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All Visible Light Switch based on the Dimethyldihydropyrene Photochromic Core

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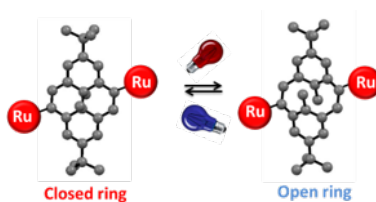
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ABSTRACT. Two photoswitchable compounds that can operate under visible light irradiation are prepared and investigated using spectroscopic and computational studies. These all-visible systems are based on the dimethyldihydropyrene (DHP) / cyclophanediene (CPD) photochromic couple connected either to a bipyridine (bpy) unit or to a (tris(bpy)ruthenium(II)) complex through a pyridinium bridge. In these compounds, the DHP to CPD isomerization and the reverse CPD to DHP conversion can be triggered by illumination with red (>630 nm) and blue (460 nm) light respectively. The unambiguous and reversible response of these systems triggered by visible light make them potential candidates for biological purposes and electronic devices.

TOC GRAPHICS



KEYWORDS. Photochromism, dimethyldihydropyrene, visible switch, ruthenium complexes

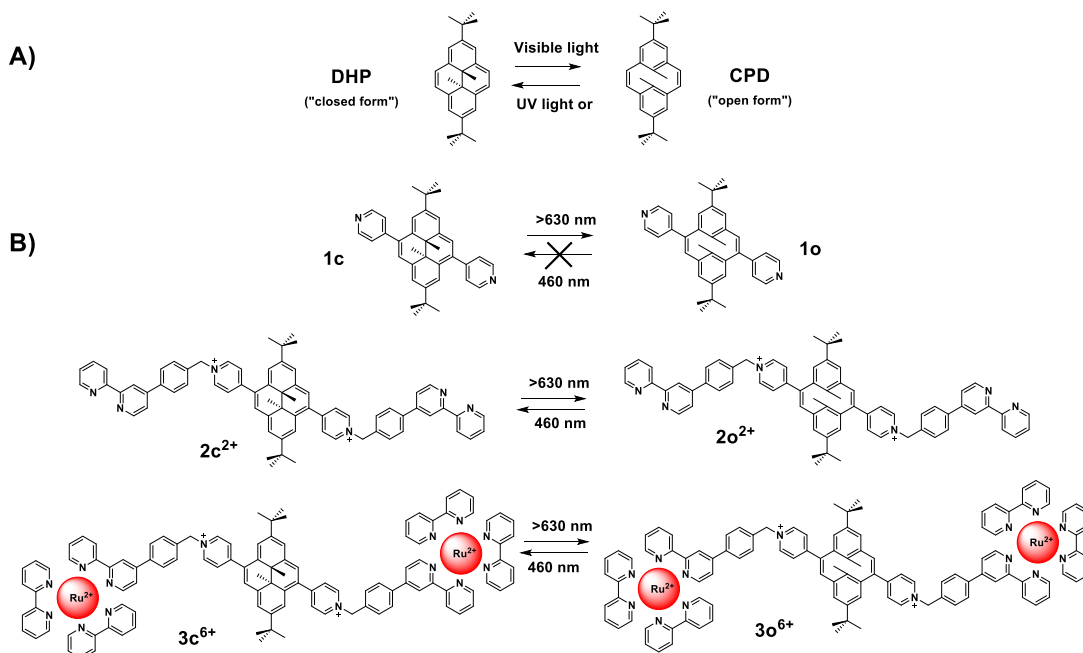
The research area of photochromic molecules is a very active and promising topic due to the great variety of possible applications notably, in molecular electronic devices and machines.^{1,2} These particular molecules can be converted reversibly between two isomers that possess different optical and electronic properties by combining visible and UV light irradiations. Recently, huge efforts have been made to develop biological applications involving photochromic molecules.^{3,4} However, for such applications it is necessary to avoid the use of UV-light because of undesired degradations and the low penetration in biological tissues.⁵

