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Synthesis and Photochemistry of a Two-Position Ru(terpy)(phen)(L)$^{2+}$ Scorpionate Complex

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A dissymmetric 1,10-phenanthroline chelate (N-phen-S) bearing two polyether chains terminated by two monodentate ligands of the benzonitrile (N) and dialkylesulfoxide (S) types was synthesized, characterized, and coordinated to ruthenium. The corresponding Ru(terpy*)(N-phen-S)$^{2+}$ complexes (terpy* = 4′-(3,5-ditertiobutylphenyl)-2,2′;6′,2″-terpyridine) were fully characterized as being two coordination isomers of the scorpionate type with one of the two tails occupying the sixth position on the coordination sphere. Photoexpulsion of the coordinated tail led to opening of the ruthena-macrocycle and subsequent rearrangement of the bidentate chelate. This rearrangement consisted of a 90° rotation of the phenanthroline around the ruthenium atom. Selective irradiation of one isomer in a mixture of the two was undertaken using band-pass filters; this resulted in an enrichment of the nonirradiated isomer in the mixture. Thermal back-coordination of the tail was investigated in the dark. It took place quantitatively from the corresponding ruthenium chloride complex by trapping of the anion with silver salts.

Introduction

Induction of molecular motion in a controlled fashion under the action of an external signal, either to mimic some of the functions of biological motors or in relation to artificial molecular switches, machines, and devices, is particularly challenging.[1,2] As far as synthetic systems are concerned, catenanes and rotaxanes occupy a special position,[1,3−9] but noninterlocking systems such as scorpionates, metal-translocating ligands, or metallamacrocycles based on hemilabile multidentate ligands have also been investigated.[10−16] In many systems, motion at the molecular level has been triggered by electrochemical[17−21] or chemical[22−24] signals. In particular, light irradiation has also been reported to produce molecular movements, either alone[9,25−30] or in conjunction with a redox chemical reaction.[17,18,31] Purely photonic stimuli are particularly promising, as the environ-

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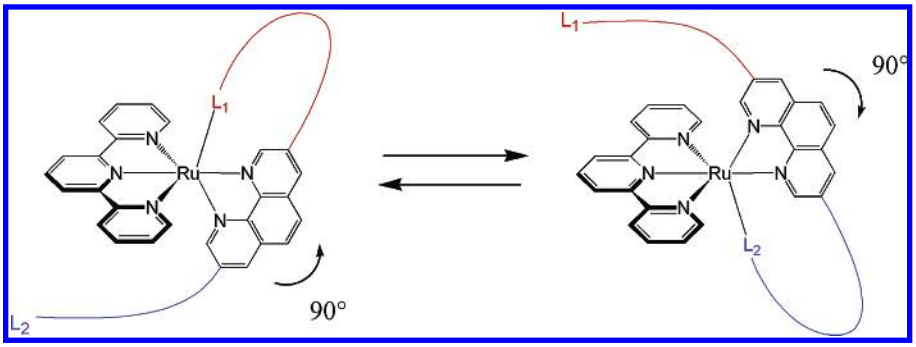

Figure 1. Design of a two-position molecular scorpionate based on the Ru(terpy)(phen)(L)$^{2+}$ moiety.

ment of the system in motion is not altered by the addition of chemical entities. Most of these systems contain a photoisomerizable group such as azobenzene or alkene. Our group has proposed another approach for light-driven machines based on multicomponent ruthenium(II) complexes.[26,32,33] In these systems, ligand photosubstitution reactions are used to set the molecule in motion. Such a process requires thermal population of the ligand-field excited state (^{3}LF) from the triplet metal-to-ligand charge-transfer (^{3}MLCT) excited state. In Ru(diimine)$_3^{2+}$-based systems, the ligand to be photoexpelled is a hindered chelate of the 6,6′-dimethyl-2,2′-bipyridine type (dmbp) inscribed in a ring. Another family of complexes with the general formula Ru(terpy)(phen)(L)$^{2+}$ (where L is a monodentate ligand) has also recently been investigated as new building blocks for light-controlled molecular machines.[11,34−36] Visible light irradiation of such complexes leads to the selective expulsion of the monodentate ligand L and subsequent replacement by a solvent molecule. The syntheses of complexes of the type Ru(terpy)(phen)(L)$^{2+}$ were described with a large variety of monodentate ligands (water, acetonitrile, benzonitrile derivatives, pyridines substituted in the 3, 4 or 5 positions, sulfoxides, and thioethers).[35,36] The absorption maxima of these complexes vary with the nature of the monodentate ligands, from ∼430 nm for dialkylsulfoxides to 515 nm for the chloride ion. Control of the irradiation wavelength should allow selective photoexpulsion of one type of ligand in a mixture of complexes with different coordinated monodentate ligands, L.

In 2001, Schofield et al. synthesized one of the first prototypes of a molecular machine based on the Ru(terpy)(phen)(L)$^{2+}$ core.[11] It was a scorpionate molecule where a monodentate ligand, L_1, of the benzonitrile type was attached to the terpyridine ligand by a long and flexible poly(ethylene glycol) chain. The benzonitrile ligand was shown both in solution and in the solid state to be coordinated to the ruthenium atom. White light irradiation of the complex led to selective and quantitative photoexpulsion of L_1, with an opening of the ruthena-macrocycle and replacement of the benzonitrile by a solvent molecule. The presence of the covalent arm allowed the monodentate ligand to stay close to the complex, which resulted in an easy thermal back-coordination of the benzonitrile ligand to the ruthenium center. In neat acetone, the ring-closing reaction was quantitative within 1 day at room temperature or 2 h at reflux.

This new scorpionate-type complex is based on a dissymmetric 1,10-phenanthroline chelate bearing two tails functionalized by a benzonitrile group and a dialkylesulfoxide group (Figure 1).

In a Ru(terpy)(N−N)(L)$^{2+}$ complex, when the bidentate chelate N−N is dissymmetric, two different isomers may exist.[34] The change from one isomer to the other implies a 90° rotation of the bidentate chelate around the ruthenium atom. As depicted in Figure 1, such a rotation changes the ability of the two monodentate ligands to coordinate, as only the one which is on the side of the coordination site may bind to the metal (Figure 1). Once bound, the monodentate ligands play the role of a wedge that holds the bidentate chelate in one position or the other. A suitable combination of monodentate ligands was L_1 = benzonitrile and L_2 = dialkylesulfoxide since it was important to avoid as much overlapping of the ^{1}MLCT absorption bands of both isomers as possible so that selective irradiation could be performed. The model complexes Ru(terpy*)(phen)(MeOBN)$^{2+}$ and Ru(terpy*)(phen)(DMSO)$^{2+}$ (terpy* = 4′-(3,5-ditertiobutylphenyl)-2,2′;6′,2″-terpyridine, MeOBN = 2,6-dimethoxybenzonitrile, and DMSO = dimethyl sulfoxide) showed ^{1}MLCT absorption bands far enough from each other in the visible region (465 and 431 nm, respectively).[36] These two ligands were attached to the phenanthroline chelate by rigid phenyl linkers followed by flexible polyether "tails" (Scheme 1). The length of these tails was estimated on CPK models of both isomers of the ruthenium scorpionate.

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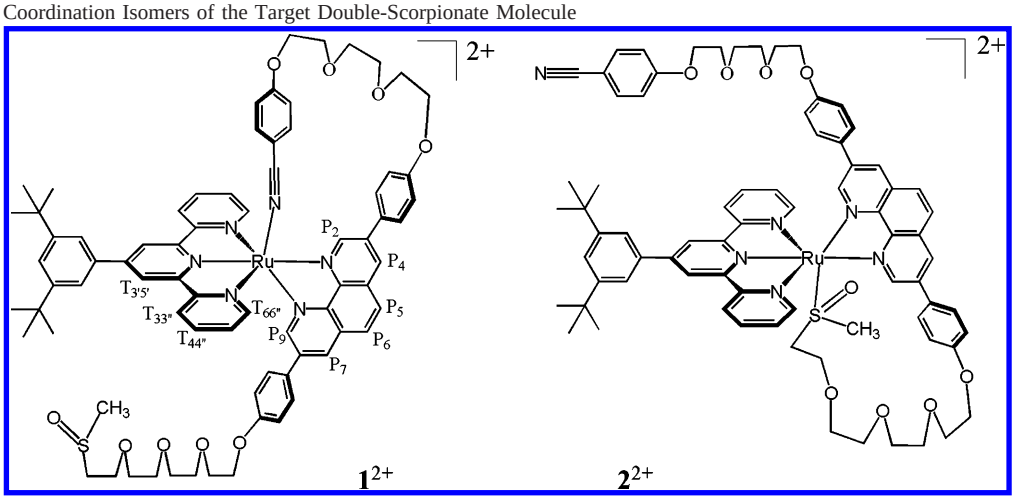
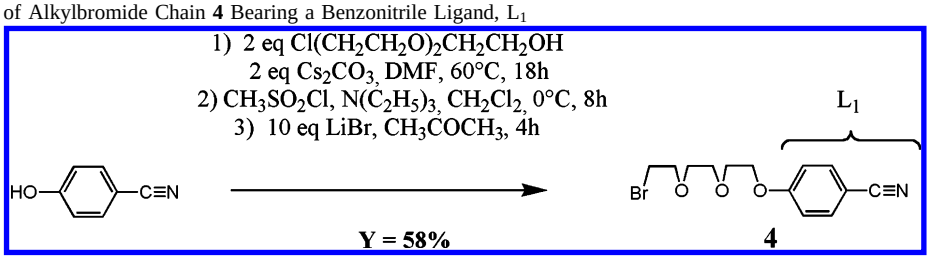
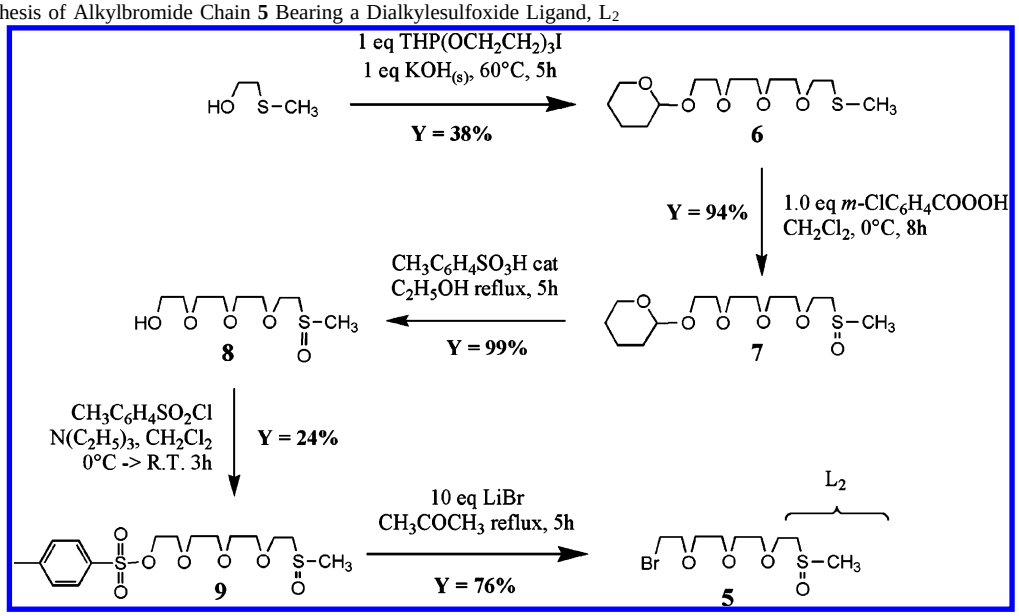
Scheme 1. Two Coordination Isomers of the Target Double-Scorpionate Molecule



