Ru^{II}-Polypyridine Complexes Covalently Linked to Electron Acceptors as Wires for Light-Driven Pseudorotaxane-Type Molecular Machines**

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Abstract: An investigation has been performed on the design of light-driven, pseudorotaxane-type, mechanical molecular machines based on wires made up of an electron-transfer photosensitizer covalently linked to an electron acceptor. Compounds (2,2′-bipyridine)$_2$Ru(2,2′-bipyridine-5-(CH$_2$)-1-(4,4′-bipyridinium)-1′-CH$_2$-R)$^{4+}$ ($\mathbf{1}^{4+}$), (4,4′-(Me)$_2$-2,2′-bipyridine)$_2$Ru(2,2′-bipyridine-5-(CH$_2$)$_4$-1-(4,4′-bipyridinium)-1′-CH$_2$-Me)$^{4+}$ ($\mathbf{2}^{4+}$), and (2,2′:6′,2″-terpyridine)Ru(2,2′:6′,2″-terpyridine-4′-phenylene-2-(2,7-diazapyrenium)-7-CH$_2$-R)$^{4+}$ ($\mathbf{3}^{4+}$), where $R = -C_6H_4-(O-CH_2-CH_2)_2-O-Ph$) have been prepared and their photochemical and photophysical processes have been investigated in butyronitrile fluid solution (room temperature) and rigid matrix (77 K). At room temperature the triplet metal-to-ligand charge-transfer (^{3}MLCT) excited state of the Ru-based unit of $\mathbf{1}^{4+}$ is quenched by a very fast ($k_q > 5 \times 10^9\,s^{-1}$) electron-transfer process. For $\mathbf{2}^{4+}$, where the Ru-based and electron-acceptor units are separated by four methylene groups, the value of the quenching constant is $6.2 \times 10^8\,s^{-1}$. In $\mathbf{3}^{4+}$, the potentially fluorescent S_1 excited state of the diazapyrenium unit is quenched by the Ru-based moiety with a rate constant $\geq 1 \times 10^{11}\,s^{-1}$. In rigid matrix at 77 K, the ^{3}MLCT excited state of the Ru-based moiety is not quenched by the bipyridinium or diazapyrenium moiety, whereas both the fluorescence and phosphorescence of the diazapyrenium moiety of $\mathbf{3}^{4+}$ are completely quenched by the MLCT levels of the Ru-based moiety through energy transfer. Excitation spectra of the Ru-based emission show that, in a rigid matrix at 77 K, the excitation of the bipyridinium moiety leads to population of the ^{3}MLCT excited state of the Ru-based moiety. The above wires and a crown ether (1/5DN38C10) containing two 1,5-dioxynaphthalene electron-donor units self-assemble to give pseudorotaxane systems. Light-induced dethreading of a pseudorotaxane has been achieved and valuable information has been gathered concerning the design of more efficient systems. A spin-off of these studies has been the design of pseudorotaxanes in which the dethreading/rethreading process can be controlled by chemical stimuli.

Keywords: charge transfer • energy transfer • molecular devices • self-assembly • rotaxanes

Introduction

Currently, we are engaged in the design and construction of simple mechanical molecular machines[1–5] based on pseudorotaxanes, rotaxanes, and catenanes[6] whose structure is essentially controlled by π-electron-deficient and π-electron-rich aromatic-stacking and hydrogen-bonding interactions.[7] Since such interactions can be switched on and off by redox processes, it occurred to us to use photoinduced electron-transfer reactions to bring about the mechanical displacements.[1–3]

Because of a unique combination of chemical stability, redox properties, luminescence intensity, and excited-state lifetime, the complexes of the polypyridine-type family

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(prototype: $[Ru(bpy)_3]^{2+}$, in which bpy = 2,2′-bipyridine) have been used extensively during the past 20 years as photosensitizers in a variety of intermolecular electron-transfer processes.[8–11] More recently, these compounds have also been used to obtain photoinduced energy- or electron-transfer processes in suitably-designed supramolecular (multicomponent) systems.[12–14]

Our first attempt[2, 3] to design a photochemically driven, mechanical molecular machine was based on the use of an external electron-transfer photosensitizer ($[Ru(bpy)_3]^{2+}$ or 9-anthracenecarboxylic acid). Starting from the pseudorotaxane constituted by a wire containing the 1,5-dioxynaphthalene electron-donor unit threaded through the cavity of a cyclophane containing two 4,4′-bipyridinium electron-acceptor units, we found that light excitation of the photosensitizer in the presence of a sacrificial electron donor [e.g., triethanolamine (TEOA)] causes single-electron transfer to the electron-acceptor unit of the ring component (Figure 1a). This reduction decreases the donor–acceptor interaction between the component parts of the pseudorotaxane, which is the driving force for the self-assembly. As a consequence, the thread component dethreads from the cavity of the cyclophane. If oxygen is allowed to enter the irradiated solution, which is stored in the dark, the reduced ring is reoxidized, the donor–acceptor interaction restored, and the thread component rethreads through the cyclophane once more.

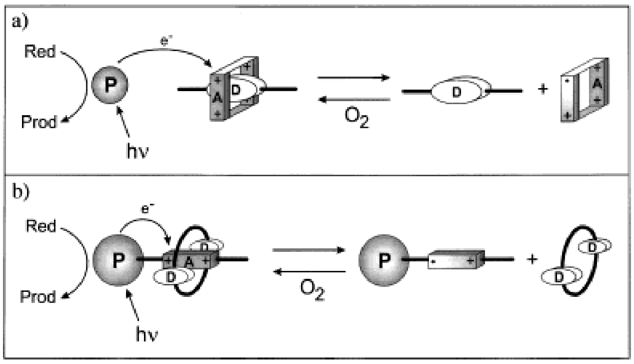


Figure 1. Schematic representation of the light-induced dethreading of a pseudorotaxane by use of a) an external and b) an incorporated photosensitizer. The photosensitizer **P** is an excited-state electron donor (e.g., $[Ru(bpy)_3]^{2+}$ **4**$^{2+}$); **Red** is a sacrificial reductant (e.g., triethanolamine); **Prod** are species originating from irreversible oxidation of **Red**; **A** and **D** are electron-acceptor and electron-donor units, respectively. Rethreading can be obtained by oxidation of the photoreduced electron-acceptor unit. For more details, see text.

