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Photochromic and Redox Properties of Bisterpyridine Ruthenium Complexes Based on Dimethyldihydropyrene Units as Bridging Ligands

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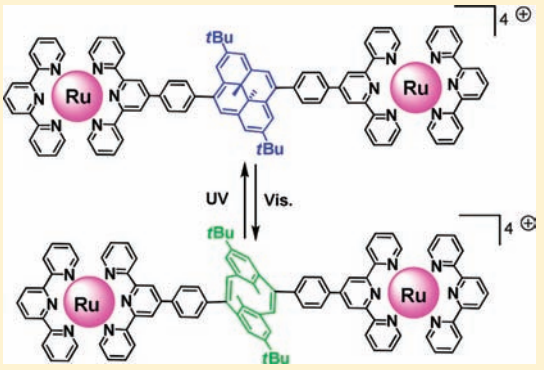
ABSTRACT: We report herein the synthesis and characterization of four new bisterpyridine dinuclear ruthenium complexes containing the dimethyldihydropyrene (DHP) photochrome as bridging ligand. A synthetic strategy has been developed based on a Suzuki coupling reaction to synthesize these novel terpyridine−DHPs. The reactivity of these different ligands and dinuclear ruthenium complexes with light was examined by ^{1}H NMR and monitoring the changes in their absorption spectra upon irradiation at controlled wavelengths. The free ligands and their corresponding ruthenium complexes all displayed photochromic properties with highly efficient conversion between the closed stable isomers (DHP) and their open forms (CPD). The properties of the compounds in their closed and open forms were investigated by cyclic voltammetry, spectroscopy, and luminescence measurements.



INTRODUCTION

Molecular switches, i.e., molecular systems that can be reversibly converted between two or more different well-defined and stable states by application of an external stimulus such as light, electricity, or a chemical process, are the subject of intensive research.[1] In particular, optical switches appear very attractive for construction of molecular devices and materials because their control can be achieved using light at different wavelengths, which is an easily controllable and clean energy that does not need direct contact or connection.[1,2] For example, some fascinating studies have already demonstrated applications of spiropyran,[3] fulgides,[4] or dithienylethene[2a,3−5] derivatives in electronic devices (e.g., memories, logic gates, molecular wires) or for construction of mechanical work based on geometrical structural changes of individual molecules induced by external stimuli.

In this context, a very promising strategy for the elaboration of multifunctional materials is to covalently combine organic photochromic derivatives with metal complexes.[6] Indeed, metal complexes can have well-defined and tunable optical, redox, and magnetical properties, and their association with optical switches may result in multiresponsive molecular assemblies that can find applications in many domains, such as in electronics (molecular logic gates, switchable molecular wires...), energy conversion, catalysis, or sensors. In particular, bipyridine and terpyridine metal complexes have been widely employed because of their high stability, well-defined geometries, and appealing redox, photophysical, and photochemical properties.[7] For instance, Nishihara and co-workers constructed a number of polypyridyl−transition metal complexes bearing azobenzene units and carried out a systematic study of their trans/cis isomerization and the concurrent change of the photophysical and electrochemical properties.[8] Terpyridine or bipyridine metal complexes associated with a photochromic dithienylethene (DTE) unit were also investigated by Abruña and co-workers.[9] It was shown that their photochemical and electrochemical properties could be finely tuned by changing the metal centers, the arrangement of terpyridine and dithienylcyclopentene units, and the terminal substituents. In particular, a dinuclear complex bridged by an open DTE was found to be inert to ultraviolet photoirradiation when Os^{II}, Ru^{II}, or Fe^{II} was used, while the Co^{II} system underwent efficient photochemical cyclization.[9a]

Here, we report the synthesis and characterization of a series of dinuclear ruthenium−bisterpyridine complexes containing the dimethyldihydropyrene (DHP)[10,11] photochrome moiety as a bridge, and one mononuclear-DHP complex is also presented (**L_1Ru**−**L_5Ru**, Chart 1).

Our objective was to investigate the photochromic, redox, and luminescence properties of the DHP unit when covalently coupled to terpyridine metal complexes and to evaluate the potentialities of these systems for further applications in switchable devices or materials. In addition, as fatigue resistance and thermal stability are among the most important requirements that a photochromic material should accomplish in order to be suitable for use as a molecular switch in devices useful as memory media, thermal reclosing rates and lifetimes of some of the compounds synthesized have been determined.

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Chart 1. Mono- and Bis-Ruthenium Complexes L_1Ru-L_5Ru

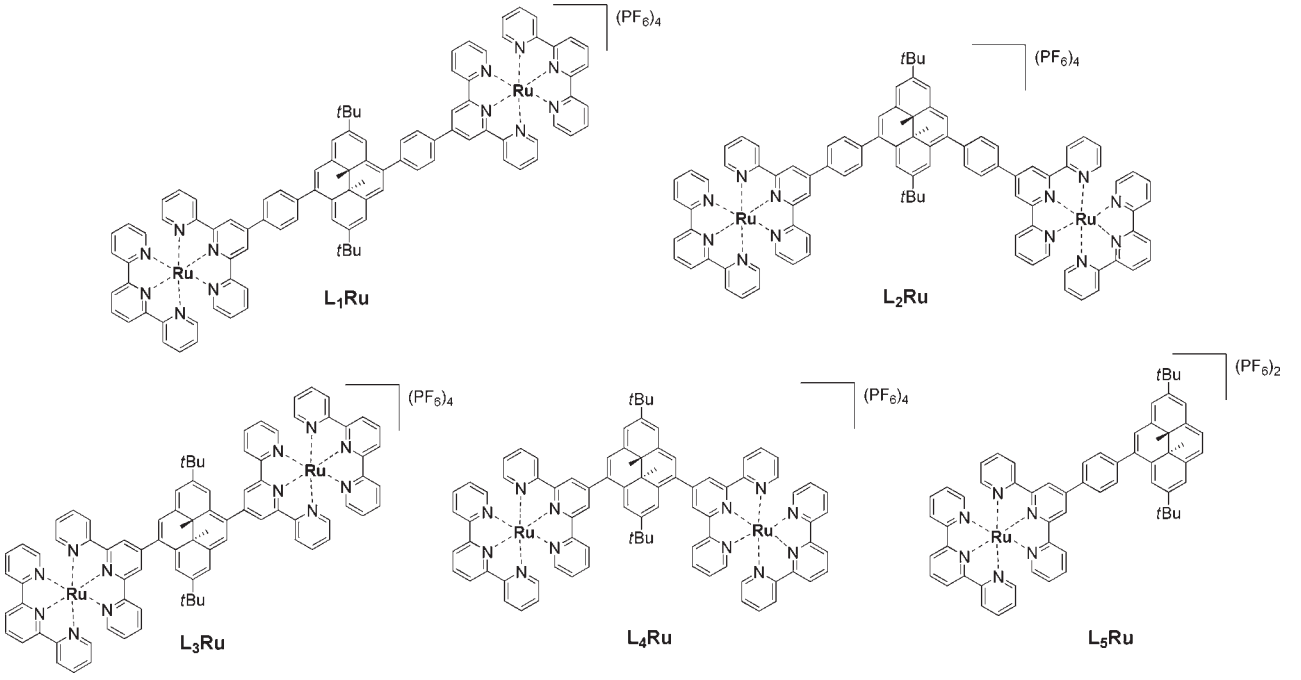
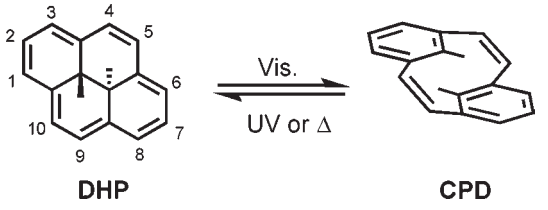


Chart 2. Optically Triggered Interconversion of the Dimethyldihydropyrene (DHP)/Cyclophanediene (CPD) System



The DHP photochrome, which was essentially exploited by Mitchell and co-workers[11,12] and belongs to the family of diarylethene, is a large π-conjugated system that can be quantitatively optically and reversibly converted to its less π-conjugated cyclophanediene (CPD) isomers (Chart 2). Interestingly, it represents a rare example of negative-T-photochrome, i.e., the colorless open form (CPD) usually reverts both photochemically and thermally to the colored and more stable DHP closed isomer.

A great advantage of the DHP moiety is that it can be chemically modified in many various ways and thus constitutes a real molecular platform ideally suitable for construction of multifunctional architectures. Nevertheless, compared to other organic photochromic molecules such as the well-known dithienylcyclopentene,[5] DHP derivatives have been much less intensively studied because of much longer synthetic pathways involved to afford them and examples of DHP systems associated to metal complexes are still rare.[13] Recently, a reversible photoswitching of the electronic communication between two ferrocenyl groups bridged by a DHP unit through π-conjugated ethynyl connectors was demonstrated.[13d] In contrast, no photoisomerization occurred when the two ferrocene units were replaced by stronger donor pentamethylferrocene moieties that probably quench the photoexcited state of the system preventing the ring opening of the DHP. This result shows that the properties of the DHP unit can be finely tuned and strongly depend on its environment.

RESULTS AND DISCUSSION

Synthesis of the Ligands. The five new bisterpyridine (L_1-L_4) and monoterpyridine (L_5) ligands (Chart 3) were all prepared using the same methodologies involving bromination of the DHP unit and Suzuki cross-coupling reactions. The synthetic procedure for L_1 is represented in Scheme 1.