Scheme 2. Synthesis of Alkylbromide Chain **4** Bearing a Benzonitrile Ligand, L_1



Scheme 3. Synthesis of Alkylbromide Chain **5** Bearing a Dialkylesulfoxide Ligand, L_2



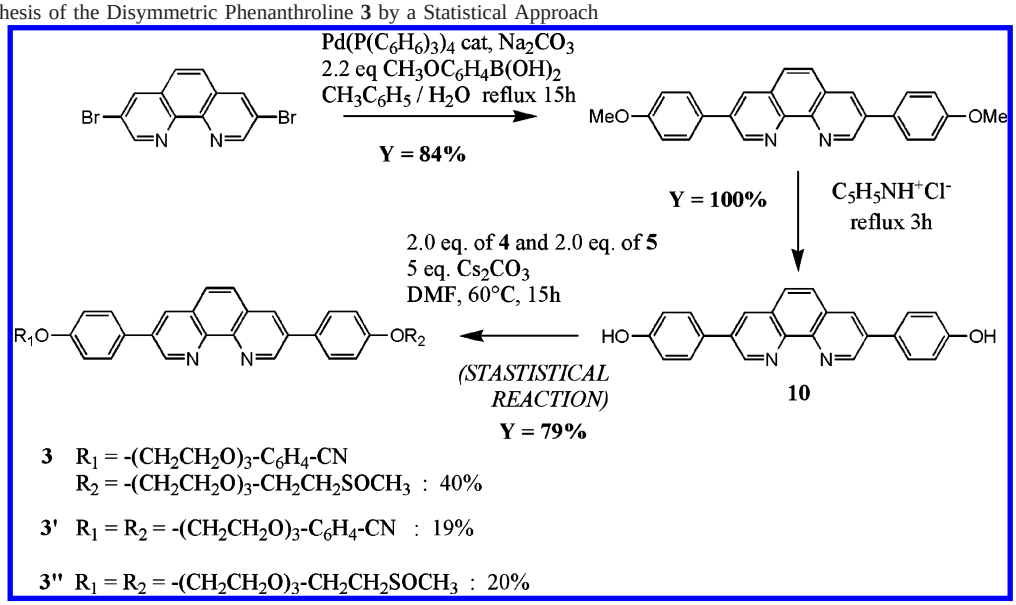
In this paper, we describe the synthesis, characterization, and photoreactivity of the two isomers of a double scorpionate molecule, complexes $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ (Scheme 1). Notably, the motion of the phenanthroline chelate is reported to take place during irradiation at room temperature. Thermal coordination of the tail is also reported, which allows one to envision future conversion of one isomer into the other.

Results

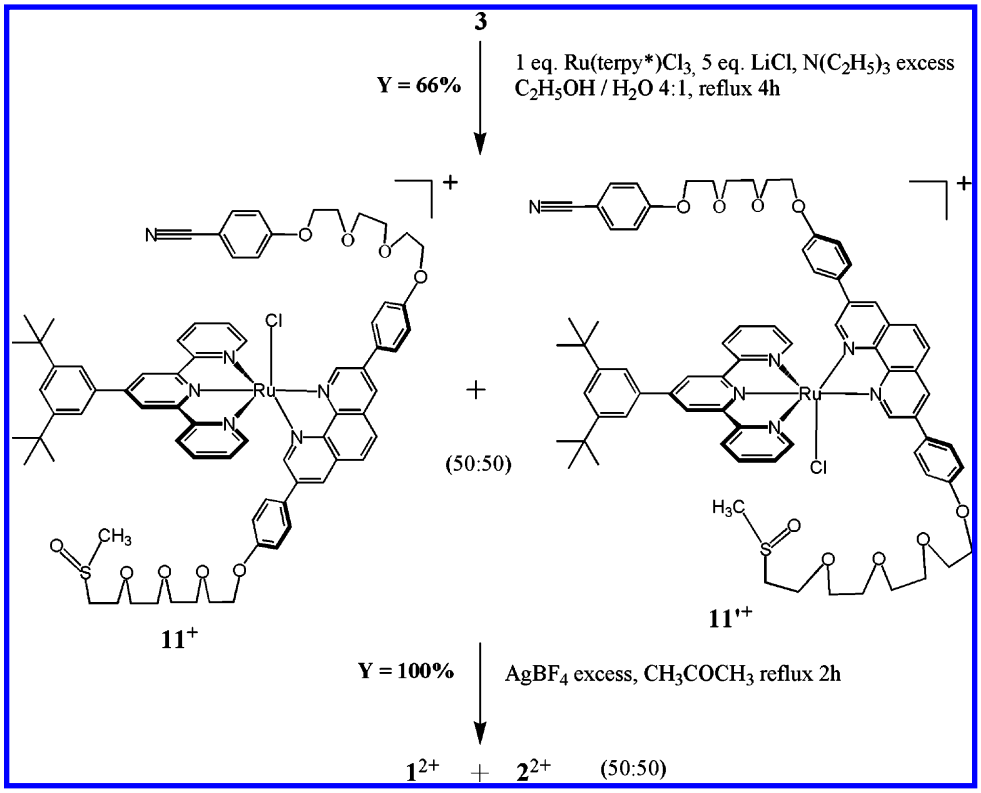
Synthesis of the 3,8-Dissymmetrically Substituted Phenanthroline 3. A statistical Williamson reaction between 3,8-di(hydroxyphenyl)-1,10-phenanthroline and an equimolar mixture of the two alkylbromides **4** and **5** was chosen to synthesize the bidentate chelate **3** (see Scheme 4), bearing the two tails of the scorpionate. The syntheses of the two alkylbromides **4** and **5** are depicted in Schemes 2 and 3, respectively.

In the synthesis of **4**, the first Williamson reaction led to an inseparable mixture of the desired benzonitrile derivative and the starting triethylene glycol monochlorohydrin. This mixture was used in the mesylation and bromination steps, and **4** could be obtained after chromatography on a 3 g scale. In the synthesis of **5**, alcohol **8** was tosylated instead of mesylated as the latter option led to a water soluble compound; hence it was difficult to extract. The moderate hydrophilicity of tosylate **9** probably explains the low yield

Scheme 4. Synthesis of the Disymmetric Phenanthroline **3** by a Statistical Approach



Scheme 5. Synthesis of the Two Coordination Isomers $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$



of this step. The sulfoxide chain **5** was prepared on a 700 mg scale. The main starting material for the 3,8-disubstituted 1,10-phenanthroline is the symmetric 3,8-dibromo-1,10-phenanthroline (Scheme 4).[37]

This symmetric molecule was turned into 3,8-dianisyl-1,10-phenanthroline using standard Suzuki cross-coupling conditions.[38] Methoxy groups were efficiently removed in refluxing pyridinium chloride to produce 3,8-di(parahydroxyphenyl)-1,10-phenanthroline (compound **10**).[39] Symmetric diphenol **10** was further reacted in a dissymmetric Williamson reaction using an equimolar mixture of **4** and **5**, bearing at their ends the two ligands L_1 (benzonitrile) and L_2 (dialkylesulfoxide). The dissymmetric Williamson reaction yielded a mixture of three phenanthrolines: the dissymmetric one bearing two different ligands (L_1-phen-L_2, compound **3**) and two symmetric ones bearing two monodentate ligands of the same kind (**3′** = L_1-phen-L_1 and **3″** = L_2-phen-L_2). Separation of this mixture by chromatography and isolation

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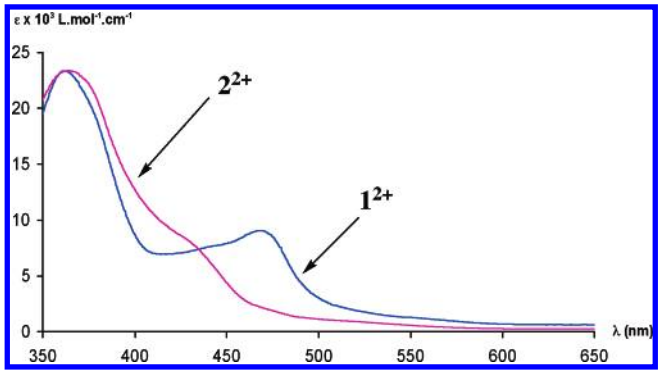


Figure 2. UV-vis spectra of $\mathbf{1}^{2+}$ (blue) and $\mathbf{2}^{2+}$ (violet) in acetone.

of the dissymmetric product was possible because of the higher polarity of the sulfoxide chain compared to the benzonitrile chain. The 40% isolated yield of **3** was close to the maximum theoretical value (50%). Compound **3** was prepared on a 200 mg scale. It was characterized by ^{1}H 1D NMR, 2D COSY, ROESY, HSQC, HMBC NMR, and FAB mass spectrometry.