Abstract in Italian: *Nell'ambito degli studi intrapresi sulla progettazione e sintesi di macchine molecolari fotochimiche basate su pseudorotassani, sono state preparate tre molecole filiformi costituite da un sensibilizzatore di trasferimento elettronico [un complesso polipiridinico di* Ru^{II}*] legato covalentemente ad un gruppo elettron accettore (4,4′-dipiridinio o 2,7-diazapirenio). Le proprietà fotofisiche e fotochimiche di queste tre specie e di opportuni composti modello sono state esaminate in butirronitrile a temperatura ambiente e in matrice rigida a 77 K. A temperatura ambiente, lo stato eccitato di tripletto MLCT del complesso di* Ru^{II} *nel composto (2,2′-dipiridile)*$_2$*Ru(2,2′-dipiridile-5-(CH*$_2$*)-1-(4,4′-dipiridinio)-1′-CH*$_2$*-R)*$^{4+}$ *[in cui R = -C*$_6$*H*$_4$*(OCH*$_2$*CH*$_2$*)*$_2$*OPh] viene disattivato mediante un processo di trasferimento elettronico molto veloce (*$k_q > 5 \times 10^9\,s^{-1}$*). Per (4,4′-(Me)*$_2$*-2,2′-dipiridile)*$_2$*Ru(2,2′-dipiridile-5-(CH*$_2$*)*$_4$*-1-(4,4′-dipiridinio)-1′-CH*$_2$*-Me)*$^{4+}$*, in cui il complesso di* Ru^{II} *e l'unità elettron accettrice sono separati da quattro gruppi metilene, il valore della costante di spegnimento è* $6.2 \times 10^8\,s^{-1}$*. Nel composto (2,2′:6′,2″-terpiridile)Ru(2,2′:6′,2″-terpiridile-4′-fenilene-2-(2,7-diazapirenio)-7-CH*$_2$*-R)*$^{4+}$ *(R come sopra), lo stato eccitato* S_1 *dell'unità diazapirenio, potenzialmente fluorescente, è disattivato dal complesso terpiridinico di* Ru^{II} *(*$k_q \geq 1 \times 10^{11}\,s^{-1}$*). In matrice rigida, lo stato eccitato* ^{3}*MLCT del complesso metallico non è influenzato dai gruppi dipiridinio o diazapirenio, mentre sia la fluorescenza che la fosforescenza di (2,2′:6′,2″-terpiridile)Ru(2,2′:6′,2″-terpiridile-4′-fenilene-2-(2,7-diazapirenio)-7-CH*$_2$*-R)*$^{4+}$ *sono completamente spente a causa di un processo di trasferimento di energia ai livelli MLCT dell'unità contenente* Ru^{II}*. Lo spettro di eccitazione dell'emissione dovuta al complesso di* Ru^{II} *mostra che, a 77 K, si ha popolazione del suo stato eccitato* ^{3}*MLCT in seguito ad eccitazione del gruppo dipiridinio. I composti filiformi esaminati si assemblano spontaneamente con un etere corona (1/5DN38C10) contenente unità elettron donatrici 1,5-diossinaftalene formando pseudorotassani. Per uno di questi pseudorotassani è stato possibile indurre lo sfilamento dei componenti molecolari mediante irradiazione con luce visibile. Gli studi riportati si sono rivelati di grande utilità per la progettazione di macchine molecolari fotochimiche più efficienti, nonché per la costruzione di pseudorotassani nei quali i processi di sfilamento/infilamento dei componenti si possono controllare mediante stimoli di tipo chimico.*

Currently our attention is focused on the design of a second-generation mechanical machine that is based upon a pseudorotaxane in which the photosensitizer is incorporated into a wire,[15] which in turn contains a π-electron-deficient unit (which also acts as a single-electron acceptor), and the ring component contains π-electron-rich moieties (Figure 1b). To explore the feasibility of this project, we have synthesized the wire-type systems **1**$^{4+}$, **2**$^{4+}$, and **3**$^{4+}$ shown in Figure 2a. As the photosensitizer, we have chosen either i) $[Ru(bpy)_3]^{2+}$ derivatives (**4**$^{2+}$; Figure 2b), because of their well-defined photophysical and redox properties,[9] or ii) $[Ru(tpy)_2]^{2+}$ (**5**$^{2+}$) derivatives, which exhibit less favorable photophysical properties (very short excited-state lifetimes),[14] but offer several synthetic and structural advantages for the construction of wire-type systems.[14, 16, 17] As an electron acceptor, besides the well-known 4,4′-bipyridinium unit **6**$^{2+}$,[18] we have used the 2,7-diazapyrenium unit **7**$^{2+}$ because of its high association constants with π-electron-rich crown ethers such as **8** and **9**[4] and its interesting luminescence properties.[19]

In this paper, we report the results of an investigation on the luminescence and photoinduced intramolecular energy- and electron-transfer processes that occur on excitation of the systems shown in Figure 2a, both in a fluid solution at room temperature and in a rigid matrix at 77 K. We have also investigated the self-assembly of these wires with crown ethers **8** and **9** containing two hydroquinone and two 1,5-

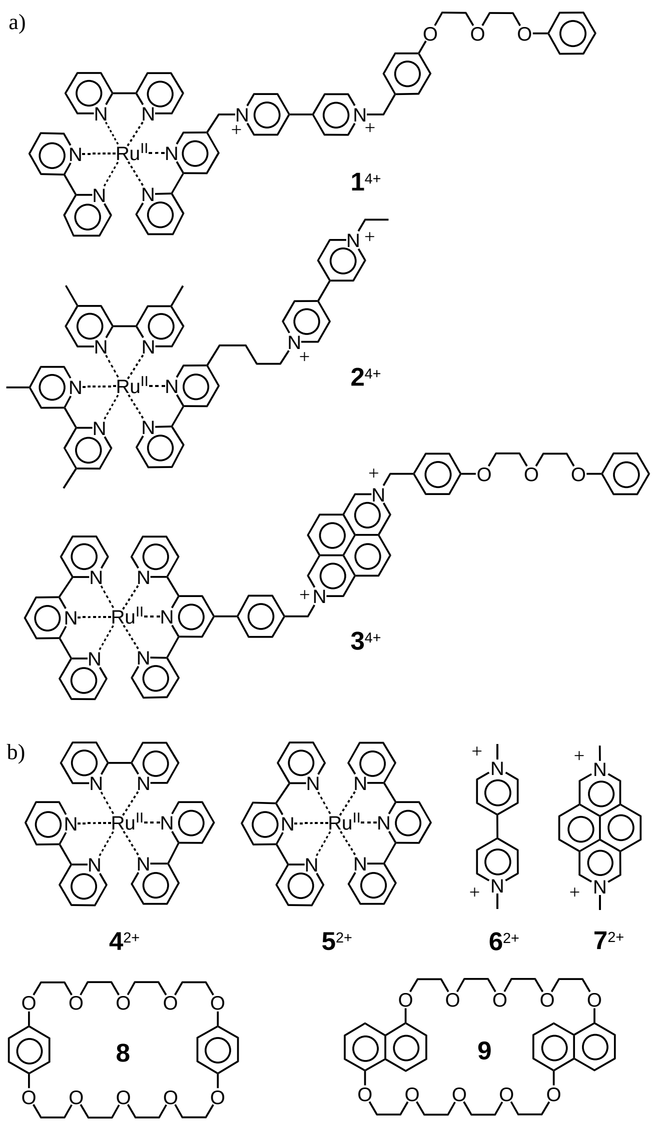


Figure 2. Structure formulas of a) the novel wire-type systems, and b) the reference compounds for the luminescent and redox-active units of the wire-type systems, and of the crown ether used as a ring for obtaining pseudorotaxanes.

dioxynaphthalene π-electron-rich units, respectively, to give pseudorotaxane superstructures. We have subsequently attempted to cause light- and chemically-induced dethreading of such systems and have been successful in our attempts in two cases. Wire-type compounds similar to those in Figure 2a have recently been investigated for other purposes by Mallouk et al.[20] and by Kelly and Rodgers.[21]

