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A New Surface-Bound Molecular Switch Based On The Photochromic Dimethyldihydropyrene With Light-Driven Release Of Singlet Oxygen Properties

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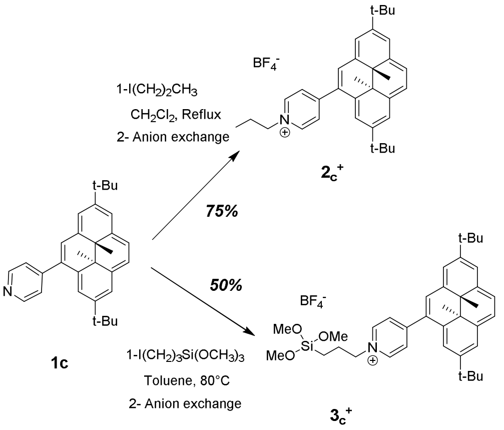
A pyridinium-substituted dimethyldihydropyrene photo-switch immobilized onto an ITO surface acts as a singlet oxygen carrier and supplier.

The design of functionalized stimuli-responsive surfaces[1] with tailored properties has given rise to an intense research activity motivated by potential applications in various fields such as bio-sensing,[2] electronic and microfluidic analytical devices.[3,4] Among the desired properties, control of singlet oxygen trapping and release is of great interest for not only chemical or biomedical purposes,[5] but also in the field of nanotechnology for the design of micrometer scale structures (lithography).[6] In both cases, the precise regulation of the oxygen singlet production is essential and light, used for the rapid and controlled generation of $^1O_2$ in a desired environment, is an elegant and non-invasive On/Off stimuli. Integration of $^1O_2$ photo-donors in appropriate materials is another key point in the perspective of practical uses. The $^1O_2$ release has been demonstrated in the cases of mono[6] or multilayer films,[7] and functionalized polymer nanoparticles.[8] However, these materials require the use of an exogenous photosensitizing agent. A much less explored but appealing strategy consists in combining oxygen photosensitizing at low energy (red light), carrying and producing properties in an immobilized all-in-one molecular system.

We recently reported that the red light irradiation ($\lambda > 630$ nm) of the coloured pyridinium-disubstituted dimethyldihydropyrene (DHP) photo-switch readily leads to the quantitative formation of the thermodynamically less stable colourless cyclophanediene form (CPD) following the opening of the central C-C bond. In the presence of dioxygen, this DHP derivative also plays the role of O_2 sensitizer. The photogenerated $^1O_2$ reacts with the CPD isomer to afford the corresponding endoperoxide-CPD species. The endoperoxide-CPD then releases $^1O_2$ thermally with a high yield of >85%.[9]

Motivated by the ability of this pyridinium-substituted DHP derivative to efficiently generate and release $^1O_2$, we report here the possibility to control $^1O_2$ production and delivery by light irradiation or heating of an ITO surface functionalized by pyridinium-substituted DHP derivatives. The challenge deals with the transfer of the $^1O_2$ generation and release properties from a homogeneous solution to a surface without loss of the efficiency of the molecular switch. For this, a novel alkyl-pyridinium-substituted DHP derivative $\mathbf{3_c}^+$ has been designed to be anchored on metal oxide surface through a silane subunit (Scheme 1). $\mathbf{2_c}^+$ was also used as a reference compound.



Scheme 1. Synthesis of compounds $\mathbf{2_c}^+$ and $\mathbf{3_c}^+$.

The targeted photo-switches $\mathbf{3_c}^+$ and $\mathbf{2_c}^+$ were synthesized starting from the previously reported[10] 2,7-di-tert-butyl-4-(4-pyridyl)-trans-10b,10c-dimethyl-10b,10c-dihydropyrene $\mathbf{1_c}$ that was reacted with an excess of (3-iodopropyl)trimethoxysilane or 3-iodopropane, respectively (Scheme 1). The crude reaction products were submitted to an anion exchange procedure

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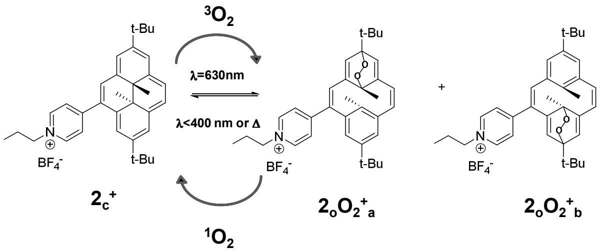
using an ion-exchange resin to afford the targeted $\mathbf{2_c^+}$ and $\mathbf{3_c^+}$ compounds as BF_4^- salts, isolated as red powders with good yields (75% and 50% respectively).