Coordination of Phenanthroline 3 to the Ruthenium. Because the two different monodentate ligands of bidentate chelate **3** were located far from the coordinating nitrogen atoms, its coordination to Ru(terpy*)Cl_3 yielded a statistical mixture of the two chloro isomers of compound Ru(terpy*)-(**3**)$(Cl)^+$, denoted $\mathbf{11}^+$ and $\mathbf{11'}^+$ (Scheme 5). These two coordination isomers could not be separated at this stage. After removal of the chloride ion by silver(I) in acetone, the two complexes $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ of Scheme 1 were isolated by chromatography.

Complexes $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ displayed identical mass spectra (an *m*/*z* value of 1487.443 instead of the 1487.439 value obtained by simulation for Ru(terpy*)(**3**)$(PF_6)^+$) but very different proton NMR and UV−vis spectra.

(i) The UV−vis spectra in acetone of the two complexes showed a ^{1}MLCT absorption maximum at 468 nm for $\mathbf{1}^{2+}$ and a shoulder around 430 nm for $\mathbf{2}^{2+}$ (Figure 2). These values were consistent with a benzonitrile group and a sulfoxide ligand coordinated to a Ru(terpy)(phen) core.[35,36]

(ii) In the proton NMR spectrum of $\mathbf{1}^{2+}$, the terpy* moiety showed symmetric signals, which was consistent with the diastereogenic sulfoxide ligand being far from the coordination sphere of the ruthenium; in contrast, both sides of the terpy* moiety in $\mathbf{2}^{2+}$ were very distinctly different. This is consistent with the sulfoxide ligand being close to the coordination sphere of the ruthenium (Figure 3). In particular, the protons P_9 (in $\mathbf{1}^{2+}$) and P_2 (in $\mathbf{2}^{2+}$) of the phenanthroline ligand appear to be strongly shielded as a consequence of their proximity to the terpyridine nucleus. (iii) ROESY correlation experiments unambiguously showed the close proximity of the protons near the ruthenium atom on the terpy* and phen chelates and the benzonitrile ligand in $\mathbf{1}^{2+}$ and the sulfoxide ligand in $\mathbf{2}^{2+}$. This experimental evidence clearly showed that complexes $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ are coordination isomers with the benzonitrile and sulfoxide ligands, respectively, coordinated to the ruthenium.

Photochemical Reactivity of $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$. Irradiation of $\mathbf{1}^{2+}$ or $\mathbf{2}^{2+}$ in Pure Form. Photoinduced expulsion of the

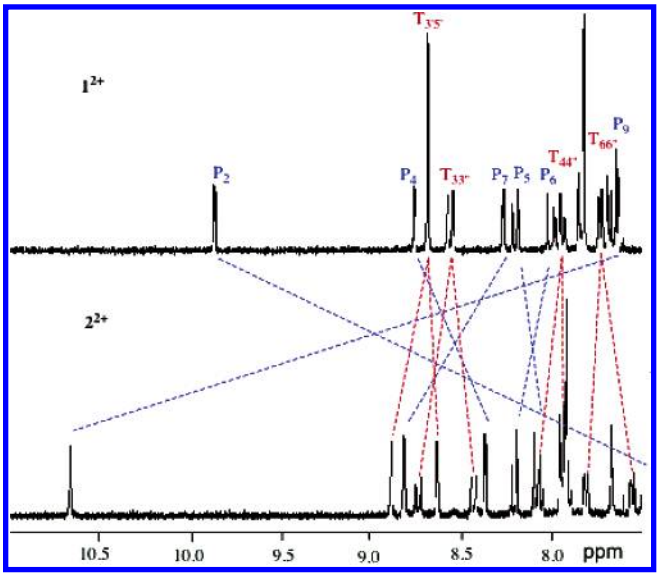
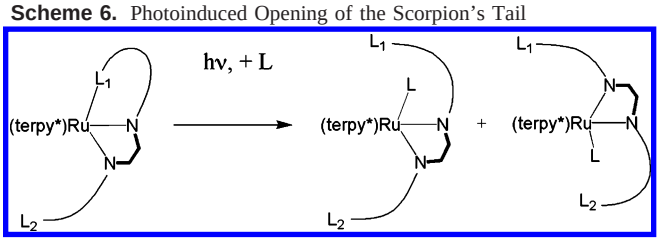


Figure 3. ^{1}H NMR spectra of $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ in $CDCl_3$ (7.5 to 11 ppm) showing the signals of the terpyridine (red) and the phenanthroline (blue). See Scheme 1 for proton assignment.

Scheme 6. Photoinduced Opening of the Scorpion's Tail



monodentate ligand L_1 (or L_2) from $\mathbf{1}^{2+}$ (or $\mathbf{2}^{2+}$) at room temperature resulted in the "open species" Ru(terpy*)(**3**)-$(L)^{n+}$, where L was a solvent molecule or a chloride anion (Scheme 6). During this process, rearrangement of the coordination sphere, corresponding to a gliding motion (90°) of the phen ligand around the rurhenium (II) center, might also take place. As a result, the irradiation product was a mixture of two isomers.

To study the photochemical isomerization process, a source of white light filtered by interference filters centered either at 470 nm or at 430 nm was used. These wavelengths corresponded to the ^{1}MLCT absorption bands of complexes $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$, respectively. During the course of the reactions, two ^{1}H NMR probes were used: (i) the α-proton of **3** that was on the side of the monodentate ligand (P_2 and P_9, see Scheme 1) and (ii) the methyl group of the sulfoxide ligand. The former was conclusive about the nature of the coordinated monodentate ligand, the latter about the exact nature of the isomer. They both enabled precise determination of the number and proportions of species in solution during the course of the photochemical reaction. The percentages of isomerization after complete ring-opening were measured, starting from a pure compound $\mathbf{1}^{2+}$ or $\mathbf{2}^{2+}$, on the photoproduct Ru(terpy*)(**3**)$(L)^{n+}$. Representative results are given Table 1.

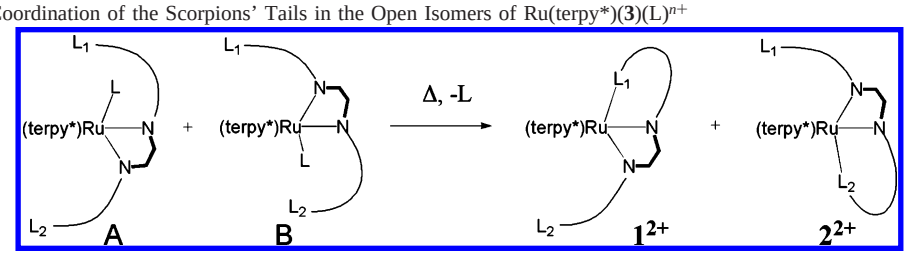
Three main tendencies appeared from the analysis of the ^{1}H NMR data. (i) In acetonitrile and acetone/water solutions (entries I, II, and V), complexes $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ led to a statistical mixture of the two open isomers of Ru(terpy*)(**3**)$(L)^{2+}$. After

Table 1. Photoexpulsion of the Tail and Photoisomerization of $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$

entry	complex	solvent system	L	irradiation time (wavelength)	yield[a] (%)	% isomerization
I	$\mathbf{1}^{2+}$	CD_3CN	CD_3CN	0.5 h (470 nm)	100	40
II	$\mathbf{1}^{2+}$	CD_3COCD_3/20% D_2O	D_2O	3 h (470 nm)	95	39
III	$\mathbf{1}^{2+}$	CD_3COCD_3/4% D_2O + Cl^-,$N(C_2H_5)_4^+$	Cl^-	3 h (470 nm)	100	14
IV	$\mathbf{1}^{2+}$	CD_2Cl_2/Cl^-,$N(C_2H_5)_4^+$	Cl^-	3 h (470 nm)	100	5
V	$\mathbf{2}^{2+}$	CD_3COCD_3/20% D_2O	D_2O	3 h (430 nm)	96	43
VI	$\mathbf{2}^{2+}$	CD_2Cl_2/Cl^-,$N(C_2H_5)_4^+$	Cl^-	3 h (430 nm)	100	9

[a] Calculated as the number of moles of both isomers of the photoproduct Ru(terpy*)(**3**)(L)$^{n+}$ divided by the number of moles of irradiated complex.

Scheme 7. Thermal Coordination of the Scorpions' Tails in the Open Isomers of Ru(terpy*)(**3**)(L)$^{n+}$



the total disappearance of the starting product, further irradiation led to an increase of the percentage of isomerization until a statistical distribution (50:50) was reached. (ii) In chlorination conditions (entries III, IV, and VI) the ring-opening process took place with negligible isomerization, leading to the open isomer Ru(terpy*)(**3**)(Cl)$^+$ (compounds $\mathbf{11}^+$ or $\mathbf{11'}^+$) where the chloride was on the same side as the original monodentate ligand. After the total disappearance of the starting product, further irradiation did not lead to an increase of the percentage of isomerization. (iii) In all cases, the photochemical product *without* isomerization was produced faster than the photochemical product *with* isomerization. Unfortunately, direct production of $\mathbf{2}^{2+}$ after irradiation of $\mathbf{1}^{2+}$, or vice-versa, was never detected. It is noteworthy that the absence of isomerization during chlorination experiments (entries IV and VI in Table 1) permitted independent ^{1}H NMR characterization of the two chloro isomers $\mathbf{11}^+$ and $\mathbf{11'}^+$.