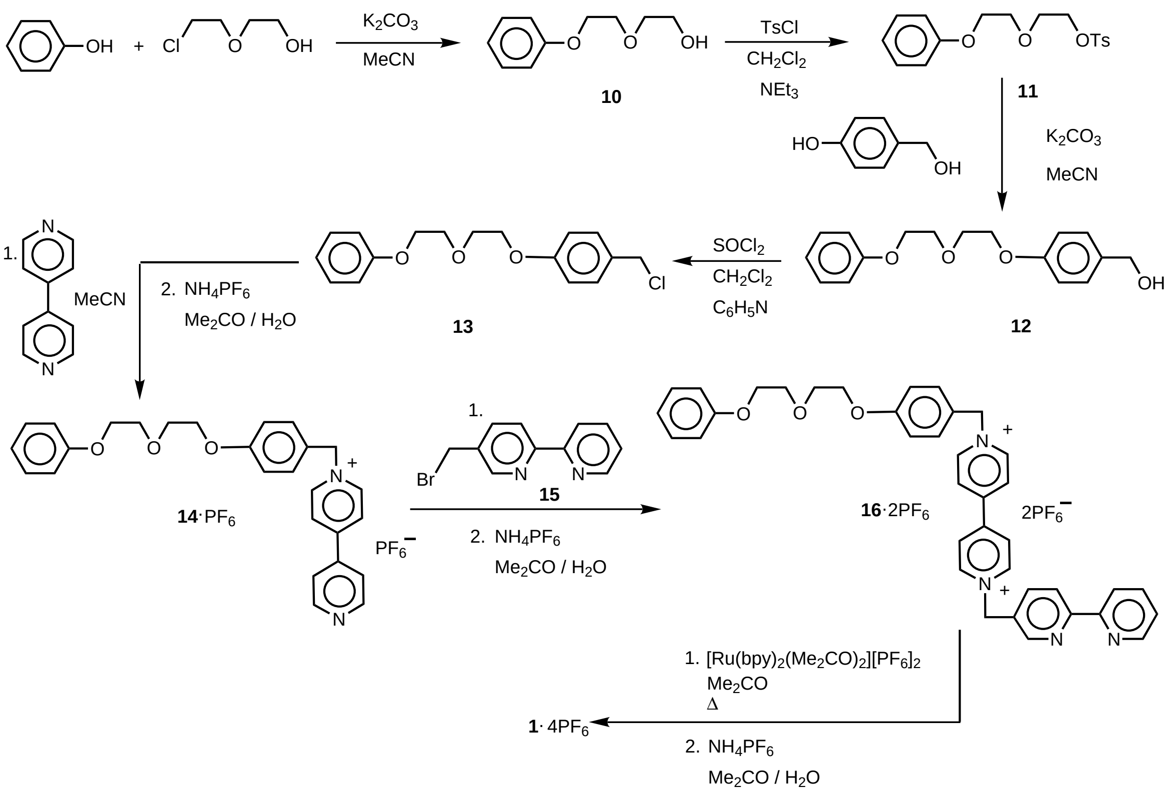
Results and Discussion

1. Strategy: The design of photochemically driven, mechanical molecular machines of the types illustrated in Figure 1 is not a trivial problem. It is clear that i) each component must exhibit suitable spectroscopic and redox properties, ii) there must be appropriate noncovalent bonding interactions between the various components to allow the self-assembly of the wire and the ring, iii) the system must be chemically stable under the operating conditions, and iv) the threading/dethreading process must result in an easily monitorable change of some properties (the most useful ones are absorption spectra, and luminescence spectra and lifetimes).

The newly designed machine, shown in Figure 1b, differs from the previous one[2, 3] (illustrated in Figure 1a) in several respects. Besides having covalently incorporated the photosensitizer into the wire, we have exchanged the position of the π-electron-deficient and π-electron-rich aromatic units in the pseudorotaxane structure, such that the π-electron-deficient aromatic bipyridinium or diazapyrenium unit is now incorporated into the thread and the π-electron-rich aromatic units into the macrocyclic component. A consequence of this modification is that there is only one electron-acceptor moiety—the organic viologen-like dication units—which equates with the single-electron transfer caused by photoexcitation. Thus, the noncovalent bonding interactions between the viologen dication and the crown ether will be switched off upon photoinduced electron transfer from the $[Ru(bpy)_3]^{2+}$ or $[Ru(tpy)_2]^{2+}$ sensitizer to the viologen dication. The 4,4′-bipyridinium unit was chosen as an electron acceptor because of its good reversible electrochemical behavior[18] and its affinity for crown ethers such as **8** and **9**. Additionally, we have also explored the possibility of using the 2,7-diazapyrenium unit since i) it binds crown ethers such as **8** and **9** more strongly than the analogous bipyridinium unit and ii) it exhibits a strong fluorescence.[4, 19] As the macrocyclic component for constructing the pseudorotaxane superstructure, we have chosen crown ethers containing two π-electron-rich units because such compounds i) bind strongly to bipyridinium and diazapyrenium dications and ii) show a strong fluorescence, particularly in the case of the naphthalene-containing crown ether **9**.[4]

The photochemical operation of the mechanical machines shown in Figure 1 is based on the presence of a sacrificial electron donor, which is capable of reducing the oxidized photosensitizer by an intermolecular process more rapidly than the intermolecular (Figure 1a) or intramolecular (Figure 1b) back-electron-transfer reaction from the reduced organic cation to the oxidized photosensitizer (vide infra). The most efficient sacrificial reductants are amines (especially TEOA) or polycarboxylate anions (e.g., oxalate anions).[22] Polycarboxylate anions are soluble only in water. Since crown ethers and the three wire-type compounds (as their hexafluorophosphate salts) shown in Figure 2a are only moderately soluble in water, but are soluble in polar organic solvents (such as MeCN and Me_2CO), we employed the organic soluble TEOA as the sacrificial electron donor.

2. Synthesis: The synthesis of **1**$\cdot$4PF_6 is illustrated in Scheme 1. Phenol was alkylated with 2-chloro(ethoxy)ethanol under basic conditions (K_2CO_3) to afford the alcohol **10**, which was tosylated to give **11**. 4-Hydroxybenzyl alcohol was then alkylated selectively with the tosylate **11**, affording the benzylic alcohol **12**. Next, the benzylic alcohol **12** was converted ($SOCl_2$) into the benzylic chloride **13**, which was used without further purification to monoalkylate 4,4′-bipyridine that, after counterion exchange (NH_4PF_6), yielded **14**$\cdot$

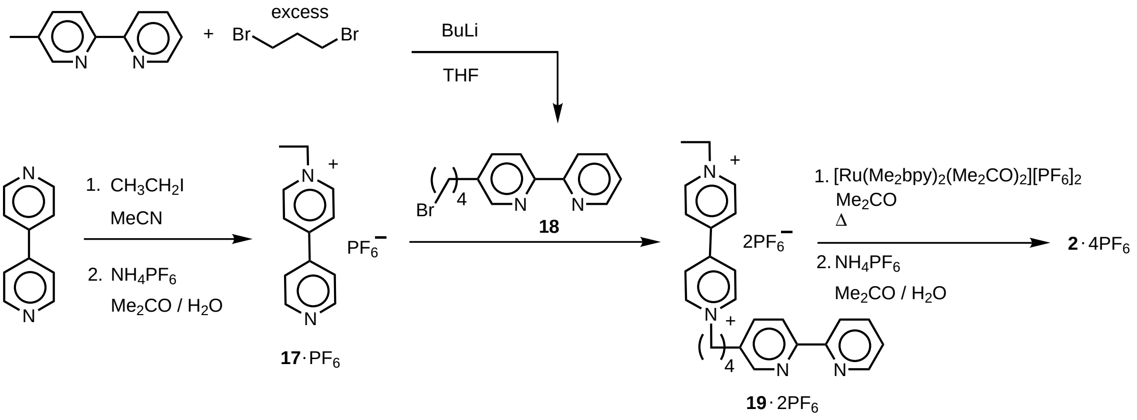


Scheme 1.