This synthesis starts from the 2,7-di-*tert*-butyldimethyldihydropyrene (**1**, DHP), the *tert*-butyl groups being introduced for synthetic and solubility reasons. **1** was prepared in seven steps employing the *tert*-butyltoluene as starting material as previously described by Tashiro[14] and improved by Mitchell.[12c] Bromination of **1** in the presence of *N*-bromosuccinimide lead to the different bromo-DHP precursors of the bisboronic-DHP derivatives required for the Suzuki cross-coupling reaction.[12c] Several synthetic strategies have been employed to afford L_1 via Suzuki cross-coupling reaction. Initial attempts to generate the corresponding boronic ester from either the 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine or the 4′-chloro-2,2′:6′,2″-terpyridine led to low yields or repeatedly failed in the second case.[15] Alternatively, the known bis-bromide DHP (**2**)[12c] was first lithiated with 2 equiv of *n*-BuLi followed by addition of the tributyl borate to give the bisboronic DHP ester (**3**), which could be used without further purification in the next step. A Suzuki coupling[16] between the bisboronic DHP ester (**3**) and the 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine afforded the desired ligand (L_1) in good yield (74%). Generation of the corresponding bisboronic DHP acid (**4**) and subsequent Suzuki cross-coupling as described

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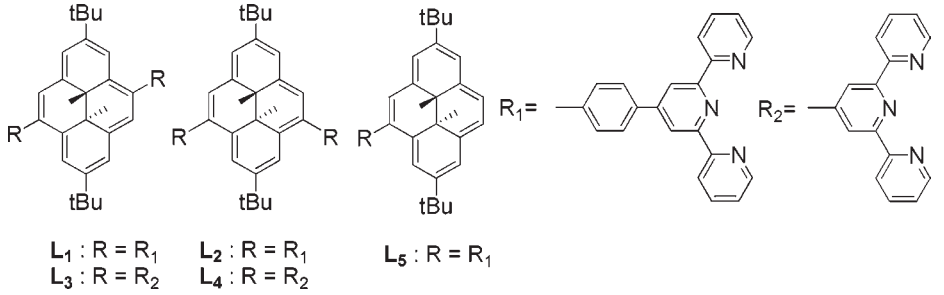
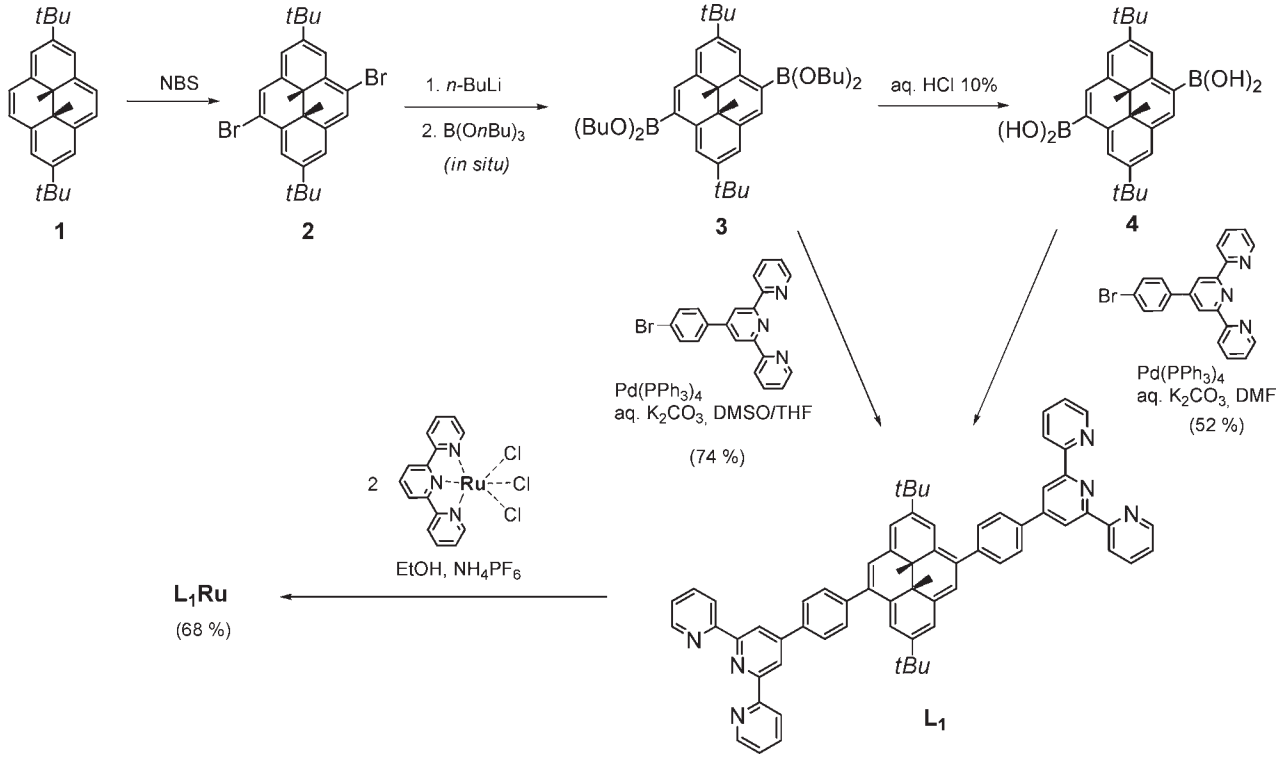
Chart 3. Bisterpyridine (L_1−L_4) and Monoterpyridine (L_5) Ligands Synthesized



Scheme 1. Overall Synthetic Pathways for Preparation of L_1 via Suzuki Cross-Coupling Reaction and Preparation of L_1Ru



above did not enhance the yield of the final product due to its low solubility in most of the organic solvents tested. The same synthetic route was employed to prepare L_2. In the case of ligands L_3 and L_4 the first step of Scheme 1 was analogous as for ligands L_1 and L_2. However, in the second step 4′-chloro-2,2′:6′,2″-terpyridine was employed instead of the 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine, leading to notably lower yields (32−40%). This fact is in good agreement with the well-known lower reactivity of the aryl chlorides in palladium-catalyzed reactions.[17] Table 1 summarizes the yields of the bridging ligands synthesized.

Full characterization for each compound is given in the Experimental Section. Analysis of the ^{1}H NMR spectra of ligands L_1−L_5 clearly corroborates that the closed forms were isolated. In each case, ^{1}H NMR peaks were observed in the negative region of the spectrum (Table 1 and Figure 1). These signals are characteristic of dihydropyrenes units in which the internal methyl protons are shielded by the strong diatropic ring current. In addition, these peaks appear slightly deshielded from those of the DHP (**1**) parent (δ = −4.04 ppm[12c]) and no longer identical to each other for L_2, L_4, and L_5 due to a loss of the symmetry.

Preparation of Mono- and Dinuclear Ruthenium Complexes (L_1Ru−L_5Ru). As depicted in Scheme 1 for L_1Ru, preparation of the ruthenium complexes L_1Ru−L_5Ru was carried out in the last step of the synthetic pathway through a divergent manner. In this approach, ligands L_1−L_5 previously synthesized after Suzuki coupling as mentioned above were directly complexed with either 1 or 2 mol equiv of (tpy)$RuCl_3$ to give the mononuclear (L_5Ru) or dinuclear (L_1Ru−L_4Ru) Ru(II) complexes, respectively. The ^{1}H NMR spectrum confirmed the metalation of the bisterpyridine−DHP ligands with a significant deshielding of the internal methyl protons that appeared at δ between −3.1 and −2.8 ppm (Table 1 and Figure 1).

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Table 1. Summary of the Preparation Yields, ^{1}H NMR, and Spectroscopic Data Obtained in the Synthesis of 1, Ligands (L_1−L_5), and Ruthenium Complexes (L_1Ru−L_5Ru)

		^{1}H NMR data for the internal methyl (DHP unit)[b]	λ_{max}, nm[d] ($\varepsilon/10^5$ L·mol^{-1}·cm^{-1})
compounds	synthetic yields (%)	closed/open	closed/open
1		−4.04 (6H)[e]/1.25 (6H)	486 (0.7)[e]
L_1	60[a]	−3.68 (6H)/1.34 (6H)	479 (0.18)/252 (1.37)
L_2	40[a]	−3.71 (3H), −3.73 (3H)/1.31 (3H), 1.35 (3H)	481 (0.22)/250 (1.45)
L_3	56[a]	−3.55 (6H)/1.28 (6H)	477 (0.25)/265 (1.71)
L_4	32[a]	−3.56 (3H), −3.58 (3H)/1.38 (3H), 1.42 (3H)	482 (0.28)/252 (1.67)
L_5	72[a]	−3.75 (3H), −3.73 (3H)/1.26 (3H), 1.36 (3H)	478 (0.23)/255 (1.02)
L_1Ru	41[c]	−2.98 (6H)/1.23 (6H)	487 (0.36)[f]/252 (1.83)
L_2Ru	35[c]	−2.93 (3H), −2.90 (3H)/1.30 (3H), 1.39 (3H)	485 (0.42)[f]/252 (1.68)
L_3Ru	47[c]	−2.86 (6H)/1.42 (3H)	486 (0.45)[f]/263 (1.54)
L_4Ru	38[c]	−2.89 (3H), −2.87 (3H)/1.46 (3H), 1.52 (3H)	489 (0.44)[f]/255 (1.27)
L_5Ru	56[c]	−3.04(3H), −3.01 (3H)/1.41 (3H), 1.47 (3H)	490 (0.43)[f]/252 (1.21)

[a] Reported yields of the ligands are calculated considering the corresponding monobromo- and dibromo-DHP's derivatives as starting material. [b] ^{1}H NMR spectra were recorded in CD_3CN. [c] Metalation yields. [d] Dimethyldihydropyrene core-based transition recorded in CH_3CN. [e] From ref 12c. [f] Overlapped with the MLCT absorption band.

