Flexible viologen cyclophanes: odd/even effects on intramolecular interactions

Mathilde Berville,^[a] Sylvie Choua,^[b] Christophe Gourlaouen,^[c] Corinne Boudon,^[d] Laurent Ruhlmann,^[d] Corinne Bailly,^[e] Saioa Cobo,^[f] Eric Saint-Aman,^[f] Jennifer Wytko^{*,[a]} and Jean Weiss,^{*,[a]}

Abstract: The ability of three bis-viologen cyclophanes to act as redox-triggered contractile switches was investigated. Odd/even effects in the formation of cyclic bis-viologens were circumvented by the use of a Zincke salt intermediate and a tetrathiafulvalene template to prepare a flexible cyclophane with hexyl linkers. Comparative spectro-electrochemical studies of this macrocycle with two other pentyl- or heptyl-linked cyclic bis-viologens showed that the development of intramolecular interactions in aqueous solution depended on the length of the bridges. This dependence was confirmed by EPR and DFT studies of the magnetic coupling in the di(radical cation) species. The anti-ferromagnetic or ferromagnetic nature of the coupling depended respectively on the odd or even number of methylene units in the spacer.

Introduction

Stimuli-responsive molecular species are of primary importance in modern host-guest chemistry and the era of molecular machines.^[1] The motion of these scaffolds stems from geometrical and conformational changes induced by light, pH changes, redox reactions, ion exchange or guest binding.^[1,2] In the more restricted field of directional molecular motions, the

oxidation or reduction of a molecular component is an easily controlled trigger, both qualitatively and quantitatively.^[3] Examples of redox-stimulated molecular motion include scissor-^[4] or tweezer-like^[5] movement, linear shuttling in rotaxanes,^[1d,6,7] as well as contraction and extension of molecular muscles built from rotaxanes.^[8] In macrocyclic structures, redox-triggered contraction driven by intramolecular π -dimerization has been described in scaffolds containing redox-active moieties such as tetrathiafulvalenes (TTF)^[5d,9] oligothiophene^[10] or perylenes,^[11] linked by flexible spacers.

Among the numerous redox-active molecules, viologens have been selected for decades as building blocks with switchable properties due to their multiple and accessible redox states. In addition, viologen derivatives form π -dimers in their radical cation state at low temperature^[12] and in aqueous or confined media.^[13] In non-cyclic, covalently linked bis-viologens, π -dimerization is also possible when appropriate, flexible alkyl spacers are present in the architecture.^[14] However, macrocycles comprised of two viologen subunits rarely form intramolecular π -dimers. For Stoddart's rigid, macrocyclic "blue-box", i.e. cyclo(bis-paraquat-*p*-phenylene)^[15] only intermolecular π -dimers have been observed in the solid state^[16] or in inclusion complexes with radical cation guests.^[17] This article describes solution studies of a series of new flexible "blue-box" analogs, or "flex-boxes" (Figure 1), in which the odd or even number of methylene groups in the alkyl chain linking the viologens contribute to the control of the intramolecular π -dimerization or similar electronic interactions.

Figure 1. Bis(viologen) cyclophanes with alkyl linkers.

Results and Discussion

Recently, our group reported the synthesis of two bis-viologen cyclophanes **1**(PF₆)₄ and **3**(PF₆)₄ with alkyl spacers and the modulation of their solid state host-guest properties upon reduction.^[18] Synthetic yields were low, unaffected by the use of templates and surprisingly sensitive to an odd or even number of carbon atoms in the intended alkyl linkers. Cyclophanes with an even number of carbons in the alkyl linkers were not produced by this method. An alternate synthetic approach employing the

- [a] Dr. M. Berville, Dr. J. A. Wytko, Dr. J. Weiss
Laboratoire de Chimie des Ligands à Architecture Contrôlée
Institut de Chimie, UMR 7177 CNRS-Université de Strasbourg
4 rue Blaise Pascal, 67008 Strasbourg, France
E-mail: jwytko@unistra.fr; jweiss@unistra.fr
- [b] Dr. S. Choua
Laboratoire de Propriétés Optiques et Magnétiques des Architectures Moléculaires
Institut de Chimie, UMR 7177 CNRS-Université de Strasbourg
4 rue Blaise Pascal, 67008 Strasbourg, France
- [c] Dr. C. Gourlaouen
Laboratoire de Chimie Quantique
Institut de Chimie, UMR 7177 CNRS-Université de Strasbourg
1 rue Blaise Pascal, 67008 Strasbourg, France
- [d] Prof. C. Boudon, Prof. L. Ruhlmann
Laboratoire d'Electrochimie et Chimie Physique du Corps Solide
Institut de Chimie, UMR 7177 CNRS-Université de Strasbourg
4 rue Blaise Pascal, 67008 Strasbourg, France
- [e] Mrs. C. Bailly
Service de Cristallographie
GDS 3648 CNRS-Université de Strasbourg
1 rue Blaise Pascal, 67008 Strasbourg, France
- [f] Dr. S. Cobo, Prof. E. Saint-Aman
Département de Chimie Moléculaire (UMR 5250), Laboratoire de Chimie Inorganique Rédox
Université Grenoble Alpes, 38000 Grenoble, France

Supporting information for this article, including binding titrations and fits, crystal packing, electrochemistry figures, EPR and DFT data, is given via a link at the end of the document.

Zincke reaction^[19,20] was designed from the assumption that the use of an electron rich template would be most efficient if applied to the cyclization of a tetracationic bis-viologen clip **5**⁴⁺ rather than to a partially quaternized bipyridine intermediate such as **4**²⁺. TTF was selected as a possible template because it forms a green charge transfer complex with the larger **3**(PF₆)₄ cyclophane. Despite the low binding constant ($K_a = 21 \pm 1 \text{ M}^{-1}$ in MeCN, see SI) of the latter with TTF, we reasoned that binding might be stronger with **2**(PF₆)₄, which should have a smaller cavity than **3**(PF₆)₄. To generate a bis-viologen clip, the hexyl-linked bis(pyridinium-pyridine)^[21] **4**²⁺ was treated with 2,4-dinitrochlorobenzene in refluxing MeCN (Scheme 1) to give the Zincke salt **5**⁴⁺ in 81% yield. Further reaction of this salt with 1,6-hexanediamine in the presence of two equivalents of TTF afforded a green crude mixture. Excess TTF was used due to its low binding constant (*vide infra*). Removal of the TTF by liquid/liquid extraction, purification by column chromatography and anion exchange afforded the cyclophane **2**(PF₆)₄ in 14% yield. When the last synthetic step was carried out in the absence of TTF, **2**(PF₆)₄ was isolated in 1.5% yield. The corresponding chloride salt, **2**Cl₄ was prepared by anion exchange using NEt₄Cl. The chloride salts of **1**⁴⁺ and **3**⁴⁺ were prepared in a similar fashion.