$\mathbf{2_c^+}$ undergoes a quantitative photo-oxygenation in organic solvents upon visible light irradiation under air ($\lambda > 630$nm, t =20 min), as judged from ^1H NMR, UV-visible spectroscopies and cyclic voltammetry. Indeed, as previously stated with similar compounds,[9] red light irradiation of the DHP populates the singlet excited state (S1) that is responsible for the isomerisation resulting from the loss of the central C-C bond.

The S1 level can also undergo intersystem crossing to generate the triplet T1 state which is efficiently quenched by oxygen.[9] The photogenerated $^1O_2$ rapidly reacts with the CPD form to afford the corresponding endoperoxide $\mathbf{2_oO_2^+}$ (Scheme 2).



Scheme 2. Photo-oxygenation of $\mathbf{2_c^+}$.

This system ($\mathbf{2_c^+}$ / $\mathbf{2_oO_2^+}$) in CD_3CN solution has been characterized by ^1H NMR spectroscopy. Due to the asymmetry of $\mathbf{2_c^+}$, the internal methyl groups are revealed by two singlets at -3.84 and -3.89 ppm. The opening of the central C–C bond results in a large low-field shift of these signals. The asymmetry of $\mathbf{2_c^+}$ is also responsible for the formation of two endoperoxide CPD isomers, $\mathbf{2_oO_2^+{}_a}$ and $\mathbf{2_oO_2^+{}_b}$, after irradiation under air, as shown by the signal splitting of the ^1H NMR features. For instance, the ^1H NMR spectrum of the irradiated solution displays two couples of singlets corresponding to the internal methyl proton signals at -0.11 ppm and 2.04 ppm, and at -0.10 ppm and 1.96 ppm, respectively. From the integration of these signals, it is seen that the photo-irradiation of the solution leads to the quantitative formation of $\mathbf{2_oO_2^+}$ and that the two isomers are obtained with a 33/67 ratio ($\mathbf{2_oO_2^+{}_a}$/$\mathbf{2_oO_2^+{}_b}$). The formation of $\mathbf{2_oO_2^+}$ has also been confirmed by mass spectrometry. A peak at m/z = 496 $[M-BF_4^-]^+$ (100 %) is detected on the spectrum.

The UV-visible spectrum of the $\mathbf{2_c^+}$ solution ($2 \cdot 10^{-5}$ M, in CH_3CN) displays four typical absorption bands (λ = 339, 417, 516, 666 nm) attributed to π–π* transitions involving the four singlet electronic states of the DHP entity (Figure 1A). During visible light irradiation under air, the intensity of the main absorption bands gradually decreases at the expense of new bands in the UV region. The quantitative consumption of $\mathbf{2_c}$ was evidenced by the full disappearance of the initial absorption band at 671 nm (S0-S1 transition).

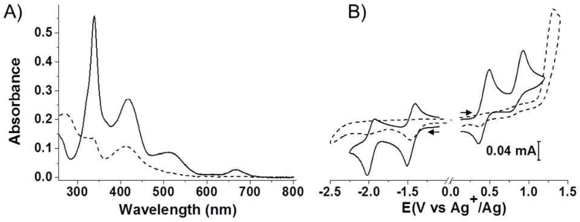


Figure 1. UV-visible absorption spectra (A, $2 \cdot 10^{-5}$ M in CH_3CN) and CV curves (B, 10^{-3} M + 0.1 M TBAP in CH_3CN solution) of $\mathbf{2_c^+}$ (full line) and $\mathbf{2_oO^{2+}}$ (dashed line, after irradiation of $\mathbf{2_c^+}$ under air, $\lambda > 630$ nm, 20 min). (0.1 $V.s^{-1}$, vitreous carbon ϕ 3 mm, E *vs* Ag^+/Ag 10 mM CH_3CN +TBAP 0.1 M, path length = 1 cm)