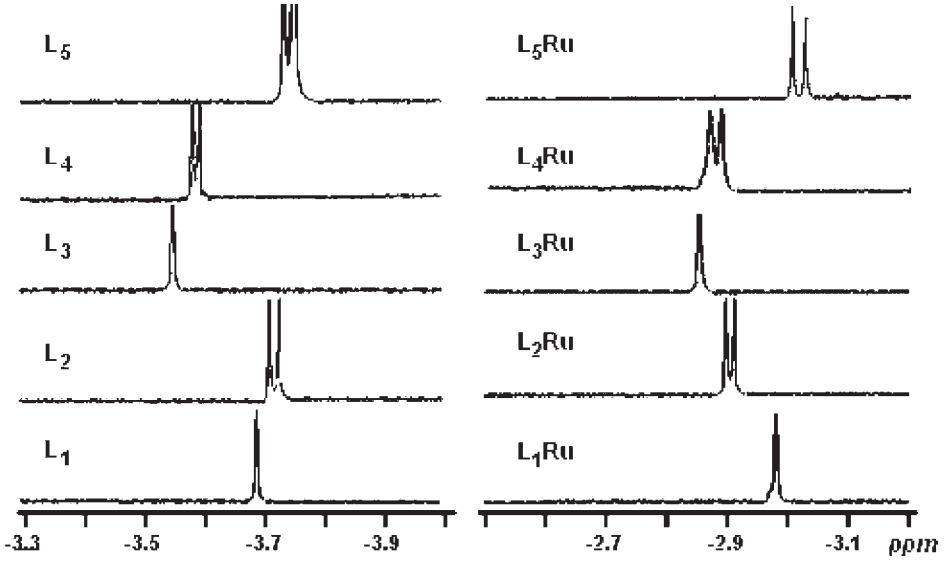

Figure 1. Partial ^{1}H NMR spectra in CD_3CN of the L_1−L_5 ligands (left) and corresponding ruthenium complexes (right) in their closed forms. Signals correspond to the internal methyl protons of the DHP unit.

■ ELECTRONIC ABSORPTION SPECTROSCOPY AND PHOTOCHROMIC BEHAVIORS

Absorption spectra of CH_3CN solutions of ligands L_1−L_5 all exhibit a typical band ($S_0 \rightarrow S_1$) of the DHP unit located in the 450−700 nm range (Table 1). Compared to the precursor **1**, it appeared that incorporation of the terpyridine functionalities did not produce a significant shift in the absorbance band with lowest energy.

The photochromic behavior of freshly prepared solutions of the systems was investigated by monitoring the changes of their absorption spectra upon irradiation with a specific wavelength of light in a 1 cm cell cooled at ∼0 °C (ice bath). Representative spectra are displayed in Figure 2. Irradiation of the green-brown solutions of ligands L_1−L_5 in their closed forms with visible light (cutoff filter $\lambda \geq 490$ nm) led to the ring opening of the DHP unit as observed by the progressive changes of the bands in the UV region and the disappearance of the long wavelength absorption bands of the ligands in the visible part of the spectrum as the light yellow cyclophanediene (CPD) isomer forms. Subsequent irradiation of the solution containing the open forms of the ligands at $\lambda = 254$ nm gave rise to regeneration of the spectrum corresponding to the initial closed form, showing the reversibility of the isomerization process.

This opening process could be also conventionally followed by ^{1}H NMR in CD_3CN, as represented in Figure 3 displaying the evolution of the spectrum upon photoirradation with visible light. Significant changes have been observed in the region corresponding

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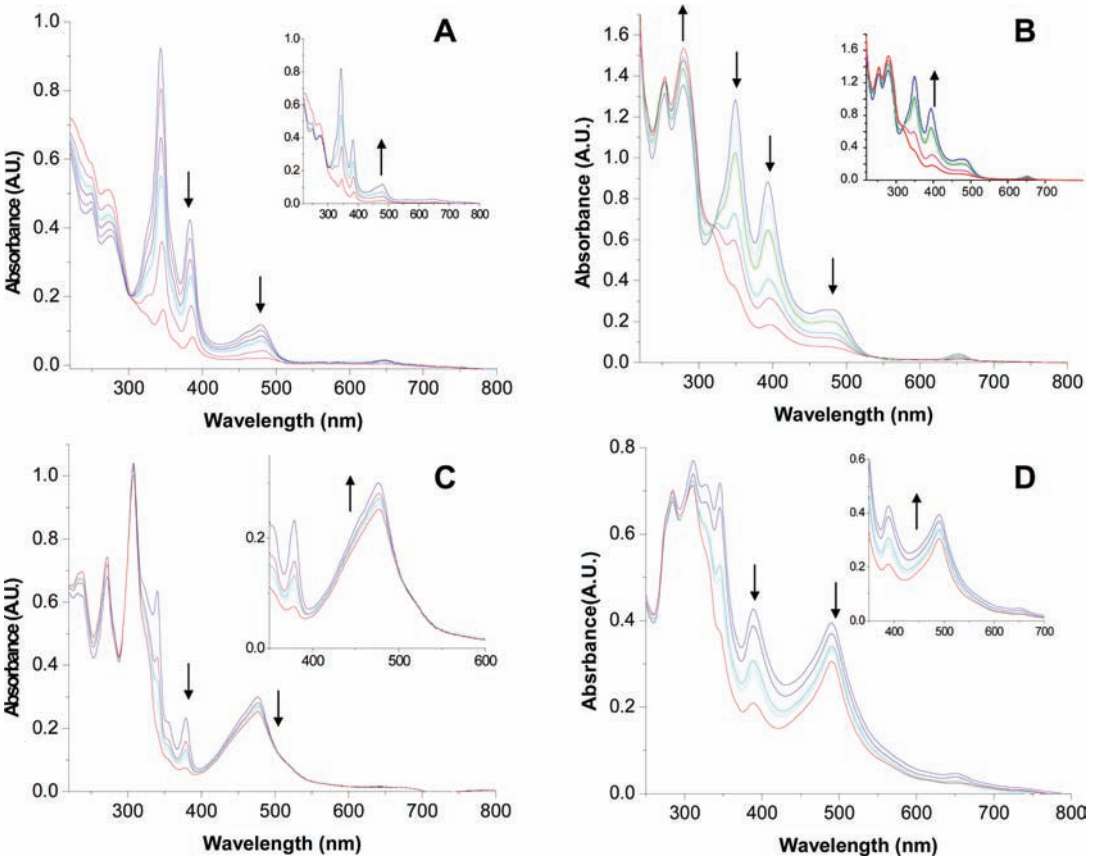

Figure 2. Evolution of the absorption spectra of solutions 10^{-5} M of (A) $\mathbf{L_1}$, (B) $\mathbf{L_2}$, (C) $\mathbf{L_1Ru}$, and (D) $\mathbf{L_2Ru}$ in CH_3CN recorded every 5 min during irradiation of the sample at $\lambda \geq 490$ nm (opening process). The blue and red spectra correspond in all the cases to the closed and open isomers, respectively. (Insets) Corresponding closing process during UV irradiation ($\lambda = 254$ nm).

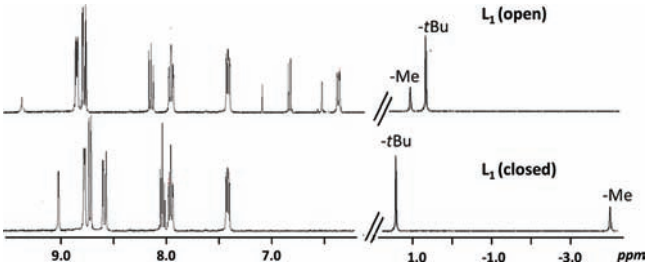

Figure 3. ^{1}H NMR of $\mathbf{L_1}$ in CD_3CN before (bottom, closed form) and after (top, open form) irradiation with visible light (cutoff filter $\lambda \geq 490$ nm).

to the internal methyl protons for $\mathbf{L_1}$ before and after irradiation. With this ligand, conversion from the closed to the open form is accompanied by a large shift from −3.7 to +1.3 ppm of the internal methyl protons. The total disappearance of the peak at −3.7 ppm could be reached, which indicates a quantitative photoconversion between isomers. Similar quasi-quantitative conversion yields were also observed for the four other ligands. These results thus indicate that associating terpyridine or phenylterpyridine to the DHP core does not result in inhibition of the switching properties of the DHP unit.

In the case of the ruthenium complexes $\mathbf{L_1Ru}$−$\mathbf{L_5Ru}$, the same DHP to CPD conversion could be reached. However, evolution of the UV−vis spectrum in the 450−700 nm range during irradiation by visible light was less marked than in the case of the free ligands because of the overlapping of the MLCT band of the bisterpyridine ruthenium(II) moiety with the low-energy band of the DHP unit (Figure 2C and 2D). When irradiated with visible light, the deep red-purple solution of the complexes in acetonitrile bleached to very pale violet in accordance with formation of the cyclophanediene isomer. However, this opening process appeared to be slightly less effective (estimated to >85%) than in the case of ligands $\mathbf{L_1}$−$\mathbf{L_5}$, probably because of some

Table 2. Kinetic Parameter Values Estimated from Experimental Data Obtained at Different Temperatures for the Thermal Isomerization Process

compound	T (K)	k (min^{-1})	$\tau_{1/2}$ (min)	E_{act} (kcal/mol)
$\mathbf{L_1}$	328	0.0273	25.4	36.6
	318	0.0056	123.3	
	311	0.0012	557.1	
$\mathbf{L_3}$	328	0.0304	22.8	36.8
	318	0.0058	118.7	
	311	0.0014	504.5	
$\mathbf{L_1Ru}$	328	0.1154	6.1	35.7
	318	0.0228	30.4	
	311	0.0057	121.6	
$\mathbf{L_3Ru}$	328	0.0737	9.4	35.2
	318	0.0149	46.5	
	311	0.0038	181.8	

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Table 3. Redox Potentials[a] of L_1−L_5 Ligands and L_1Ru−L_5Ru Complexes Before (closed forms) and After Irradiation (open forms) with Visible Light ($\lambda \geq 490$ nm)

	closed form			open form
compounds	$E_{1/2}$ (DHP^+/DHP)	E_{pa} (DHP^{2+}/DHP^+)	$E_{1/2}$ (Ru^{III}/Ru^{II})	$E_{1/2}$ ($\lvert i_{pc}\rvert/i_{pa}$)
DHP (**1**)	0.26	0.84		
$\mathbf{L_1}$	0.31	0.83		E_{pa} = 1.13[c]
$\mathbf{L_2}$	0.34	0.85		*b*
$\mathbf{L_3}$	0.32	0.81		E_{pa} = 1.14[c]
$\mathbf{L_4}$	0.33	0.84		*b*
$\mathbf{L_5}$	0.32	0.82		E_{pa} = 1.12[c]
$\mathbf{L_1Ru}$	0.32	0.85	1.08	1.04 (0.69)
$\mathbf{L_2Ru}$	0.34	0.88	1.04	1.04 (0.61)
$\mathbf{L_3Ru}$	0.36	0.90	1.10	1.09 (0.61)
$\mathbf{L_4Ru}$	0.38	0.91	1.09	1.12 (0.69)
$\mathbf{L_5Ru}$	0.33	0.84	1.05	1.06 (0.62)

[a] All potentials are given in volts referred to the Ag^+/Ag (10^{-2} M in CH_3CN) reference electrode. $E_{1/2} = (E_p^a + E_p^c)/2$ at 0.1 V s^{-1}. [b] Not measured. [c] Fully irreversible system.

slight quenching of the excited state of the DHP unit by the low-energy MLCT transition. In addition, as observed with the free ligands, the initial closed forms of $\mathbf{L_1Ru}$−$\mathbf{L_5Ru}$ could be regenerated by irradiation at 254 nm. The $\mathbf{L_1Ru}$−$\mathbf{L_5Ru}$ complexes thus display good photoconversion, and the DHP unit keeps its photochromic properties in the presence of the metal centers.