The emerald green color observed during the cyclization step in the presence of TTF suggested that the latter and the Zincke salt **5**⁴⁺ might form a sandwich-like charge transfer complex that preorganizes the viologens for the cyclization. However, a UV-visible titration of **5**(PF₆)₄ with TTF in MeCN/EtOH (3/1) demonstrated a negligible affinity (see SI) between these compounds.^[22] A charge transfer band was also observed at 765 nm upon addition of TTF to **2**(PF₆)₄ but the UV-visible titration showed a weak affinity of **2**(PF₆)₄ for TTF ($K_a = 104 \pm 2 \text{ M}^{-1}$ in MeCN) (see SI).

Scheme 1. Synthesis of cyclophane **2**⁴⁺ with hexyl linkers.

Nonetheless, the yield of cyclization significantly improved in the presence of TTF. A tentative explanation probably resides in the multi-step character of the reaction of a Zincke salt with an amine. Within the numerous steps that are reversible, except for the final one,^[23] the stabilization of only one cyclic intermediate

by the electron rich TTF might be sufficient to template the formation of **2**(PF₆)₄. The preparation of cyclophanes **1**⁴⁺ and **3**⁴⁺ via a Zincke intermediate was not tried for several reasons. First, a templated synthesis of **1**⁴⁺ is highly unlikely because the macrocyclic cavity is too small to host a TTF guest, as shown by the absence of a charge transfer band during a titration of **1**⁴⁺ with TTF (see ESI). Second, although the cavity of **3**⁴⁺ is of adequate size to host TTF,^[18] the affinity of this host and guest in solution is probably too weak to effectively template the cyclization. Thus, we did not attempt to optimize this strategy because satisfactory quantities of **1**⁴⁺ and **3**⁴⁺ could be obtained in only two steps by the previously reported method.^[18] Nevertheless, the necessity to use the strategy in Scheme 1 rather than the previously reported method for the synthesis of the hexyl-linked macrocycle **2**⁴⁺ suggests that conformational constraints imposed by the number of methylene groups of the spacer are a determining factor in the cyclization step. On several occasions, odd/even effects have also been observed in the synthesis of several other macrocycles containing alkyl spacers.^[24]

Single crystals^[25] of **2**(PF₆)₄ were obtained by slow diffusion of diisopropylether into a dilute MeCN solution of the cyclophane. In the solid state structure of **2**⁴⁺ in Figure 2, the alkyl chains have a gauche conformation. To accommodate this conformation, a torsion angle of 27° exists between the viologen units of the macrocycle. The pyridinium rings in each dicationic viologen are twisted with respect to each other, with a dihedral angle of 38° that indicates a lack of conjugation. The macrocycle is 6.15 Å high and 10.43 Å wide. No intermolecular interactions are observed in the solid state, as shown by the offset arrangement of each macrocycle in the packing of **2**⁴⁺ (see SI).

Figure 2. Solid state structure of **2**(PF₆)₄ determined by X-ray diffraction. Left: face and top view; Right: Side view. Anions (PF₆)⁻ are omitted for clarity.

The ability of the cyclophanes **1**Cl₄–**3**Cl₄ to π -dimerize in water was investigated by electrochemistry and spectro-electrochemistry. To limit the possibility of intermolecular π -dimerization, these studies were carried out at concentrations $\leq 2 \times 10^{-4} \text{ M}$. This critical concentration was determined from spectro-electrochemical studies of the one-electron reduction of aqueous methylviologen (MV²⁺) at $4 \times 10^{-4} \text{ M}$ (see SI).

Cyclic voltammetry (CV) from 0 to -1.2 V vs AgCl/Ag on either a platinum or glassy carbon (GC) electrode clearly indicated adsorption of the neutral species (i.e. the fully reduced

Table 1. Electrochemical data of derivatives observed by cyclic voltammetry (CV) and rotating disk voltammetry (RDV) in H₂O + 0.1 M KCl. All potentials are given versus AgCl/Ag, used as standard, and are uncorrected from ohmic drop.

	E^0 (V) ^[a]	ΔE_p (mV) ^[b]	E_p (V) ^[c]	$E_{1/2}$ (V)	slope (mV) ^[d]
MVCl ₂	Pt			Pt	
	-0.65	55		-0.66	60
	-0.98	50		-0.99	60
	GC			GC	
	-0.63	55		-0.65	60
	-0.99	50		-0.99	60
1Cl ₄	Pt			Pt	
	-0.49	50		-0.52	80
	-0.92	56		-0.93	40
	GC			GC	
	-0.51	65		-0.52	82
	-0.83	90		-0.93	30
2Cl ₄	Pt			Pt	
	-0.55	56		-0.56	60
	-0.83	124		-0.87	30
	GC			GC	
	-0.55	60		-0.57	75
	-0.83	124		-0.88	30
3Cl ₄	Pt		Pt		
	-0.57	90	E_{pc} : -0.91*		
			E_{pa} : -0.70*	[e]	
	GC		GC		
	-0.56	110	E_{pc} : -0.93*	[e]	
			E_{pa} : -0.69*		

[a] $E^0 = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively; [b] $\Delta E_p = E_{pa} - E_{pc}$; [c] E_p = irreversible peak potential; [d] logarithmic analysis of the wave obtained by plotting E versus $\text{Log}[I/(I_{lim}-I)]$; [e] unresolved signals. * E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials respectively with $\Delta E_p = 210$ mV (Pt) and 240 mV (GC).