In this context, several examples have been reported concerning the synthesis of azobenzene,⁵⁻⁷ stilbene⁸ and diarylethene⁹⁻¹⁵ families of photochromic molecules, in order to obtain all visible systems.¹⁶⁻²² Two main strategies may be considered *i*) a chemical modification of the photochromic moiety through the extension of its π -conjugation or/and the introduction of push pull substituents¹¹ and *ii*) an association of an additional photosensitizer that can provoke energy transfer to the photochromic unit upon visible irradiation. For example, [Ru(bpy)₃]²⁺-diarylethene derivatives (with bpy = 2,2'-bipyridine) have been reported in which irradiation on the metal to ligand charge transfer band (in the visible region) is followed by an energy transfer to the triplet state of the photochromic unit that leads to the photocyclization of the diarylethene group.⁹

Note that most cases of visible systems described to date belong to the class of positive photochromic compounds, *i.e.* systems for which the thermodynamically more stable form (often colorless) absorbs at higher energies relative to the less stable one. In contrast, the dimethyldihydropyrene (DHP, “closed form”) – cyclophanediene (CPD, “open form”) couple belongs to the class of negative photochromic compounds, where the colorless CPD isomer is thermodynamically unstable and reverts thermally to the closed form (DHP) through the closure of the central carbon–carbon bond (Scheme 1a). During the last years, dimethyldihydropyrenes, initially exploited by Boelkelheide and Mitchell,²³ have gained an increasing interest for applications in material sciences and biology.²⁴⁻²⁶ In particular, it was previously reported that the DHP/CPD couple, due to the important differences in the electronic structure between both isomers, can be used to optically modulate the conductance of electronic devices and materials.^{24,27,28} In addition, recent efforts have been made to increase the photochromic properties of the DHP/CPD couple. For example, we demonstrated that the quantum yield for the DHP to CPD conversion can be significantly enhanced by introduction of pyridinium substituents.²⁵ In a

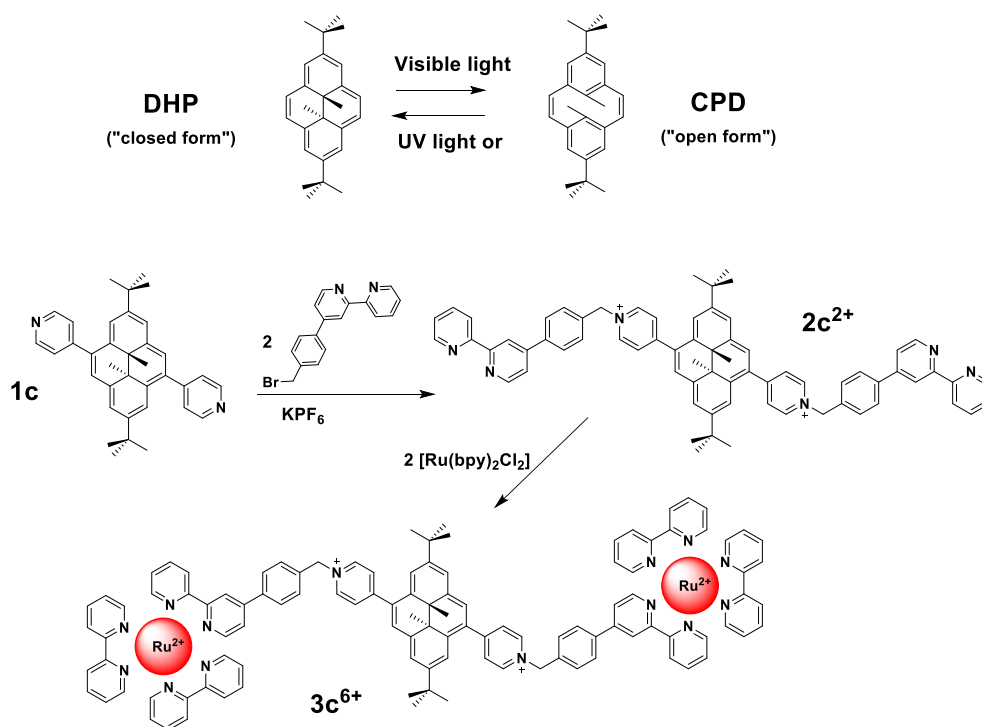
recent study, Hecht and coworkers recently reported an interesting example of push-pull system in which the DHP to CPD conversion operates under NIR light illumination.²²

In this work, our aim was to develop all-visible systems based on the DHP/CPD couple using a combination of the strategies described above. The studied compounds **2²⁺** and **3⁶⁺** are depicted in Scheme 1. Our strategy was to associate the DHP photochromic core either with a bipyridine unit (**2²⁺**) or with a [Ru(bpy)₃]²⁺ complex (**3⁶⁺**) using an electron-withdrawing pyridinium as a bridge. Such pyridinium linker was chosen in order to ensure a good quantum yield for the DHP to CPD conversion²⁵ and the [Ru(bpy)₃]²⁺ moiety in **3⁶⁺** was introduced as a photosensitizer in order to populate the triplet state of the DHP core.