THERMAL RECLOSING AND LIFETIMES OF THE CPD ISOMERS

The thermal isomerization process from the open to the closed forms was investigated in CH_3CN for compounds $\mathbf{L_1}$, $\mathbf{L_3}$, $\mathbf{L_1Ru}$, and $\mathbf{L_3Ru}$ at 38, 45, and 55 °C. In all cases, thermal closing was followed by UV−vis spectroscopy, taking advantage of the characteristic absorption band of the closed isomers located at 477−487 nm (Table 1). In addition, since $\mathbf{L_1Ru}$ and $\mathbf{L_3Ru}$ displayed an important overlapping of such a characteristic absorption band with the MLCT band, the results obtained in the case of these compounds were confirmed by following the thermal closing process by ^{1}H NMR in CD_3CN. Integration of the internal methyl protons was conveniently used to estimate the experimental rate constants in these cases. The rate constants estimated are summarized in Table 2.

Comparing the half-life time values ($\tau_{1/2}$) reported in Table 2 for compounds $\mathbf{L_1}$ and $\mathbf{L_3}$ with the previously reported for **1** at 46 °C (113 min),[12c] we can conclude that substitution of the DHP core with terpyridine derivatives does not result in significant changes concerning the thermal closing isomerization since the kinetic parameters estimated are of the same order of magnitude. In contrast, complexation of the ligands with ruthenium complexes resulted in a lower thermal stability of the corresponding open isomers for compounds $\mathbf{L_1Ru}$ and $\mathbf{L_3Ru}$ according to their $\tau_{1/2}$ values determined at 45 °C, 30.4 and 46.5 min respectively as summarized in Table 2. Thus, compared to the $\tau_{1/2}$ reported for **1**,[12c] the presence of the ruthenium complexes increased the thermal closing rate by 3.7 and 2.4 times for compounds $\mathbf{L_1Ru}$ and $\mathbf{L_3Ru}$, respectively.

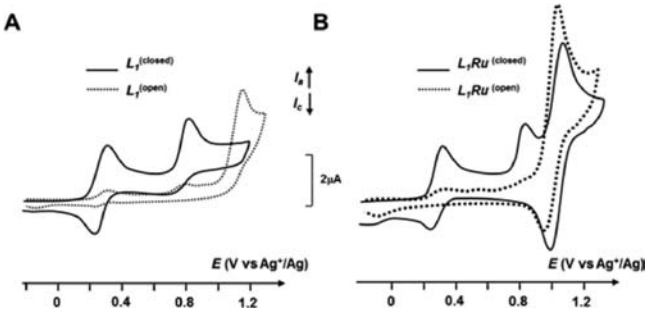

Figure 4. Cyclic voltammograms on the anodic region of millimolar solutions of (A) $\mathbf{L_1}$ and (B) $\mathbf{L_1Ru}$ before (full line) and after (dotted line) irradiation of the solutions at $\lambda \geq 490$ nm. All data were recorded in CH_3CN + $TBABF_4$. Scan rate 100 mV. s^{-1}.

ELECTROCHEMICAL BEHAVIOR

In contrast to their photochromic properties, the electrochemical behavior of the DHP derivatives reported has been much less extensively investigated.[12c,13] In this study, both the DHP (**1**) and the new $\mathbf{L_1}$−$\mathbf{L_5}$ and $\mathbf{L_1Ru}$−$\mathbf{L_5Ru}$ compounds were studied by cyclic voltammetry (CV) in CH_3CN containing tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$, 0.1 M) as supporting electrolyte. Table 3 summarizes the electrochemical data obtained for all investigated systems in their closed and open forms.

The anodic electrochemical CV curves of **1** and the tpy−DHP ligands $\mathbf{L_1}$−$\mathbf{L_5}$ recorded at a scan rate of 100 mV/s appeared to be very similar. Typical voltammetric curves obtained with $\mathbf{L_1}$ are given in Figure 4A. In their closed states, all systems displayed a first reversible wave at $E_{1/2} \approx +0.3$ V versus $Ag/AgNO_3$ (10^{-2} M in CH_3CN) attributed to the monoelectronic oxidation of the DHP unit ($DHP^{+\bullet}$/DHP couple)[13d] followed by an irreversible peak at $E_{pa} \approx +0.85$ V accompanied during the reverse scan by a new and ill-defined reduction wave at around ∼−0.2 V. This signal was attributed to the second oxidation of the DHP core (DHP^{2+}/$DHP^{+\bullet}$),[13d] and its irreversibility results from a coupled chemical reaction that follows electrogeneration of the unstable dicationic DHP^{2+} unit.

Upon photoswitching of the solutions of **1** and $\mathbf{L_1}$−$\mathbf{L_5}$ by irradiation of the electrochemical cell at $\lambda \geq 490$ nm (cutoff filter), the cyclic voltammogram of the corresponding open CPD isomers all displayed very similar features with a single and an irreversible oxidation wave at $E_{pa} \approx +1.1$ V associated to a weak reduction wave observed during the reverse scan at ∼−0.2 V. Irreversibility of the oxidation waves observed in both the open and the closed isomers was ascribed to chemical reactions that follow electron transfer, and detailed investigations using spectroelectrochemical techniques are currently under way in our laboratory in order to determine the nature of the electrogenerated product(s). However, on the basis of the CV profiles, it is clear that incorporation of the terpyridine units does not deeply modify the electrochemical behavior of the switching DHP unit. Only a modest positive shift of the first oxidation process can be outlined in the presence of the tpy substituents (up to ∼80 mV with $\mathbf{L_2}$).

The electrochemical behavior of the ruthenium complexes $\mathbf{L_1Ru}$−$\mathbf{L_5Ru}$ was then investigated (see data in Table 3). The cyclic voltammogramm of the $\mathbf{L_1Ru}$ complex in its closed state is represented in Figure 4B and displays three well-separated oxidation waves at $E_{1/2}$ = 0.32 V, E_{pa} = 0.85 V (irreversible

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Table 4. Photophysical Data of the Closed Form of Compounds 1, L_1−L_5, and L_1Ru −L_5Ru at Room Temperature in Acetonitrile Solutions

compounds	λ_{em}, nm	ϕ	τ, ns
1	648	3.0×10^{-3}	5.4
$\mathbf{L_1}$	652	2.4×10^{-3}	5.0
$\mathbf{L_2}$	652	2.5×10^{-3}	4.9
$\mathbf{L_3}$	653	2.7×10^{-3}	5.0
$\mathbf{L_4}$	660	3.1×10^{-3}	4.8
$\mathbf{L_5}$	649	2.8×10^{-3}	5.4
$\mathbf{L_1Ru}$	649	5.1×10^{-4}	5.6
$\mathbf{L_2Ru}$	649	6.6×10^{-4}	5.1
$\mathbf{L_3Ru}$	648	5.8×10^{-4}	5.4
$\mathbf{L_4Ru}$	648	5.2×10^{-4}	5.8
$\mathbf{L_5Ru}$	649	9.8×10^{-4}	5.6

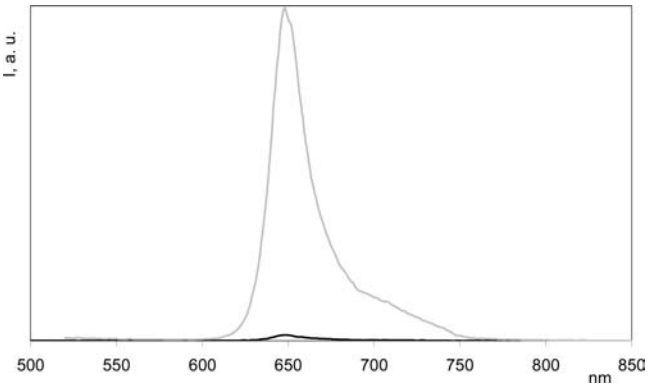

Figure 5. Emission spectra of $\mathbf{L_2Ru}$ at room temperature in acetonitrile solution before (closed form; gray line) and after (open form; black line) irradiation at $\lambda \geq 490$ nm.

oxidation), and $E_{1/2}$ = 1.08 V. By comparison with the CV curves of the metal-free $\mathbf{L_1}$−$\mathbf{L_5}$ ligands, these signals were attributed to the first and second oxidation of the DHP moiety followed by the reversible metal-centered oxidation of the two $(tpy)_2Ru$ units. Upon conversion of $\mathbf{L_1Ru}$ into its open CPD isomer by visible light irradiation, the resulting CV curve was deeply modified with a single and nonfully reversible oxidation wave ($|i_{pc}| < i_{pa}$) at $E_{1/2}$ = 1.04 V. This signal was attributed to the overlays of the reversible oxidation of the two $(tpy)_2Ru$ groups with the irreversible oxidation of the CPD (open) bridge, this last being logically responsible for the partial reversibility of the curve ($i_{pc} < i_{pa}$). It should be also outlined that the DHP (closed form) or CPD (open form) bridges are oxidized at lower or at similar potentials, respectively, than the Ru(II) centers, which logically prevent efficient electronic communication between the two $(tpy)_2Ru$ groups. For this reason, the equivalent ruthenium ions are oxidized at close potentials, giving rise to a unique observable CV wave.