Figure 3. Cyclic voltammogram of 2Cl₄ in water + 0.1 M KCl; working electrode: glassy carbon disk (GC), auxiliary electrode: Pt wire, pseudo reference electrode: Pt wire.

cyclophane) at the electrode. However, for 1Cl₄ and 2Cl₄, the first two-electron reduction leading to the di(radical cation) and the subsequent reoxidation were reversible on both glassy carbon and platinum electrodes (see Table 1 for redox potentials and SI). Figure 3 shows a cyclic voltammogram of 2Cl₄, which is

Figure 4. UV-visible-NIR monitoring of π -dimer formation during scans from -0.25 to -0.80 V vs. AgCl/Ag at 0.01 Vs⁻¹ for cyclophanes 1Cl₄, 2Cl₄, and 3Cl₄ in H₂O, [KCl] = 0.1 M, working electrode: Pt mini-grid, optical pathway = 0.1 cm.

similar to that of 1Cl₄ (see SI). For 3Cl₄, the first reduction is quasi-reversible (see SI). Thus, in the potential range from 0 to -0.8 V, spectro-electrochemical investigation of the di(radical cation) absorption properties in the near infrared (NIR) was possible for all three cyclophanes.

Again, all compounds were studied at a constant concentration of viologen units in solution with $[MV^{2+}] = 2 \times [(1-3)Cl_4]$ for comparison purposes. For 3Cl₄, no NIR absorption was detected, indicating the absence of π -dimer for 3²⁽⁺⁾. For 1Cl₄

and 2Cl_4 , while cycling from -0.25 to -0.80 V at 0.01 Vs^{-1} on an optically transparent Pt grid, the simultaneous recording of the UV-vis-NIR spectrum showed the growth of an absorption band at 878 and 900 nm, respectively. These absorptions in the NIR region are typical of the formation of π -dimers^[12a,26] and of a multi-centered bonding orbital between the two viologens of each cyclophane.^[27]

In the case of **3**, the adsorption tendency at the mini Pt grid electrode was observed even at the first reduction step giving $3^{2(++)}$. Under the same conditions at a concentration of 4×10^{-4} M in H_2O , MV^{++} shows only the first hints of intermolecular π -dimer formation (see SI). However, the absence of an absorption band in the NIR for 3Cl_4 indicates that intermolecular interactions are not present when the cyclophanes are studied at 2×10^{-4} M. Thus, the observed NIR absorption in the di(radical cationic) species $1^{2(++)}$ and $2^{2(++)}$ can be assigned to intramolecular electronic interactions resulting from a contraction of the cyclophane. These interactions do not occur in 3Cl_4 because the seven-carbon chain between the bipyridinium moieties imposes a longer distance between the two radical cationic species. On the contrary, the pentyl and hexyl chains are sufficiently short to favor interactions between the two viologens in their radical cation state, leading to the formation of a π -dimer.

Distance is not the only relevant parameter in the efficiency of the π -dimer formation. Intuitively, if the distance between the viologen radical cations were the only factor modulating the redox-triggered π -dimer formation, a five-carbon linker would be expected to be more efficient than a six-carbon connection. Experimentally, several features of the spectro-electrochemical studies of 1Cl_4 suggest a less efficient production of π -dimer than in 2Cl_4 . In the smaller cyclophane, full reduction could not be achieved during simple scanning of the reduction potential. To observe the characteristic absorption band of the intramolecular π -dimer, it was necessary to either hold the reduction potential at -0.75 V (AgCl/Ag) or perform iterative cyclic voltammetry around the first reduction potential and monitor the 200–1400 nm region. On the contrary, with the hexyl chain of cyclophane 2Cl_4 , intramolecular π -dimer formation was very fast and the evolution of the corresponding absorption band was observed during the continuous potential scan.

These observations strongly suggest that establishing electronic interactions such as π -dimer formation between two covalently linked viologens is not exclusively controlled by the length of the linker but also by its conformational flexibility. An even number of carbon atoms seems more appropriate for bringing two viologen units “face-to-face” than an odd number, as emphasized by comparing the length of the spacers.

X-band EPR spectra of di(radical cation) species provided more detailed information about the electronic structures of the cyclophanes. At room temperature, the reduced species were generated by electrolysis *in situ* at 2×10^{-4} M in water to minimize intermolecular interactions. In the case of $3^{2(++)}$, only a very weak signal was recorded (see SI). The blue color characteristic of the di(radical cationic) species appeared mostly in the vicinity of the electrode, confirming the adsorption tendency already observed in the spectro-electrochemistry studies. However, a very well resolved EPR signal was

observed for $2^{2(++)}$, revealing an exchange interaction between two radicals in the limit of a strong exchange (see SI). The EPR spectrum (Figure 5) of this di(radical cation) fits perfectly with a two spin species, with hyperfine coupling constants (hfc) divided by two compared to that of the MV^{++} reference compound under the same experimental conditions (see SI). The hfc of $2^{2(++)}$ were assigned by analogy with those of the MV^{++} radical cation.^[28] For $1^{2(++)}$, a less resolved signal (see SI) did not allow measurement of the hyperfine coupling constants.

Figure 5. X-band EPR spectrum of $2^{2(++)}$ generated by electrolysis in water $[\text{KCl}] = 0.1$ M at room temperature.

To determine the spin state of the molecules, a series of geometry optimization were undertaken, starting from the experimental crystal structures¹⁸ for $1^{2(++)}$ and $3^{2(++)}$ (further denoted as $1^{2(++)}(\text{RX1})$, $1^{2(++)}(\text{RX2})$ and $3^{2(++)}(\text{RX})$) and that of the $2^{2(++)}$ (further denoted as $2^{2(++)}(\text{RX})$) molecule was optimized starting from the structure of 2^{+} . For $1^{2(++)}$, two structures are present in the crystal and were both studied. Due to the flexible nature of the alkyl linkers in the cyclophanes, the conformation adopted in the crystal structure may not be representative of those present in solution. Other arrangements of the side chains were optimized to investigate the role of the geometry on the spin state. The structures optimized from the X-ray data are hereafter designated as RX and the other constructed conformers as GA, GB, etc. The molecules were fully optimized with no symmetry in the closed shell singlet (CSS) and open shell triplet (T) states. The energy of the open shell singlet state (OSS) was evaluated using a single point on the optimized triplet geometry (see details in ESI). The main results are summarized in Figure 6 and details concerning the geometry optimization are provided as supporting information.

For all structures, the unpaired electrons are, as expected, localized on the π system of the viologen fragments (see ESI) with negligible contribution of the alkyl side chains. A second general observation is that the CSS state is never the ground state and is typically much higher in energy than the OSS and T states, particularly for the conformers of $3^{2(++)}$. Otherwise, the energy difference between OSS and T states strongly depends on the geometry.