Irradiation of a Mixture of $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$. The following photochemical and thermal sequence of reactions was repeated several times on the same sample to test the efficiency of the selective irradiations: (i) 1 h of band-pass irradiation at 470 nm in acetone/water, (ii) addition of NEt_4-Cl into the irradiation vessel and stirring 24 h at room temperature in the dark and isolation of the resulting complexes, and (iii) 2 h of reflux in acetone with $AgBF_4$ and isolation of the resulting complexes. Because the replacement of the coordinated solvent (acetone or water) by Cl^- and the thermal coordination of the tails on the ruthenium chloride species are quantitative processes, (vide infra) these experiments should allow us to determine if selective irradiation favors the formation of one isomer with respect to the other. The $\mathbf{1}^{2+}$/$\mathbf{2}^{2+}$ ratios after step 3, starting from a pure sample of $\mathbf{1}^{2+}$, were measured by ^{1}H NMR, and the following results were obtained: 62:38 ratio after run 1 and a 44:56 ratio after run 2.

Thermal Coordination of the Scorpion's Tail. This reaction yielded the corresponding mixture of the initially irradiated product ($\mathbf{1}^{2+}$ or $\mathbf{2}^{2+}$) and its isomer ($\mathbf{2}^{2+}$ or $\mathbf{1}^{2+}$, respectively; see Scheme 7) from a mixture of the two open isomers of Ru(terpy*)(**3**)(L)$^{n+}$.

Table 2. Thermal Back-Coordination of the Tail

starting A/B ratio	L in Ru(terpy*)(**3**)(L)$^{n+}$	conditions	ratio $\mathbf{1}^{2+}$/$\mathbf{2}^{2+}$ X′/Y′	scorpionate yield (%)[a]
60:40	D_2O	acetone 2 h reflux	60:40	60
95:5	Cl^-	$AgBF_4$ (excess) acetone 2 h reflux	95:5	100
40:60	D_2O	acetone 2 h reflux	40:60	60
8:92	Cl^-	$AgBF_4$ (excess) acetone 2h reflux	8:92	100

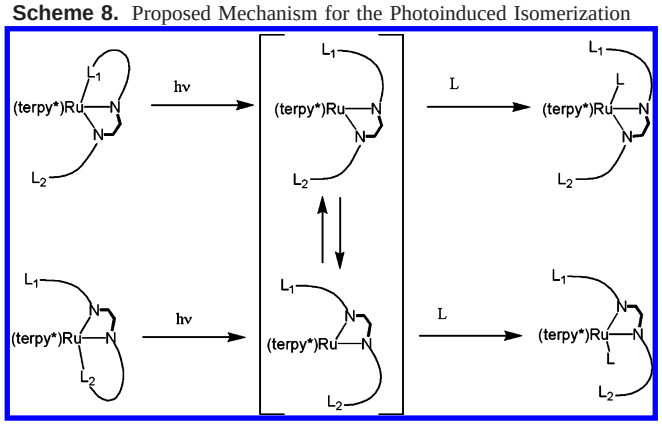
[a] Calculated by dividing the sum of the numbers of moles of $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ by the total number of moles of all Ru(terpy*)(**3**)(L)$^{n+}$ species detected by ^{1}H NMR.

Back-coordination of the scorpion's tail was too slow at room temperature to take place during irradiation. Irradiation of the mixture at 40 °C did not give better results. An X/Y mixture of the two isomers of Ru(terpy*)(**3**)(L)$^{n+}$ generated photochemically was heated in the dark, yielding a X′/Y′ mixture of the closed scorpionates $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$. Within the experimental uncertainty of ^{1}H NMR analysis, there was no change of the isomer ratio in thermal conditions (X′ = X and Y′ = Y). The yields and final $\mathbf{1}^{2+}$/$\mathbf{2}^{2+}$ compositions are given in Table 2. No thermal reaction takes place in CH_3-CN, probably because the acetonitrile ligand is so strongly bound to the ruthenium(II) center that it cannot be displaced by Cl^-, L_1, or L_2.

Discussion

Ruthenium chemistry is known to be controlled by kinetics, and because of their polydentate nature, the terdentate and bidentate chelates in Ru(terpy)(phen)(L)$^{n+}$ complexes are strongly bound to the ruthenium atom. No detectable Ru(II)-dialkylesulfoxide linkage isomerization was observed for the monodentate ligand under the experimental conditions used. In previous works, such an isomerization process required particular media, such as DMSO solution, ionic liquid, or polymer films.[40−42] In addition, other published works were consistent with the hypothesis of a

Scheme 8. Proposed Mechanism for the Photoinduced Isomerization



dissociative mechanism for the photosubstitution reaction of L in Ru(terpy*)(phen)(L)$^{2+}$ complexes.[34,36,43,44] Isomerization of **3** was supposed to occur on the photochemically produced pentacoordinated species (see Scheme 8). The longer such pentacoordinated species last in solution, the higher the isomerization percentage should be in the reaction. When the nonhindering and symmetric nature of phenanthroline **3** close to the ruthenium center is considered, a long-lived unsaturated intermediate would lead to a 1:1 statistical composition of both isomers of the photoproduct Ru(terpy*)-(**3**)(L)$^{n+}$. In this hypothesis, the kinetics for the coordination of an entering ligand, L, to the pentacoordinated species is critical for the degree of isomerization after irradiation. If coordination of L is slow compared to the isomerization process (Scheme 8), this latter reaction will take place preferentially. Thus, a 1:1 mixture of the final isomers (A and B of Figure 7) will be obtained. This was probably the case in weakly coordinating solvents (Table 1, entries II and V). In contrast, if the coordination step leading to the 6-coordinated complex is fast versus isomerization, isomerization will not be favored. The chlorination reactions (Table 1, entries IV and VI) fit well with this interpretation.

The interconversion between **1**$^{2+}$ and **2**$^{2+}$ would require the tail of the scorpion to come back thermally. As such a process did not take place spontaneously during band-pass irradiation at room temperature, the thermal reaction was tested in the dark (Table 2). With L = D_2O, the tail slowly came back to coordinate the ruthenium center in wet acetone. The moderate yield of this reaction prevented a second irradiation of the same sample. Because the acetone was wet, catalytic processes involving Ru(terpy*)(**3**)$(H_2O)^{2+}$ are suspected to be responsible for secondary reactions.[45−48] With L = Cl^-, the use of silver salts enabled trapping of the chloride ion. As a result, coordination of the tail was fast and quantitative. In all cases, no significant changes in the isomer ratios were detected after thermal back-coordination. As a consequence, one cannot exclude the hypothesis of an associative mechanism for such intramolecular thermal reactions.

To take advantage of the efficiency of *both* photoinduced isomerization in acetone/water *and* thermal back-coordination from L = chloride, we designed a sequence where (i) the tail was photoexpelled and replaced by water with isomerization, (ii) the water was replaced by chloride at room temperature, yielding a mixture of **11**$^+$ and **11′**$^+$, and (iii) chloride was trapped by silver(I) in acetone, leading to back-coordination of the tail. Repeating these three steps on the same sample allowed us to gradually enrich an initially pure sample of **1**$^{2+}$ in **2**$^{2+}$. After two runs, starting from a mixture of **1**$^{2+}$ and **2**$^{2+}$, a 44:56 ratio was obtained, which was beyond the theoretical 50:50 statistical limit. This experiment proves that the second irradiation with an interference filter centered at 470 nm was selective on isomer **1**$^{2+}$ and left **2**$^{2+}$ untouched. However, the inherent experimental complexity of this photochemical sequence (3 precipitations) obviously limited the potential of the herein described scorpionate molecule as a photochemically controlled molecular switch. The long and flexible nature of the polyether chain may be a limiting factor for the back-coordination of the tail.

Conclusion

Two ruthenium(II) polypyridyl complexes, **1**$^{2+}$ and **2**$^{2+}$, were synthesized and fully characterized by absorption spectroscopy, mass spectrometry, and ^{1}H and ^{13}C nuclear magnetic resonance. Their scorpionate nature was demonstrated, and they were shown to be coordination isomers. Because of the different natures of their coordinated monodentate ligands, their ^{1}MLCT absorption bands were different enough to show selective irradiation by wavelength selection. Photoinduced expulsion of the coordinated tail led to two processes: (i) opening of the ruthena-macrocycle and coordination of a solvent molecule, S, to the ruthenium and (ii) isomerization of the complex, corresponding to a 90° rotation of the phenanthroline in its plane and around the ruthenium atom, occurring on the transient pentacoordinated species. These two processes were studied in different solvents showing either strong or poor coordinating properties. Photoinduced opening of the ruthena-macrocycle was shown to be quantitative, but isomerization was a slower process. Thermal back-coordination of the tail was investigated in the dark; it was not followed by further rotation of the bidentate chelate. With water as the monodentate ligand, isomerization was efficient and led to a statistical mixture of the two open isomers of Ru(terpy*)(**3**)$(H_2O)^{2+}$; however, thermal recoordination had a low yield. In contrast, with chloride as the monodentate ligand, isomerization did not take place during irradiation but back-coordination was quantitative. It was experimentally shown that band-pass filters permitted selective irradiation of one isomer in a

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mixture of $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$. This led to partial enrichment of the mixture of the nonirradiated isomer.

Experimental Section

^{1}H NMR spectra were acquired on a Brucker AVANCE 300 (300 MHz) a Bruker AVANCE 400 (400 MHz), or a Bruker AVANCE 500 (500 MHz) spectrometer, using the deuterated solvent as the lock and the residual solvent as the internal reference. Mass spectra were obtained by using a VG ZAB−HF(FAB) spectrometer, a VG-BIOQ triple quadrupole, positive mode, or a Bruker MicroTOF spectrometer (ES-MS). UV−vis spectra were recorded with a Kontron Instruments UVIKON 860 spectrometer at room temperature.