Scheme 1. A) Principle of the DHP/CPD couple and B) photoisomerization processes of **1c, **2c²⁺** and **3c⁶⁺** into **1o**, **2o²⁺**, and **3o⁶⁺**, respectively.**

The synthetic routes for the preparation of 2^{2+} and 3^{6+} are shown in Scheme 2. The bis(pyridine)-DHP derivative reacted with two molar equivalents of 4'-(4-bromomethylphenyl)-2,2'-bipyridine. The crude reaction product was subjected to an anion exchange procedure to afford the targeted PF₆⁻ pyridinium salt 2^{2+} , isolated upon filtration as a red powder. The preparation of the ruthenium(II) complex 3^{6+} has been carried out by reacting one molar equivalent of 2^{2+} with two molar equivalents of Ru(bpy)₃Cl₂. The metal complex was isolated by silica gel column chromatography using a mixture of CH₃CN/CH₃OH/aqueous sat. NaCl as eluent. The obtained product was subjected to an anion exchange procedure with aqueous KPF₆. Synthetic details and characterizations are described in the supplementary information.



Scheme 2. Synthesis of $2c^{2+}$ and $3c^{6+}$.

Investigation of the photo-opening isomerization (DHP → CPD)

The photoisomerization reactions between the closed and the open isomers of the different systems were investigated in the 300 nm–800 nm range using diluted samples in acetonitrile as solvent (Figure 1). The closed compounds exhibit four main absorption bands in the visible region. Based on time-dependent density functional theory (TD-DFT) calculations, these four bands were assigned to π – π^* transitions in **1c** and **2c²⁺**. In **3c⁶⁺** these π – π^* transitions were also present but the third band, with a shoulder centered at 456 nm, also involves metal-to-ligand charge transfer (MLCT) transitions from the ruthenium center to the bpy ligands (Table 1).

Compared to the absorption spectrum of the parent DHP compound **1c**,²⁴ most of the absorption bands of the pyridinium substituted DHP derivatives **2c²⁺** and **3c⁶⁺** appear red shifted. In particular, the lowest energy absorption band (in the 650-750 nm region) is shifted of about -0.1 eV. This effect is attributed to the introduction of the electron-withdrawing pyridinium group and was previously rationalized by theoretical calculations.²⁵ The computed red-shift of the lowest transition energy between **1c** and **2c²⁺** is 0.165 eV at TD-DFT level, in good agreement with experimental data. Note that the π – π^* transitions of the DHP core in **3c⁶⁺** are almost identical to the π – π^* transitions computed in **2c²⁺**. They remain thus unaffected by the presence of the ruthenium centers.

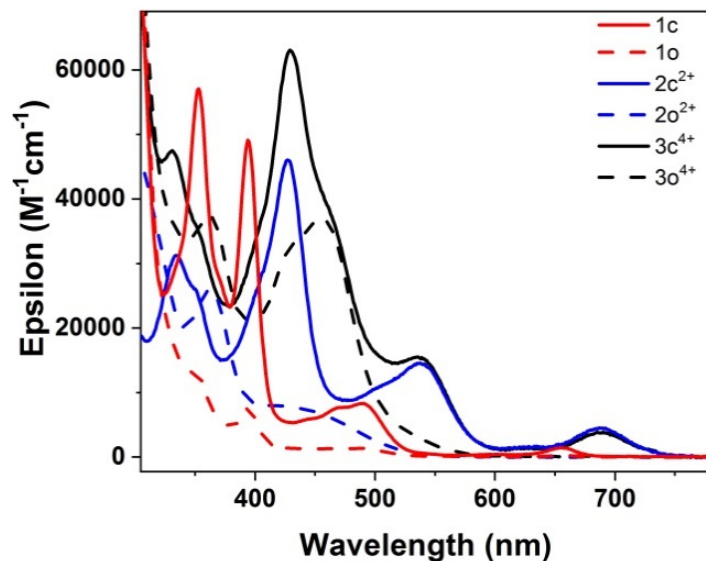


Figure 1. Absorption spectra of the investigated dimethyldihydropyrene derivatives, **1** (red curves), **2²⁺** (blue curves) and **3⁴⁺** (black curves) in their closed (solid lines) and open (dashed lines) forms. Solvent: CH₃CN; room temperature.