Figure 6. Optimized geometries of (a) $12^{(\bullet\bullet)}(\text{T})$, (b) $22^{(\bullet\bullet)}(\text{GB,CSS})$, (c) $32^{(\bullet\bullet)}(\text{RX,T})$, (d) $12^{(\bullet\bullet)}(\text{GA,OSS})$, (e) $22^{(\bullet\bullet)}(\text{GE,OSS})$, (f) $32^{(\bullet\bullet)}(\text{GA,OSS})$.

For $12^{(\bullet\bullet)}$, the most stable state is the OSS of $12^{(\bullet\bullet)}$ (GA), although the triplet state of this optimized structure is close enough in energy (270 cm^{-1}) to be thermally accessible (see Table S2); particularly at room temperature. By analogy with the solid state structure, an open shell singlet of $12^{(\bullet\bullet)}(\text{RX2, OSS})$ lies only 326 cm^{-1} higher in energy than $12^{(\bullet\bullet)}(\text{GA, OSS})$. In both structures the viologens are not parallel, their average planes exhibiting dihedral angles of 37° ($12^{(\bullet\bullet)}(\text{GA, OSS})$) and 61° ($12^{(\bullet\bullet)}(\text{RX, OSS})$) with respect to one another. The two structures differ mainly by the orientation of one of the side chains (Figures 6a-d) and are probably in equilibrium in the solution. The closest carbon-carbon edge-to-edge distance is $3.6\text{ \AA}$ in both conformers illustrates the attempted development of electronic intramolecular interactions hampered by the distortion of the side-chains. The lowest energy conformer, $22^{(\bullet\bullet)}(\text{GE, OSS})$ (Figure 6e), corresponds to an OSS. However, the triplet state of this same structure, $22^{(\bullet\bullet)}(\text{GE, T})$ and the CCS state of a second optimized conformer, $22^{(\bullet\bullet)}(\text{GB, CSS})$, are respectively only 77 cm^{-1} and 82 cm^{-1} above $22^{(\bullet\bullet)}(\text{GE, OSS})$. In $22^{(\bullet\bullet)}(\text{GB, CSS})$, the two viologens are almost perfectly superimposed (Figure 6b), which is not the case for the other structures. At the closest point, the carbon atoms of the two viologens are separated by $3.0\text{ \AA}$. The two viologen subunits in conformer $22^{(\bullet\bullet)}(\text{GE, OSS})$ adopt a tilted geometry of their mean planes similar with a 55° dihedral angle similar to that of $12^{(\bullet\bullet)}(\text{GA, OSS})$ and $12^{(\bullet\bullet)}(\text{RX2, OSS})$. Within an energy range of 600 cm^{-1} , at least four other possible conformers were identified for $22^{(\bullet\bullet)}$ (see ESI); therefore this molecule is significantly more flexible than $12^{(\bullet\bullet)}$. Due to such small energy differences, $22^{(\bullet\bullet)}$ can thermally adopt many different conformations and spin states. The calculated OSS ground state of cyclophane $22^{(\bullet\bullet)}$ fits well with the EPR data described above.

The results for $32^{(\bullet\bullet)}$ are completely different from those of the other two cyclophanes. For this compound, none of the calculated conformers are lower in energy than the crystal structure (see ESI). Only two conformers, $32^{(\bullet\bullet)}(\text{GA, T})$ (Figure 6c) and $32^{(\bullet\bullet)}(\text{GA, OSS})$, are reasonably close in energy to the crystal structure. Furthermore, our calculations do not clearly indicate the spin state of the molecule because $32^{(\bullet\bullet)}(\text{RX, T})$ and $32^{(\bullet\bullet)}(\text{RX, OSS})$ are almost perfectly degenerate. In the latter,

shown in Figure 6c, the nearly parallel viologens are within the range of van der Waals contacts ($3.3\text{--}3.6\text{ \AA}$) necessary for π -dimer interactions. Yet this intramolecular interaction is obviously not favored in solution, as demonstrated by the lack of an absorption band in the NIR during spectroelectrochemical experiments.

These results may be related to the structures and more precisely to the relative arrangement of the two viologen planes. As observed in a reported bis-viologen²⁹ or in verdazyl-based analogues,^[30] small variations of the geometry can greatly modify the nature of the ground state in pairs of organic radicals. In these flexible boxes, the length of the spacer and its parity modifies the parallel character of the two viologens. With a pentyl chain, the structure of $12^{(\bullet\bullet)}$ is relatively rigid and imposes an angle between the planes of the two viologens. Although the antiferromagnetic OSS state is favored, intramolecular π -type interactions would be inefficient because of the molecule's ground state geometry. The longer 6-membered chain of $22^{(\bullet\bullet)}$ allows greater distortions of the two viologen planes, in turn weakening the antiferromagnetic character and allowing several conformers. EPR and spectro-electrochemistry results indicate that in solution the two viologens act as unpaired radicals and form π -dimer interactions. In the longest 7-membered chain of $32^{(\bullet\bullet)}$, the flexibility is even greater than in the shorter alkyl chains, allowing large distortions in which the viologen planes are no longer superimposed, such as in $32^{(\bullet\bullet)}(\text{GA, OSS})$ in Figure 6f. However, in solution this cyclophane must adopt the most stable ground state geometry in which the viologens are too far apart to form intramolecular interactions.

Conclusion

The use of an efficient strategy allowed us to circumvent the odd/even selection tendency observed in the synthesis of flexible bis-viologen cyclophanes and to prepare a cyclophane bearing alkyl linkers with six carbon atoms, thus completing this family of cyclophanes. Comparative electrochemistry studies of the varying ability of the three cyclophanes $14\text{--}34$ to π -dimerize in solution upon reduction have been combined with EPR

measurements and DFT calculations. The results suggest that odd/even effects not only impact the synthesis of viologen cyclophanes, but also influence the flexibility of the cyclic structures and consequently, their ability to contract and develop intramolecular electronic interactions. Thus, in the design of redox addressable hosts or molecular switches, odd and even effects have to be considered very carefully when choosing the connection between redox active species. Simple adjustments and geometric changes are suitable to adjust the response of the molecular device, for instance its spin state or its responsiveness.