4′-(2,5-Ditertiobutylphenyl)-2,2′;6′,2″-terpyridine (terpy*),[49] triethyleneglycol monoiodide (3,6-dioxa-1-hydroxy-8-iodooctane),[50] and 3,8-dianisyl-1,10-phenanthroline[51] were prepared according to literature procedures. Tetraethylammonium chloride was dried overnight under vacuum. 1,10-Phenanthroline hydrochloride, acetonitrile, 2-(2-(2-chloroethoxy)ethoxy)ethanol, 2-methylthioethanol, and parahydroxybenzonitrile were commercial products. $RuCl_3 \cdot xH_2O$ was kindly provided by Johnson Matthey Inc. Dichloromethane was distilled under CaH_2. Acetone was distilled and dried over sodium sulfate. KPF_6 was used as a 40 g/L aqueous solution, and KNO_3 was used as a saturated aqueous solution. In every synthesis of ruthenium complexes, chromatography fractions were worked up as follows: addition of an excess of KPF_6, evaporation of acetone until precipitation, filtration, washing with water, recovery from the P4 frit with acetone, and drying under vacuum.

2-(2-(2-Paracyanophenylethoxy)ethoxy)ethanol. A suspension of 11.3 g of cesium carbonate (34.8 mmol) in 75 mL of dimethylformamide was put under argon; 2.07 g of parahydroxybenzonitrile (17.4 mmol) in 25 mL of DMF was added dropwise without a noticeable color change. The suspension was heated at 60 °C, and a solution containing 5.86 g of 2-(2-(2-ethoxy)ethoxy)-chloroethanol (34.8 mmol) in 25 mL of DMF was added dropwise under argon. The reaction vessel was stirred under argon at 60 °C overnight (18 h), and the DMF was removed under vacuum. Water and DCM were added, and the aqueous phase was extracted three times with dichloromethane. The organic phases were combined, washed with NaOH (0.1 M), water, and brine, and evaporated to dryness to yield 6.56 g of crude oil. This material was put on a silica gel chromatography column using DCM/MeOH (2%) as the eluent. The main fraction was collected; the solvent evaporated, and the residue was weighed (5.69 g). NMR analysis revealed that the oil was a mixture of the product and the starting chlorotriethyleneglycol. TLC (silica, alumina) showed that these two compounds could not be separated by chromatography. The sample was used for the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (d, 2H, a, $J = 8.9$ Hz), 6.94 (d, 2H, b, $J = 9.0$ Hz), 4.15 (t, 2H, α, $J = 4.6$ Hz), 3.85 (t, 2H, β, $J = 4.8$ Hz), 3.75−3.56 (m, 8H, $\gamma\delta\epsilon\zeta$), 2.53 (s, 1H, OH). ^{13}C NMR (300 MHz, $CDCl_3$): δ 162.1 (c), 134.0 (a), 119.2 (d), 115.4 (b), 104.2 (CN), 72.6−69.4 ($\beta\gamma\delta\epsilon$), 67.7 ($\zeta$), 61.7 (α).

Compound 4. The preceding mixture of alcohols (1.01 g) was dissolved in 50 mL of dichloromethane and cooled to 0 °C under argon; 10 mL of distilled triethylamine was added. A solution containing 0.80 mL of mesyl chloride in 20 mL of dry dichloromethane was added dropwise at 0 °C within 20 min. The solution was stirred at 1 °C for 4 h and at room temperature overnight. Fifty milliliters of water was added at 0 °C under vigorous stirring. The aqueous phase was extracted with dichloromethane, and the combined organic phases were washed with water and brine, dried on Na_2SO_4, and evaporated under vacuum. Yield: 1.57 g of a yellowish oil. NMR analysis showed the presence of the chloromesyltriethyleneglycol. This mesylate mixture was dissolved in 20 mL of acetone and transferred into a solution of 3.85 g (44.3 mmol) of lithium bromide in 100 mL of acetone. The solution was refluxed under argon for 4 h. The acetone was removed under vacuum, water and DCM were added, and the aqueous phase was extracted with dichloromethane. The combined organic phases were washed with water and brine and evaporated to dryness. The crude product was chromatographed on silica gel (eluent DCM/MeOH 0.5%). The bromochlorotriethyleneglycol was removed to yield 736 mg of the analytically pure bromide **4** (76% from the starting alcohol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (d, 2H, a, $J = 9.1$ Hz), 6.92 (d, 2H, b, $J = 8.9$ Hz), 4.12 (t, 2H, ζ, $J = 4.7$ Hz), 3.83 (t, 2H, ϵ, $J = 4.9$ Hz), 3.75 (t, 2H, β, $J = 6.2$ Hz), 3.70−3.60 (m, 4H, $\gamma\delta$), 3.41 (t, 2H, α, $J = 6.2$ Hz). ^{13}C NMR (300 MHz $CDCl_3$): δ 162.1 (c), 133.9 (a), 119.2 (d), 115.4 (b), 104.0 (CN), 71.2, 70.8, 70.6, 70.5, 69.4 ($\beta\gamma\delta\epsilon$), 67.8 ($\zeta$), 30.5 (α). IE-MS: *m*/*z* (calcd) 313.0 (313.0 $[M]^+$), 194.9 (195.0 $[M - OC_6H_4CN]^+$), 145.0 (146.1 $[M - Br(CH_2CH_2O)_2 + H]^+$), 106.9 (107.0 $[M - (OCH_2CH_2)_2OC_6H_4CN]^+$), 102.0 (102.0 $[M - Br(CH_2CH_2O)_3]^+$).

Compound 6. Potassium hydroxyde (2.74 g, 48.9 mmol) was ground in a mortar and put into a 50 mL two-necked round-bottom flask. A condensor was adapted, and the flask was put under argon and heated to 60 °C. 2-Methylthioethanol (4.25 mL, 48.9 mmol) was added dropwise under efficient stirring, and the suspension was stirred for 15 min; 16.8 g (48.9 mmol) of triethylene glycol monoiodide was then added dropwise to ensure that the internal temperature did not go higher than 70 °C. The reaction mixture was stirred at 60 °C for 4 h. The mixture was cooled to room temperature; 80 mL of water and 80 mL of dichloromethane were added, and the aqueous phase was extracted three times with dichloromethane. The combined organic phases were washed with water and brine and dried over sodium sulfate; the solvent was removed under vacuum. The crude mixture (14.4 g) was put in an alumina column and eluted with a DCM/hexane mixture (from 1:1 to 1:0). The starting iodo chain and the elimination product were removed to yield the substitution product **6** as a colorless oil. Yield: 5.65 g (38%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.60 (t, 1H, a, $J = 3.5$ Hz), 3.88−3.78, 3.67−3.53, 3.52−3.42 (m, 2H, 13H and 1H resp, α, β, γ, δ, ϵ, ζ, η, e), 2.66 (t, 2H, θ, $J = 6.9$ Hz), 2.11 (s, 3H, CH_3(SO)), 1.90−1.40 (m, 6H, b, c, d). ^{13}C NMR (300 MHz, $CDCl_3$): δ 99.0 (a), 70.7−70.5 ($\gamma\delta\epsilon\zeta$), 70.4 ($\eta$), 66.7 (α), 62.3 ($\beta$), 53.5 (e), 33.5 ($\theta$), 30.7, 25.5, 19.6 (b, c, d), 16.1 (CH_3-(SO)). IE-MS: *m*/*z* (calcd) 307.1 (308.1 $[M - H]^+$), 233.1 (233.1 $[M - CH_3SCH_2CH_2]^+$), 225.1 (225.1 $[M - THP + 2H]^+$), 206.0 (206.1 $[M - THPOH]^+$), 119.1 (119.1 $[M - THPO(CH_2CH_2O)_2]^+$), 92.0 (92.1 $[M - THP(OCH_2CH_2)_3 + H]^+$), 85.1 (85.1 $[M - CH_3S(CH_2CH_2O)_4]^+$), 75.1 (75.1 $[M - THPO(CH_2CH_2O)_4]^+$).

Compound 7. Thioether **6** (752 mg, 2.44 mmol) was dissolved under argon in 75 mL of dichloromethane, and the mixture was cooled to 0 °C; 504 mg of *m*-chloroperbenzoic acid (75% pure with 25% of *m*-chlorobenzoic acid, 2.44 mmol) was dissolved in 50 mL of dichloromethane. This solution was added dropwise to the thioether solution at 0 °C, and the mixture was stirred at 0 °C for 8 h under argon. The solution was quenched with 50 mL of saturated aqueous sodium carbonate without letting the temperature

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go over 15 °C. The mixture was extracted three times with dichloromethane; the combined organic phases were washed with brine, dried on sodium sulfate, and evaporated. The crude product was put on an alumina column, and the remaining starting material was removed with DCM/MeOH (0.5%) The sulfoxide was eluted with DCM/MeOH (1%). Yield: 746 mg of sulfoxide **7** (94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.63 (dd, 1H, a, $J = 2.8$, 4.2 Hz), 3.95−3.80, 3.70−3.55, 3.55−3.45 (m, 4H, 11H and 1H resp, $\alpha\beta\gamma\delta\epsilon\zeta$, e), 3.05−2.85 (m, 2H, θ), 2.64 (s, 3H, CH_3(SO)), 1.90−1.45 (m, 8H, b + c + d). ^{13}C NMR (300 MHz, $CDCl_3$): δ 99.1 (a), 70.7−70.5 ($\gamma\delta\epsilon\zeta$), 66.7 ($\alpha$), 63.7 ($\eta$), 62.4 ($\beta$), 54.9 ($\theta$), 53.4 (e), 39.3 ($CH_3$(SO)), 30.7, 25.5, 19.6 (b, c, d). IE-MS: *m*/*z* (calcd) 325.2 (325.2 $[M + H]^+$), 307.3 (307.3 $[M - OH]^+$), 295.2 (295.1 $[M - CH_3O + 2H]^+$), 241.2 (241.1 $[M - THP + 2H]^+$), 197.1 (197.1 $[M - THPOCH_2CH_2 + 2H]^+$), 153.1 (153.0 $[M - THP\text{-}(OCH_2CH_2)_2 + 2H]^+$), 85.1 (85.1, $[M - CH_3S(CH_2CH_2O)_4]^+$), 63.1 (63.0 $[M - THP(OCH_2CH_2)_4]^+$).