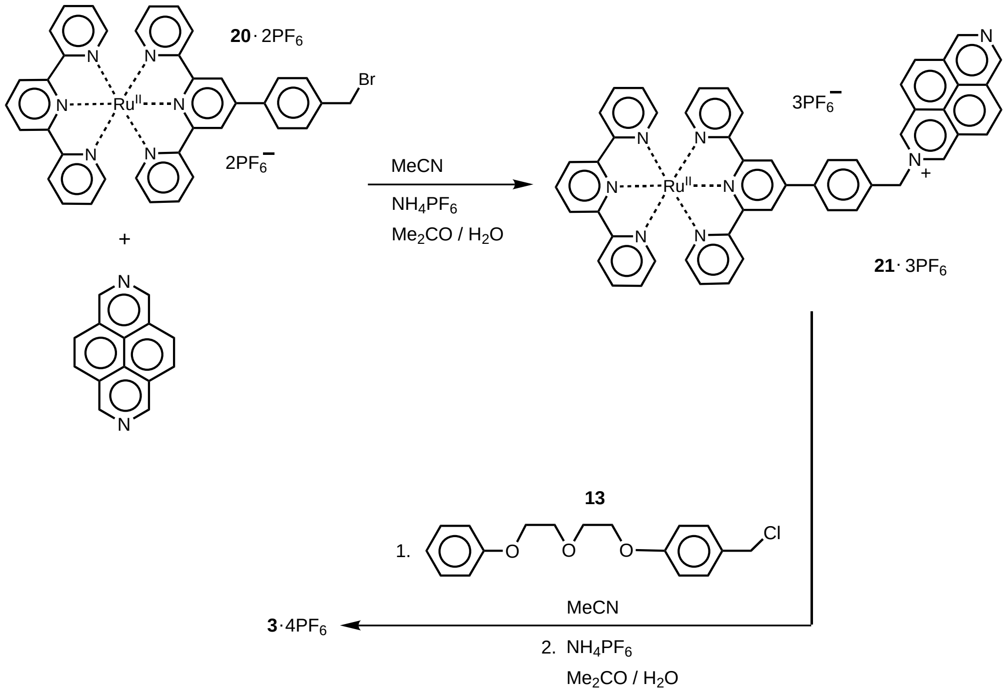
$4PF_6$. A second quaternization was then performed on the pyridine moiety of **14**·PF$_6$ with the benzylic bromide **15** affording **16**·2PF$_6$ after counterion exchange with (NH$_4$PF$_6$). [Ru(bpy)$_2$Cl$_2$] was heated under reflux in Me$_2$CO with an equimolar proportion of AgPF$_6$ to generate the pure solvo-complex, [Ru(bpy)$_2$(Me$_2$CO)$_2$][PF$_6$]$_2$. The precipitated AgCl was removed by filtration and the resulting filtrate was added slowly to a solution of **16**·2PF$_6$ in Me$_2$CO, yielding the desired tetracationic **1**$^{4+}$ as its tetrakis(hexafluorophosphate) salt in 68% yield.

The synthesis of **2**·4PF$_6$ is illustrated in Scheme 2. 4,4′-Bipyridine was monoalkylated with EtI to afford the monoquat derivative **17**·PF$_6$,[23] after counterion exchange. The anion of 5-methyl-2,2′-bipyridine, formed by deprotonation with BuLi, was alkylated with 1,3-dibromopropane[20a] to give the bromide **18**. The monoquat derivative **17**·PF$_6$ was quaternized with the alkylbromide **18** to afford, after counterion exchange (NH$_4$PF$_6$), the dicationic salt **19**·2PF$_6$. [Ru(Me$_2$bpy)$_2$Cl$_2$][24] was converted to its solvo-complex (Me$_2$CO and AgPF$_6$), before being added slowly to a solution of **19**·2PF$_6$ in Me$_2$CO, giving the desired tetracationic salt **2**$^{4+}$ in 55% yield.

The synthesis of **3**·4PF$_6$ is illustrated in Scheme 3. [Ru(tpy)Cl$_3$][25] was treated with 4′-(*p*-bromomethylphenyl)-2,2′:6′,2″-terpyridine[26] to afford, after counterion exchange (NH$_4$PF$_6$), the ruthenium complex **20**·2PF$_6$. 2,7-Diazapyrene[27] was monoalkylated with **20**·2PF$_6$ that, after counterion exchange (NH$_4$PF$_6$), yielded **21**·3PF$_6$. The monoquat derivative **21**·3PF$_6$ was quaternized with benzylic chloride **13** yielding the desired tetracationic salt **3**·4PF$_6$ in 49% yield.



Scheme 2.



Scheme 3.

3. Pseudorotaxanes: When progressively more and more bis-*p*-phenylene-34-crown-10 (BPP34C10; **8**) or 1,5-dinaphtho-38-crown-10 (1/5DN38C10; **9**) is added to solutions of the viologen dications such as $\mathbf{16}^{2+}$ and $\mathbf{19}^{2+}$ in MeCN, a deep orange or purple color, respectively, appears as a result of the charge-transfer interactions between the π-electron-rich aromatic rings of the crown ether and the π-electron-deficient viologen unit incorporated within the thread components. Qualitative evidence for the pseudorotaxane formation was obtained from mass spectrometry, in which it was evident that there were peaks corresponding to the loss of one then two hexafluorophosphate counterions from the pseudorotaxanes. Table 1 lists the FABMS data for selective photoactive wires and model viologen compounds, and their respective pseudorotaxanes.

Table 1. LSIMS[a] data for the threads $\mathbf{16}\cdot 2PF_6$, $\mathbf{1}\cdot 4PF_6$ and $\mathbf{2}\cdot 4PF_6$, and their inclusion complexes[b] with the crown ethers **8** and **9**.

	M[c]	$[M - PF_6]^+$	$[M - 2PF_6]^+$
$\mathbf{16}\cdot 2PF_6$	887	741	596
$[\mathbf{16}\cdot\mathbf{8}][PF_6]_2$	1422	1277	1132
$[\mathbf{16}\cdot\mathbf{9}][PF_6]_2$	1522	–	–
$\mathbf{1}\cdot 4PF_6$	1590	1445	1300
$[\mathbf{1}\cdot\mathbf{8}][PF_6]_4$	2127	1982	1836
$[\mathbf{1}\cdot\mathbf{9}][PF_6]_4$	2227	–	–
$\mathbf{2}\cdot 4PF_6$	2000	–	–
$[\mathbf{2}\cdot\mathbf{8}][PF_6]_4$	–	1837	1694
$[\mathbf{2}\cdot\mathbf{9}][PF_6]_4$	–	1937	1794

[a] Liquid secondary ion mass spectometry (LSIMS) was carried out on a VG-Zab Spec mass spectrometer (accelerating voltage, 8 kV; resolution, 2000). Spectra were recorded in the positive-ion mode at a scan speed of 5 s per decade. Samples were dissolved in a small volume of 3-nitrobenzyl alcohol. [b] Samples were prepared in MeCN (0.5 mL) with 1 equiv of crown ether and 1 equiv of thread (3–6 μmol). [c] The molecular weight of the appropriate hexaflourophosphate salt.

Further qualitative evidence for the formation of a pseudorotaxanelike complexation was obtained from changes in the chemical-shift values (Δδ) in the ^{1}H NMR spectra of the photoactive wires before and after the addition of an equimolar amount of the crown ethers. For example, the aromatic protons of uncomplexed **8** resonate at $\delta = 6.75$. However, on complexation with $\mathbf{16}^{2+}$, an upfield shift of 0.28 ppm is observed.

The association constants for several pseudorotaxane-type structures obtained from electron-acceptor threads and electron-donor rings (or vice versa) have been previously reported.[2–6, 28] The values of the association constants between $\mathbf{2}^{4+}$ and **9** in ethanol and MeCN, or between $\mathbf{3}^{4+}$ and **9** in ethanol, have been estimated to be $2 \times 10^4\,\mathrm{M}^{-1}$ and $7 \times 10^5\,\mathrm{M}^{-1}$, respectively, by fluorescence-quenching measurements (see Experimental Section). More details will be given in Section 6.