Experimental Section

Synthetic generalities. Compound **4**(PF₆)₂ was synthesized by a reported method.^[31] Reagents and solvents of reagent-grade were purchased and used without further purification. Column chromatography was performed with silica gel from Merck (Kieselgel 60; 40–63 µm). Mass spectra analyses were performed by le Service de Spectrométrie de Masse de l'Institut de Chimie, Université de Strasbourg. Elemental analyses were performed by le Service d'Analyse Elementaire de l'Institut de Chimie, Université de Strasbourg. ¹H NMR spectra were recorded on Bruker Advance 400 (400 MHz) or 500 (500 MHz) spectrometers. Chemical shifts were determined by taking the solvent as a reference: CD₃CN (1.94 ppm).

Compound 5(PF₆)₄. Compound **4**(PF₆)₂ (2.0 g, 2.9 mmol) and 1-chloro-2,4-dinitrobenzene (5.90 g, 29.1 mmol) in MeCN (20 mL) were stirred and refluxed under argon for 72 h. After cooling to r.t., the white precipitate was filtered, washed with MeCN and dissolved in a minimum of a mixture of water and acetone until complete dissolution. After addition of a saturated aqueous KPF₆ solution (15 mL), the mixture was concentrated, filtered, washed with water and dried under vacuum to afford **5**(PF₆)₄ as a white solid (6.14 g, 4.7 mmol, 81%). ¹H NMR (500 MHz, CD₃CN, 25 °C) δ = 1.51 (m, 4H), 2.07 (m, 4H), 4.66 (t, J = 7.6 Hz, 4H), 8.16 (d, J = 8.6 Hz, 2H), 8.51 (d, J = 6.6 Hz, 4H), 8.63 (d, J = 6.8 Hz, 4H), 8.86 (dd, J = 8.6 Hz, J = 2.5 Hz, 2H), 8.97 (d, J = 6.6 Hz, 4H), 9.14 (d, J = 6.8 Hz, 4H), 9.20 (d, J = 2.5 Hz, 2H). ¹³C NMR (125 MHz, CD₃CN, 25 °C) δ = 25.8, 31.5, 62.9, 123.2, 128.3, 128.5, 131.4, 132.5, 138.9, 144.2, 146.6, 147.6, 150.3, 151.0, 153.9. ESI HRMS: m/z calc. [C₃₈H₃₄N₈O₈P₂F₁₂]²⁺ = 510.0886, found [M⁴⁺ 2PF₆]⁺ = 510.853; m/z calc. [C₃₈H₃₄N₈O₈PF₆]³⁺ = 291.7375, found [M⁴⁺ PF₆]⁺ = 291.7358 and m/z calc. [C₃₈H₃₄N₈O₈]⁴⁺ = 182.5619, found [M⁴⁺] = 182.5612.

Cyclophane 2(PF₆)₄. 1,6-Hexanediamine (0.546 g, 4.7 mmol) was added to a solution of compound **5**(PF₆)₄ (6.17 g, 4.7 mmol) and tetrathiafulvalene (1.92 g, 9.4 mmol) in a mixture of MeCN/EtOH (415 mL, (3/1)). The green solution was stirred at r.t. under argon atmosphere for 12 h. The solvent was evaporated and the crude product was dissolve in MeCN. Saturated Et₄NCl in MeCN was added until no further precipitation was observed. The resulting precipitate was filtered. The solid was dissolved in water and continuously extracted for 2 days with CHCl₃. The aqueous phase became red. The aqueous phase was evaporated and purified by column chromatography (SiO₂, MeCN/MeOH/H₂O/sat. NH₄Cl_{aq} (2/1/1/1)). The fractions containing the product were concentrated then dissolved in H₂O. A saturated aqueous solution of KPF₆ was added until no further precipitation was observed. The resulting precipitate was filtered; the solid was washed with H₂O and dried under vacuum to give compound **2**(PF₆)₄ as a white solid (0.69 g, 0.65 mmol, 14%). ¹H NMR (500 MHz, CD₃CN, 25 °C) δ = 0.94 (m, 8H), 1.96 (m, 8H), 4.60 (t, J = 5.8 Hz, 8H), 8.23 (d, J = 6.5 Hz, 8H), 8.79 (d, J

= 6.5 Hz, 8H). ¹³C NMR (125 MHz, CD₃CN, 25 °C) δ = 25.6, 30.9, 63.0, 127.8, 146.4, 150.5. ESI HRMS: calc. [C₃₂H₄₀N₄PF₆]³⁺ = 208.4293, found [M⁴⁺ PF₆]⁺ = 208.4321 and m/z calc. [C₃₂H₄₀N₄]⁴⁺ = 120.0808, found [M⁴⁺] = 120.0815. E.A. (%) calcd for C₃₂H₄₂N₄P₄F₂₄ (1060.18): C 36.24, H 3.80, N 5.28, found: C 35.95, H 3.78, N 5.26.

Anion exchange: A saturated solution of Et₄NCl in MeCN was added to a saturated solution of **1**(PF₆)₄, **2**(PF₆)₄ or **3**(PF₆)₄ in MeCN until no further precipitation was observed. After filtration, the solid was washed with MeCN and dried under vacuum to give compound **1**Cl₄, **2**Cl₄ or **3**Cl₄, respectively, as a white solid.

X-ray crystallography. The crystals were placed in oil, and a single crystal was selected, mounted on a glass fiber and placed in a low-temperature N₂ stream. X-Ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 38 mm. The cell parameters were determined (APEX2 software)^[32] from reflections taken from three sets of 12 frames, each at 10 s exposure. The structure was solved by direct methods using the program SHELXS-2013.^[33] The refinement and all further calculations were carried out using SHELXL-2013.^[33] The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F². A semi-empirical absorption correction was applied using SADABS in APEX2;^[32] transmission factors: T_{min}/T_{max} = 0.6353 / 0.7458.

Electrochemistry: Materials. Pure water was used throughout. It was obtained by passing water through a Milli-RO4 unit and subsequently through a Millipore Q water purification set. KCl was commercial product from Prolabo (RP Normapur, purity ≥99.5 %).

Electrochemistry Measurements. Electrochemical measurements were carried out in H₂O containing 0.1 M KCl in a classical three-electrode cell by cyclic voltammetry (CV) and rotating-disk voltammetry (RDV). The working electrode was a glassy carbon disk (GC, 3 mm in diameter), the auxiliary electrode a Pt wire, and the pseudo reference electrode a Pt wire. The cell was connected to an Autolab PGSTAT30 potentiostat (Eco Chemie, Holland) driven by a GPSE software running on a personal computer. All potentials are given vs. Fc⁺/Fc as well vs. AgCl/Ag used as internal reference and are uncorrected from ohmic drop.

