

## Supporting Text

### Materials and Methods

**Synthesis.** The synthesis and the electrochemical and spectroscopic properties of  $1^{6+}$ , its dumbbell-shaped component  $2^{6+}$ , and the model compound of the photosensitizer unit  $3^{2+}$  (Scheme 1) have been previously reported (1).

**Spectroelectrochemical Measurements.** Spectroelectrochemical measurements in acetonitrile Romil-Hi-Dry were performed in situ with a custom-made OTTLE (optically transparent thin layer electrochemical) cell (2) by using an Agilent Technologies 8543 diode array spectrophotometer. The working and counter electrodes were Pt minigrids ( $\approx 0.3 \text{ cm}^2$ ), and the quasi-reference electrode was an Ag wire; all three electrodes are melt-sealed into a polyethylene spacer. The thickness of the layer, determined by spectrophotometry, was  $180 \text{ }\mu\text{m}$ .

**Photophysical Measurements.** Measurements were carried out on acetonitrile Merck Uvasol solutions with concentrations ranging from  $5.0 \times 10^{-5}$  to  $1.0 \times 10^{-4} \text{ mol}\cdot\text{liter}^{-1}$ . UV-Vis absorption spectra were recorded at room temperature on air-equilibrated solutions with a PerkinElmer  $\lambda 40$  spectrophotometer. Luminescence spectra were obtained with a PerkinElmer LS-50 spectrofluorimeter, equipped with a Hamamatsu R928 phototube, on solutions degassed with four freeze-pump-thaw cycles and sealed under vacuum ( $7 \times 10^{-9} \text{ bar}$ ). The experimental error on the wavelength values is estimated to be  $\pm 1 \text{ nm}$ .

**Flash Photolysis Experiments.** Luminescence decay and transient absorption experiments were performed in acetonitrile Merck Uvasol by exciting the sample with  $10 \text{ ns}$  (fwhm) pulses of a Continuum Surelite I-10 Nd:YAG laser. In the transient absorption studies, a  $150\text{-W}$  Xe lamp (Applied Photophysics model 720; power supply, model 620) perpendicular to the laser beam was used as a probing light; for the kinetic investigations in the  $0\text{--}10 \text{ }\mu\text{s}$  time window, a pulsing unit (Applied Photophysics model 03-102,  $2\text{-ms}$  pulses) was also employed. Excitation was performed at  $\lambda = 532 \text{ nm}$ , obtained by frequency doubling. A shutter was placed between the

lamp and the sample and opened only during the measurements to prevent phototube fatigue and photodecomposition. Suitable pre- and post-cutoff and bandpass filters were also used to avoid photodecomposition and interferences from scattered light. The light was collected in a PTI monochromator (model 01-001; 1,200 lines/mm grating; slit width, 0.25 mm; resolution, 1 nm), detected by a Hamamatsu R928 tube, and recorded on a Tektronix TDS380 (400 MHz) digital oscilloscope connected to a PC. Synchronous timing of the system was achieved by means of a built-in-house digital logic circuit. Each decay was obtained by averaging at least 20 pulses.

The accuracy on the wavelength values was estimated to be  $\pm 2$  nm. The experimental error was 4% for the lifetime values and 20% for the quantum yield of the photoinduced electron transfer processes.

## Luminescence Data

The luminescence lifetime values at different temperatures for rotaxane  $\mathbf{1}^{6+}$ , dumbbell-shaped component  $\mathbf{2}^{6+}$ , and reference compound  $\mathbf{3}^{2+}$  are reported in Table 3.

The electron transfer rate constant  $k_{et}$  (step 2, Scheme 2a) can be obtained from Eq. **S1**:

$$k_{et} = \frac{1}{\tau} - \frac{1}{\tau_0} , \quad (\text{S1})$$

where  $\tau$  is the luminescence lifetime and  $\tau_0$  is the luminescence lifetime of the reference compound  $\mathbf{3}^{2+}$ , taken as the time constant for the deactivation of  $*\mathbf{P}^{2+}$  by all pathways other than electron transfer (step 3, Scheme 2a). The quantum yield values for the electron transfer process can be obtained from Eq. **S2**:

$$\Phi_{et} = k_{et} \times \tau . \quad (\text{S2})$$

The results obtained are gathered in Table 3.