The electrochemical behaviour of the closed form $\mathbf{2_c^+}$ in CH_3CN is similar to what was previously reported for pyridinium-disubstituted DHP derivatives (Figure 1B).[3b] In the region of positive potentials, two anodic waves are observed at $E_{1/2}$ = +0.42 V (reversible) and E_{pa} = +0.92 V (irreversible), respectively, accounting for the formation of the radical cation and the non-stable corresponding di-cation. In the region of negative potentials, two reversible cathodic waves at $E_{1/2}$ = -1.46 V and -1.97 V are observed. They are attributed to the one-electron reduction of the pyridinium unit and of the DHP core, respectively. The electrochemical behaviour of the $\mathbf{2_c^+}$ electrolytic solution is deeply modified after its visible irradiation under air. One irreversible anodic signal attributed to the two-electron oxidation of the generated $\mathbf{2_oO_2^+}$ is seen at E_{pa} = +1.31 V. Two irreversible cathodic signals are also detected at -1.50 V and -2.01 V and they correspond to electron transfers centred on the pyridinium unit and the endoperoxide-CPD core, respectively.

The de-oxygenation process coupled with the ring-closure back reaction to the $\mathbf{2_c^+}$ form could be readily performed upon irradiation with UV light (254 nm, 3 min, $2 \cdot 10^{-5}$ M) without noticeable degradation, or thermally (45°C, 5h) as judged from the full recovery of the initial ^1H NMR and UV-visible spectroscopy features for $\mathbf{2_c^+}$ (see SI). As for the pyridinium-disubstituted DHP/CPD couple studied under air,[9] the ring-closure process is accompanied by the release of singlet oxygen which could be sensed by EPR technique based on the detection of the 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy (4-oxo-TEMPO) free radical formed upon oxidation of 2,2,6,6-tetramethyl-4-piperidone (4-oxo-TMP) in the presence of singlet oxygen (see SI).

The interesting ability of $\mathbf{2_c^+}$ / $\mathbf{2_oO_2^+}$ to efficiently generate and release $^1O_2$ in solution prompted us to investigate the immobilization of the trimethoxysilane analogue $\mathbf{3_c^+}$ as an organic layer onto a pre-treated ITO surface.[11] The substrates were dipped in 1 mM CH_3CN solution of $\mathbf{3_c^+}$ at room temperature during 12 h, in the absence of light, leading to the formation of the film $\mathbf{3_c^+/ITO}$. The functionalized surface has been investigated by X-ray photoelectron and absorption spectroscopies, atomic force microscopy (AFM) and by electrochemical analysis.

X-ray photoelectron spectroscopy (XPS) has been used as a versatile tool to analyse the surface chemical composition after grafting. High resolution XPS spectra at the Si (2p), C (1s), N (1s), and O (1s) core levels show the emergence or the increase of the peak components at their respective binding energies relative to carbon (285.0 eV), nitrogen (399.9 eV), silicium (102.3 eV) and oxygen (530.1 - 532.5 eV) confirming the occurrence of the grafting (see SI). The O (1s) multi-peak structure can be explained by the signature of overlapping components due to bulk In_2O_3 and SnO_2 (530.1 eV), to OH groups on the pre-treated ITO samples and to the methoxy groups belonging to $\mathbf{3_c}^+$ (532.5 eV).[12] The effective anchorage of $\mathbf{3_c}^+$ onto ITO was also checked by cyclic voltammetry restricted to the first oxidative process undergone by the DHP core in order to preserve the functionalized layer from degradation following its over-oxidation (Figure 2A). The CV curve of $\mathbf{3_c}^+$**/ITO** in CH_2Cl_2 electrolytic solution shows the expected reversible oxidation wave at $E_{1/2}$ = +0.40 V, close to the one observed with $\mathbf{2_c}^+$. The shape of this wave ($\Delta E_p \sim 0$ V at low scan rates) is characteristic of the nernstian electrochemical behaviour for immobilized electro-active species with linear variation of the peak intensity as a function of the scan rate. Integration of the anodic wave recorded at low scan rate (10 $mV.s^{-1}$) yields an apparent surface concentration of $(2.4\pm0.3)\cdot10^{-10}$ $mol.cm^{-2.}$ From AFM observation, it is seen that the layer of $\mathbf{3_c}^+$**/ITO** (Figure 3) can be described as a 4 nm thickness disperse monolayer. The UV-visible spectrum of the organic layer (Figure 2B) has been also recorded to confirm the chemical structure of the deposit. The typical absorption bands of the DHP entity are observed at 342, 411, 503 and 656 nm. From the absorbance value at 342 nm (see SI), the surface coverage has been estimated at $(2.0 \pm 0.6)\cdot10^{-10}$ $mol.cm^{-2}$, close to the value determined by cyclic voltammetry.