UV-Vis-NIR and IR Spectroelectrochemical Measurements. UV-Vis-NIR spectroelectrochemical experiments were performed with an optically transparent thin-layer electrochemical (OTTLE) cell (University of Reading UK, Hartl, F.)^[34] equipped with a Pt mini-grid working electrode and CaF₂ optical windows. IR spectroelectrochemical experiments were performed with an optically transparent thin-layer electrochemical (OTTLE) cell (University of Reading UK, Hartl, F.)^[34] equipped with a Pt mini-grid working electrode and KBr optical windows. UV-Vis-NIR spectroelectrochemical analyses have been carried out with a Zeiss MCS 601 UV-vis-NIR diode array spectrometer. Spectrophotometric analyses of the films have been conducted using a 0.1 mol L⁻¹ solution of KCl in H₂O. IR spectroelectrochemical analyses have been carried out with a Bruker Vertex 70 spectrometer at 1 cm⁻¹ resolution (16 scans).

EPR experiments. EPR spectra were recorded with an ESP 300E spectrometer (Bruker) operating at X-band and equipped with a standard TE102 rectangular cavity. Computer simulations of the EPR spectra were performed with the help of Winsim (NIEH Public Software) software. Radical cations were generated *in situ* by electrolysis in a flat, quartz

microcell. Electrolyses were performed at controlled potential with a three electrode configuration under argon using a platinum wire as the working electrode, a platinum wire as the auxiliary electrode and a silver wire as the pseudo reference electrode. A dilute aqueous solution (2×10^{-4} M) of compounds **1Cl₂**, **2Cl₂** or **3Cl₂** was prepared with KCl (0.1 M) as supporting electrolyte. A concentration of 4×10^{-4} M in water was used for the methylviologen reference.

Computational details. All calculations were performed with ADF 2013 package. The DFT level of calculations with B3LYP functional was used associated with a TZP basis set. Dispersion corrections with Grimme3 model were employed. PCM model of water was added. All the geometries were first optimized on the basis of the triplet states. Then starting from this geometry and wave function, the open shell singlet was obtained applying the spin-flip procedure. The geometry was then optimized again for this new wave function.

Acknowledgements

This work was supported by the Agence National de la Recherche (ANR-12-BS07-0014-01, PRIMO project), the Université de Strasbourg and the CNRS. We thank Vincent Robert for fruitful discussions about this research.

