supset \mathbf{2}$-$H^{3+}$ and **2**-$H^{3+} \subset$ **3** two-component systems, it was calculated that an equimolar mixture of the three components at 5.0×10^{-5} M concentration should contain 27% of the $\mathbf{1}^{2+} \supset \mathbf{2}$-$H^{3+} \subset$ **3** triad, assuming that the two connections do not interfere with each other.

Addition of a 5.0×10^{-5} M solution of **2**-H^{3+} to an equimolar solution of component $\mathbf{1}^{2+}$ caused (Figure 4) a decrease of the luminescence intensity of the $[Ru(bpy)_3]^{2+}$ unit to 40% of its initial value. This result indicates that, in such a solution, 60% of the $\mathbf{1}^{2+}$ and **2**-H^{3+} species is threaded to give $\mathbf{1}^{2+} \supset \mathbf{2}$-$H^{3+}$ and 40% of each of the two components $\mathbf{1}^{2+}$ and **2**-H^{3+} is free. After successive addition of 1 equiv of component **3**, we found that (i) the $[Ru(bpy)_3]^{2+}$ luminescence intensity was unaffected, (ii) the fluorescence intensity of component **3** was partially quenched, and (iii) the CT band at 527 nm, characteristic of the interaction between the bipyridinium unit of **2**-H^{3+} and **3**, was observed. The result noted under point (i) demonstrates that the connection between $\mathbf{1}^{2+}$ and **2**-H^{3+} is not affected by **3**. Because a quantitative evaluation of the intensity of the fluorescence band of **3** was difficult, because of inner filter effects[37] caused by overlapping (Figure 2) between the absorption spectrum of $\mathbf{1}^{2+}$ with both the absorption and fluorescence spectra of **3**, we have used the intensity at 527 nm of the CT absorption band to estimate the fractions of **2**-H^{3+} and $\mathbf{1}^{2+} \supset \mathbf{2}$-$H^{3+}$ threaded with **3**. Titration of a solution containing 5.0×10^{-5} M $\mathbf{1}^{2+}$ and **2**-H^{3+} with **3** gave spectroscopic changes identical to those obtained from the titration of **2**-H^{3+} alone with **3**. Moreover, the intensity of the CT band of the **2**-$H^{3+} \subset$ **3** adduct did not change upon addition of $\mathbf{1}^{2+}$. These results show that the connection between **2**-H^{3+} and **3** is not affected by the presence of $\mathbf{1}^{2+}$. From the absorbance at 527 nm, we estimated that 45% of the crown ether is engaged in CT interactions; that is, **3** is threaded by either **2**-H^{3+} or $\mathbf{1}^{2+} \supset \mathbf{2}$-$H^{3+}$. Since under the experimental conditions used, the $\mathbf{1}^{2+}$

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(37) Credi, A.; Prodi, L. *Spectrochim. Acta, Part A* **1998**, *59*, 154−170.