## Transient Absorption Experiments in the Absence of the Electron Relay

**Transient Absorption Spectra.** The transient absorption spectral changes observed upon flash excitation of  $\mathbf{1}^{6+}$  are reported in Fig. 5. The transient spectrum in the *inset*, which was recorded 6  $\mu\text{s}$  after light excitation, exhibits the features of the monoreduced 4,4'-bipyridinium unit  $\mathbf{A}_1^+$  (3), and a residual bleaching in the spectral region of the ground state absorption of  $\mathbf{P}^{2+}$ . There is no evidence of formation of the monoreduced 3,3'-dimethyl-4,4'-bipyridinium unit,  $\mathbf{A}_2^+$ , whose spectrum (4) is substantially different from that of  $\mathbf{A}_1^+$ . These results indicate that the species formed upon light excitation of  $\mathbf{1}^{6+}$  is a compound in which an electron has been transferred from the  $^*\mathbf{P}^{2+}$  excited state to the  $\mathbf{A}_1^{2+}$  unit. Note that there is no isosbestic point at  $\lambda$  around 400 nm. The same results have been obtained for dumbbell  $\mathbf{2}^{6+}$ .

It should be noted that, on the basis of the redox potentials of the  $\mathbf{P}^{2+}$ ,  $\mathbf{A}_1^{2+}$  and  $\mathbf{A}_2^{2+}$  ( $E_{1/2}(\mathbf{A}_2^{2+}/\mathbf{A}_2^+) = -0.74$  V versus SCE) units, the observed electron transfer from  $^*\mathbf{P}^{2+}$  to  $\mathbf{A}_1^{2+}$  could occur by a two-step mechanism, i.e., photoinduced transfer from  $^*\mathbf{P}^{2+}$  to  $\mathbf{A}_2^{2+}$  followed by a charge shift from  $\mathbf{A}_2^+$  to  $\mathbf{A}_1^{2+}$ . We did not observe the transient absorption bands typical of the  $\mathbf{A}_2^+$  unit, indicating that either  $\mathbf{A}_2^{2+}$  is not involved in the electron transfer process, or the  $\mathbf{A}_2^+$  species disappears as soon as it is formed. The fact that the rate constant of luminescence quenching is larger for  $\mathbf{2}^{6+}$  than for  $\mathbf{1}^{6+}$  (Table 3) is an evidence for the one-step route, because in the case of the two-step route one would expect similar quenching rate constants for the two compounds. Moreover, the higher value of the rate constant found for  $\mathbf{2}^{6+}$  is consistent with direct electron transfer from  $^*\mathbf{P}^{2+}$  to  $\mathbf{A}_1^{2+}$ , which lies in the normal Marcus region (5,6), because such a process is more exoergonic in  $\mathbf{2}^{6+}$  compared with  $\mathbf{1}^{6+}$ .

Nanosecond laser excitation of model compound  $\mathbf{3}^{2+}$  in degassed acetonitrile solution produced (Fig. 6) an increase in absorption below 400 nm and a bleaching in the spectral region of the ground-state absorption (400-500 nm). These changes are consistent with the formation of the  $^3\text{MLCT}$  excited state of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  type ( $\mathbf{P}^{2+}$ ) unit. The apparent bleaching observed above 580 nm is originated by the luminescence of the  $\mathbf{P}^{2+}$  unit. The decay time of the transient absorption spectrum (Fig. 6, *inset*) and that of the Ru-based luminescence are in full agreement.

It is important to note that an isosbestic point between the absorption spectra of the ground and excited states of  $\mathbf{3}^{2+}$  was found at  $\lambda_{\text{iso}} = 398$  nm. This observation and the fact that the spectrum

of  $\mathbf{A}_1^+$  possesses a very intense band peaking in the same region (Fig. 1) allowed us to monitor the formation and decay of the  $\mathbf{A}_1^+$  unit in the case of  $\mathbf{1}^{6+}$  and  $\mathbf{2}^{6+}$ , and hence to measure the rate constants for the forward ( $*\mathbf{P}^{2+}$  to  $\mathbf{A}_1^{2+}$ , step 2, Scheme 2a) and the back ( $\mathbf{A}_1^+$  to  $\mathbf{P}^{3+}$ , steps 5 and 6; see below) electron transfer processes. Typical transient absorption kinetics recorded at  $\lambda_{\text{iso}}$  are shown in Fig. 7.