When irradiated at 460 nm, compound **1c** is converted to its opened isomer with a quantum yield $\phi_{c \rightarrow o} = 0.4\%$.²⁵ In the case of the **2c²⁺** and **3c⁴⁺** derivatives, irradiation at lower energy ($\lambda > 630$ nm), corresponding to light absorption at the lowest energy band (690 nm), gives a quantitative ring-opening, with a quantum yield 20-fold higher compared to **1c** (Table 2).²⁵ Such increase of the photo-opening efficiency is consistent with the measured ring-opening quantum yields observed for previously reported pyridinium-appended DHPs. In accordance with our previously reported theoretical studies,^{25,29} this effect was attributed to the fact that the photo-active HOMO→LUMO state responsible for the initial isomerization process towards CPD becomes S₁ in the presence of electrowithdrawing pyridinium groups such as in **2c²⁺** and **3c⁴⁺** compounds, whereas it is S₂ in **1c** (Table 1).

Table 1. Lowest electronic transitions computed at TD-DFT level in acetonitrile.

Compound	λ (nm)	f^b	Transitions ^c
s			
1c	577	0.004	0.45(H→L+1)+0.41(H-1→L)
	492	0.038	0.55(H→L)
	385	0.687	0.40(H-1→L)-0.38(H→L+1)
	341	0.933	0.50(H-1→L+1)
1o	359	0.113	0.67(H→L)
	278	0.524	0.62(H-1→L+1)
	273	0.113	0.42(H-2→L)
	249	0.727	0.44(H→L+2)
2c²⁺	625	0.087	0.54(H→L)
	539	0.277	0.44(H-1→L)+0.39(H→L+1)
	409	1.093	0.52(H→L+1)-0.39(H-1→L)
	366	0.303	0.54(H-1→L+1)
2o²⁺	407	0.413	0.65(H→L)
	324	0.816	0.65(H-1→L+1)
	288	0.007	0.44(H-6→L)+0.37(H→L+4)
	280	0.641	0.42(H→L+4)-0.41(H-6→L)
3c⁶⁺	638	0.123	0.57(H→L)
	549	0.355	0.47(H-1→L)+0.38(H→L+4)
	498	0.017	MLCT
	451	0.255	MLCT
	435	0.321	MLCT
	429	0.256	MLCT
3o⁶⁺	412	1.207	0.53(H→L+4)-0.38(H-1→L)
	498	0.017	MLCT
	451	0.165	MLCT
	436	0.409	MLCT
	429	0.247	MLCT
	416	0.504	0.65(H→L)
	329	0.550	0.47(H-3→L+1)

^aComputed at TD-CAM-B3LYP/6-311G** level, except for MLCT transitions computed at TD-B3LYP/6-311G** level (see Supp. Info.). ^bOscillator strengths. ^cEigenvectors with main configurations (H: HOMO, L: LUMO). Main contributing orbitals shown in Table S1.

Absorption bands of the investigated open isomers are also quite different. Indeed, while no absorption is observed for **1o** in the visible range, cyclophanedienes **2o⁺** and **3o⁺** display a broad band in the visible region around 400-500 nm (Figure 1 and Table S3). The extinction coefficient at 460 nm is 7300 and 37000 L.mol⁻¹.cm⁻¹ for **2o⁺** and **3o⁺** respectively. This feature is consistent with the computed absorption spectra (Table 1). While the first electronic transition appears around 360 nm for **1o**, the photo-active HOMO→LUMO transition is found at $\lambda > 400$ nm in **2o⁺** and **3o⁺**. In addition, the remarkable quantitative photoconversion of **1c** and **2c⁺** to their corresponding open isomers upon irradiation at *ca.* 460 nm and > 630 nm, respectively can be explained by the fact that the corresponding CPDs absorb at much shorter wavelengths. Thus, no back reaction (photocyclization) can occur at these wavelengths, which is a manifestation of negative photochromic systems.