Compound 8. Protected alcohol **7** (725 mg, 2.24 mmol) was dissolved in 250 mL of ethanol; a catalytic amount of *p*-toluenesulfonic acid was added, and the solution was refluxed under argon for 5 h. The solvent was evaporated to dryness, and the yield was 533 mg of analytically pure **8** (99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.92 (m, 2H, α), 3.71 (t, 2H, β), 3.66 (s, 8H, $\gamma\delta\epsilon\zeta$), 3.59 (t, 2H, η), 3.06−2.84 (m, 2H, θ), 2.63 (s, 3H, CH_3(SO)), 2.50 (broad s, 1H, OH). ^{13}C NMR (300 MHz, $CDCl_3$): δ 72.5 (α), 70.6−70.3 ($\gamma\delta\epsilon\zeta$), 63.6 ($\eta$), 61.6 ($\beta$), 54.7 ($\theta$), 39.1 ($CH_3$(SO)). FAB-MS: *m*/*z* (calcd) 241.2 (240.1 $[M + H]^+$).

Compound 9. Alcohol **8** (516 mg, 2.15 mmol) and *p*-toluenesulfonyl chloride (744 mg, 3.90 mmol) were dissolved in 80 mL of distilled dichloromethane. The solution was put under argon and cooled to 0 °C. Four milliliters of triethylamine (28.9 mmol) was added at 0 °C; the solution was stirred at this temperature for 30 min and then at room temperature for 3 h. The reaction was quenched by the addition of 408 mg of Na_2CO_3 in 30 mL of water, and the mixture was stirred for 30 min at room temperature. Fifty milliliters of saturated $NaHCO_3$ was added, and the aqueous phase was extracted three times with dichloromethane. The organic phases were collected and evaporated, and the crude material was purified by chromatography on alumina (eluent DCM/MeOH 1%). Yield: 206 mg of tosylate **9** (24%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, 2H, a, $J = 8.3$ Hz), 7.32 (d, 2H, b, $J = 8.0$ Hz), 4.13 (t, 2H, β, $J = 4.2$, 5.4 Hz), 3.88 (m, 2H, α), 3.68−3.56 (m, 10H, $\gamma\delta\epsilon\zeta\eta$), 3.05−2.93, 2.91−2.81 (m, 2H, θ), 2.60 (s, 3H, CH_3(SO)), 2.42 (s, 3H, CH_3(Ts)). ^{13}C NMR (300 MHz, $CDCl_3$): δ 144.9 (d), 133.0 (c), 129.9 (a), 128.0 (b), 70.8, 70.7, 70.6, 70.5 ($\gamma\delta\epsilon\zeta$), 69.3 ($\alpha$), 68.8 ($\beta$), 63.7 ($\eta$), 54.9 ($\theta$), 39.3 ($CH_3$(SO)), 21.7 ($CH_3$(Ts)).

Compound 5. Tosylate **9** (179 mg, 0.454 mmol) and lithium bromide (395 mg, 4.54 mmol) were dissolved in 25 mL of acetone, and the mixture was refluxed under argon for 4 h. The acetone was evaporated, and the crude product was purified by chromatography on silica (eluent DCM/MeOH 5%). Yield: 105 mg of bromide **5** (76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.92−3.88 (m, 2H, η), 3.80 (t, 2H, β, $J = 6.3$ Hz), 3.65 (broad s, 8H, $\gamma\delta\epsilon\zeta$), 3.46 (t, 2H, α, $J = 6.3$ Hz), 3.00−2.85 (m, 2H, θ), 2.63 (s, 3H, CH_3-(SO)). ^{13}C NMR (300 MHz, $CDCl_3$): δ 71.3 (β), 70.8 (γ), 70.7 (δ), 70.7 (ϵ), 70.6 (ζ), 63.7 (η), 55.0 (θ), 39.4 (CH_3(SO)), 30.5 (α). IE-MS: *m*/*z* (calcd) 303.1 (303.0 $[M + H]^+$), 223.0 (223.1 $[M - Br]^+$), 196.0 (195.0 $[M - CH_3SOCH_2CH_2O]^+$), 179.1 (179.0 $[M - BrCH_2CH_2O]^+$), 151.0 (151.0 $[M - CH_3SO(CH_2CH_2O)_2]^+$), 135.1 (135.1 $[M - Br(CH_2CH_2O)_2]^+$), 107.0 (107.0 $[M - CH_3\text{-}SO(CH_2CH_2O)_3]^+$), 91.1 (91.1 $[M - Br(CH_2CH_2O)_3]^+$), 63.1 (63.1 $[M - BrCH_2CH_2(OCH_2CH_2)_3]^+$).

Compound 10. Forty-four milliliters of 37% hydrochloric acid was slowly added to 40 mL of pyridine in a three-necked 100 mL round-bottom flask. A distillation apparatus was adapted, and the water was distilled off under argon until the internal temperature in the flask reached 220 °C. The pyridinium chloride was cooled to 140 °C, and 1.00 g (2.56 mmol) of 3,8-dianisylphenanthroline was added as a solid under argon. The mixture was heated at reflux (221 °C) for 3 h. The heating was stopped when the temperature was 140 °C and 100 mL of water was slowly added. The reaction mixture was homogenized and transferred into a 500 mL Erlenmeyer flask with 200 mL of water and 100 mL of ethanol. The yellow suspension was neutralized with 0.1 M sodium hydroxide solution until the pH of the liquid phase was stable (7.5). The solid was filtered off using a Millipore filter and dried under vacuum using P_2O_5 as a drying agent. Yield: 933 mg (100%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.90 (s, 2H, PhOH), 9.38 (s, 2H, P_2), 8.84 (d, 2H, P_4, $J = 2.2$ Hz), 8.11 (s, 2H, P_5), 7.83 (d, 4H, P_a, 8.8 Hz), 6.99 (d, 4H, P_b, $J = 8.8$ Hz). ^{13}C NMR (500 MHz, DMSO-d_6, assignments were done according to HSQC and HMBC correlation experiments): δ 158.0 (P_c), 146.6 (P_2), 140.7 (P_6), 134.7 (P_3), 133.1 (P_4), 128.3 (P_a), 127.0 (P_5), 126.2 (P_d), 116.0 (P_b). P_7 could not be assigned. Anal. Calcd for $C_{24}H_{16}N_2O_2{\cdot}HCl{\cdot}2H_2O$: C, 65.98; H, 4.84; N, 6.41. Found: C, 65.49; H, 4.82; N, 6.24.

Compound 3. 3,8-Di(parahydroxyphenyl)-1,10-phenanthroline (20 mg, 55 μmol) was dissolved in 10 mL of DMF. The solution was put under argon, and 89 mg of cesium carbonate (275 μmol) was added; in less than two minutes, the yellow solution turned bright orange. A solution containing 36 mg of **4** (110 μmol) and 34 mg of **5** (110 μmol) in 12 mL of DMF was prepared and added to the phenolate solution. A condensor was adapted, and the reaction mixture was degassed and heated at 60 °C under argon for 24 h. The DMF was pumped under vacuum; water and dichloromethane were added, and the aqueous phase was extracted three times with DCM. The organic phases were combined, washed with water and brine, and evaporated to dryness. This crude material was put on a neutral alumina column and eluted with DCM/MeOH (1%). The positions of the three phenanthrolines in the column were followed with a UV lamp, and the three compounds were collected separately. Yield: 18 mg of **3** (44%) and 9 mg of each of the two symmetric phenanthrolines **3′** and **3″**. Characterization of **3**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.38 (s, 2H, $P_2 + P_9$), 8.32 (d + d, 2H, $P_4 + P_7$), 7.84 (s, 2H, $P_5 + P_6$), 7.70 (d + d, 4H, $P_{a3} + P_{a8}$), 7.54 (d, 2H, P_a, $J = 8.9$ Hz), 7.08 (d + d, 4H, $P_{b3} + P_{b8}$), 6.95 (d, 2H, P_b, $J = 8.9$ Hz), 4.23−4.15 (m, 6H, $\alpha_3 + \alpha_8 + \zeta_3$), 3.92−3.87 (m, 8H, $\beta_3 + \beta_8 + \epsilon_3 + \eta_8$), 3.76−3.66 (m, 12H, $\gamma_3 + \delta_3 + \gamma_8 + \delta 8 + \epsilon_8 + \zeta_8$), 3.03−2.83 (m, 2H, θ_8), 2.61 (s, 3H, CH_3(SO)). ^{13}C NMR (400 MHz, $CDCl_3$, assigments were made according to HSQC and HMBC 2D ^{1}H−^{13}C HETCORR experiments): δ 162.2 (P_c), 159.34, 159.30 (P_{c3}, P_{c8}), 149.35 ($P_2 + P_9$), 144.8 ($P_{11} + P_{12}$), 135.3 ($P_{d3} + P_{d8}$), 134.1 (P_a), 132.7 ($P_4 + P_7$), 130.3 ($P_3 + P_8$), 128.7 ($P_{a3} + P_{a8}$), 128.5 ($P_{13} + P_{14}$), 127.2, 127.1 (P_5, P_6), 119.3 (P_{CN}), 115.5, 115.4 (P_b, $P_{b3} + P_{b8}$), 104.2 (P_d), 71.1, 71.0, 71.0, 70.8, 70.6 ($\gamma_3 + \gamma_8 + \delta_3 + \delta_8 + \epsilon_8 + \zeta_8$), 69.9, 69.8 ($\beta_3 + \beta_8$), 69.6 ($\epsilon_3$), 67.9 ($\zeta_3$), 67.7, 67.7 ($\alpha_3 + \alpha_8$), 63.7 ($\eta_8$), 54.9 ($\theta_8$), 39.3 ($CH_3$(SO)). FAB MS: *m*/*z* (calcd) 820.2 (820.3 $[M + H]^+$).