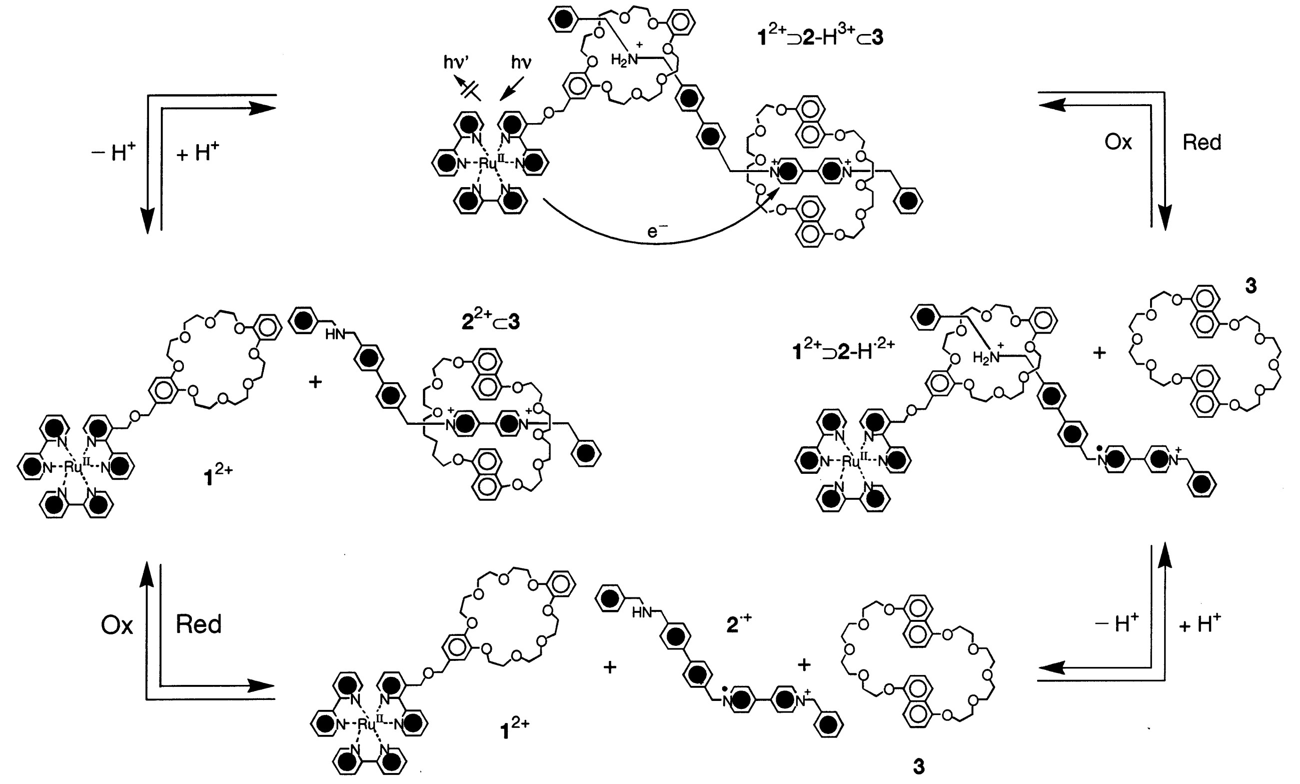

Figure 10. Photoinduced electron transfer in the **1**$^{2+}$ $\supset$ **2**-H^{3+} $\subset$ **3** self-assembled system and control of the two plug/socket functions by acid/base or redox stimulation.

$\supset$ **2**-H^{3+} species is 60% and the free **2**-H^{3+} species is 40%, it follows that 27% of the **3** species is engaged with the **1**$^{2+}$ $\supset$ **2**-H^{3+} two-component system to give the **1**$^{2+}$ $\supset$ **2**-H^{3+} $\subset$ **3** triad (Figure 10). The invariance of the [Ru(bpy)$_3$]$^{2+}$ luminescence intensity on addition of **3** to a solution already containing **1**$^{2+}$ and **2**-H^{3+} (point i) not only shows that the **1**$^{2+}$ $\supset$ **2**-H^{3+} connection is not affected by **3** but also that quenching of the [Ru(bpy)$_3$]$^{2+}$ excited state occurs both in the **1**$^{2+}$ $\supset$ **2**-H^{3+} and **1**$^{2+}$ $\supset$ **2**-H^{3+} $\subset$ **3** adducts with the same rate constant (2.8×10^{8} s^{-1}).

On addition of tributylamine to the solution containing the three components, the luminescence intensity of free [Ru(bpy)$_3$]$^{2+}$ is recovered, as expected because of the disengagement of component **1**$^{2+}$ from both **2**-H^{3+} and **2**-H^{3+} $\subset$ **3**.

Since one-electron reduction of the bipyridinium moiety of component **2**-H^{3+} leads to its dethreading from **3** (vide supra), it can be expected that photoinduced electron transfer from **1**$^{2+}$ to **2**-H^{3+} in the **1**$^{2+}$ $\supset$ **2**-H^{3+} $\subset$ **3** triad (Figure 10) leads to the disconnection of the crown-ether socket **3** from the rest of the system. Such a photoinduced disassembly would indeed compromise the performance of the supramolecular system as a molecular-level extension device, unless the transferred electron is rapidly removed from the reduced bipyridinium unit.