The other investigated systems $\mathbf{L_2Ru}$−$\mathbf{L_5Ru}$ all displayed very similar behaviors to the $\mathbf{L_1Ru}$ complex with three oxidation waves in their closed forms and a unique wave at ∼1.0−1.1 V in their open states (see Table 3). The number, position, or nature of the $(tpy)_2Ru$ moiety appeared to have only a small effect on the potentials observed for the different redox couples with shifts ≤100 mV (see Table 3). Logically, a smaller intensity of the peaks corresponding to the $Ru^{III/II}$ couple was observed with the $\mathbf{L_5Ru}$ system that incorporates only one $(tpy)_2Ru$ unit instead of two in the four other complexes.

PHOTOPHYSICAL PROPERTIES

The luminescence properties of all compounds at room temperature have been studied in acetonitrile solutions before and after irradiation with visible light, i.e., in their open and closed forms. The results are gathered in Table 4, and an example of data is represented in Figure 5. In the case of the ligands $\mathbf{L_1}$−$\mathbf{L_5}$, the closed forms exhibited emission maxima in the range 649−660 nm, with quantum yields around 3×10^{-3} and lifetimes in the nanosecond time scale (see Table 4). The emission spectra were very narrow with very small Stokes shifts, indicating that the nature of the emitting state is singlet. Previous photophysical studies and laser flash photolysis experiments on variously substituted DHPs have determined that their relatively low quantum yields of fluorescence arise from the fact that the singlet excited states mainly decay to the ground state of the DHPs by nonradiative channels (>95%).[18] The remaining excitation energy is converted by (i) formation of the CPD forms (ring opening occurs from the singlet excited state), (ii) intersystem crossing to the triplet excited state of the CPD forms, and (iii) fluorescence processes. After extensive irradiation of $\mathbf{L_1}$−$\mathbf{L_5}$ by visible light, the CPD open forms were obtained and loss of conjugation of the annulene ring resulted in an important blue shift of the absorption spectra as well as a loss of fluorescence on passing from the closed to the open forms.

Concerning the DHP-bearing ruthenium complexes, compounds $\mathbf{L_1Ru}$−$\mathbf{L_5Ru}$, in the closed forms they exhibited weak luminescence with maxima at similar wavelengths as the tpy−DHP analogous ligands. The monoexponential lifetimes were all about 5 ns, like in the case of the tpy−DHP photoswitches (Table 4). Considering the narrow shapes of the emission spectra as well as their energies and lifetimes, the emission could be attributed to deactivation of the switching part of the systems. This result is not surprising since the luminescence properties of the $(tpy)_2Ru$-like complexes are very weak and their emission lifetimes and quantum yields are very low (τ = 0.25 ns; $\phi < 10^{-5}$);[19] therefore, emission from the Ru complex part of the molecules was not detected. The quantum yields were 5-fold lower with respect to the free ligands; this decrease is likely due to the increased number of vibrational modes in the molecules compared to the $\mathbf{L_1}$−$\mathbf{L_5}$ compounds. As expected during continuous irradiation of the solutions of $\mathbf{L_1Ru}$−$\mathbf{L_5Ru}$ in acetonitrile at $\lambda \geq 490$ nm, the luminescence intensity decreased: the metal complexes displayed the same behavior as the tpy−DHP compounds, which corroborates that the emitting excited states are centered on the photoswitches. However, as observed by ^{1}H NMR, the conversion between DHP and CPD forms was slightly less effective. As a consequence, a very weak residual emission from the closed form was still detected after irradiation. The ratio of the emission quantum yields of the closed forms when compared to the open forms is ca. 1/60 in the case of the metal complexes and 1/110 in the case of the free ligands. The luminescence quantum yields of the open forms of all compounds are about 10^{-5}.

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Table 5. Ring-Opening Isomerization of Compounds 1, L_2, L_3, L_2Ru, and L_3Ru in Acetonitrile Solutions[a]

compounds	$\phi/10^{-3}$
1	1.3 ± 0.3
$\mathbf{L_2}$	0.5 ± 0.1
$\mathbf{L_3}$	0.20 ± 0.01
$\mathbf{L_2Ru}$	0.08 ± 0.01
$\mathbf{L_3Ru}$	0.08 ± 0.02

[a] Errors correspond to average deviations.

RING-OPENING ISOMERIZATION QUANTUM YIELDS

The ring-opening quantum yield of some of the representative compounds (**1**, L_2, L_3, L_2Ru, L_3Ru) was determined by actinometry, i.e., by comparing the change in absorption upon irradiation at 468 nm during specific time periods for the compounds with unknown quantum yield to the change in absorption for a standard with a photochemical process for which the quantum yield is known when irradiated at the same wavelength. The potassium ferrioxalate actinometer was used as a primary standard;[20,21] the results are presented in Table 5.

The ring-opening quantum yield of compound **1** was measured to compare with literature values and agreed with them.[18,22] The low value indicates that the transannular bond cleavage is intrinsically a low-efficiency process. Two explanations have been suggested: (i) the mechanism of isomerization is an activated process with a weak probability and (ii) the photocleavage could arise via biradical formation from the singlet excited state.[23] The presence of terpyridine or phenylterpyridine substituents on **1** in (4,9) or (4,10) positions, molecules L_3 and L_2, respectively, slightly lowers the quantum yield. Coordination of ruthenium centers on the polypyridine ligands (L_2Ru and L_3Ru) further decreases the ring-opening efficiency, which appears to be more than 1 order of magnitude smaller than in the case of compound **1**.

CONCLUSION

The synthesis of four dinuclear (L_1Ru–L_4Ru) and one mononuclear (L_5Ru) bisterpyridine ruthenium complexes covalently connected to the dimethyldihydropyrene photoswitch has been successfully accomplished. It was shown by ^{1}H NMR, UV–vis spectroscopy, electrochemical, and luminescence measurements that the presence of the ruthenium complexes does not induce negative effects on the photochromic behavior of the DHP unit, and all investigated complexes and ligands exhibited reversible isomerization between closed and open isomers by alternate irradiation with visible ($\lambda \geq 490$ nm) and UV (254 nm) light. The electrochemical behavior of the Ru(II) complexes was shown to be strongly dependent on the form of the systems with three separated oxidation waves in the 0–1.2 V range in the closed isomer and only one observable wave at ~1.1 V in the open one. In addition, the DHP derivatives exhibited luminescence properties with light emission in the range 649–660 nm. Upon opening of the photochromic unit by visible light, the loss of conjugation of the annulene ring of the CPD moiety resulted in an important blue shift of the absorption spectra as well as a loss of fluorescence. In addition, kinetic parameters (rate constants, half-life times, and activation energies) have been also determined for the thermal ring-closing process taking place from the most unstable isomer (CPD). The data estimated from measurements performed at three different temperatures is on the same order of magnitude as that previously reported for other DHP derivatives. Lifetimes close to 4–5 days at room temperature can be estimated from the experimental data and support the potential of the compounds here reported for molecular electronics applications. To our knowledge, this work represents the first example of DHP covalently associated to polypyridyl metal complexes, and these results show that these systems are very promising candidates for further developments in molecular electronics, as logic gates, molecular memories, or single-molecule devices. In addition, the designed ligands have well-defined linear (L_1 and L_3) or V-shaped (L_2 and L_4) geometries that are particularly suitable for construction of supramolecular light-responsive polynuclear 1D chains[24] or rings.[25]

EXPERIMENTAL SECTION

General Procedures. All air-sensitive reactions were performed under a dry argon atmosphere using standard Schlenk techniques. Solvents were dried over appropriate drying agents and distilled before use. All other solvents and reagents were purchased and used as received. ^{1}H and ^{13}C NMR spectra were recorded at 298 K on a Bruker 400 MHz NMR spectrometer in CD_2Cl_2 (unless specified for ligands L_1–L_5) using the solvent residual peak for calibration (5.15 ppm) and in CH_3CN (unless specified for L_1Ru–L_5Ru) using the solvent residual peak for calibration (1.92 ppm). Mass spectra were recorded on a CL-ESI/ApCI-ITD (Agilent 1100 and Esquire 3000+Bruker Daltonics) system using methane as a carrier gas for chemical ionization. Elemental analyses were performed by the Service Central d'Analyses, CNRS, Lyon, France.

Electrochemical Measurements. Electrochemical experiments were conducted in a conventional three-electrode cell under an argon atmosphere at 293 K using a CH Instrument (CHI660B). Measurements were done with solutions of the compounds (~0.5 mM) in CH_3CN containing tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$, 0.1 M) as supporting electrolyte. The reference electrode was $Ag/AgNO_3$ (10 mM in CH_3CN containing 0.1 M $TBABF_4$). The potential of the regular ferrocene/ferrocenium (Fc/Fc^+) redox couple in acetonitrile is 0.07 V under our experimental conditions. The working electrode was a carbon disk (3 mm in diameter) polished with 1 μm diamond paste before each use.

Thermal-Closing Isomerization Process. The thermal-closing process has been investigated by UV–vis at three different temperatures.[12c,13a–13c] In order to estimate kinetic parameters concerning such isomerization process from the closed to the open forms, diluted solutions of the L_1, L_3, L_1Ru, and L_3Ru have been prepared in CH_3CN and irradiated in an ice bath with $\lambda \geq 490$ nm to afford their corresponding open isomers photochemically. Afterward, aliquots of the initial solution have been taken and evolution of their UV–vis spectra followed at three different temperatures. In particular, the kinetic measurements have been carried out in all cases studied at 311, 318, and 328 K. The absorption maximum located around 480 nm and characteristic of the DHP core has been selected to relate the absorbance as a function of time with the concentration of the closed isomer in solution. The concentration of the open isomer could be determined assuming that no degradation of the samples occurs during the time of the experiments and as a result the kinetic constant of the thermal closing could be determined according to a first-order chemical process. Due to the noticeable overlapping of the MLCT band with the absorption band mentioned above characteristic of the DHP isomer additional experiments where carried out to follow the process by ^{1}H NMR.