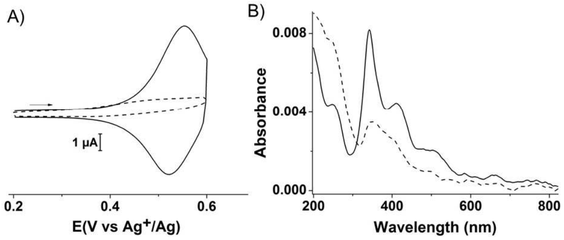


Figure 2. CV curves (A) and UV-visible absorption spectra (B) of $\mathbf{3_c}^+$**/ITO** (full line) and $\mathbf{3_o}^+\mathbf{O_2}$**/ITO** (dashed line, after irradiation of $\mathbf{3_c}^+$**/ITO** under air, λ> 630nm, 60 min). CV curve recorded in CH_2Cl_2 + TBAP 0.1 M solution (0.05 $V.s^{-1}$, ITO 1 cm^2, E *vs* Ag/Ag^+ 10 mM CH_3CN +TBAP 0.1M).

Visible light irradiation (λ > 630 nm) of the surface under air during 60 min at room temperature leads to the formation of the immobilized endoperoxide $\mathbf{3_o}^+\mathbf{O_2}$**/ITO**. As for $\mathbf{2_c}^+$ in solution, this result is revealed from UV-visible spectroscopy (Figure 2B) by the disappearance of the initial $\mathbf{3_c}^+$**/ITO** UV-visible spectrum along with the emergence of the one for $\mathbf{3_o}^+\mathbf{O_2}$**/ITO.** The electrochemical response of the functionalized surface evolves accordingly with the disappearance of the first reversible anodic signal characteristic of $\mathbf{3_c}^+$**/ITO** (Figure 2A).

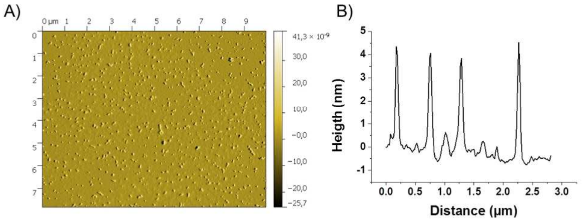


Figure 3. Representative AFM images (A) and cross-sections (B) of $\mathbf{3_c}^+$**/ITO** monolayer.

The back reaction from $\mathbf{3_o}\mathbf{O_2}^+$**/ITO** to $\mathbf{3_c}^+$**/ITO** was carried out by thermal pathway or upon UV light irradiation. As judged from UV-visible spectroscopy and cyclic voltammetry, the back reaction is quantitative for temperatures between 25 °C and 45 °C, the initial state being reached after 5 h at 45 °C. However, UV irradiation (λ = 254 nm for 2 min at room temperature) of the immobilized oxygenated compound leads to a slight degradation after several opening-closure cycles under air, a decrease of 30% in the absorbance at 341 nm being measured after 6 cycles.