**Electron Transfer Quantum Yield.** The quantum yield of the photoinduced electron transfer processes can be calculated by the transient absorption data as the ratio between the concentration of  $\mathbf{A}_1^+$  species formed by electron transfer and the total concentration of excited states produced by photoexcitation:

$$\Phi_{\text{et}} = \frac{[\mathbf{A}_1^+]}{[*\mathbf{P}]} = \frac{\Delta A(\lambda_{\text{iso}}) / \varepsilon(\lambda_{\text{iso}})}{|\Delta A(458)| / \varepsilon(458)}, \quad (\text{S3})$$

where  $\Delta A(\lambda_{\text{iso}})$  and  $\Delta A(458)$  are the transient absorption change at zero time monitored respectively at  $\lambda_{\text{iso}}$  and at the wavelength of maximum bleaching of the ground-state absorption of the  $\mathbf{P}^{2+}$  component.  $\varepsilon(\lambda_{\text{iso}})$  and  $\varepsilon(458)$  are the molar absorption coefficients of either  $\mathbf{1}^{6+}$  or  $\mathbf{2}^{6+}$ , respectively, at  $\lambda_{\text{iso}}$  (which is approximately equal to the  $\lambda_{\text{max}}$  of the UV band of  $\mathbf{A}_1^+$ ;  $\varepsilon_{\text{max}} = 35,000 \text{ liters}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) and at 458 nm, i.e., the  $\lambda_{\text{max}}$  of the visible absorption band of the  $\mathbf{P}^{2+}$  component ( $\varepsilon_{\text{max}} = 14,800 \text{ liters}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ). Such  $\Delta A$  values were obtained from the preexponential factors of the corresponding fitting profiles. Alternatively,  $\Phi_{\text{et}}$  can be estimated from the relative magnitude of the preexponential factors in the double exponential law employed to fit the recovery of the ground-state absorption in the 450-nm region.

## Transient Absorption Experiments in the Presence of Phenothiazine as an Electron Relay

**Shift of the Transient Absorption Maximum.** The motion of the ring towards station  $\mathbf{A}_2^{2+}$  upon reduction of  $\mathbf{A}_1^{2+}$  is expected to cause changes in the absorption spectrum of the rotaxane  $\mathbf{1}^{5+}$ , because it is likely that the two interconverting conformations,<sup>†</sup> B' and C' (Scheme 2b), have different absorption spectra. In the case of rotaxane  $\mathbf{1}^{5+}$ , we have indeed observed a shift of the  $\mathbf{A}_1^+$  band, while no shift was observed for the ringless compound  $\mathbf{2}^{6+}$  (Figs. 8 – 10).

**Kinetic Analysis.** The absorption spectrum of  $\mathbf{1}^{5+}$  at a certain time  $t$  can be described as

$$F(\lambda, t) = f_{B'}(\lambda) \times x_{B'}(t) + f_{C'}(\lambda) \times x_{C'}(t) \quad (\text{S4})$$

where  $f_{B'}(\lambda)$  and  $f_{C'}(\lambda)$  are the functions that describe the absorption spectra of conformations B' and C', and  $x_{B'}(t)$  and  $x_{C'}(t)$  are their time-dependent molar fractions, respectively. In principle, the spectra and time profiles can be extracted from the absorption spectra recorded as a function of time after introduction of one electron into the  $\mathbf{A}_1^{2+}$  station. However, since a deconvolution of the transient absorption spectra is too complicated, we decided to look at changes of parameters that can be determined more easily from the experiments, such as, for instance, the position of the absorption bands of the 4,4'-bipyridinium radical cation,  $\mathbf{A}_1^+$ . In particular, the UV band peaking at  $\approx 390$  nm is strong enough to be monitored with high precision and is so sharp that even minor differences in its position are easily detectable. We have found that the shift of this band obeys a first order law (see Fig. 3):

$$\left| \lambda_{\max, t} - \lambda_{\max, \infty} \right| = \left| \lambda_{\max, 0} - \lambda_{\max, \infty} \right| e^{-k_{\lambda} \times t} . \quad (\text{S5})$$