Electronic Spectroscopic and Photophysical Experiments. Electronic absorption spectra were recorded on a Cary 300 or a Cary 50 Scan UV−vis spectrophotometer using acetonitrile as solvent. Emission spectra were recorded in CH_3CN at room temperature on a Varian Cary Eclipse fluorescence spectrophotometer. Samples were placed in 1 cm path length quartz cuvettes. Luminescence lifetimes measurements were performed after irradiation at λ = 400 nm obtained by the second harmonic of a titanium:sapphire laser (picosecond Tsunami laser spectra physics 3950-M1BB and 39868-03 pulse picker doubler) at a 800 kHz repetition rate. Fluotime 200 from AMS technologies was used for the decay acquisition. It consists of a GaAs microchannel plate photomultiplier tube (Hamamatsu model R3809U-50) followed by a time-correlated single-photon counting system from Picoquant (PicoHarp300). The ultimate time resolution of the system is close to 30 ps. Luminescence decays were analyzed with Fluofit software available from Picoquant. Emission quantum yields ϕ were determined at room temperature in acetonitrile solutions (λ_{ex} = 430 nm) using the optically dilute method.[26] $[Ru(bpy)_3]^{2+}$ (bpy =2,2′-bipyridine) in air-equilibrated aqueous solution was used as quantum yield standard (ϕ = 0.028).[27] Experimental uncertainties are as follows: absorption maxima, 2 nm; molar absorption, 20%; emission maxima, 5 nm; emission lifetimes, 10%; emission quantum yields, 20%.

Photo-Opening Isomerization Quantum Yields Measurement. Potassium ferrioxalate actinometer was used as a primary standard. The change in absorption upon irradiation at 468 nm (band-pass filter) during specific time periods for compounds **1**, $\mathbf{L_2}$, $\mathbf{L_3}$, $\mathbf{L_2Ru}$, and $\mathbf{L_3Ru}$ was compared to the change in absorption for the actinometer irradiated at the same wavelength. The monitoring wavelengths were 235, 476, and 643 nm for **1**, 476 and 643 nm for $\mathbf{L_2}$ and $\mathbf{L_3}$, and 378 and 643 nm for $\mathbf{L_2Ru}$ and $\mathbf{L_3Ru}$. The compounds were dissolved in acetonitrile; the concentration was such that the absorbance at 468 nm was higher than 1.9. The solution of the actinometer was 0.15 M in a 0.05 M H_2SO_4 aqueous solution. After each irradiation, 8 μL of the irradiated solution was placed into a 2 mL volumetric flask. A 100 μL amount of sodium acetate buffer solution (pH = 3.5) and 16 μL of 0.01 M 1,10-phenanthroline aqueous solution were then added, and the volume was completed with distilled water. The photoreduction of the actinometer was followed at 510 nm. The absorption spectra for each compound were recorded after each irradiation time without further handling, and the total time was such that the isomerization of the compound was less than 10%. The ring-opening quantum yields ϕ_x were calculated according to eq 1

$$\phi_x = \frac{\phi_s \varepsilon_s \Delta A_x V_x t_s}{\varepsilon_x \Delta A_s V_s t_x} \quad (1)$$

where ϕ_s is the quantum yield of the standard, ε is the molar extinction coefficient at the monitoring wavelength, ΔA is the change in absorbance at the monitoring wavelength, V is the volume of solution, and t is the irradiation time. The subscripts s and x refer to the standard and the compound of unknown quantum yield, respectively.

Synthesis. 2,7-Di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**1**), 4,9-dibromo-2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b-10c-dihydropyrene (4,9-Br_2-DHP, **2**), and 4,10-dibromo-2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b-10c-dihydropyrene (4,10-Br_2-DHP) were prepared following the procedure reported by Mitchell.[12c]

4-Bromo-2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b-10c-dihydropyrene (4-Br-DHP). To a solution containing the DHP (150 mg, 0.44 mmol) in dry CH_2Cl_2 (80 mL) at −40 °C was slowly added with stirring under argon atmosphere a solution containing NBS (78 mg, 0.44 mmol) in dry DMF (15 mL). After addition, the reaction mixture was stirred for an additional hour at room temperature. Cyclohexane (100 mL) and water were subsequently added. The green organic phase was separated and dried. The green product was purified over silica gel using cyclohexane/CH_2Cl_2 (6:1) as eluant and subsequently recrystallized, giving 210 mg of the 4-Br-DHP.

^{1}H NMR/ppm (400 MHz, CD_2Cl_2): −3.93 (s, 3H), −3.95 (s, 3H), 1.65 (s, 9H), 1.72 (s, 9H), 8.47 (br s, 3H), 8.56 (d, 1H), 8.62 (s, 2H), 8.80 (d, 1H).

Ligand $\mathbf{L_1}$. $\mathbf{L_1}$ was prepared by a Suzuki coupling reaction between the 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine and the bisboronic ester, **3**, following two different methods.

Method A. To a solution of 4,9-Br_2-DHP (**2**, 100 mg, 0.199 mmol) in dry diethyl ether (5 mL) at −78 °C was added dropwise *n*-butyllithium (160 μL of a 2.5 M solution in hexane). The initial green solution became dark reddish. After stirring for 1 h at this temperature, tributyl borate (108 μL, 0.400 mmol) was added and the solution was further stirred for 48 h at room temperature. This solution was then evaporated to dryness to isolate the crude bis-boronic DHP ester (**3**).

A two-necked flask was charged with 75 mg of crude 4,9-$[B(OnBu)_2]_2$DHP (**3**, ∼0.174 mmol), 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine (93 mg, 0.348 mmol) and $Pd(PPh_3)_4$ (23 mg, 0.020 mmol) under an argon atmosphere. To the flask was then added well-degassed toluene (10 mL) and sodium carbonate (5 mL, 2 M). The mixture was refluxed for 36 h. The solvent was removed, and the residue was washed with water and then diethyl ether. The residue was extracted into dichloromethane, and the solution was dried ($MgSO_4$) and evaporated. The residue was chromatographed on silica gel using hexane as eluent to elute first the unreacted dibromide. Polarity of the eluent was gradually increased up to hexane/ethyl acetate (50:50) to elute 80 mg of product as a dark brown solid further purified by recrystallization from methanol.

Method B. In this procedure, the synthesis was carried out using the bisboronic acid, 4,9-$[B(OH)_2]_2$DHP (**4**). Aqueous hydrochloric acid 10% (6.25 mL) was added directly to the solution described above containing **3** and further stirring continued up to 3 additional hours. After this period, the layers were separated and the aqueous phase was extracted with diethyl ether. At this point, the procedure followed was analogous to that described above when using the bis-boronic ester, **3** (method A).

Yield (method A): 60%. ^{1}H NMR/ppm (400 MHz, CD_3CN): −3.68 (s, 6H), 1.61 (s, 18H), 7.30−7.36 (m, 4H), 7.86 (d, 4H), 7.90−8.10 (m, 8H), 8.44 (br s, 2H), 8.48 (s, 2H), 8.58 (br s, 2H), 8.65 (d, 4H), 8.75 (d, 4H, overlapped), 8.98 (s, 4H). ^{13}C NMR/ppm (100 MHz, CD_3CN): 156.8 (4C), 155.1 (4C), 149.9 (4C), 145.9 (2C), 139.6 (4C), 138.5 (2C), 137.8, 137.2, 136.9, 131.3, 128.4 (8C), 127.9 (4C), 126.5, 124.2 (2C), 123.5 (2C), 122.7, 121.9, 121.5, 121.3, 121.1, 120.9, 120.5 (4C), 120.3, 117.8 (4C), 114.1, 36.9, 36.2, 32.5, 31.9, 29.7, 14.1 (4C). CI MS *m/z:* 960.1 ($M + H^+$). Anal. Calcd for $C_{68}H_{58}N_6$: C, 85.14; H, 6.09; N, 8.76. Found: C, 84.86; H, 6.37; N, 8.77.

Ligands $\mathbf{L_2}$−$\mathbf{L_5}$. Preparation of ligands $\mathbf{L_2}$−$\mathbf{L_5}$ has been performed following the procedure described for $\mathbf{L_1}$, starting from the corresponding brominated-DHP precursors, and in the case of $\mathbf{L_3}$ and $\mathbf{L_4}$, 4′-chloro-2,2′:6′,2″-terpyridine was employed instead of 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine.

$\mathbf{L_2}$. Yield (method A): 40%. ^{1}H NMR/ppm (400 MHz, CD_3CN): −3.73 (s, 3H), −3.71 (s, 3H), 1.66 (s, 9H), 1.68 (s, 9H), 7.32−7.40 (m, 4H), 7.66 (d, 4H), 7.94−8.01 (m, 8H), 8.40 (br s, 2H), 8.45 (s, 2H), 8.52 (br s, 2H), 8.67 (d, 4H), 8.70 (d, 4H, overlapped), 8,75 (s, 4H). ^{13}C NMR/ppm (100 MHz, CD_3CN): 157.7 (4C), 155.1 (4C), 149.9 (4C), 145.9 (2C), 139.6 (4C), 138.5 (2C), 137.8, 137.2, 136.9, 131.3, 128.4 (8C), 128.4 (4C), 126.5, 124.3 (4C), 122.7, 121.9, 121.5, 121.3, 121.1, 120.9, 120.5 (4C), 120.3, 117.8 (4C), 114.1, 36.9, 36.2, 32.1, 31.7, 29.3, 14.4 (4C). CI MS *m/z:* 960.3 ($M + H^+$). Anal. Calcd for $C_{68}H_{58}N_6$: C, 85.14; H, 6.09; N, 8.76. Found: C, 85.27; H, 6.29; N, 8.44.