Keywords: viologen • cyclophane • pi-dimer • electrochemistry

- [1] For reviews see: a) P. Ceroni, A. Credi, M. Venturi, *Chem. Soc. Rev.*, **2014**, 43, 4068-4083; b) E. R. Kay, Leigh, c) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem. Int. Ed.* **2000**, 39, 3348-3391; c) S. Erbas-Cakmak, D. A. Leigh, C. T. McTernan, A. L. Nussbaumer, *Chem. Rev.* **2015**, 115, 10081-10206; d) E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem. Int. Ed.* **2007**, 46, 72-191; e) ed. J. F. Stoddart, *Acc. Chem. Res.* **2000**, 100, 406, special issue on Molecular Machines; f) K. Kinbara, T. Aida, *Chem. Rev.* **2005**, 105, 1377-1400; g) W. R. Browne, B. L. Feringa, *Nat. Nanotechnol.* **2006**, 1, 25-35; h) Y. Shira, J.-F. Morin, T. Sasaki, J. M. Guerrero, J. M. Tour, *Chem. Soc. Rev.* **2006**, 35, 1043-1055.
- [2] For selected examples: a) J. Chen, S. J. Wezenberg, B. L. Feringa, *Chem. Commun.* **2016**, 52, 6765-6768; b) T. Lang, E. Graf, N. Kyritsakas, M. W. Hosseini, *Chem. Eur. J.* **2012**, 18, 10419-10426; c) Y. Yamada, M. Okamoto, K. Furukawa, T. Kato, K. Tanaka, *Angew. Chem. Int. Ed.* **2012**, 51, 709-713; d) F. Niess, V. Duplan, J.-P. Sauvage, *J. Am. Chem. Soc.* **2014**, 136, 5876-5879; e) F. Niess, V. Duplan, C. S. Diercks, J.-P. Sauvage, *Chem. Eur. J.* **2015**, 21, 14393-14400; f) S. Ø. Scottwell, J. D. Crowley, *Chem. Commun.* **2016**, 52, 2451-2464; g) K. Miwa, Y. Furusho, E. Yashima, *Nat. Chem.* **2010**, 2, 444-449; h) N. Zigon, M. W. Hosseini, *Chem. Commun.* **2015**, 51, 12486-12489.
- [3] a) J. W. Lee, I. Hwang, W. S. Jeon, Y. H. Ko, S. Sakamoto, K. Yamaguchi, K. Kim, *Chem. Asian J.* **2008**, 3, 1277-1283; b) J. Sun, Y. Wu, Y. Wang, Z. Liu, C. Cheng, K. J. Hartlieb, M. R. Wasielewski, J. F. Stoddart, *J. Am. Chem. Soc.* **2015**, 137, 13484-13487.
- [4] a) A. Iordache, M. Oltean, A. Milet, F. Thomas, B. Baptiste, E. Saint-Aman, C. Bucher, *J. Am. Chem. Soc.*, **2012**, 134, 2653-2671; b) A. Takai, T. Yasuda, T. Ishizuka, T. Kojima, M. Takeuchi, *Angew. Chem., Int. Ed. Engl.* **2013**, 52, 9167-9171.
- [5] For selected examples see: a) A. Iordache, M. Retegan, F. Thomas, G. Royal, E. Saint-Aman, C. Bucher, *Chem. Eur. J.* **2012**, 18, 7648-7653; b) C. Kahlfuss, A. Milet, J. Wytko, J. Weiss, E. Saint-Aman, C. Bucher *Org. Lett.* **2015**, 17, 4058-4061; c) M. H. Düker, H. Schäfer, M. Zeller, V. A. Azov, *J. Org. Chem.* **2013**, 78, 4905-4912; d) C. Beijger, C. M. Davis, J. S. Park, V. M. Lynch, J. B. Love, J. L. Sessler, *Org. Lett.* **2011**, 13, 4902-4905; e) V. J. Chebny, R. Shukla, S. V. Lindeman, R. Rathore, *Org. Lett.* **2009**, 11, 1939-1942; f) J. Lyskawa, M. Sallé, J. Y. Balandier, F. Le Derf, E. Levillain, M. Allain, P. Viel, S. Palacin, *Chem. Commun.* **2006**, 2233-2235; g) G. Pognon, C. Boudon, K. J. Schenk, M. Bonin, B. Bach, J. Weiss *J. Am. Chem. Soc.* **2006**, 128, 3488-3489; h) M. Hardouin-Lerouge, P. Hudhomme, M. Sallé, *Chem. Soc. Rev.* **2011**, 40, 30-43; i) J. Leblond, A. Petitjean, *ChemPhysChem*, **2011**, 12, 1043-1051.
- [6] a) R. A. Bissell, E. Córdova, A. E. Kaifer, J. F. Stoddart, *Nature*, **1994**, 369, 133-137; b) J.-P. Collin, P. Gavina and J.-P. Sauvage, *New J. Chem.* **1997**, 21, 525-528.
- [7] For several reviews, see: a) S. Durot, F. Reviriego, J.-P. Sauvage, *Dalton Trans.* **2010**, 39, 10557-10570; b) M. Xue, Y. Yang, X. Chi, X. Yan, F. Huang, *Chem. Rev.* **2015**, 115, 7398-7501; c) J. F. Stoddart, *Chem. Rev.* **2009**, 38, 1802-1820.
- [8] For recent reviews, see: a) F. Niess, V. Duplan, J.-P. Sauvage, *Chem. Lett.* **2014**, 43, 964-974; b) C. J. Bruns, J. F. Stoddart, *Acc. Chem. Res.* **2014**, 47, 2186-2199;
- [9] a) K. Takimiya, Y. Aso, F. Ogura, T. Otsubo, *Chem. Lett.* **1995**, 735-736; b) M. Brøndsted Nielsen, N. Thorup, J. Becher, *J. Chem. Soc., Perkin Trans. 1*, **1998**, 1305-1308; c) H. Spanggaard, J. Prehn, M. B. Nielsen, E. Levillain, M. Allain, J. Becher, *J. Am. Chem. Soc.* **2000**, 122, 9486-9494; d) K. Takimiya, A. Oharuda, Y. Aso, F. Ogura, T. Otsubo, *Chem. Mater.* **2000**, 12, 2196-2204; e) K. Takimiya, N. Thorup, J. Becher, *Chem. Eur. J.* **2000**, 6, 1947-1954; f) M. Iyoda, M. Hasegawa, Y. Miyake, *Chem. Rev.* **2004**, 104, 5085-5113; g) J. O. Jeppesen, M. Brøndsted Nielsen, J. Becher, *Chem. Rev.* **2004**, 104, 5115-5131; h) W. Wang, S. M. Dyar, D. Cao, A. C. Fehrenbach, N. Horwitz, M. T. Colvin, R. Carmieli, C. L. Stern, S. K. Day, M. R. Wasielewski, J. F. Stoddart, *J. Am. Chem. Soc.* **2012**, 134, 19136-19145; i) K.-i. Nakamura, Y. Okada, T. Shirahata, Y. Misaki, *Chem. Lett.* **2014**, 43, 708-710.
- [10] J. Casado, K. Takimiya, T. Otsubo, F. J. Ramírez, J. J. Quirante, R. Ponce Ortiz, S. R. González, M. Moreno Oliva, J. T. López Navarrete, *J. Am. Chem. Soc.* **2008**, 130, 14028-14029.
- [11] D. F. Schlosser, M. Moos, C. Lambert, F. Würthner, *Adv. Mater.* **2013**, 25, 410-414.
- [12] E. M. Kosower, J. L. Cotter, *J. Am. Chem. Soc.* **1964**, 86, 5524-5527
- [13] a) J. W. Lee, Hwang, W. S. Jeon, Y. H. Ko, S. Sakamoto, K. Yamaguchi, K. Kim, *Chem.-Asian J.* **2008**, 3, 1277-1283; b) T. Zhang, S. Sun, F. Liu, J. Fan, Y. Pang, L. Sun X. Peng, *Phys. Chem. Chem. Phys.* **2009**, 11, 11134-11139; c) J. W. Lee, S. Samal, N. Selvapalam, H.-J. Kim, K. Kim, *Acc. Chem. Res.* **2003**, 36, 621-630.
- [14] a) S. J. Atherton, S. J.; Tsukahara, K. T.; Wilkins, R. C. *J. Am. Chem. Soc.* **1986**, 108, 3380-3385; b) Furue, M.; Nozokura, S. I. *Bull. Chem. Soc. Jpn.* **1982**, 55, 513-516; c) Deronzier, A.; Galland, B.; Vieira, M. *Nouv. J. Chim.* **1982**, 97-100; d) Furue, M.; Nozokura, S. I. *Chem. Lett.* **1980**, 9, 821-824.; e) Hirayama, F. *J. Chem. Phys.* **1965**, 42, 3163
- [15] (a) B. Odell, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, D. J. Williams, *Angew. Chem., Int. Ed. Engl.* **1988**, 27, 1547-1550; b) J. F. Stoddart, H. M. Colquhoun, *Tetrahedron*, **2008**, 64, 8231-8263.
- [16] J. C. Barnes, A. C. Fahrenbach, D. Cao, S. M. Dyar, M. Frasconi, M. A. Giesener, D. Benítez, E. Tkatchouk, O. Chernyashevskyy, W. H. Shin, H. Li, S. Sampath, C. L. Stern, A. A. Sarjeant, K. J. Hartlieb, Z. Liu, R. Carmieli, Y. Y. Botros, J. W. Choi, A. M. Z. Slawin, J. B. Ketterson, M. R. Wasielewski, W. A. Goddard III, J. F. Stoddart, *Science*, **2013**, 339, 429-433.
- [17] a) A. Trabolsi, N. Khashab, A. C. Fahrenbach, D. C. Friedman, M. T. Colvin, K. K. Cotí, D. Benítez, E. Tkatchouk, J.-C. Olsen, M. E. Belowich, R. Carmielli, H. A. Khatib, W. A. Goddard III, M. R. Wasielewski, J. F. Stoddart, *Nature Chem.* **2010**, 2, 42-49; b) A. C.