Brouwer *et al.* (8) demonstrated that, if the bands can be described with gaussian functions, and the displacement  $\Delta\lambda_{\max}$  of the maximum wavelength is small compared to band width, the shift

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<sup>†</sup> For the sake of simplicity we will use the term “conformations” for rotaxane structures that differ only for the position of the ring. These structures, however, should be referred to as co-conformations. For a definition of co-conformation, see ref. 7.

of  $\lambda_{\max}$  is directly related to the change in the relative populations of the two conformations. For a detailed discussion of this method, see the supplementary material of ref. 8.

Since the shift can be quantitatively related to the ring displacement,  $k_\lambda$  can be taken as  $k_{rd}$ , Table 1 (i. e.  $k_4$  in Scheme 2*b*). The time dependence of the  $\lambda_{\max}$  at 303 K for compounds  $\mathbf{1}^{6+}$  and  $\mathbf{2}^{6+}$  is shown in Fig. 3. The temperature dependence of the rate constants is shown in Fig. 11.

In our system the picture is complicated by the fact that both conformations of the monoreduced rotaxane  $\mathbf{1}^{5+}$  disappear because of the bimolecular recombination with the phenothiazine radical cation. The kinetic scheme that can be used to discuss this problem is Scheme 3, taken from Scheme 2*b*.

It can be shown that when  $k_9$  and  $k_{10}$  are not too different from each other, the rate constant of the  $\mathbf{A}_1^+$  absorption band shift (Eq. S5; see, e. g., Fig. 3) still corresponds to the rate constant of the ring displacement  $k_4$  in Schemes 2 and 3.

From Scheme 3, the following differential equations can be obtained:

$$\frac{d[B']}{dt} = -k_4[B'] - k_9[B'][\mathbf{ptz}^+] \quad (\text{S6})$$

$$\frac{d[C']}{dt} = +k_4[B'] - k_{10}[C'][\mathbf{ptz}^+] . \quad (\text{S7})$$

The disappearance of B' and C' is monitored through the decrease of the intensity of the UV band of their  $\mathbf{A}_1^+$  unit, whose intensity is practically the same for both conformations. Therefore, the intensity decay of the monitored signal,  $I$ , is given by:

$$\frac{dI}{dt} \propto \frac{d([B'] + [C'])}{dt} = -k_9[B'][\mathbf{ptz}^+] - k_{10}[C'][\mathbf{ptz}^+] . \quad (\text{S8})$$

From the experimental viewpoint the signal is fitted according to Eq. S7:

$$\frac{dI}{dt} \propto \frac{d([B'] + [C'])}{dt} = -k_{ptz}[\mathbf{ptz}^+]([B'] + [C']) . \quad (\text{S9})$$

By combining Eqs. S8 and S9 the following relationship between  $k_{ptz}$ ,  $k_9$ , and  $k_{10}$  is obtained:

$$k_{\text{ptz}} = k_9 \frac{[\text{B}']}{[\text{B}'] + [\text{C}']} + k_{10} \frac{[\text{C}']}{[\text{B}'] + [\text{C}']} . \quad (\text{S10})$$

When in Eq. **S10** the molar fractions of [B'] and [C'] are replaced by the Eqs. **S11** and **S12**, obtained on the basis of Scheme 2*b*,

$$\frac{[\text{B}']}{[\text{B}'] + [\text{C}']} = \frac{k_9[\text{ptz}^+]}{k_9[\text{ptz}^+] + k_4} , \quad (\text{S11})$$

$$\frac{[\text{C}']}{[\text{B}'] + [\text{C}']} = \frac{k_4}{k_9[\text{ptz}^+] + k_4} , \quad (\text{S12})$$

the expression of  $k_{\text{ptz}}$  becomes:

$$k_{\text{ptz}} = k_9 \frac{k_9[\text{ptz}^+]}{k_9[\text{ptz}^+] + k_4} + k_{10} \frac{k_4}{k_9[\text{ptz}^+] + k_4} . \quad (\text{S13})$$