4. Reference compounds: In order to understand the photochemical and photophysical properties of a multicomponent species, it is important to know the behavior of the isolated components.[13] As far as the photosensitizer is concerned, for both $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$ we can take $[Ru(bpy)_3]^{2+}$ ($\mathbf{4}^{2+}$) as a reference compound since its properties are only slightly affected by methyl substitution.[9] For $\mathbf{3}^{4+}$, the reference compound is $[Ru(tpy)_2]^{2+}$ ($\mathbf{5}^{2+}$), whose properties are not strongly affected by phenyl substitution in the 4′-tpy position.[14a] For the electron-acceptor units, suitable reference compounds are the 1,1′-dimethyl-4,4′-bipyridinium dication ($\mathbf{6}^{2+}$) and the N,N′-dimethyl-2,7-diazapyrenium dication ($\mathbf{7}^{2+}$).

5. Absorption spectra, luminescence properties, and photoinduced processes of the wire-type compounds: Absorption and luminescence data for the wire-type compounds $\mathbf{1}^{4+}$–$\mathbf{3}^{4+}$

and for the reference compounds **4**$^{2+}$, **5**$^{2+}$, **6**$^{2+}$, and **7**$^{2+}$, all represented in Figure 2, are collected in Table 2.

Table 2a. Absorption and luminescence properties at 298 K[a] of the wires **1**$^{4+}$, **2**$^{4+}$, and **3**$^{4+}$, and reference compounds.

	Absorption[b]		Fluorescence[c]			Phosphorescence[d]		
	λ_{max} [nm]	ε_{max} [L mol^{-1} cm^{-1}]	λ_{max} [nm]	τ [ns]	I_{rel}	λ_{max} [nm]	τ [ns]	I_{rel}
1^{4+}	286	79000				–	–	< 1
	451	11000						
2^{4+}	287	94000				615	1.6	≈ 5
	457	14500						
3^{4+}	279	54000	–	–	< 1	–	–	–
	308	65000						
	421[e]	14400[e]						
	482	20300						
4^{2+}	287	72000				610	190	1000
	451	12000						
5^{2+}[f]	270	46000				629	0.25	< 0.1
	307	28000						
	474	10400						
6^{2+}	260	19000						
7^{2+}	418[g]	15000[g]	428	9.7	1000			

[a] Butyronitrile solution, unless otherwise noted. [b] MeCN solution. [c] DAP-based. [d] Ru-based. [e] λ_{max} and lowest energy feature of a structured band of the DAP^{2+} subunit. [f] Data from ref. [14a]. [g] λ_{max} and lowest energy feature of a structured band.

Table 2b. Luminescence properties at 77 K[a] of the wires **1**$^{4+}$, **2**$^{4+}$, and **3**$^{4+}$, and reference compounds.

	Fluorescence[b]		Phosphorescence[b]		Phosphorescence[c]	
	λ_{max} [nm]	τ [ns]	λ_{max} [nm]	τ [ms]	λ_{max} [nm]	τ [μs]
1^{4+}					600	6.6
2^{4+}					597	5.6
3^{4+}	–	–	–	–	632	12
4^{2+}					580	6.1
5^{2+}[d]					607	10.6
7^{2+}	424	10.7	586	900		

[a] Butyronitrile rigid matrix. [b] DAP-based. [c] Ru-based. [d] Data from ref. [14a].

The absorption spectra at room temperature of **1**$^{4+}$, and of the **4**$^{2+}$ and **6**$^{2+}$ reference compounds are shown in Figure 3. The Ru^{II} complex **4**$^{2+}$ shows the well-known, very intense ligand-centered (LC) bands in the UV region and moderately intense metal-to-ligand charge-transfer (MLCT) bands in the visible region. The viologen dication **6**$^{2+}$ shows only a moderately intense band in the UV region. The absorption spectrum of **1**$^{4+}$ is practically equal to the sum of the spectra of the two component units. As shown in Table 2, **6**$^{2+}$ is not luminescent, whereas **4**$^{2+}$ shows a relatively strong emission from its lowest energy ^{3}MLCT level. In butyronitrile fluid solution at room temperature, the strong luminescence of the Ru-based unit of **1**$^{4+}$ is quenched by a factor of at least 10^3. The rate constant of the quenching process ($k_q > 5 \times 10^9$ s^{-1}) evaluated from the luminescence-intensity quenching [Eq. (6) in the Experimental Section] is not inconsistent with the value ($k_q = 5.9 \times 10^{10}$ s^{-1}) obtained by Mallouk, et al.[20] from picosecond transient-spectroscopy experiments carried out in MeCN solution on the very similar $[(bpy)_2Ru(Mebpy)-CH_2-viologen-CH_3]^{4+}$ system. These researchers have also shown that the quenching process is due, as expected, to electron transfer from the ^{3}MLCT excited state of the Ru-based unit to the 4,4′-bipyridinium unit and that the back electron-transfer reaction is very fast ($k_q = 4.0 \times 10^{10}$ s^{-1}).

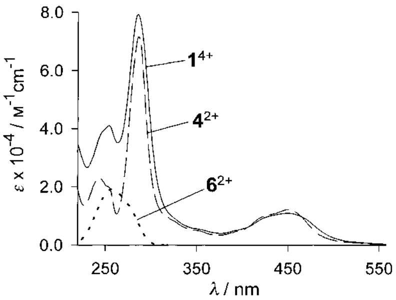


Figure 3. Absorption spectra in MeCN solution at room temperature of **1**$^{4+}$ (—), **4**$^{2+}$ (- - -), and **6**$^{2+}$ (···).

In a rigid matrix at 77 K, the luminescence of the Ru-based moiety of **1**$^{4+}$ is not quenched at all (Table 2). Under such conditions, in fact, the electron-transfer quenching process is most likely endoergonic because of the lack of solvent repolarization (vide infra).[29] The excitation spectrum of the Ru-based emission in a rigid matrix at 77 K shows that excitation of the 4,4′-bipyridinium unit leads to emission from the Ru-based unit. This observation indicates that an energy-transfer process takes place from the bipyridinium to the Ru-based unit, but the efficiency of the process is difficult to evaluate because an intense absorption band of the Ru-based component overlaps with the absorption band of the bipyridinium unit (Figure 3).

In **2**$^{4+}$, the presence of four methylene groups between the Ru-based unit and the 4,4′-bipyridinium unit slows down the rate of the photoinduced- (forward) and back-electron-transfer processes. In a fluid solution at room temperature the luminescence of the Ru-based unit of this system can be clearly seen (Table 2). Its intensity, however, is strongly quenched compared with that of the reference compound **4**$^{2+}$ and its lifetime is 1.6 ns—120 times shorter than that of **4**$^{2+}$. By use of Equation (5) [see Experimental Section], a rate constant of 6.2×10^8 s^{-1} is obtained from the excited-state quenching, which compares well with the value of 6.5×10^8 s^{-1} obtained by Mallouk et al.[20] for an analogous compound not carrying methyl-substituents on the bpy ligands. In a rigid matrix at 77 K, the luminescence of the Ru-based moiety of **2**$^{4+}$ is not quenched (Table 2) and excitation of the 4,4′-bipyridinium unit leads to emission of the Ru-based unit, as described for the system **1**$^{4+}$.