Study of photo-closing reactions (CPD→DHP)

Irradiation of **2o⁺** and **3o⁺** at 460 nm (monochromatic light) results in the photoconversion to their corresponding closed isomers **2c⁺** and **3c⁺** with yields of 80% and 94%, respectively. In contrast, illumination of a solution containing the parent CPD **1o** at the same wavelength does not lead to the formation of the closed state **1c**. Thus, the large bathochromic shift in **2o⁺** and **3o⁺** allows for a fully reversible switch operating in the visible region. TD-DFT calculations corroborate these results and the absence of photocyclization of **1o** when illuminated in the visible region is attributed to the absence of electronic transitions in this spectral region (the lowest energy transition occurring in the UV range). The fact that incomplete photoconversion

are observed for the cyclization of **2o²⁺** and **3o⁶⁺** is attributed to the absorption of **2c²⁺** and **3c⁶⁺** at 460 nm (see Figure 1 and Table 1) leading logically to a photo-stationary state (PSS).

Photoisomerization quantum yields for the ring-closure reactions ($\phi_{o\rightarrow c}$) by visible irradiation were investigated using the method of Rau *et al.*³⁰ and yields of 32 % and 21% were obtained for **2o²⁺** and **3o⁶⁺**, respectively (Table 2). Note that these values are comparable with the quantum yields for photocyclization of CPD derivatives (around 30%) performed with UV illumination.³¹ It should be pointed out that the photocyclization quantum yield of **3o⁶⁺** is lower than that of **2o²⁺**, while the corresponding photoconversion yield is higher for **3o⁶⁺** (94%) compared to **2o²⁺** (80%). The main difference between the two systems arises from the MLCT transitions present in **3o⁶⁺** and **3c⁶⁺**. Upon irradiation at 460 nm, **3o⁶⁺** absorbs both in its photo-active HOMO→LUMO state (computed at 416 nm; Table 1) and in bright singlet MLCT states (computed around 440 nm; Table 1), whereas **2o²⁺** light absorption populates only the HOMO→LUMO state. The presence of lower triplet MLCT states (Table S2) is responsible for efficient intersystem crossing in **3o⁶⁺**, as already known for polypyridine ruthenium(II) complexes.³²⁻³⁴ As the two lowest triplet excited states are ³(π, π^*) centered on DHP (Table S2), an energy transfer (by internal conversion) from the metal to the triplet state of the photochromic unit can be expected. As the triplet state is not expected to play an important role in the photoisomerization mechanism of DHPs, it is thus not surprising to observe a lower photocyclization quantum yield in the coordinated compound **3o⁶⁺**. For the closed-ring isomer **3c⁶⁺**, the picture is fairly similar. The MLCT transitions are unchanged compared to **3o⁶⁺** showing that the isomerization state does not affect these transitions. However, in **3c⁶⁺**, the triplet MLCT states are degenerate with the lower ³(π, π^*) centered on DHP (Table S2), suggesting an efficient formation of these unreactive states responsible for the lowering of the ring-opening quantum yield in the coordinated compound **3c⁶⁺**.

Table 2. Quantum yields (Φ) and photostationary state compositions (PSS) for ring-opening and cyclization reactions.

Compounds	λ_{irr} (nm)	Φ (%)	PSS composition
1c → 1o	478	0.4	100 % 1o
1o → 1c	460	-	0 %
2c²⁺ → 2o²⁺	687	8	100 % 2o²⁺
2o²⁺ → 2c²⁺	460	32	80% 2c²⁺
3c⁶⁺ → 3o⁶⁺	690	8	100 % 3o⁶⁺
3o⁶⁺ → 3c⁶⁺	460	21	94% 3c⁶⁺

Transient absorption spectroscopy studies

More details on the closing mechanism were studied using femtosecond transient absorption spectroscopy in the UV-visible range. Difference absorption spectra until 2.5 nanosecond for **2o²⁺** and **3o⁶⁺** after 470 nm femtosecond excitation pulse are shown in Figure 2. Evolution of transient absorption spectra for **2o²⁺** is characteristic of the photo-dynamics of CPD (Figure 2a). In few hundred of femtosecond a broad difference absorption spectrum assigned to Franck-Condon excited states is growing and gives a transient spectrum at 350 femtoseconds characterized by four bands: three positive bands (maximum at 380 nm, 505 nm and 590 nm) for excited states and one negative band (peaking at 430 nm) from the depopulation of ground state (same maximum in comparison with steady state spectra of **2o²⁺** that has a shoulder at 442 nm, Figure 1). There is then a minor picosecond dynamic that is a signature of some vibrational relaxations