- Fahrenbach, J. C. Barnes, D. A. Lanfranchi, H. Li, A. Coskun, J. J. Gassensmith, Z. Liu, D. Benítez, A. Trabolsi, W. A. Goddard III; M. Elhabiri, J. F. Stoddart, *J. Am. Chem. Soc.*, **2012**, *134*, 3061-3072;
- [18] M. Berville, L. Karmazin, J. A. Wytko, J. Weiss, *Chem. Commun.* **2015**, 51, 15772-15775.
- [19] T. Zincke, G. Heuser, W. Möller, *Liebigs Ann.* **1904**, 333, 296-345.
- [20] The Zincke reaction was previously used in the cyclization step of several viologen-containing macrocycles: H. M. Colquhoun, B. W. Greenland, Z. Zhu, J. S. Shaw, C. J. Cardin, S. Burattini, J. M. Elliott, S. Basu, T. B. Gasa, J. F. Stoddart, *Org. Lett.* **2009**, *11*, 5238-5241.
- [21] J. B. Wittenberg, P. Y. Zavaliji, L. Issacs, *Angew. Chem. Int. Ed.* **2013**, *52*, 87-94.
- [22] For the titration, the initial concentration of **5**(PF₆)₄ was nearly identical to that in the cyclization reaction. The binding constant is $0.9 \pm 0.4 \text{ M}^{-1}$ in MeCN/EtOH (3/1).
- [23] a) S. Kunugi, T. Okubo, N. Ise, *J. Am. Chem. Soc.* **1976**, *98*, 2282-2287; b) E. N. Marvell, G. Caple, I. Shahidi, *J. Am. Chem. Soc.* **1970**, *92*, 5641-5645.
- [24] a) F. B. L. Cougnon, N. Ponnuswamy, N. A. Jenkins, G. D. Pantoş, J. K. M. Sanders, *J. Am. Chem. Soc.* **2012**, *134*, 19129-19135; b) A. Torres-Huerta, H. Höpfel, H. Tlahuext, I. F. Hernández-Ahuactzi, M. Sánchez, R. Reyes-Martínez, D. Morales-Morales, *Eur. J. Inorg. Chem.* **2013**, 61-69; c) K. E. Jelfs, E. G. B. Eden, J. L. Culshaw, S. Shakespeare, E. O. Pyzer-Knapp, H. P. G. Thompson, J. Bacsa, G. M. Day, D. J. Adams, A. I. Copper, *J. Am. Chem. Soc.* **2013**, *135*, 9307-9310.
- [25] CCDC-1051149 contain(s) the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data%5Frequest/cif. Crystallization solvents: MeCN/diisopropylether; Crystal size: 0.30 x 0.22 x 0.15 mm; Identification: (C₃₂H₄₀N₄)(PF₆)₄; formula: C₃₂H₄₀F₂₄N₄P₄; Formula Weight: 1060.56 g/mol; Color: Colorless; Crystal system: orthorhombic; Space group: Pnna, Unit cell dimensions (Å and deg): a = 15.0492(7) Å, b = 25.0265(11) Å, c = 11.7886(6) Å, α = 90°, β = 90°, γ = 90°; Volume: 4439.9(4) Å³, Z = 4; Density: 1.587 mg/m³, Temperature: 173(2) K; Absorption coefficient: 0.302 mm⁻¹; 2θmax: 58.06 deg.; Reflections collected: 26441; Reflections unique: 5915; Goodness of fit: 1.049; R₁ = 0.0777; wR₂ = 0.2348.
- [26] a) M. Itoh, E. M. Kosower, *J. Am. Chem. Soc.* **1967**, *89*, 3653-3656; b) M. Itoh, E. M. Kosower, *J. Am. Chem. Soc.* **1968**, *90*, 1843-1849.
- [27] a) J. M. Lü, S. V. Rosakha, J. K. Kochi, *J. Am. Chem. Soc.* **2003**, *125*, 12161-12171; b) Y. Jung, M. Head-Gordon, *J. Phys. Chem. Chem. Phys.* **2004**, *6*, 2008-2011; c) J. J. Novoa, P. La Fuente, R. E. Del Sesto, J. S. Miller, *Angew. Chem. Int. Ed.*, **2001**, *40*, 2540-2545; c) Y. H. Tian, M. Kertesz, *J. Phys. Chem. A*, **2011**, *115*, 13942-13949.
- [28] J. C. Evans, C. R. Morris, C. C. Rowland, *Tetrahedron*, **1987**, *43*, 5329-5334.
- [29] A. Iordache, R. Kannappan, E. Méta, M.-C. Duclos, S. Pellet-Rostaing, M. Lemaire, A. Milet, E. Saint-Aman, C. Bucher, *Org. Biomol. Chem.* **2013**, *11*, 4383-4389.
- [30] a) M. Vérot, N. Bréfuel, J. Pécaut, C. Train, V. Robert, *Chem. Asian J.*, **2012**, *7*, 380-386; b) J.-B. Rota, B. Le Guennic, V. Robert, *Inorg. Chem.* **2010**, *49*, 1230-1237.
- [31] Adapted from: A. Iordache, M. Retegan, F. Thomas, G. Royal, E. Saint-Aman, C. Bucher, *Chem. Eur. J.*, **2012**, *18*, 7648-7653.
- [32] "M86-E01078 APEX2 User Manual", Bruker AXS Inc., Madison, USA, 2006.
- [33] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.
- [34] M. Krejčík, M. Daněk, F. J. Hartl, *J. Electroanal. Chem.* **1991**, *317*, 179-187.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Text for Table of Contents

*Mathilde Berville, Corinne Boudon,
Laurent Ruhlmann, Sylvie Choua,
Maxime Bernard, Corinne Bailly,
Jennifer Wytke,* Jean Weiss,* Saioa
Cobo and Eric Saint-Aman*

Page No. – Page No.

**Flexible viologen cyclophanes:
odd/even effects on π -dimerization**

Layout 2:

FULL PAPER

((Insert TOC Graphic here; max. width: 11.5 cm; max. height: 2.5 cm))

*Author(s), Corresponding Author(s)**

Page No. – Page No.

Title

Text for Table of Contents