Complex $11^+{\cdot}PF_6^-$. Seventeen milligrams of Ru(terpy*)Cl_3 (27 μmol) and 5 mg of lithium chloride (27 μmol) were weighed in a 50 mL two-necked round-bottom flask; 5 mL of water and 10 mL of ethanol were added, and the suspension was put under argon. Eighteen milligrams of phenanthroline **3** (22 μmol) was dissolved in 10 mL of hot ethanol, and this solution was transferred to the reaction vessel. The mixture was degassed and heated at reflux under argon for 5 h. Aqueous KPF_6 and distilled water were added

to the cooled solution; the ethanol was removed under vacuum, and the violet precipitate was filtered on a P4 frit and washed with water. The solid was recovered with acetone and evaporated to dryness. The mixture of chloro isomers was put on a silica gel column and eluted with an acetone/water/saturated $KNO_{3(aq)}$ mixture (300:15:2). The violet band was collected, precipitated with KPF_6 and water, filtered, washed with water, recovered with acetone, and evaporated to dryness. Yield: 22 mg of a 1:1 mixture of the two isomers [**11**][PF_6]. UV−vis ($CHCl_3$): λ_{max} (ϵ) 367.5 (33 800), 516.5 nm (11 000 M^{-1} cm^{-1}). ES MS: *m*/*z* (calcd) 1377.449 (1377.444 [M − PF_6]$^+$).

Preparation and Characterization of Isomer 11$^+$. Three milligrams of [**1**][PF_6]$_2$ (1.8 μmol) was weighed in a conical flask; 3 mg (18 μmol) of dry tetraethylammonium chloride was added, and an NMR tube was prepared using CD_2Cl_2 as the solvent. The tube was irradiated for 2 h at 25 °C with a xenon 1000 W lamp fitted with a water filter and an Andover 470FS10-50 interference filter. The color of the solution changed from orange to violet. The solution was transferred into a flask containing 30 mL of saturated KPF_6 aqueous solution, and the ruthenium complex precipitated. It was filtered, washed thoroughly with water, recovered with acetone, and vacuum dried. Yield: 2.8 mg (100%) of [**11**][PF_6] as a 95:5 mixture of the two isomers **11**$^+$/**11′**$^+$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 10.77 (d, 1H, P_2, J = 1.9 Hz), 8.89 (d, 1H, P_4, J = 2.0 Hz), 8.63 (s, 2H, $T_{3'5'}$), 8.49 (d, 2H, $T_{33''}$, J = 8.0 Hz), 8.34−8.32 (m, 2H, P_5 + P_7), 8.13 (d, 1H, P_6, J = 9.0 Hz), 8.03 (d, 2H, P_{a3}, J = 6.7 Hz), 7.88 (td, 2H, $T_{44''}$, J = 7.6, 1.4 Hz), 7.79 (d, 1H, P_9, J = 1.9 Hz), 7.78 (d, 2H, T_o, J = 1.9 Hz), 7.70 (t, 1H, T_p, J = 1.7 Hz), 7.62 (m, 2H, $T_{66''}$), 7.56 (d, 2H, P_a, J = 9.0 Hz), 7.23 (d, 2H, P_{a8}, J = 8.9 Hz), 7.21−7.17 (m, 4H, $T_{55''}$ + P_{b3}), 6.99 (d, 2H, P_b, J = 9.0 Hz), 6.93 (d, 2H, P_{b8}, J = 8.8 Hz), 4.23 (m, 2H, α_3), 4.18 (m, ζ_3), 4.08 (m, 2H, α_8), 3.89 (m, 2H, β_3), 3.86 (m, 2H, ϵ_3), 3.82 (m, 2H, η_8), 3.77 (m, 2H, β_8), 3.73 (s, 4H, γ_3 + δ_3), 3.64−3.62 (m, 2H, γ_8), 3.60−3.58 (m, 2H, δ_8), 3.58 (s, 4H, ϵ_8 + ζ_8), 2.96−2.76 (m, 2H, θ_8), 2.53 (s, 3H, CH_3(SO)), 1.49 (s, 18H, tBu).

Preparation and Characterization of Isomer 11′$^+$. Three milligrams (1.8 μmol) of [**2**][PF_6]$_2$ was weighed in a conical flask; 3 mg (18 μmol) of dry tetraethylammonium chloride was added, and an NMR tube was prepared using CD_2Cl_2 as the solvent. The tube was irradiated for 2 h at 25 °C with a xenon 1000 W lamp fitted with a water filter and an Andover 430FS10-50 interference filter. The color of the solution changed from yellow to violet. The solution was transferred into a flask containing 30 mL of saturated KPF_6 aqueous solution, and the ruthenium complex precipitated. It was filtered, washed thoroughly with water, recovered with acetone, and vacuum dried. Yield: 2.8 mg of [**11**][PF_6] as a 9:91 mixture of the two isomers **11**$^+$/**11′**$^+$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 10.78 (d, 1H, P_2, J = 1.9 Hz), 8.90 (d, 1H, P_4, J = 2.0 Hz), 8.63 (s, 2H, $T_{3'5'}$), 8.49 (d, 2H, $T_{33''}$, J = 8.0 Hz), 8.32 (d, 1H, P_5, J = 9.0 Hz), 8.31 (d, 1H, P_7, J = 1.8 Hz), 8.13 (d, 1H, P_6, J = 9.0 Hz), 8.03 (d, 2H, P_{a3}, J = 6.7 Hz), 7.88 (td, 2H, $T_{44''}$, J = 7.6, 1.4 Hz), 7.79 (d, 1H, P_9, J = 1.9 Hz), 7.78 (d, 2H, T_o, J = 1.9 Hz), 7.70 (t, 1H, T_p, J = 1.7 Hz), 7.62 (m, 2H, $T_{66''}$), 7.51 (d, 2H, P_a, J = 9.0 Hz), 7.22−7.17 (m, 6H, P_{a8} + $T_{55''}$ + P_{b3}), 6.95 (d, 2H, P_b, J = 9.0 Hz), 6.89 (d, 2H, P_{b8}, J = 8.8 Hz), 4.25 (m, 2H, α_3), 4.13 (m, ζ_3), 4.04 (m, 2H, α_8), 3.90 (m, 2H, β_3), 3.86 (m, 2H, ϵ_3), 3.82 (m, 2H, η_8), 3.77 (m, 2H, β_8), 3.65 (s, 4H, ϵ_8 + ζ_8), 3.63 (s, 4H, γ_3 + δ_3), 3.64−3.62 (m, 2H, γ_8), 3.60−3.58 (m, 2H, δ_8), 3.03−2.80 (m, 2H, θ_8), 2.57 (s, 3H, CH_3(SO)), 1.48 (s, 18H, tBu).

1^{2+}·2PF_6^- and 2^{2+}·2PF_6^-. Eighteen milligrams (93 μmol) of silver tetrafluoroborate were dissolved in 10 mL of acetone and put under argon. A solution of 22 mg (15 μmol) of [**11**][PF_6] as an equimolar mixture of both isomers dissolved in 20 mL of acetone was transferred into the flask, the reaction mixture was degassed and refluxed under argon in the dark for 2 h. The silver chloride precipitate was removed by filtration on Celite, the complexes were precipitated by the addition of KPF_6 and water, filtered, washed with water, recovered with acetone, and dried under vacuum. The crude material was put on a fine silica gel column and eluted with an acetone/water/saturated KNO_3 mixture 300:6:1. The yellow band was collected, precipitated with KPF_6, filtered, washed with water, recovered with acetone, and dried to give 12 mg of [**2**][PF_6]$_2$. The polarity of the eluent was increased to 75:6:1, and the orange band on the column was collected, precipitated with KPF_6, filtered, washed with water, recovered with acetone and evaporated to dryness to yield 12 mg of [**1**][PF_6]$_2$.