The absorption spectra of **3**$^{4+}$, and of the **5**$^{2+}$ and **7**$^{2+}$ reference compounds at room temperature in MeCN solution are shown in Figure 4. $[Ru(tpy)_2]^{2+}$ exhibits very intense LC bands in the UV region and moderately intense, broad MLCT bands in the visible, whereas **7**$^{2+}$ shows, besides a very intense band around 260 nm, two moderately intense, structured bands in the 300–450 nm region. The absorption spectrum of **3**$^{4+}$ almost matches the sum of the spectra of **5**$^{2+}$ and **7**$^{2+}$. The lack of exact matching can be attributed to the fact that the reference compounds are slightly different from the two

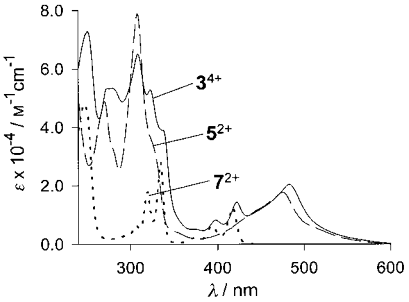


Figure 4. Absorption spectra in MeCN solution at room temperature of $\mathbf{3}^{4+}$ (—), $\mathbf{5}^{2+}$ (- - -), and $\mathbf{7}^{2+}$ ($\cdots$).

chromophoric units of the wire-type compound. The emission spectra of the three compounds in butyronitrile rigid matrix are shown in Figure 5. The diazapyrenium dication $\mathbf{7}^{2+}$ shows both fluorescence and phosphorescence. The ^{3}MLCT band of $\mathbf{5}^{2+}$ lies at slightly lower energy than the phosphorescence band of $\mathbf{7}^{2+}$. One can see that in the emission spectrum of $\mathbf{3}^{4+}$ at 77 K only one band is present, which is very similar to that of the reference compound $\mathbf{5}^{2+}$.

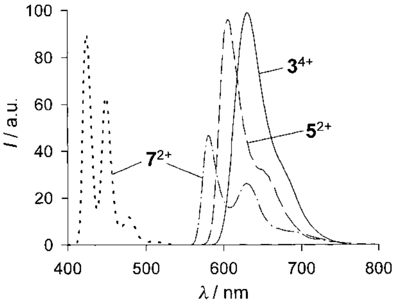


Figure 5. Emission spectra in butyronitrile rigid matrix at 77 K of $\mathbf{3}^{4+}$ (—), $\mathbf{5}^{2+}$ (- - -), and $\mathbf{7}^{2+}$ (fluorescence, $\cdots$; phosphorescence, -·-·-·-).

The photoinduced processes taking place in $\mathbf{3}^{4+}$ can be discussed with reference to the energy-level diagram shown in Figure 6. The energy values for the ^{3}MLCT, S_1, and T_1 levels have been obtained from the highest energy feature of the emission spectra at 77 K; as a rough estimation of the energy of ^{1}MLCT, we have taken the maximum of the corresponding absorption band. The energy of the $\mathbf{P}^+$–$\mathbf{A}^-$ charge-transfer level is assumed to be that obtained from the reduction potentials of $[\mathrm{Ru(tpy)_2}]^{3+}$ (+1.30 V, vs SCE)[14a] and $\mathbf{7}^{2+}$ (−0.44 V, vs Ag/AgCl)[27] species. As mentioned when discussing the previous wire-type compounds, one can expect that the $\mathbf{P}^+$–$\mathbf{A}^-$ level to be somewhat destabilized in rigid matrix at 77 K because of the lack of solvent repolarization.[29]

As schematically depicted in Figure 6, at room temperature excitation of the Ru-based unit (**P**) leads to formation of its ^{3}MLCT level, which is expected to transfer an electron to the DAP-based unit (**A**) to give the $\mathbf{P}^+$–$\mathbf{A}^-$ species. Although this process is expected to be relatively fast, its occurrence cannot be proved by luminescence measurements, since the isolated Ru-based unit (i.e., the reference compound $\mathbf{5}^{2+}$) is already substantially nonemissive (Table 2). The efficiency of the coupling of the two units (**P** and **A**) is shown by the quenching of the strong fluorescence of the diazapyrenium-based unit (Table 2 and Figure 5). From Equation (6) [see Experimental Section], a lower limiting value of $1\times10^{11}\,\mathrm{s}^{-1}$ is obtained for the rate constant of this quenching reaction. As illustrated by the schematic energy-level diagram of Figure 6, quenching of the fluorescence of the diazapyrenium-based unit can occur by energy or electron transfer.

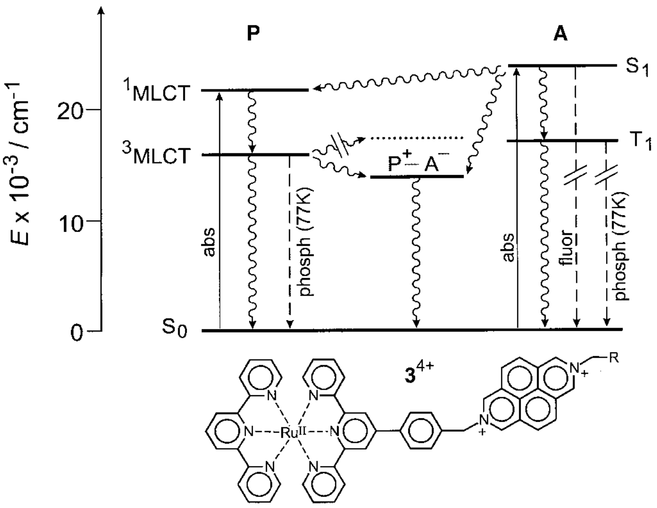


Figure 6. Energy-level diagram for $\mathbf{3}^{4+}$ in a simplified representation in which **P** (photosensitizer) and **A** (electron acceptor) stand for the two component units. The most relevant absorption (full lines), emission (dashed lines), and radiationless (wavy lines) processes are indicated. The horizontal dotted line represents an estimation of the $\mathbf{P}^+$–$\mathbf{A}^-$ energy level in rigid matrix at 77 K. For more details, see text.

In a rigid matrix at 77 K, the luminescence of the Ru-based unit of $\mathbf{3}^{4+}$ is not affected by the presence of the diazapyrenium-based unit, confirming that the electron-transfer quenching process of the ^{3}MLCT level cannot occur under such conditions because of the destabilization of the $\mathbf{P}^+$–$\mathbf{A}^-$ species (Figure 6). It is interesting to note, however, that the quenching of the S_1 excited state of the diazapyrenium-based unit occurs very rapidly also in rigid matrix at 77 K ($k_q \geq 1\times10^{11}\,\mathrm{s}^{-1}$). Although the exoergonicity of the electron-transfer quenching process on excitation of S_1 is so large that it is possible that it could take place even in rigid matrix,[29] the strict similarity between absorption and excitation spectra indicates that the quenching process takes place by energy transfer. It should also be noticed that at 77 K the T_1 excited state of the diazapyrenium-based unit is quenched by the lower lying ^{3}MLCT level of the Ru-based unit (Table 2).

6. Photoinduced dethreading of the pseudorotaxane structures

6.1. Strategy: The photoinduced dethreading of a pseudorotaxane as illustrated in Figure 1b can only occur if light excitation disrupts the donor–acceptor interaction. As already described, light excitation of wires $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$ causes an electron-transfer process with oxidation of the photosensitizer and reduction of the electron acceptor (in the following equations, the photosensitizer and electron-acceptor moieties of the wires will be schematically indicated by Ru^{2+} and A^{2+}, respectively).