Conclusions

We have investigated the photochemical, photophysical, and electrochemical properties of the three molecular components **1**$^{2+}$, **2**-H^{3+}, and **3** (Figure 1b), their self-assembled **1**$^{2+}$ $\supset$ **2**-H^{3+} and **2**-H^{3+} $\subset$ **3** two-component systems, and the **1**$^{2+}$ $\supset$ **2**-H^{3+} $\subset$ **3** three-component system. We have shown that, on the basis of the properties incorporated into the three components, the **1**$^{2+}$ $\supset$ **2**-H^{3+} and **2**-H^{3+} $\subset$ **3** connections can be controlled *reversibly* and *independently* by acid/base and redox external inputs, respectively (Figure 10). In the fully connected **1**$^{2+}$ $\supset$ **2**-H^{3+} $\subset$ **3** system, light excitation of the [Ru(bpy)$_3$]$^{2+}$ unit of component **1**$^{2+}$ is followed by electron transfer to the bipyridinium unit of component **2**-H^{3+}, which is plugged into component **3**. Therefore, the triad mimics, at the molecular level, the function played by a macroscopic electrical extension cable.

It should be noted that the **1**$^{2+}$ $\supset$ **2**-H^{3+} $\subset$ **3** supramolecular triad (Figure 10) is in fact a pentad,[38] because it is made of five distinct molecular-level subunits: [Ru(bpy)$_3$]$^{2+}$, a DB24C8 crown ether, a secondary dialkylammonium center, a bipyridinium unit, and a 1/5DN38C10 crown ether. *Its operation is governed by three different types of stimuli (light, acid/base, redox), and its behavior can be monitored by changes in one electrochemical, two light-emission, and two light-absorption signals.*

The results reported in this paper constitute a further demonstration that looking at supramolecular chemistry from the viewpoint of functions, keeping in mind the devices of macroscopic world, is a very interesting exercise for a chemist. This kind of research leads, indeed, to a better understanding of the principles that govern intermolecular interactions as well as of the effects caused by external energy inputs on supramolecular systems.

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[38] For recent reviews on multicomponent systems, see: (a) Gust, D.; Moore, T. A.; Moore, A. L. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, 2001; Vol. 3, Part II, Chapter 2. (b) Scandola, F.; Chiorboli, C.; Indelli, M. T.; Rampi, M. A. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, 2001; Vol. 3, Part II, Chapter 3. (c) Chang, C. J.; Brown, J. D. K.; Chang, M. C. J.; Baker, E. A., Nocera, D. G. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, 2001; Vol. 3, Part II, Chapter 4.

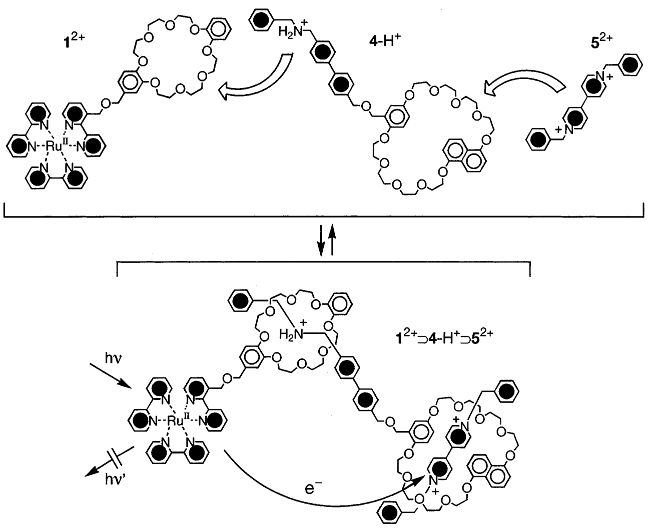

Figure 11. Improved molecular-level model of a macroscopic extension obtained by exchanging the bipyridinium moiety of component **2**-H^{3+} with a suitable appended crown ether capable of binding a bipyridinium dication.