Characterization of 1^{2+}·2PF_6^-. ^{1}H NMR (500 MHz, acetone-d_6): δ 10.23 (d, 1H, P_2, J = 1.9 Hz), 9.25 (d, 1H, P_4, J = 2.0 Hz), 9.24 (s, 2H, $T_{3'5'}$), 8.89 (m, 2H, J = 8.9, 2.5, 1.3 Hz), 8.52 (d, 1H, P_5, J = 8.9 Hz), 8.33 (d, 1H, P_6, J = 9.0 Hz), 8.15−8.12 (m, 4H, $T_{66''}$ + $T_{44''}$), 8.10 (d, 2H, T_o, J = 1.7 Hz), 8.03 (d, 1H, P_9), 8.02 (d, 2H, P_{a3}, J = 6.6 Hz), 7.82 (t, 1H, T_p, J = 1.7 Hz), 7.80 (d, 2H, BN_a, J = 9.1 Hz), 7.41 (m, 4H, $T_{55''}$ + P_{a8}), 7.21 (d, 2H, BN_b, J = 9.1 Hz), 7.21 (d, 2H, P_{b3}, J = 8.9 Hz), 6.95 (d, 2H, P_{b8}, J = 8.9 Hz), 4.39 (m, 2H, ξ_3, J = 4.5 Hz), 4.35 (t, 2H, α_3, J = 5.3 Hz), 4.13 (t, 2H, α_8, J = 4.7 Hz), 3.83−3.79 (m, 8H, η_8 + ϵ_3 + β_3 + β_8), 3.66−3.55 (m, 12H, γ_3 + δ_3 + γ_8 + δ_8 + ϵ_8 + ξ_8), 2.97−2.90 (m, 1H, θ''_8), 2.82−2.74 (m, 1H, θ'_8), 2.50 (s, 3H, CH_3(SO)), 1.51 (s, 18H, tBu). ^{13}C NMR (500 MHz, acetone-d_6, assigments were made according to HSQC and HMBC 2D ^{1}H−^{13}C HETCORR experiments): δ 164.0 (BN_c), 160.2 (P_{c3}), 160.0 (P_{c8}), 158.5 ($T_{22''}$), 157.7 ($T_{2'6'}$), 154.1($T_{66''}$), 151.3 (P_2), 151.1 ($T_{4'}$), 149.5 (P_9), 146.3 (P_8), 145.3 (P_3), 138.6 ($T_{44''}$), 136.6 (T_i), 135.4 (BN_a), 133.2 (P_7), 133.2 (P_{14}), 132.4 (P_{13}), 132.3 (P_4), 131 (P_{11}), 130.3 (P_{12}), 129.3 (P_{a3}), 128.8 (P_5), 128.7 (P_{d3}), 128.4 (P_{a8}), 128.4 ($T_{55''}$), 128.0 (P_6), 127.5 (P_{d8}), 126.3 (BN_d), 124.7 ($T_{33''}$), 124.5 (T_p), 122.3 (T_o), 122.2 (T_m), 122.0 ($T_{3'5'}$), 116.2 (P_{b3}), 116.2 (BN_b), 115.3 (P_{b8}), 101.2 (CN), 69 (β_3 − ϵ_3), 69 (β_8 − ζ_8), 68.5 (ζ_3), 68 (α_3), 67.6 (α_8), 64.3 (η_8), 53.9 (θ_3), 38.4 (CH_3(SO)), 35.0 (C(Me_3)), 30.8 (Me_3). ES-MS: *m*/*z* (calcd) 1487.42 (1487.44 [M − PF_6]$^+$), 671.231 (671.238 [M − 2PF_6]$^{2+}$). UV−vis (acetone): λ_{max} (ϵ) 362 nm (23 300), 468 nm (9090 L mol^{-1} cm^{-1}).

Characterization of 2^{2+}·2PF_6^-. ^{1}H NMR (500 MHz, acetone-d_6): δ 10.84 (d, 1H, P_9, J = 1.9 Hz), 9.37 (d, 1H, $T_{3'}$, J = 1.45 Hz), 9.29 (d, 1H, P_7, J = 1.9 Hz), 9.29 (d, 1H, $T_{5'}$, J = 1.44 Hz), 8.94 (d, 1H, T_3, J = 7.7 Hz), 8.88 (d, 1H, P_4, J = 1.9 Hz), 8.84 (d, 1H, $T_{3''}$, J = 7.8 Hz), 8.50 (d, 1H, P_6, J = 8.9 Hz), 8.32 (d, 1H, P_5, J = 8.9 Hz), 8.31 (d, 1H, $T_{6''}$, J = 4.9 Hz), 8.23 (td, 1H, T_4, J = 7.9,1.5 Hz), 8.18−8.14 (m, 2H, T_6 + $T_{4''}$), 8.10 (d, 2H, P_{a8}, J = 8.8 Hz), 8.09 (d, 2H, T_o, J = 1.7 Hz), 7.84 (t, 1H, T_p, J = 1.7 Hz), 7.80 (d, 1H, P_2, J = 1.9 Hz), 7.57 (d, 2H, BN_a, J = 9.0 Hz), 7.52 (ddd, 1H, T_5, J = 1.3, 5.6, 7.5 Hz), 7.47 (d, 2H, P_{b8}, J = 8.9 Hz), 7.44 (ddd, 1H, $T_{5''}$), 7.39 (d, 2H, P_{a3}, J = 8.9 Hz), 7.06 (d, 2H, BN_b, J = 9.0 Hz), 6.89 (d, 2H, P_{b3}, J = 8.8 Hz), 4.49 (dddd, 2H, α_8, J = 2.1, 5.8, 13.5, 41.6 Hz), 4.22 (t, 2H, ζ_3, J = 4.7 Hz), 4.11 (m, 1H, η_8), 4.07 (t, 2H, α_3, J = 4.9 Hz), 4.03 (m, 1H, η'_8), 3.88 (m, 2H, β_3), 3.86 (m, 1H, β_8), 3.83 (m, 2H, ϵ_3), 3.80 (m, 1H, β'_8), 3.76 (m, 1H, θ_8), 3.66 (m, 2H, γ_3), 3.61 (m, 2H, ζ_8), 3.59 (m, 2H, δ_3), 3.59 (m, 2H, γ_8), 3.57 (m, 2H, ϵ_8), 3.52 (m, 2H, δ_8), 2.99 (m, 1H, θ'_8), 2.63 (s, 3H, CH_3(SO)), 1.50 (s, 18H, tBu). ^{13}C NMR (500 MHz, acetone-d_6, assignments were done according to HSQC and HMBC 2D ^{1}H−^{13}C HETCORR experiments): δ 162.4 (BN_c), 161.0 (P_{c8}), 160.2 (P_{c3}), 157.9 ($T_{6'}$), 157.7 ($T_{2'}$), 157.6 ($T_{22''}$), 155.1 (P_9), 154.7 (T_6), 154.2 ($T_{6''}$), 152.5 (T_m), 147.4 (P_2), 147.1 (P_8), 144.5 (P_3), 140.1 ($T_{44''}$), 136.4 ($T_{4'}$), 134.5 (P_{13}), 134.4 (P_4), 134.0 (BN_a), 133.0 (P_7), 133.0 (P_{14}), 131.2 (P_{12}), 130.4 (P_{11}), 129.6 ($T_{5''}$), 129.5

(T_5), 129.0 (P_6), 128.8 (P_{a8}), 128.6 (P_{a3}), 128.0 (P_5), 127.9 (P_{d8}), 127.1 (P_{d3}), 126.1 ($T_{3''}$), 125.8 (T_3), 124.9 (T_i), 124.9 (T_p), 123.7 ($T_{3'}$), 123.3 ($T_{5'}$), 122.4 (T_o), 118.7 (BN_d), 117.4 (P_{b8}), 115.5 (P_{b3}), 115.5 (BN_b), 103.5 (CN), 68.7 (α_8), 68.6 (η_8), 68.1 (ζ_3), 67.6 (α_3), 54.8 (θ_8), 69.3−71.1 ($\beta_3 - \epsilon_3$), 69.1−71.0 ($\beta_8 - \zeta_8$), 38.5 (CH_3-(SO)), 34.9 (C(Me_3)), 31.0 (Me_3). ES-MS*: m/z* (calcd) 1487.443 (1487.439 $[M - PF_6]^+$), 671.242 (671.238 $[M - 2PF_6]^{2+}$). UV−vis (acetone): λ_{max} (ϵ) 362 (23 400), shoulder at 428 nm (8330 L mol^{-1} cm^{-1}).

Irradiation Experiments. In a typical experiment, 3 mg of $\mathbf{1}^{2+}\cdot 2PF_6^-$ or $\mathbf{2}^{2+}\cdot 2PF_6^-$ (1.8 μmol) was weighed in a vial; the deuterated solvent was added (CD_3CN, an acetone-d_6/D_2O mixture 9:1, or 20 equiv of tetraethylammonium chloride in CD_2Cl_2), and an NMR tube was prepared in the dark. A reference spectrum was taken at $t = 0$, and the course of the reaction was followed by ^1H NMR. Irradiations were performed under the following conditions. The NMR tubes were fitted to a glass cell thermostated at $T = 25$ °C. The lamp was a high pressure 1000 W xenon arc lamp providing a parallel beam of white light, and the beam was filtered by a 10 cm thick water filter filled with running water at 5 °C and by an Andover interference filter with $\Delta\lambda = 10$ nm, centered either at 430 (for $\mathbf{2}^{2+}$) or 470 nm ($\mathbf{1}^{2+}$) (reference of the filters, 430FS10-50 and 470FS10-50, respectively).

Characterization of Ru(terpy*)(3)(D_2O)$^{2+}\cdot 2PF_6^-$. ^1H NMR (300 MHz, acetone-d_6/D_2O (20%)): δ 10.26 (d, 1H, $P_{2,9}$), 9.17 (d, 1H, P_4), 9.06 (s, 2H, $T_{3'5'}$), 8.77 (d, 2H, $T_{33''}$), 8.51 (m, 1H, P_7), 8.45 (d, 1H, P_5), 8.23 (d, 1H, P_6), 8.14 (d, 2H, P_{a3}), 8.01 (td, 2H, $T_{44''}$), 7.99 (d, 2H, T_o), 7.94 (m, 2H, $T_{66''}$), 7.80 (d, 1H, P_9), 7.71 (t, 1H, T_p), 7.62 (d, 2H, P_a), 7.36−7.19 (m, 6H, $P_{a8} + T_{55''} + P_{b3}$), 7.09 (d, 2H, P_b), 6.89 (d, 2H, P_{b8}), 4.31−3.52 (m, 12H, $\alpha_3 - \zeta_3 + \alpha_8 - \eta_8$), 3.13−2.88 (m, 2H, θ_8), 2.63 (s, 3H, CH_3(SO) on the side of D_2O) or 2.59 (s, 3H, CH_3(SO) opposite to D_2O), 1.43 (s, 18H, tBu). UV−vis (acetone/water): λ_{max} (ϵ) 505 nm (7900 L mol^{-1} cm^{-1}). MS ES: *m/z* (calcd) 671.26 (671.24 $[M - 2PF_6 - D_2O]^{2+}$), 680.8 (681.2 $[M - 2PF_6]^{2+}$).

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