As for the reference system $\mathbf{2_c}^+/\mathbf{2_o}\mathbf{O_2}^+$, the release of singlet oxygen during the closing process was detected by EPR technique (Figure 4).[13]

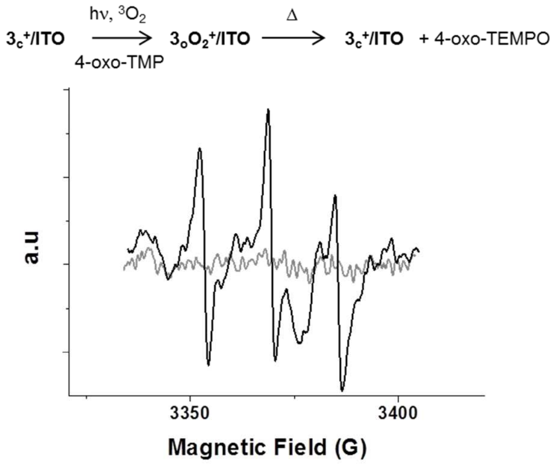


Figure 4. EPR spectra (room temperature) of nitroxide radical generated in a 1M water solution of 4-oxo-TMP and in the presence of $\mathbf{3_o}\mathbf{O_2}^+$**/ITO** previously formed upon irradiation of $\mathbf{3_c}^+$**/ITO** (under air, λ> 630nm, 60 min); grey line: initial spectrum; black line: after thermal relaxation in the absence of light.

A $\mathbf{3_o}\mathbf{O_2}^+$**/ITO** layer was allowed to undergo the closing process thermally in a 1M aqueous solution of 4-oxo-TEMP. The signal of the generated 4-oxo-TEMPO free radical is clearly seen on the EPR spectrum of the solution (Figure 4). This spectrum is very similar to the one of commercial 4-oxo-TEMPO radical dissolved in water with the hyperfine splitting constant equal to 16 G and the g factor equal to 2.0056.

The photo-induced reversible binding of $^1O_2$ to the immobilized compound **3_c^+** was further confirmed by XPS measurements focussing on the O (1s) core level. High resolution XPS spectra have been recorded for **3_c^+/ITO** samples before and after irradiation process under air (Figure 5). The thermal back reaction from **$3_oO_2^+$/ITO** to **3_c^+/ITO** was carried out by thermal pathway. Upon irradiation under air, the intensity of the component located at 532.5 eV increases. The ratio between the two main peaks at 530.0 eV and 532.5 eV rises from 0.73 (**3_c^+/ITO**) to 0.89 (**$3_oO_2^+$/ITO**) due to an additional contribution in the range of the binding energy for oxygen-oxygen bond reflecting the formation of the endoperoxide **$3_oO_2^+$/ITO**.[14] After thermal release of oxygen, the **3_c^+/ITO** initial XPS spectrum is restored.

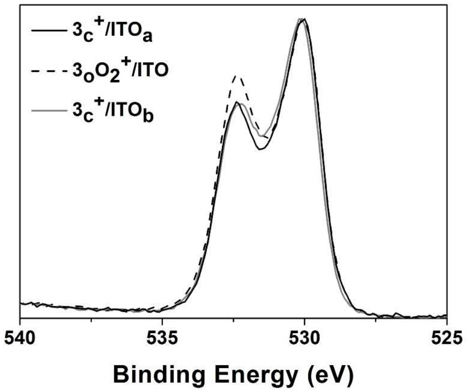


Figure 5. High resolution XPS spectra of the O(1s) bands of **3_c^+/ITO$_a$**, **$3_oO_2^+$/ITO** and **3_c^+/ITO$_b$** thermally recovered.

Conclusions

In summary, we have demonstrated that the efficient reactivity towards oxygen of a pyridinium-substituted DHP can be transferred to an ITO surface. Under air and upon red light irradiation, the opening process of the photo-switch in solution and on the surface is accompanied by the formation of an endoperoxide which releases singlet oxygen during the back reaction that can be rapidly achieved thermally and by UV irradiation; this device thus stocks and produces singlet oxygen on request. Such a feature allows to envision the use of this compound, as photoresist, in photolithography, providing an efficient tool for surface etching under simple and ecological conditions.

Notes and references

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