Ligand $\mathbf{L_3}$. Yield (method A): 56%. ^{1}H NMR/ppm (400 MHz, CD_3CN): −3.55 (s, 6H), 1.70 (s, 18H), 7.32−7.40 (m, 4H), 7.86 (d, 4H), 8.51 (br s, 2H), 8.53 (s, 2H), 8.55 (s, 2H), 8.60 (d, 4H), 8.75 (d, 4H), 8.95 (s, 4H). ^{13}C NMR/ppm (100 MHz, CD_3CN): 157.5 (4C),

155.7 (4C), 149.3 (4C), 145.5 (2C), 139.9 (4C), 138.3 (2C), 137.8, 137.5, 136.7, 131.1, 128.4 (8C), 128.7 (4C), 126.2, 124.1 (4C), 122.3, 121.5 (2C), 121.1 (2C), 120.7, 120.4 (4C), 120.3, 117.3 (4C), 114.6, 36.7, 36.5, 32.4, 31.7, 29.6, 14.1 (2C), 13.9 (2C). CI MS *m/z:* 808.1 (M + H^+). Anal. Calcd for $C_{56}H_{50}N_6$: C, 83.34; H, 6.24; N, 10.41. Found: C, 83.60; H, 6.29; N, 10.11.

Ligand L_4. Yield (method A): 32%. ^{1}H NMR/ppm (400 MHz, CD_3CN): −3.58 (s, 3H), −3.56 (s, 3H), 1.67 (s, 9H), 1.70 (s, 9H), 7.32−7.40 (m, 4H), 8.03 (d, 4H), 8.45 (br s, 2H), 8.49 (s, 2H), 8.61 (br s, 2H), 8.65 (d, 4H), 8.72 (d, 4H), 8.99 (s, 4H). ^{13}C NMR/ppm (100 MHz, CD_3CN): 156.9 (4C), 155.3 (4C), 149.5 (4C), 146.3 (2C), 138.9 (4C), 138.1 (2C), 137.3, 137.0, 136.5, 131.0, 129.7 (4C), 128.4, 124.1 (4C), 122.7, 121.9, 121.5, 121.3, 121.1, 120.9, 120.5 (4C), 120.3, 117.8 (4C), 114.1, 36.9, 36.1, 32.4, 31.6, 28.7, 14.3 (4C). CI MS *m/z:* 808.0 (M + H^+). Anal. Calcd for $C_{56}H_{50}N_6$: C, 83.34; H, 6.24; N, 10.41. Found: C, 83.56; H, 6.41; N, 10.03.

Ligand L_5. Yield (method A): 72%. ^{1}H NMR/ppm (400 MHz, CD_3CN): −3.57 (s, 3H), −3.73 (s, 3H), 1.65 (s, 9H), 1.68 (s, 9H), 7.35−7.39 (m, 2H), 7.70 (d, 2H), 7.92−8.00 (m, 4H), 8.42 (br s, 3H), 8.51 (s, 1H), 8.58 (br s, 3H), 8.69 (d, 2H), 8.76 (d, 2H), 8.85 (s, 2H). ^{13}C NMR/ppm (100 MHz, CD_3CN): 157.3 (2C), 155.1 (2C), 150.1 (2C), 149.6, 146.5, 139.3 (2C), 138.5 (2C), 137.8, 137.2, 136.9, 131.3, 129.6 (4C), 128.4 (4C), 126.5, 124.3 (2C), 122.9, 122.3, 121.7, 121.3, 121.1, 120.9, 120.5 (2C), 120.3, 117.3 (2C), 115.3, 36.9, 36.2, 32.1, 31.7 (2C), 29.3, 14.5, 14.0. CI MS *m/z:* 652.8 (M + H^+). Anal. Calcd for $C_{47}H_{45}N_3$: C, 86.60; H, 6.96; N, 6.45. Found: C, 86.92; H, 6.84; N, 6.24.

Preparation of L_1Ru. L_1 (35 mg, 0.043 mmol) and [(tpy)$RuCl_3$] (38 mg, 0.086 mmol) were dissolved in EtOH (40 mL). A few drops of *N*-ethylmorpholine were added. The reaction mixture was heated under reflux for 48 h, then filtered through Celite, and washed with EtOH. The filtrate was concentrated under reduced pressure, and aqueous NH_4PF_6 was added to precipitate the product. The crude product was filtered, washed with diethyl ether, and dissolved in CH_3CN. It was purified by column chromatography on silica gel (CH_3CN:H_2O:saturated KNO_3 7:2:2). The third orange band (orange-red) was collected and concentrated under reduced pressure. Aqueous $NH_4PF_6$was added to precipitate the product, which was collected and washed with diethyl ether and dissolved in CH_3CN. Removal of solvent gave [4,9-[$Ru(tpy)_2]_2$−DHP]$(PF_6)_4$ (**L_1Ru**) as a dark red powder.

Yield: 41%. ^{1}H NMR/ppm (400 MHz, CD_3CN): −2.98 (s, 6H), 1.72 (s, 18H), 7.12 (t, 8H), 7.25 (d, 4H), 7.35 (d, 4H), 7.42 (d, 4H), 7.82 (m, 4H), 7.98 (m, 6H), 8.25 (d, 4H), 8.48 (br s, 6H), 8.51 (s, 2H), 8.67 (br s, 2H), 8.70 (d, 4H), 8,75 (d, 4H), 8.98 (s, 4H) . MALDI-MS: 2207.9 [M], 2063.0 [M − PF_6]$^+$, 1918.1 [M − $2PF_6$]$^{2+}$, 1773.1 [M − $3PF_6$]$^{3+}$, 1293.2 [M − Ru − tpy − $4PF_6$]$^+$, 986.3 [M − Ru − tpy − Phtpy − $4PF_6$]$^+$. Anal. Calcd for $C_{98}H_{80}F_{24}N_{12}P_4Ru_2$: C, 53.31; H, 3.65; N, 7.61. Found: C, 53.72; H, 3.76; N, 7.22.

Preparation of L_2Ru−L_5Ru. These complexes were prepared from a similar procedure as described above for **L_1Ru** starting from the corresponding L_2−L_5 ligands. In the case of **L_5Ru**, 1 mol equiv of [(tpy)$RuCl_3$] per ligand was used.

L_2Ru. Yield: 35%. ^{1}H NMR/ppm (400 MHz, CD_3CN): −2.93 (s, 3H), −2.90 (s, 3H), 1.69 (s, 9H), 1.73 (s, 9H), 7.05 (t, 8H), 7.21 (d, 4H), 7.38 (m, 4H), 7.42 (d, 4H), 7.78 (m, 4H), 8.01 (m, 6H), 8.23 (d, 4H), 8.42 (br s, 2H), 8.55 (s, 6H), 8.67 (br s, 2H), 8.75 (d, 4H), 8.84 (d, 4H), 9.02 (s, 4H). MALDI-MS: 2208.2 [M], 2062.8 [M − PF_6]$^+$, 1918.3 [M − $2PF_6$]$^{2+}$, 1772.9 [M − $3PF_6$]$^{3+}$, 1293.0 [M − Ru − tpy − $4PF_6$]$^+$. Anal. Calcd for $C_{98}H_{80}F_{24}N_{12}P_4Ru_2$: C, 53.31; H, 3.65; N, 7.61. Found: C, 53.54; H, 3.55; N, 7.47.

L_3Ru. Yield: 47%. ^{1}H NMR/ppm (400 MHz, CD_3CN): −2.86 (s, 6H), 1.70 (s, 18H), 7.12 (t, 8H), 7.42 (m, 4H), 7.71(m, 4H), 8.01 (m, 6H), 8.19 (d, 4H), 8.42 (br s, 2H), 8.58 (s, 6H), 8.65 (br s, 2H), 8.72 (d, 4H), 8.81 (d, 4H), 9.05 (s, 4H). MALDI-MS: 2055.8 [M], 1911.0 [M− PF_6]$^+$, 1765.8 [M − $2PF_6$]$^{2+}$, 1621.1 [M − $3PF_6$]$^{3+}$, 910.3 [M − Ru − 2tpy − $4PF_6$]$^+$. Anal. Calcd for $C_{86}H_{72}F_{24}N_{12}P_4Ru_2$: C, 50.25; H, 3.53; N, 8.18. Found: C, 50.49; H, 3.63; N, 8.02.

L_4Ru. Yield: 38%. ^{1}H NMR/ppm (400 MHz, CD_3CN): −2.89 (s, 3H), −2.87 (s, 3H), 1.69 (s, 9H), 1.73 (s, 9H), 7.05 (t, 8H), 7.45 (m, 4H), 7.78 (m, 4H), 8.05 (m, 6H), 8.20 (d, 4H), 8.46 (br s, 2H), 8.58 (s, 6H), 8.69 (br s, 2H), 8.75 (d, 4H), 8.80 (d, 4H), 8.95 (s, 4H). MALDI-MS: 2055.6 [M], 1910.61 [M − PF_6]$^+$, 1765.5 [M − $2PF_6$]$^{2+}$, 1620.7 [M − $3PF_6$]$^{3+}$, 1141.5 [M − Ru − tpy − $4PF_6$]$^+$. Anal. Calcd for $C_{86}H_{72}F_{24}N_{12}P_4Ru_2$: C, 53.31; H, 3.65; N, 7.61. Found: C, 53.59; H, 3.70; N, 7.28.

L_5Ru. Yield: 56%. ^{1}H NMR/ppm (400 MHz, CD_3CN): −3.04 (s, 3H), −3.01 (s, 3H), 1.65 (s, 9H), 1.70 (s, 9H), 7.10 (t, 4H), 7.21 (d, 2H), 7.35 (m, 2H), 7.40 (d, 2H), 7.75 (m, 2H), 8.05 (m, 3H), 8.20 (m, 3H), 8.42 (br s, 2H), 8.53 (s, 3H), 8.67 (br s, 2H), 8.78 (br d, 3H), 8.82 (d, 2H), 9.00 (s, 2H). MALDI-MS: 1276.2 [M], 1131.2 [M − PF_6]$^+$, 986.3 [M − $2PF_6$]$^{2+}$, 884.7 [M − Ru − $2PF_6$ − 1H]$^+$. Anal. Calcd for $C_{62}H_{56}F_{12}N_6P_2Ru$: C, 58.35; H, 4.42; N, 6.59. Found: C, 58.67; H, 4.75; N, 6.87.