The photoinduced electron-transfer process [Eqs. (1) and (2)] is followed by a very fast back-electron-transfer reaction

[Eq. (3)]. Therefore, the occurence of the photoinduced electron-transfer process in the wire of a pseudorotaxane

$$\mathrm{Ru}^{2+}\text{–}\mathbf{A}^{2+}\text{–} + h\nu \rightarrow {}^{*}\mathrm{Ru}^{2+}\text{–}\mathbf{A}^{2+}\text{–} \tag{1}$$

$${}^{*}\mathrm{Ru}^{2+}\text{–}\mathbf{A}^{2+}\text{–} \rightarrow \mathrm{Ru}^{3+}\text{–}\mathbf{A}^{+}\text{–} \tag{2}$$

$$\mathrm{Ru}^{3+}\text{–}\mathbf{A}^{+}\text{–} \rightarrow \mathrm{Ru}^{2+}\text{–}\mathbf{A}^{2+}\text{–} \tag{3}$$

system cannot cause dethreading of the crown ether, since this process, requiring extensive nuclear motions, is much slower. Dethreading can only occur if the photoinduced process leads to a permanent reduction of the electron acceptor. This result can be obtained when a suitable sacrifical electron donor (Red) is present in the solution. In such a case, a fast reaction between the sacrifical electron donor and the oxidized photosensitizer unit of the wire [Eq. (4)] can compete with the intra-wire back-electron transfer reaction [Eq. (3)].

$$\mathrm{Ru}^{3+}\text{–}\mathbf{A}^{+}\text{–} + \mathrm{Red} \rightarrow \mathrm{Ru}^{2+}\text{–}\mathbf{A}^{+}\text{–} + \mathrm{Products} \tag{4}$$

Permanent reduction of the electron-acceptor unit of the wire can thus be obtained and dethreading can follow (Figure 1b). The most suitable sacrifical electron donors are amines, particularly TEOA. Introduction of amines into our systems, however, is problematic. The wire type compounds $\mathbf{1}^{4+}$, $\mathbf{2}^{4+}$, and $\mathbf{3}^{4+}$ are stable in ethanol, acetonitrile, and dichloromethane solution both in the dark and under light excitation. In aprotic solvents, however, addition of amines causes the decomposition of $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$, as a result of a nucleophilic attack by the amine nitrogen on the electrophilic methylene groups adjacent to the bipyridinium units; this breaks the covalent bond between the Ru-complex and the electron acceptor. This decomposition process is clearly shown by luminescence measurements. For $\mathbf{1}^{4+}$ and $\mathbf{2}^{4+}$ in MeCN solution at room temperature, the emission of the Ru^{2+}-based moieties are strongly quenched by the covalently-linked bipyridinium electron acceptor ($\mathbf{A}^{2+}$). Upon addition of TEOA, while the absorption spectrum of the solution remains unaffected, the Ru-based luminescence progressively increases, indicating the separation of the two moieties; this process, however, is not observed in ethanol. In the case of $\mathbf{3}^{4+}$, addition of TEOA to an MeCN solution causes completely different spectral changes.[4] Upon subsequent addition of $\mathrm{CF_3COOH}$ the changes in the absorption spectrum are fully reversed and no fluorescence of free diazapyrenium-based units is observed. This behavior is consistent with the amine forming an adduct with the diazapyrenium unit and not chemically degrading $\mathbf{3}^{4+}$.

6.2. Pseudorotaxane of the $\mathbf{2}^{4+}$ *wire*: Since the back electron-transfer reaction in $\mathbf{2}^{4+}$ is not too fast ($3.2 \times 10^{9}\,\mathrm{s}^{-1}$ in the analogous Mallouk's compound),[20] and it is slower than in $\mathbf{1}^{4+}$, it appeared feasible to obtain permanent reduction of the 4,4′-bipyridinium unit under continuous-irradiation conditions in EtOH in the presence of TEOA as sacrificial electron donor [Eq. (4)]. Irradiation with visible light ($\lambda > 350$ nm) of a $3 \times 10^{-5}\,\mathrm{M}$ EtOH solution of $\mathbf{2}^{4+}$ (as $\mathrm{PF_6^-}$ salt) containing 0.01 M TEOA caused noticeable spectral changes (Figure 7), indicating more than 90% reduction of the 4,4′-bipyridinium electron-acceptor unit. When the irradiation was stopped and oxygen was allowed to enter the irradiated solution, the spectral changes were reversed and the original absorption spectrum was again obtained. Therefore, this system seemed suitable to be used as a photoactive wire of a mechanical machine of the type shown in Figure 1b.

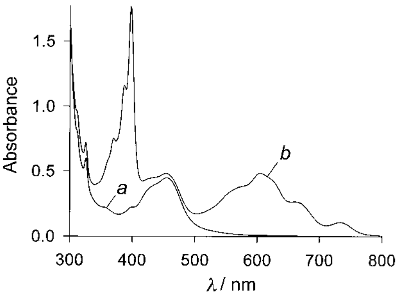


Figure 7. Spectral changes upon irradiation of an EtOH solution containing $3 \times 10^{-5}\,\mathrm{M}$ $\mathbf{2}^{4+}$, $3 \times 10^{-5}\,\mathrm{M}$ $\mathbf{9}$, and 0.01 M TEOA: a) initial spectrum; b) spectrum at the end of the irradiation (complete reduction of the electron-acceptor unit).

Since $\mathbf{6}^{2+}$ and crown ethers such as **8** and **9** self-assemble into pseudorotaxane structures,[30] we prepared an EtOH solution containing $3 \times 10^{-5}\,\mathrm{M}$ $\mathbf{2}^{4+}$ and $3 \times 10^{-5}\,\mathrm{M}$ $\mathbf{9}$. It is known[4] that when the crown ether **9** is complexed in the rotaxane structure, the fluorescence of the 1,5-dioxynaphthalene units is quenched because of the presence of low-energy excited states due to the interaction with the electron-acceptor 4,4′-bipyridinium unit of the wire. From the residual fluorescence intensity of **9** (compared with that of a reference solution containing only **9**), we determined that in the two component solution 30% of **9** was complexed with the $\mathbf{2}^{4+}$ wire.[31] Light excitation of this system under the same conditions as those described above for $\mathbf{2}^{4+}$ alone led to the permanent, almost quantitative reduction of the 4,4′-bipyridinium units of the wire (as shown by the formation of the characteristic absorption bands around 400 and 600 nm, Figure 7). Under such conditions, we expected dethreading of crown ether **9** from $\mathbf{2}^{4+}$ as schematically indicated in Figure 1b, with a corresponding increase in the fluorescence intensity of the crown ether ($\lambda_{\max} = 345$ nm). An increase in the fluorescence intensity was indeed observed, indicating that the photoinduced dethreading process does take place.

If oxygen is allowed to enter the irradiated solution, the 4,4′-bipyridinium unit is oxidized (as shown by the disappearence of the visible absorption bands) and rethreading takes place (as shown by the decrease of the fluorescence intensity of the crown ether). Quantitatively, however, the increase in the fluorescence intensity was about two-thirds that expected for quantitative dethreading. In principle, this incomplete recovery of the crown ether fluorescence intensity could be due to a quenching of the excited state of **9** by the reduced acceptor unit of $\mathbf{2}^{4+}$. However, this possibility can be ruled out in our system because i) it is implausible that **9** remains assembled around the reduced acceptor, and ii) the short excited-state lifetime of the 1,5-dioxynaphthalene units (7 ns in MeCN) and the very low concentration of the wire do not allow the occurrence of a bimolecular dynamic quenching process.

In an attempt to elucidate the lack of quantitative recovery of the crown fluorescence, we performed experiments which showed that **9** gives an adduct not only with $\mathbf{6}^{2+}$, but also with $\mathbf{4}^{2+}$, and that the fluorescence of **9** is quenched even in the case of its adduct with $\mathbf{4}^{2+}$. The values of the association constant of the adducts of the crown ether **9** with $\mathbf{4}^{2+}$ and $\mathbf{6}^{2+}$ are about 5000 and 15000 M^{-1}, respectively. Therefore, in the ethanol solution containing $\mathbf{2}^{4+}$ and **9**, only about three-quarters of the quenching of the fluorescence of **9** was due to the formation of a pseudorotaxane-type structure (i.e., association of **9** with the 4,4′-bipyridinium moiety of $\mathbf{2}^{4+}$), whereas the remaining quenching was due to association of **9** with the photosensitizer moiety. It follows that upon photoreduction of 4,4′-bipyridinium moiety of $\mathbf{2}^{4+}$ at most three-quarters of the quenching can be recovered. This is in good agreement with the results obtained (two-thirds recovery), if one considers the experimental uncertainity of the fluorescence measurements. Clearly, to obtain more precise results one should start with a system exhibiting a much larger association constant between the electron-donor ring and the electron-acceptor unit of the wire.