(intramolecular and cooling), *i.e.* the depopulation and positive bands at 590 nm decrease slightly without any change of the shape of the transient spectrum until 7 ps. Finally, from 7 ps and until 2.5 nanoseconds depopulation and positive bands of excited states decrease concomitantly with the growing of two positive bands at 430 nm and 540 nm. At 2.5 nanoseconds the spectrum is similar to the one of **2c*** steady state absorption spectrum with the characteristic band at 690 nm (Figure 2b). A global decay analysis was done (supporting information) that allows us to build a model. A hot excited state is growing in 162 fs +/- 3 fs, relaxes in 1.89 ps +/- 0.01 ps to a cold intermediate state that decays with the formation of **2c*** in 948 ps +/- 12 ps. Two isosbestic points are clearly observed at 395 nm and 565 nm, *i.e.* the relaxation of the intermediate excited state is giving either **2c*** (32%) or **2o*** (68%, back reaction) without any existence of other intermediate or deactivation pathways.

As expected from steady state results **3o*** transient absorption spectra in the picosecond time scale is exhibiting different bands and time evolution (Figure 2c). At 350 femtoseconds, the transient spectrum has the same number of bands than **2o***. However, in this case, the depopulation band corresponds to a broad band centered at 440 nm and the first positive band superior to 500 nm is red-shifted with a maximum at 520 nm that account for MLCT excited state of the ruthenium tris(bipyridine) moiety. In addition, there is a clear picosecond evolution of the latter band that shifts its maximum to 530 nm at 16 ps. Then one can observe the beginning of the recovery of depopulation band concomitantly with the decay of the positive band at 370 and 530 nm. As ruthenium triplet MLCT excited state has a lifetime of 400 nanosecond, positive bands at 370 nm, 520 nm and 580 nm are mainly assigned to this state. Altogether global decay analysis shows that singlet MLCT excited state led in 163 fs +/- 1 fs to localized triplet MLCT and a non relaxed DHP excited states. Excited state localized on DHP

relax in 5.50 ps +/- 0.11 ps to a cold excited state localized on the DHP core that decays in 1.957 ns +/- 0.043 ns to generate $3\mathbf{c}^{6+}$ or to go back to $3\mathbf{o}^{6+}$ in the ground state.