From this equation (at  $t = 0$ ), by using for  $k_{\text{ptz}}$ ,  $k_{10}$ ,  $k_4$ , and  $[\text{ptz}^+]$  the experimentally determined values of  $k_{\text{ptz}}$  for  $\mathbf{1}^{6+}$ ,  $k_{\text{ptz}}$  for  $\mathbf{2}^{6+}$ ,  $k_{\text{rd}}$  (Table 1), and  $2.5 \times 10^{-6} \text{ mol}\cdot\text{liter}^{-1}$ , respectively, the value of  $k_9$  at each temperature can be obtained (in Table 2 the values of  $k_9[\text{ptz}^+]_0$ , more easily comparable with  $k_4$ , are reported).

To check the validity of the kinetic scheme, we have performed simulation experiments by using the kinetic parameters determined as described above. Numerical solution of Eqs. **S6** and **S7** gives the concentration time profiles of B' and C'.  $[\text{B}']_0$  is estimated from the transient absorption data (see above), and  $[\text{C}']_0 = 0$ . Eq. **S4** can then be used to obtain the shape of the transient absorption band (the concentrations of the conformations must be used in place of the molar fractions). These simulations (Fig. 12) reproduce nicely the spectral changes observed in the 370–410 range upon laser excitation of the rotaxane in the presence of **ptz**.

## Ring Displacement Efficiency

**Intramolecular Mechanism.** For the intramolecular mechanism, the efficiency of ring displacement can be obtained from Scheme 4, taken from Scheme 2a.

It is worthwhile noticing that the value of the rate constant for the forward ring displacement ( $k_4$ ) in the intramolecular case is assumed to be equal to that determined in the presence of **ptz**. Since the oxidation state of the photosensitizer during the ring shuttling is 2+ in the experiments in the presence of the electron donor, and 3+ in the intramolecular case,  $k_4$  may be slightly different in the two cases as a result of long-range electrostatic interactions. However, considering the large distance between the  $\mathbf{P}^{2+}$  (or  $\mathbf{P}^{3+}$ ) unit and  $\mathbf{A}_1^+$ , and the fact that the moving ring **R** is uncharged, we expect this effect to be negligible.

The value of  $k_5$  can be obtained from the following equation

$$k_{\text{bet}} = [k_5/(k_5 + k_4)]k_5 + [k_4/(k_4 + k_5)]k_6, \quad (\text{S14})$$

where  $k_{\text{bet}}$  and  $k_6$  are the experimental values for  $\mathbf{1}^{6+}$  and  $\mathbf{2}^{6+}$ , and  $k_4$  is  $k_{\text{rd}}$  (Table 1).

Since  $k_6$  is much larger than  $k_{\text{rd}}$  (Table 1), conformer C has to disappear (step 6) as soon as it is formed (step 4). Therefore, *under these conditions*, the measured rate constant for signal decay is given by  $k_{\text{bet}} = k_5 + k_4$ , *regardless of the ring displacement efficiency*, and  $k_5 = k_{\text{bet}} - k_4$ . The values obtained are reported in Table 2.

**Mechanism Assisted by ptz.** For the **ptz**-assisted mechanism the efficiency of ring displacement is given by  $\eta_{\text{rd}} = k_4/(k_4+k_9[\mathbf{ptz}^+]_0)$  (at  $t = 0$ ). By using the experimentally determined  $k_{\text{rd}}$  for  $k_4$  and the values of  $k_9[\mathbf{ptz}^+]_0$  reported in Table 2, the ring displacement efficiencies in the 284-303 temperature range have been obtained (Table 2). It is interesting to note that these data, referring to  $t = 0$ , represent the minimum efficiency values: as the reaction proceeds  $[\mathbf{ptz}^+]$  decreases and, as a consequence, the competition between steps 4 and 9 (Scheme 2b) becomes more and more successful.