6.3. Pseudorotaxane of the $\mathbf{3}^{4+}$ wire: This system was synthesized in an attempt to explore the possibility of using the 2,7-diazapyrenium unit as an electron-acceptor component of the wire. Such a unit is known to give a pseudorotaxane-type adduct with the crown ether **9**, which exhibits a very large association constant.[4] Titration of an MeCN solution of $\mathbf{3}^{4+}$ (1.0×10^{-4} M) with **9** caused an increase in absorbance in the visible region (e.g., at 490 nm) and a decrease in the fluorescence intensity of **9** (compared with a reference solution containing only **9**), as expected when the formation of the pseudorotaxane occurs.[4, 37] From the titration curve, a value of about 7×10^5 M^{-1} was obtained for the association constant, showing that in a solution containing 5×10^{-5} M $\mathbf{3}^{4+}$ and 1×10^{-4} M **9** almost 100% of the $\mathbf{3}^{4+}$ molecules are complexed in a pseudorotaxane structure. This favorable equilibrium was an excellent starting point. However, when we added 0.01 M TEOA to the solution to perform the photochemical experiments, we observed a strong color change (from orange to greenish) that was found to be due to the formation of an adduct beween the diazapyrenium-unit of the $\mathbf{3}^{4+}$ wire and TEOA, as described previously. Other amines (e.g., hexylamine and tributylamine) were found to behave in a similar way. The adduct between the DAP unit and amines is so strong that the addition of the amine causes dethreading of the pseudorotaxane structure in the dark. While this result prevented us from performing photochemically induced dethreading experiments, it opened the way to the design of systems in which dethreading and rethreading can be chemically controlled, as described in detail elsewhere.[4, 32]

Conclusions

We have synthesized three wire-type compounds containing a photosensitizer and an electron-acceptor unit. The investigations have shown that the theoretically ideal design of light-driven pseudorotaxane-type mechanical machines based on wires made of an electron-transfer photosensitizer covalently-linked to an electron acceptor (Figure 1b) is not simple in practice, because of incompatibilities between the various components of the system. A wire like $\mathbf{2}^{4+}$ is appropriate from a photochemical viewpoint, but the association constant between the 4,4′-bipyridinium electron-acceptor unit of the wire and the electron-donor moieties of the ring **9** is not sufficiently large to allow quantitative formation of pseudorotaxane species. Under such conditions, however, photoinduced dethreading of the fraction of pseudorotaxane species present in the solution has been demonstrated. When the 4,4′-bipyridinium electron-acceptor unit was replaced by the 2,7-diazapyrenium one, which is much more appropriate from the viewpoint of association, we found that the system was incompatible with the sacrificial electron donor used in the photochemical cycle. As a spin-off of these studies, we have discovered that one can design pseudorotaxane systems in which the dethreading/rethreading process can be controlled by chemical stimuli.

We have also shown that, in the first two wire-type systems displayed in Figure 2a, the ^{3}MLCT excited state of the Ru-based unit is quenched by very fast electron transfer to the bipyridinium or diazapyrenium unit in fluid polar solvents, whereas this process does not take place in rigid matrix at 77 K because of the lack of solvent repolarization. In $\mathbf{3}^{4+}$, the strong fluorescence of the DAP unit is strongly quenched ($k_q \geqslant 1 \times 10^{11}$ s^{-1}) by the Ru-based unit both in fluid solution at room temperature and in rigid matrix at 77 K. In the latter case, the excitation spectrum shows that the quenching process takes place by an energy-transfer mechanism.

Experimental Section

General methods: Chemicals were purchased from Aldrich and used as received. Solvents were dried (MeCN and CH_2Cl_2 were distilled over CaH_2 under nitrogen) and reagents were purified where necessary by literature methods.[33] All the syntheses were carried out with no protection against ambient light. [Ru(tpy)Cl_3],[25] 4′-(*p*-bromomethylphenyl)-2,2′:6′,2″-terpyridine,[26] 2,7-diazapyrene,[27] 5-methyl-2,2′-bipyridine,[34] and the crown ethers **8**[35] and **9**[36] were prepared according to published literature procedures. Thin-layer chromatography (TLC) was carried out on aluminium sheets precoated with Merck 5735 Kieselgel 60F. Developed plates were dried and examined under UV light. Column chromatography was carried out with Kieselgel 60 (0.040–0.063 mm mesh, Merck 9385). Melting points were determined with an Electrothermal 9200 melting point apparatus and are uncorrected. Microanalyses were performed by the University of Sheffield Microanalytical Service. Low-resolution mass spectra (MS) were obtained from a Kratos Profile instrument operating in electron impact (EIMS) or chemical ionization (CI) modes, while fast atom bombardment (FABMS) were recorded on a Kratos MS80 spectrometer operating at 8 keV in the positive-ion mode at a scan speed of 10 s per decade (with a krypton or xenon primary atom beam in conjunction with a 3-nitrobenzyl alcohol (NOBA) matrix). ^{1}H NMR spectra were recorded on a Bruker AC300 (300 MHz) (with the deuterated solvent as lock and residual solvent or tetramethylsilane as internal reference) spectrometers. ^{13}C NMR spectra were recorded on a Bruker AC300 (75 MHz) spectrometer with the JMOD pulse sequence. The description of the experimental procedure and characterization by mass spectroscopy, ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis are given as Supporting Information.

The absorption spectra were recorded in MeCN (Merck Uvasol™) solution. The luminescence experiments were carried out in MeCN or butyronitrile (Fluka) solution at room temperature and in butyronitrile rigid matrix at 77 K. The concentration of the solution was of the order of 10^{-5} M. Absorption and emission spectra were recorded with a Perkin–Elmer λ6 spectrophotometer and a Perkin–Elmer LS-50 spectrofluorimeter, respectively. Fluorescence lifetimes were measured with an Edinburgh 199 single-photon counting instrument. Photochemical experiments were carried out with a tungsten halogen lamp (150 W, 24 V, $\lambda > 350$ nm). The photoinduced electron-transfer reactions, including the dethreading experiments on the pseudorotaxane based on $\mathbf{2}^{4+}$ in the presence of a sacrificial electron donor, were performed in degassed EtOH (Merck Uvasol™) solutions. The chemical dethreading of the pseudorotaxane based on $\mathbf{3}^{4+}$ was performed in MeCN solution. For more details on the choice of the experimental conditions see the Results and Discussion section. In the measurement of the luminescence intensity, a correction for the fraction of absorbed light by the relevant chromophoric unit had to be performed.[37] Experimental errors are as follows: luminescence intensity, 15%; luminescence lifetimes, 10%. Association constants were evaluated by titration methods following changes in the absorption or emission bands.[3, 4, 37] The values of association constants between bipyridinium-based threads and crown ethers **8** and **9** are given as Supporting Information. The rate constants of the intercomponent energy- and electron-transfer quenching processes were evaluated by the use of Equations (5) or (6)

$$k_q = \frac{1}{\tau} - \frac{1}{\tau_0} \qquad (5)$$

$$k_q = \frac{1}{\tau}\left(\frac{I_0}{I} - 1\right) \qquad (6)$$

I_0 and τ_0 are the luminescence intensity and lifetime of the reference compound, and I and τ are the luminescence intensity and lifetime of the wire-type compound under the same experimental and instrumental conditions.

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