It should be noted that the photoinduced electron-transfer process in the $\mathbf{1}^{2+} \supset \mathbf{2}\text{-H}^{3+} \subset \mathbf{3}$ system does not take place from the $\mathbf{1}^{2+}$ to the **3** component of the supramolecular system, but rather from the "external" molecular moiety of $\mathbf{1}^{2+}$ to the bipyridinium unit of component **2**-H^{3+} that is threaded into **3**. To improve upon this system in supramolecular terms, the bipyridinium moiety of component **2**-H^{3+} should be exchanged (Figure 11) with a suitable appended crown ether capable of binding a bipyridium dication. Such a $\mathbf{1}^{2+} \supset \mathbf{4}\text{-H}^{+} \supset \mathbf{5}^{2+}$ system would more closely resemble a macroscopic extension cable, where the wire component has a plug-and-socket function instead of two plugs as in the system examined. In the case of the system shown in Figure 11, light excitation would transfer an electron from the first to the fifth unit of the pentad.

This design and other designs for constructing more intricate molecular-level electrical extension cables are currently under investigation in our laboratories.

Experimental Section

General Synthetic Methods. All chemicals were purchased from Aldrich and were used as received. Solvents were dried according to literature procedures.[39] Analytical thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel (Merck 5554). Column chromatography was performed on silica gel 60 (Merck 40−60 nm, 230−400 mesh). Melting points (mp's) were determined on an Electrothermal 9200 apparatus. ^{1}H NMR spectra were recorded on a Bruker AC-300 at 300 MHz. ^{13}C NMR Spectra were recorded on a Bruker AC-300 at 75.5 MHz using broad band decoupling at 25 °C. The chemical shift values are expressed as δ values, and the coupling constant values (J) are in hertz. The following abbreviations are used for the signal multiplicities or characteristics: s, singlet; d, doublet; t, triplet; m, multiplet. Fast atom bombardment mass spectrometry (FABMS) was performed on a ZAB-SE mass spectrometer, equipped with a krypton primary atom beam, and utilizing a *m*-nitrobenzyl alcohol matrix.

Syntheses. (2-Pyridacyl)pyridium Iodide (7·I). Iodine (40.7 g, 0.16 mol) in warm pyridine (140 mL) was added under nitrogen to a solution of 2-acetylpyridine (60 mL). The reaction mixture was stirred at 80 °C for 4 h. After cooling, the precipitated solid was collected by filtration and washed with pyridine (75 mL). The black solid was then added to a boiling suspension of carbon (1 spatula) in EtOH (2 L). Following hot filtration, (2-pyridacyl)pyridium iodide (**7**·I) (36.03 g, 69%) was obtained as yellow-green solid. ^{1}H NMR (300 MHz, CD$_3$SOCD$_3$) δ 6.52 (s, 2H), 7.82−7.86 (m, 1H), 8.06−8.09 (m, 1H), 8.12−8.17 (m, 1H), 8.27−8.31 (m, 2H), 8.71−8.77 (m, 1H), 8.87−8.89 (m, 1H), 9.02−9.04 (m, 2H); ^{13}C NMR (75 MHz, CD$_3$SOCD$_3$) δ 66.7, 122.1, 127.8, 129.2, 138.2, 146.3, 146.4, 149.6, 150.5, 191.5.

5-Methyl-2,2′-bipyridine (8). (2-Pyridacyl)pyridium iodide (**7**·I) (32.6 g, 0.10 mmol), methacrolein (7.88 g, 0.11 mmol), and ammonium acetate (17.35 g, 0.23 mmol) were dissolved in formamide (312 mL). The reaction mixture was stirred at 75 °C for 6 h. After addition of H$_2$O, the reaction mixture was extracted with Et$_2$O. The combined organic solution was washed with brine and dried (MgSO$_4$). The solvent was removed in vacuo, and the residue was subjected to column chromatography (SiO$_2$; CH$_2$Cl$_2$/MeOH, 20:1) to yield 5-methyl-2,2′-bipyridine (**8**) (16.8 g, 99%) as an orange oil. ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.36 (s, 3H), 7.23−7.27 (m, 1H), 7.58−7.61 (m, 1H), 7.74−7.80 (m, 1H), 8.25 (d, J = 8.1 Hz, 1H), 8.31−8.35 (m, 1H), 8.48 (d, J = 1.8 Hz, 1H), 8.63, 8.65 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 18.3, 120.6, 120.8, 123.4, 133.4, 136.9, 137.5, 149.1, 149.6, 153.6, 156.3.