If the concentration of **ptz** were larger than that used in our experiments, reductive quenching of  $\mathbf{*P}^{2+}$  by **ptz** could also take place (9)





In such a case, Scheme 2b should be slightly modified. However, such a reductive quenching process (for electron transfer processes in covalently linked  $[\text{Ru}(\text{bpy})_3]^{2+}/\text{ptz}$  compounds, see refs. 10,11,12,13,14,15,16,17,18,19) would be immediately followed by intramolecular electron transfer generating  $\mathbf{A}_1^+$  surrounded by the ring so that, as far as ring shuttling is concerned, such a reductive quenching would eventually lead to the same result as the primary photoinduced electron transfer (step 2). In fact, the occurrence of the reductive quenching process would improve the efficiency of formation of  $\mathbf{A}_1^+$ , since such a process would compete with the intrinsic decay of the excited state.

### Determination of the Rate Constant for the Nuclear Reset

The rate constant for the nuclear reset (process 7 in Scheme 2) can be estimated from electrochemical experiments. Since the reduction potentials of the two conformations of  $\mathbf{1}^{6+}$  are different, the cyclic voltammograms of the rotaxane are expected to exhibit kinetic complications as soon as the time-scale of the experiment approaches that of the interconversion between the two conformations, i.e., that of ring movements. This is indeed what was observed in experiments performed on  $\mathbf{1}^{6+}$  with a conventional microdisk electrode in *N,N*-dimethylformamide at  $-55^\circ\text{C}$  (M.C.-L., A.C., and J.F.S., unpublished results.). At room temperature, the reversibility of the electrochemical processes indicates that the rates of the electrochemically induced ring movements are faster than the highest scan rate ( $20 \text{ V}\cdot\text{s}^{-1}$ ) used in the conventional electrochemical experiments. Unfortunately, attempts to investigate the electrochemical behavior of  $\mathbf{1}^{6+}$  at room temperature by using ultramicroelectrodes with very fast scan rates (up to  $3 \times 10^6 \text{ V}\cdot\text{s}^{-1}$ ) were unsuccessful because of severe adsorption phenomena on both Pt and glassy carbon electrodes.

An upper limit for the time constant of the nuclear reset process at room temperature can be determined, considering that the time-scale  $\tau$  accessible with a cyclic voltammetric experiment at temperature  $T$  is estimated (20) as

$$\tau = \frac{RT}{\nu F}, \quad (\text{S16})$$

where  $F$  is Faraday's constant and  $v$  is the potential scan rate. At 298 K with a scan rate of 20  $\text{V}\cdot\text{s}^{-1}$ ,  $\tau$  corresponds to 1.3 ms. Hence, the nuclear reset must be faster than  $\approx 1$  ms.

### Determination of the Energy Levels Involved in the Photoinduced Shuttling

The relative energies of the levels represented in Fig. 4 were estimated from the results of the spectroscopic and electrochemical experiments. The energy of the  $*\mathbf{P}^{2+}$  excited state (level E in Fig. 4) was calculated from the onset of the phosphorescence band of  $\mathbf{1}^{6+}$  at 77 K. The energy difference between levels C and D was determined from the  $\mathbf{P}^{3+}/\mathbf{P}^{2+}$  reduction potential (+1.15 V versus SCE for  $\mathbf{1}^{6+}$ ) and the potential for the  $\mathbf{A}_1^{2+}/\mathbf{A}_1^+$  reduction when such unit is not encircled by the ring ( $-0.36$  V for  $\mathbf{2}^{6+}$ ); the electrostatic work term can be neglected since the two units involved in the electron transfer are far apart and the rotaxane molecules bear a 6+ charge in all instances.

The energy differences between levels B–C and levels D–A are the most important ones because they represent, respectively, the Boltzmann-weighted thermodynamic driving forces for the forward and backward motion of the ring. Such energies can be estimated on the basis of the square scheme shown in Scheme 5, taking into consideration only the energy differences related to the position of the ring; therefore,  $\Delta G^\circ_3 = 0$ .