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REFERENCES

(1) (a) Feringa, B. L., *Molecular Switches*; Wiley-VCH: Weinheim, 2001. (b) Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines: Concepts and Perspectives for the Nanoworld*; Wiley-VCH: Weinheim, 2008. (c) Leigh, D. A.; Zerbetto, F.; Kay, E. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 72.

(2) (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685. (b) Saha, S.; Stoddart, J. F. *Chem. Soc. Rev.* **2007**, *36*, 77. (c) Kawata, S.; Kawata, Y. *Chem. Rev.* **2000**, *100*, 1777.

(3) (a) Berkovic, G.; Krongauz, V.; Weiss, V. *Chem. Rev.* **2000**, *100*, 1741. (b) Baron, R.; Onopriyenko, A.; Katz, E.; Lioubashevski, O.; Willner, I.; Wang, S.; Tian, H. *Chem. Commun.* **2006**, 2147. (c) Guo, X.; Huang, L.; O'Brien, S.; Kim, P.; Nuckolls, C. *J. Am. Chem. Soc.* **2005**, *127*, 15045.

(4) Yokoyama, Y. *Chem. Rev.* **2000**, *100*, 1717.

(5) (a) Morimoto, M.; Irie, M. *J. Am. Chem. Soc.* **2010**, *132*, 14172–14178. (b) Yamaguchi, T.; Taniguchi, W.; Ozeki, T.; Irie, S.; Irie, M. *J. Photochem. Photobiol. A: Chem.* **2009**, *207*, 282. (c) Irie, M.; Kobatake, S.; Horichi, M. *Science* **2001**, *291*, 1769. (d) Areephong, J.; Browne, W. R.; Katsonis, N.; Feringa, B. L. *Chem. Commun.* **2006**, 3930. (e) Kudernac, T.; Katsonis, N.; Browne, W. R.; Feringa, B. L. *J. Mater. Chem.* **2009**, *19*, 7168. (f) Tian, H.; Yang, S. *Chem. Soc. Rev.* **2004**, *33*, 85. (g) Liu, Y.; Lagrost, C.; Costuas, K.; Tchouar, N.; Bozec, H. L.; Rigaut, S. *Chem. Commun.* **2008**, 6117. (h) Dulic, D.; van der Molen, S. J.; Kudernac, T.; Jonkman, H. T.; de Jong, J. J. D.; Bowden, T. N.; van Esch, J.; Feringa, B. L.; van Wees, B. J. *Phys. Rev. Lett.* **2003**, *91*, 207402.

(6) (a) Akita, M. *Organometallics* **2011**, *30*, 43. (b) Kume, S.; Nishihara, H. *Dalton Trans.* **2008**, 3260 and references therein. (c) Aubert, V.; Guerchais, V.; Ishow, E.; Hoang-Thi, K.; Ledoux, I.; Nakatani, K.; Le Bozec, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 577–580. (d) Sud, D.; McDonald, R.; Branda, N. R. *Inorg. Chem.* **2005**, *44*, 5960. (e) Lee, J. K.-W; Ko, C.-C.; Wong, K. M.-C.; Zhu, N.; Yam, V. W.-W. *Organometallics* **2007**, *26*, 12. (f) Nishihara, H. *Bull. Chem. Soc. Jpn.*

2005, *77*, 407. (g) Jukes, R. T. F.; Adamo, V.; Hartl, F.; Belser, P.; De Cola, L. *Coord. Chem. Rev.* **2005**, *249*, 1327. (h) Tanaka, Y.; Inagaki, A.; Akita, M. *Chem. Commun.* **2007**, 1169–1171.

(7) (a) Constable, E. C. *Chem. Soc. Rev.* **2007**, *36*, 246. (b) Schubert, S. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892. (c) Harriman, A.; Ziessel, R. *Chem. Commun.* **1996**, 1707. (d) Balzani, V.; Juris, A.; Venturi, M. *Chem. Rev.* **1996**, *96*, 759. (e) Barigelletti, F.; Flamigni, L. *Chem. Soc. Rev.* **2000**, *29*, 1. (f) Eryazici, I.; Moorefield, C. N.; Newkome, G. R. *Chem. Rev.* **2008**, *108*, 1834. (g) Jukes, R. T. F.; Bozic, B.; Belser, P.; De Cola, L.; Hartl, F. *Inorg. Chem.* **2009**, *48*, 1711. (h) Jukes, R. T. F.; Kuhni, J.; Salluce, N.; Belser, P.; De Cola, L.; Hartl, F. *Dalton Trans.* **2009**, 3993.(i) Schubert, U. S.; Hofmeier, H.; Newkome, G. R. *Modern Terpyridine Chemistry*; Wiley-VCH: Weinheim, 2006.

(8) (a) Nishihara, H. *Coord. Chem. Rev.* **2005**, *249*, 1468. (b) Yutaka, T.; Kurihara, M.; Kubo, K.; Nishihara, H. *Inorg. Chem.* **2000**, *39*, 3438. (c) Yutaka, T.; Mori, I.; Kurihara, M.; Mizutani, J.; Kubo, K.; Furusho, S.; Matsumura, K.; Tamai, N.; Nishihara, H. *Inorg. Chem.* **2001**, *40*, 4986. (d) Yutaka, T.; Mori, I.; Kurihara, M.; Mizutani, J.; Tamai, N.; Kawai, T.; Irie, M.; Nishihara, H. *Inorg. Chem.* **2002**, *41*, 7143. (e) Yutaka, T.; Mori, I.; Kurihara, M.; Mizutani, J.; Tamai, N.; Nishihara, H. *Inorg. Chem.* **2003**, *42*, 6306.

(9) (a) Zhong, Y.-W.; Vilà, N.; Henderson, J. C.; Flores-Torres, S.; Abrũna, H. D. *Inorg. Chem.* **2007**, *46*, 10470. (b) Zhong, Y.-W.; Vilà, N.; Henderson, J. C.; Abrũna, H. D. *Inorg. Chem.* **2009**, *48*, 991.

(10) Blattmann, H. R.; Meuche, D.; Heilbronner, E.; Molyneux, R. J.; Boekelheide, V. *J. Am. Chem. Soc.* **1965**, *87*, 130.

(11) Mitchell, R. H. *Eur. J. Org. Chem.* **1999**, *1999*, 2695.

(12) See for example:(a) Robinson, S. G.; Sauro, V. A.; Mitchell, R. H. *J. Org. Chem.* **2009**, *74*, 6592. (b) Mitchell, R. H.; Bandyopadhyay, S. *Org. Lett.* **2004**, *6*, 1729. (c) Mitchell, R. H.; Ward, T. R.; Chen, Y. S.; Wang, Y.; Weerawarna, S. A.; Dibble, P. W.; Marsella, M. J.; Almutairi, A.; Wang, Z. Q. *J. Am. Chem. Soc.* **2003**, 2974.

(13) (a) Fan, W.; Berg, D. J.; Mitchell, R. H.; Barclay, T. M. *Organometallics* **2007**, *26*, 4562. (b) Zhang, R.; Fan, W.; Twamley, B.; Berg, D. J.; Mitchell, R. H. *Organometallics* **2007**, *26*, 1888–1894. (c) Mitchell, R. H.; Brkic, Z.; Sauro, V. A.; Berg, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 7581. (d) Muratsugu, S.; Kume, S.; Nishihara, H. *J. Am. Chem. Soc.* **2008**, *130*, 7204.

(14) Tashiro, M.; Yamato, T. *J. Am. Chem. Soc.* **1982**, *104*, 3701.

(15) Aspley, C. J.; Williams, J. A. G. *New J. Chem.* **2001**, *25*, 1136.

(16) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

(17) (a) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176–4211.(b) In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: New York, 1998. (c) Tsuji, J. *Palladium Reagents and Catalysts, Innovations in Organic Synthesis*; Wiley: New York, 1995.

(18) Sheepwash, M. A. L.; Mitchell, R. H.; Bohne, C. *J. Am. Chem. Soc.* **2002**, *124*, 4693.

(19) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309.

(20) Parker, C. A. *Proc. R. Soc. London, Ser. A* **1953**, *220*, 104.

(21) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

(22) Murakami, S.-I.; Tsutsui, T.; Saito, S.; Yamato, T.; Tashiro, M. *Nippon Kagaku Kaishi* **1988**, 221.

(23) Boggio-Pasqua, M.; Bearpark, M. J.; Robb, M. A. *J. Org. Chem.* **2007**, *72*, 4497.

(24) (a) Friese, V. A.; Kurth, D. G. *Coord. Chem. Rev.* **2008**, *252*, 199. (b) Gasnier, A.; Royal, G.; Terech, P. *Langmuir* **2009**, *25*, 8751. (c) Dobrawa, R.; Lysetska, M.; Ballester, P.; Grune, M.; Wurthner, F. *Macromolecules* **2005**, *38*, 1315.

(25) (a) Perera, S.; Li, X.; Soler, M.; Schultz, A.; Wesdemiotis, C.; Moorefield, C.; Newkome, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 6539. (b) Newkome, G. R.; Cho, T. J.; Moorefield, C. N.; Cush, R.; Russo, P. S.; Godínez, L. A.; Saunders, M. J.; Mohapatra, P. *Chem.—Eur. J.* **2002**, *8*, 2946. (c) Li, S.; Moorefield, C. N.; Wang, P.; Shreiner, C. D.; Newkome, G. R. *Eur. J. Org. Chem.* **2008**, *19*, 3328.

(26) Demas, N. J.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991–1024.

(27) Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697–2705.