5-Bromomethyl-2,2′-bipyridine (9). 5-Methyl-2,2′-bipyridine (**8**) (2.80 g, 16.4 mmol), *N*-bromosuccinimide (2.93 g, 16.4 mmol), and AIBN (673 mg, 4.1 mmol) were dissolved in CCl$_4$ (250 mL). The reaction mixture was stirred at 45 °C for 24 h. The solvent was evaporated, and the residue was purified by column chromatography (SiO$_2$; CHCl$_3$/Me$_2$CO, 30:20) to yield 5-bromomethyl-2,2′-bipyridine (**9**) (987 mg, 48%) as a yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.51 (s, 2H), 7.27−7.32 (m, 1H), 7.77−7.85 (m, 2H), 8.37 (d, J = 8.1 Hz, 2H), 8.65−8.67 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 29.7, 121.0, 121.2, 124.0, 133.6, 137.0, 137.6, 149.2, 149.3, 155.5, 156.0.

Crown Ether Derivative 11. Sodium hydride (15.1 mg, 0.63 mmol), hydroxymethyl-functionalized[19] dibenzo[24]crown-8 **10** (288 mg, 0.60 mmol), and 5-bromomethyl-2,2′-bipyridine (**9**) (153 mg, 0.62 mmol) were dissolved in PhMe (60 mL). The reaction mixture was heated under reflux for 15 h. The solvent was removed, and the residue was dissolved in CH$_2$Cl$_2$ and washed with H$_2$O and brine. After the removal of solvent, the residue was purified by column chromatography (SiO$_2$; CH$_2$Cl$_2$/MeOH, 90:10) to obtain the bipyridine-containing crown ether **11** (156 mg, 40%) as a yellow solid. ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.79 (s, 8H), 3.88 (t, J = 4.2 Hz, 8H), 4.14 (t, J = 4.2 Hz, 8H), 4.48 (s, 2H), 4.56 (s, 2H), 6.81−6.90 (m, 7H), 7.25−7.31 (m, 1H), 7.76−7.82 (m, 2H), 8.36 (d, J = 8.0 Hz, 2H), 8.61−8.66 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 69.1, 63.9, 69.4, 69.8, 71.2, 72.2, 113.6, 114.0, 120.8, 121.1, 121.4, 123.7, 130.9, 133.8, 136.4, 136.5, 136.9, 148.5, 148.7, 148.8, 148.9, 149.2, 155.6, 155.9. MS(FAB) *m/z* 669 [M + Na]$^+$, 647 [M]$^+$.

Component 1·2PF$_6$. A solution of *cis*-bis(2,2′-bipyridine)dichlororuthenium(II) hydrate[20] (96.9 mg, 0.2 mmol) in a mixture of EtOH/H$_2$O (13.5 mL, 3:1 v/v) was added to a refluxing solution of bipyridine-containing crown ether **11** (129 mg, 0.2 mmol) in a mixture of EtOH/H$_2$O (13.5 mL, 3:1 v/v). The reaction mixture was heated under refluxed for 24 h. The solvent was evaporated, and the residue was purified by column chromatography (SiO$_2$; MeOH/2 M NH$_4$Cl$_{\text{aq}}$/MeNO$_2$, 7:2:1) to afford component **1**·2PF$_6$ (70 mg, 43%) after counterion exchange. ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.67−3.73 (m, 12H), 3.75−3.83 (m, 6H), 4.02−4.08 (m, 4H), 4.11−4.14 (m, 2H), 4.33 (s, 2H), 4.40−4.42 (m, 2H), 6.67−6.88 (m, 5H), 7.26 (t, J = 6.4 Hz, 1H), 7.98−8.07 (m, 6H), 8.33 (d, J = 8.0 Hz, 1H), 8.42−8.49 (m, 6H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 14.1, 23.4, 25.6, 29.5, 29.8, 29.9, 30.0, 30.1, 30.2, 30.3, 30.4, 32.4, 35.5, 64.0, 123.1, 125.3, 126.85, 128.6, 138.8, 149.3, 152.6, 152.7, 157.8, 157.9, 158.0, 173.9. MS(FAB) *m/z* 1373.1 [M + Na]$^+$, 1205.2 [M − PF$_6$]$^+$, 1030.3 [M − 2PF$_6$]$^+$.