$\Delta G^\circ_1$  could be determined from the shift of the potential for the reduction of the  $\mathbf{A}_1^{2+}$  unit when it is encircled by the ring with respect to that of the free unit. However, the reduction potential of  $\mathbf{A}_1^{2+}$  in  $\mathbf{1}^{6+}$  measured by cyclic voltammetry in our conditions does not necessarily correspond to the actual halfwave potential for the  $\mathbf{A}_1^{2+}/\mathbf{A}_1^+$  couple surrounded by  $\mathbf{R}$ , since a chemical rearrangement, i.e., ring displacement, which is fast on the time-scale of the voltammetric experiments, is coupled to the electron transfer process (20,21). This reduction potential should be determined, for instance, on a rotaxane where the ring is not allowed to move away from the  $\mathbf{A}_1^+$  unit. Such a compound was not available; therefore, we attempted to estimate the relevant potential value from thermodynamic data obtained for the pseudorotaxane formed in acetonitrile between the ring  $\mathbf{R}$  and the 1,1'-dimethyl-4,4'-bipyridinium dication, taken as a model compound for the  $\mathbf{A}_1^{2+}$  unit. Since it is known (see, e.g., refs. 22 and 23) that the one-electron reduction of

the bipyridinium unit causes the disassembly of the pseudorotaxane, we have assumed that the free energy change associated to the formation of a pseudorotaxane between **R** and the bipyridinium cation  $\mathbf{A}_1^+$  is zero. The shift in the reduction potential of the bipyridinium unit due to ring complexation can be calculated from the stability constant  $K$  of the pseudorotaxane (21):

$$\Delta E = \frac{-RT \ln K}{F} . \quad (\text{S17})$$

The constant  $K$  was experimentally determined to be 1,300 liters·mol<sup>-1</sup> from spectrophotometric titrations at room temperature; therefore,  $\Delta E$  results to be about -185 mV. This value is in fair agreement with a reduction potential shift of approximately -200 mV found (24) from digital simulations of the voltammetric curves for a rotaxane where a 4,4'-bipyridinium unit is surrounded by an electron donor crown ether similar to the ring **R**. Additionally, the potential shift measured (25) for a 4,4'-bipyridinium unit surrounded by the ring **R** in a catenane structure corresponds to -150 mV.  $\Delta G^\circ_1$  can thus be calculated:

$$\Delta G^\circ_1 = -n F \Delta E = +17.8 \text{ kJ}\cdot\text{mol}^{-1} . \quad (\text{S18})$$

The driving force for the backward motion (nuclear reset) can be determined from the value of the thermodynamic constant associated with the equilibrium between the two conformations of  $\mathbf{1}^{6+}$ . Since the minority conformation of  $\mathbf{1}^{6+}$  (the one with the ring surrounding the  $\mathbf{A}_2^{2+}$  station) could not be detected by <sup>1</sup>H NMR spectroscopy,<sup>‡</sup> an equilibrium constant of at least 20 was estimated, corresponding to  $\Delta G^\circ_4 = -7.5 \text{ kJ}\cdot\text{mol}^{-1}$ .

Finally,  $\Delta G^\circ_2$  was determined on the basis of the thermodynamic cycle shown in Scheme 5:

$$\Delta G^\circ_1 + \Delta G^\circ_2 + \Delta G^\circ_3 + \Delta G^\circ_4 = 0 \quad (\text{S19})$$

$$\Delta G^\circ_2 = -\Delta G^\circ_1 - \Delta G^\circ_3 - \Delta G^\circ_4 = -10.3 \text{ kJ}\cdot\text{mol}^{-1} \quad (\text{S20})$$

The energy differences between levels B–C and levels D–A in Fig. 4 are therefore 10.3 and 7.5 kJ·mol<sup>-1</sup>, respectively.

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<sup>‡</sup> The detection limit for the <sup>1</sup>H NMR technique in this particular experiment was estimated to be <5%.

It should be emphasized that some of these energy values were calculated under specific, albeit reasonable, assumptions, and should be taken only as indicative estimates.