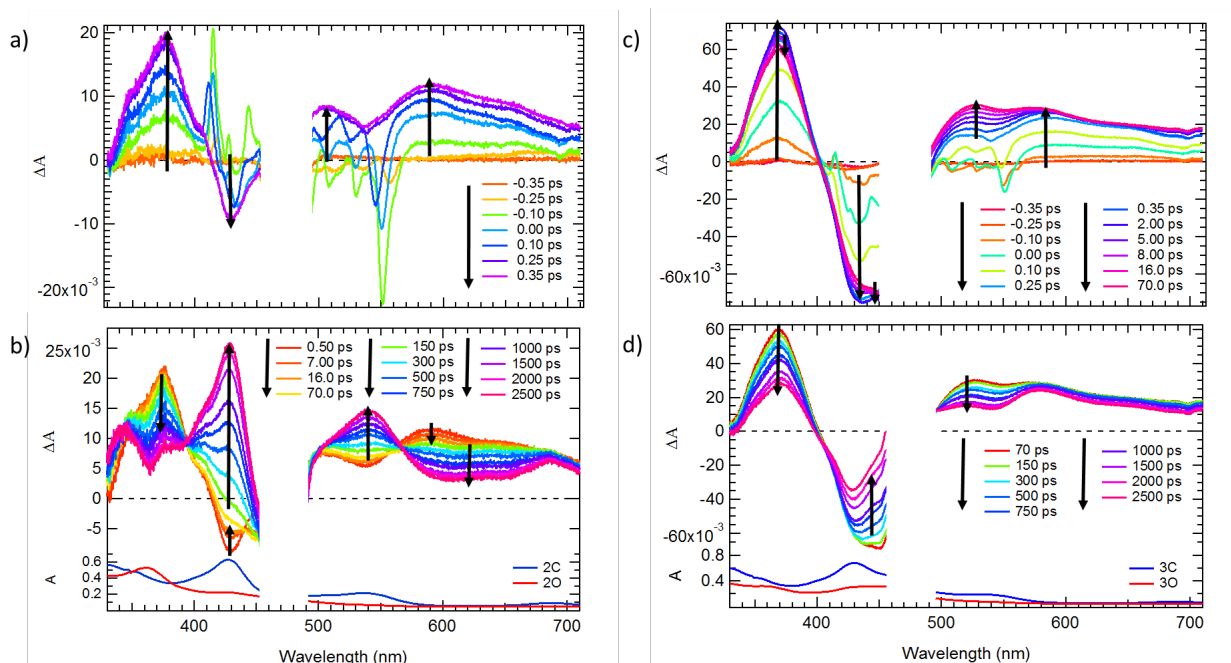


Figure 2. Ultrafast transient difference absorption spectra of $2\mathbf{o}^{6+}$ (a,b) and $3\mathbf{o}^{6+}$ (c,d) in acetonitrile. Spectra were recorded at different time delays from femtosecond to nanosecond following a 470 nm femtosecond laser excitation. The region near 470 nm is a blind zone due to laser scattering. Steady state absorption spectra of open and closed forms are also shown in panel b and d.

Investigation of the fatigue resistance

For potential practical applications as molecular switches, the investigated compounds must fulfill several requirements and in particular resistance to photochemical fatigue, *i.e.*, a loss of performance in photochromic conversion over time due to degradation reactions. This aspect was investigated by monitoring the UV-visible absorptions of 2^{2+} and 3^{6+} (Figure 3). During alternating irradiation processes at > 630 nm and 460 nm, corresponding to the opening and closing

reactions, respectively, we were not able to detect any sign of photodegradation for 2^{2+} compound over ten cycles, in contrast to previously studied pyridinium-dimethyldihydropyrene derivatives³⁵ where recovery of the closed states were realized by UV irradiation. This result clearly shows the advantage of all-visible photochromic systems.

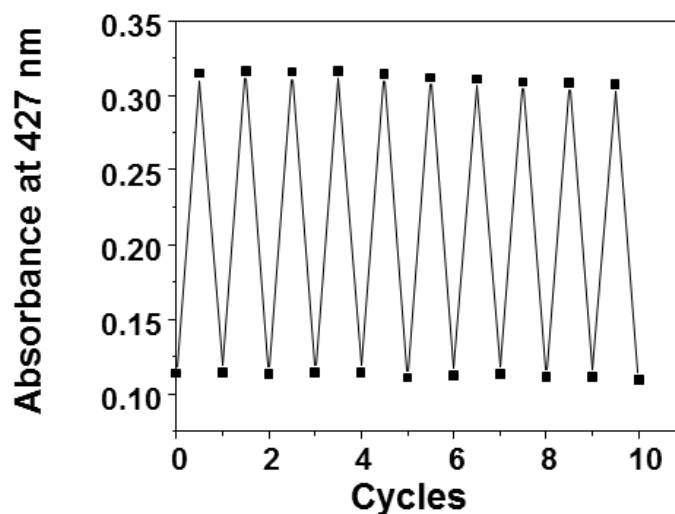


Figure 3. Fatigue resistance of $2c^{2+}$ measured at $\lambda_{\max} = 430$ nm during alternating switching cycles consisting of ring-opening (irradiation at $\lambda_{\text{irr}} > 630$ nm, $t = 600$ s) and ring-closing (irradiation at $\lambda_{\text{irr}} = 460$ nm, $t = 90$ s) of a $2 \cdot 10^{-5}$ M acetonitrile under inert atmosphere. Illumination with a 500 W Hg-Xe lamp.

In conclusion, we have synthesized two original dimethyldihydropyrene-based photoswitchable derivatives that can reversibly operate exclusively by visible light irradiation. The functionalization of the dimethyldihydropyrene with bipyridine-phenyl-pyridinium units leads to a large bathochromic shift on the absorption spectra allowing the use of red and blue light irradiation for the ring opening and closing processes. Furthermore, the introduction of

ruthenium tris-bipyridine in **3**⁺ increases the photostationary state of the ring closing from 80 to 94%, which confirms the value of incorporating a photosensitization unit.

Supporting Information. General procedure, TD-DFT calculations, Emission spectra, Additional UV-visible data, Fatigue resistance measurements, Kinetic data.

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