Component 2-H·3PF$_6$. A solution of *N*-benzyl-4-pyridium-4′-pyridine[21] (**12**·PF$_6$) (350 mg, 0.89 mmol) and 4,4′-bis(chloromethyl)-

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(39) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon: Oxford, 1989.

1,1′-biphenyl (1.12 g, 4.5 mmol) in MeCN (20 mL) was heated under reflux for 16 h. After cooling, the precipitated solid was collected by filtration and washed with CH_2Cl_2. After counterion exchange (NH_4PF_6/H_2O/Me_2CO), the product and benzylamine (95 mg, 0.89 mmol) were dissolved in MeCN (20 mL) and heated under reflux. The solvent was removed, and the residue was purified by column chromatography (SiO_2, MeOH/2 M NH_4Cl_{aq}/$MeNO_2$, 7:2:1) to afford component **2**-H·3PF_6 (258 mg, 30%) after counterion exchange (NH_4PF_6/H_2O). ^{1}H NMR (500 MHz, CD_3CN) δ 4.31 (s, 2H), 4.75 (s, 2H), 5.85 (s, 2H), 5.89 (s, 2H), 7.51−7.82 (m, 18H), 8.39 (d, $J = 6.8$ Hz, 2H), 8.41 (d, $J = 6.8$ Hz, 2H), 9.00 (d, $J = 6.8$ Hz, 2H), 9.03 (d, $J = 6.8$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 45.6, 51.3, 64.2, 64.6, 127.3, 127.4, 127.4, 127.9, 127.9, 128.9, 129.2, 129.3, 129.5, 129.8, 129.9, 130.0, 130.1, 130.8, 131.7, 132.4, 137.7, 139.5, 141.7, 145.4, 150.2, 150.3. MS(FAB) *m*/*z* 824.7 $[M - PF_6]^+$, 678.3 $[M - H\text{-}2PF_6]^+$.

Photophysical Experiments. All the measurements were performed at room temperature in air-equilibrated CH_2Cl_2/MeCN (98:2, v/v) solutions. PF_6^- ions were the counterions in the case of all the cationic compounds. UV−vis absorption spectra were recorded with a Perkin-Elmer λ6 spectrophotometer. Uncorrected luminescence spectra were obtained with a Perkin-Elmer LS-50 spectrofluorimeter equipped with a Hamamatsu R928 phototube. Luminescence lifetimes were measured by time-correlated single-photon counting with Edinburgh Instruments DS199 equipment. The exciting light ($\lambda = 320$ nm) was produced by a gas arc lamp (model nF900, filled with D_2) that delivered pulses of about 1 ns (fwmh). The light emitted was filtered by using a cutoff filter ($\lambda = 565$ nm). The detector was a cooled Hamamatsu R928 photomultiplier. The estimated experimental errors are 2 nm on band maxima and ±5% on the molar absorption coefficients, fluorescence intensity, and fluorescence lifetime values.

Electrochemical Experiments. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) experiments were carried out in argon-purged CH_2Cl_2/MeCN (90:10, v/v) at room temperature with an Autolab 30 multipurpose instrument interfaced to a personal computer. The working electrode was a glassy carbon electrode (0.08 cm^2, Amel); its surface was routinely polished with a 0.05 mm alumina−water slurry on a felt surface, immediately prior to use. In all cases, the counter electrode was a Pt spiral, separated from the bulk solution with a fine glass frit, and an Ag wire was used as a quasireference electrode. Ferrocene was present as an internal standard. The concentrations of the compounds were of the order of 5×10^{-4} M; the experiments were carried out in the presence of 5×10^{-2} M $TBAPF_6$. Cyclic voltammograms were obtained with sweep rates in the range 0.05−0.5 V s^{-1}; DPV experiments were performed with a scan rate of 20 or 4 mV s^{-1}, a pulse height of 75 or 10 mV, and a duration of 40 ms. The reversibility of the observed processes was established by using the criteria of (i) separation of 60 mV between cathodic and anodic peaks, (ii) the close-to-unity ratio of the intensities of the cathodic and anodic currents, and (iii) the constancy of the peak potential on changing sweep rate in the cyclic voltammograms. The same half-wave potential values were obtained from the DPV peaks and from an average of the cathodic and anodic CV peaks, as expected for reversible processes. The potential values are in volts versus SCE; the experimental error was estimated to be ±10 mV.

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