1. Ashton, P. R., Ballardini, R., Balzani, V., Credi, A., Dress, K. R., Ishow, E., Kleverlaan, C. J., Kocian, O., Preece, J. A., Spencer, N., *et al.* (2000) *Chem. Eur. J.* **6**, 3558–3574.
2. Krejčík, M., Daněk, M. & Hartl, F. (1991) *J. Electroanal. Chem.* **317**, 179–187.
3. Watanabe, T. & Honda, K. (1982) *J. Phys. Chem.* **86**, 2617–2619.
4. McAskill, N. A. (1984) *Aust. J. Chem.* **37**, 1579–1592.
5. Yonemoto, E. H., Saupe, G. B., Schmehl, R. H., Hubig, S. M., Riley, R. L., Iveson, B. L. & Mallouk, T. E. (1994) *J. Am. Chem. Soc.* **116**, 4786–4795.
6. Kelly, L. A. & Rodger, M. A. J. (1995) *J. Phys. Chem.* **99**, 13132–13140.
7. Fyfe, M. C. T. & Stoddart, J. F. (1997) *Acc. Chem. Res.* **30**, 393–401.
8. Brouwer, A. M. Frochot, C., Gatti, F. G., Leigh, D. A., Mottier, L., Paolucci, F., Roffia, S. & Wurpel G. W. H. (2001) *Science* **291**, 2124–2128.
9. Hoffman, M. Z., Bolletta, F., Moggi, L. & Hug, G. L. (1989) *J. Phys. Chem. Ref. Data* **18**, 219–543.
10. Striplin, D. R., Reece, S. Y., McCafferty, D. G., Wall, C. G., Friesen, D. A., Erickson, B. W. & Meyer, T. J. (2004) *J. Am. Chem. Soc.* **126**, 5282–5291.
11. Maxwell, K. A., Sykora, M., DeSimone, J. M. & Meyer, T. J. (2000) *Inorg. Chem.* **39**, 71–75.
12. Hu, Y.-Z., Tsukiji, S., Shinkai, S., Oishi, S., Dürr, H. & Hamachi, I. (2000) *Chem. Lett.* 442–443.
13. Klumpp, T., Linsenmann, M., Larson, S. L., Limoges, B. R., Buerssner, D., Krissinel, E. B., Elliott, C. M. & Steiner, U. E. (1999) *J. Am. Chem. Soc.* **121**, 1076–1087.
14. Treadway, J. A., Chen, P., Rutherford, T. J., Keene, F. R. & Meyer, T. J. (1997) *J. Phys. Chem. A* **101**, 6824–6826.
15. Larson, S. L., Elliott, C. M. & Kelley, D. F. (1996) *Inorg. Chem.* **35**, 2070–2076.
16. Larson, S. L., Elliott, C. M. & Kelley, D. F. (1995) *J. Phys. Chem.* **99**, 6530–6539.
17. Opperman, K. A., Mecklenburg, S. L. & Meyer, T. J. (1994) *Inorg. Chem.* **33**, 5295–5301.

18. Larson, S. L., Cooley, L. F., Elliott, C. M. & Kelley, D. F. (1992) *J. Am. Chem. Soc.* **114**, 9504–9509.
19. Cooley, L. F., Larson, S. L., Elliott, C. M. & Kelley, D. F. (1991) *J. Phys. Chem.* **95**, 10694–10700.
20. Bard, A. J. & Faulkner, L. R. (2001) *Electrochemical Methods* (Wiley, New York), Ch. 12.
21. Kaifer, A. E. & Gómez-Kaifer, M. (1999) *Supramolecular Electrochemistry* (Wiley-VCH, Weinheim), Ch. 9.
22. 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., *et al.* (1997) *Chem. Eur. J.* **3**, 152–170.
23. Ashton, P. R., Ballardini, R., Balzani, V., Constable, E. C., Credi, A., Kocian, O., Langford, S. J., Preece, J. A., Prodi, L., Schofield, E. R., *et al.* (1998) *Chem. Eur. J.* **4**, 2413–2422.
24. Ashton, P. R., Ballardini, R., Balzani, V., Baxter, I., Credi, A., Fyfe, M. C. T., Gandolfi, M. T., Gómez-López, M., Martínez-Díaz, M.-V., Piersanti, A., *et al.* (1998) *J. Am. Chem. Soc.* **120**, 11932–11942.
25. Ashton, P. R., Ballardini, R., Balzani, V., Credi, A., Gandolfi, M. T., Menzer, S., Pérez-García, M.-L., Prodi, L., Stoddart, J. F., Venturi, M., *et al.* (1995) *J. Am. Chem. Soc.* **117**, 11171–11197.