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A Photochromic Supramolecular Memory With Non-Destructive Readout

*Joakim Kärnbratt, Martin Hammarson, Shiming Li, Harry L. Anderson, Bo Albinsson, and Joakim Andréasson**

The use of molecules as elements for information processing and storage is a fast developing research field.[1] Replacing the materials traditionally used for the abovementioned purposes with molecular entities implies a change of paradigm for miniaturization, power consumption, etc. The light-induced color change of photochromic molecules makes them ideal candidates for optically controlled functions, as the absorption of the two isomers in different spectral regions may denote 0 or 1 — the universal digital language. Several approaches to photochromic molecular memories have been reported, and one of the most pressing problems addressed in these studies is how the stored information is to be retrieved optically without concomitant loss of data.[2-9] This is referred to as a non-destructive readout process. Monitoring the absorption of either isomeric form in the readout process is not a feasible approach since the distribution between the two isomers is affected, with resulting loss of information. Here we describe how a pyridine-decorated photoswitch from the dithienylethene (**DTE**) family is used together with a porphyrin dimer ($\mathbf{P_2}$) to constitute a supramolecular memory with non-destructive readout capability. Porphyrins have been used as fluorescent reporters in various other photochromic molecular architectures designed for similar purposes.[10-14] In the vast majority of these cases, the photoinduced isomerization process switches electron transfer reactions *on* and *off*, and the porphyrin emission intensity is concomitantly toggled between a *low* and a *high* state (quenched or not quenched). As described below, our approach has instead been to harness the isomerization-induced *structural* changes of $\mathbf{P_2}$, which in turn are reflected in the spectral properties of the dimer. As these changes are probed in a spectral region outside the photochromically active absorption bands of **DTE**, the state of the memory is preserved in the readout process.

Photoresponsive constructs containing the **DTE** backbone have been extensively utilized for optically controlled molecular logic applications due to their excellent thermal stability and fatigue resistance.[15-19] Figure 1 shows the structures and the isomerization scheme of the **DTE** derivative used in this work. Several research groups have used the same pyridine-appended **DTE** derivative for, e.g., non-destructive readout purposes, although the functional principles used differ from the approach that we have taken.[3, 4, 10, 20] The open form, **DTEo**, is isomerized to the closed one using UV light. The photostationary distribution after exposure to 302 nm UV light (ca. 1.5 mW cm^{-2}) is essentially 100% in the closed form **DTEc**, as judged by NMR measurements. This is also the case for the open form after the reverse isomerization when triggered by broadband visible light ($\lambda > 450$ nm, ca. 100 mW cm^{-2}).

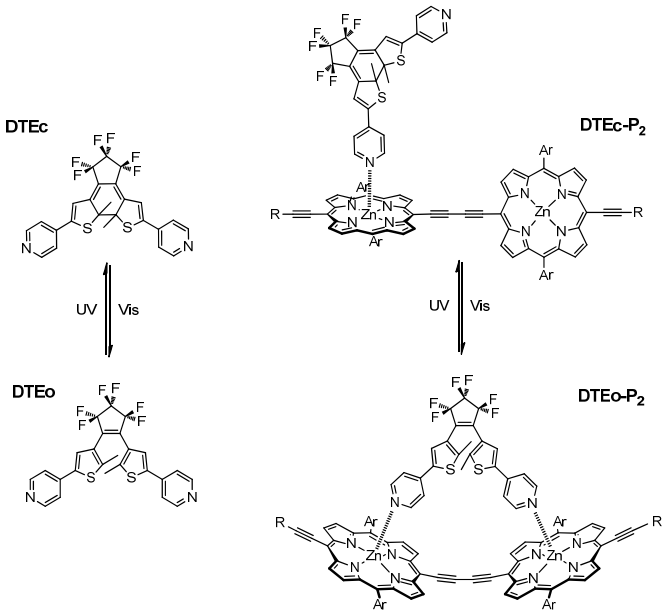

Figure 1. Isomeric forms of the pyridine-appended **DTE** photoswitch and the **DTE-$\mathbf{P_2}$** complex (Ar=3,5-di(octyloxy)phenyl, R=Si(C_6H_{13})$_3$). For **DTEc-$\mathbf{P_2}$**, the formation of higher complexes have been left out for simplicity (see text for details).

Under the specified light densities, the time constant for the closing and the opening reactions were 6 s and 45 s, and the corresponding quantum yields in methanol solution have been reported to be 0.57 and 0.014.[20] Thermal interconversions were not observed over several weeks. As shown in Figure 2a, **DTEo** (red dotted line) absorbs exclusively in the UV region; its longest-wavelength absorption band is at 303 nm. **DTEc** (blue solid line) displays absorption also in the visible region with a band centered around 594 nm. Neither form absorbs at wavelengths longer than ca 725 nm.

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Supporting information for this article with details of the synthesis, the experimental procedure, and the binding isotherms is available on the WWW under http://www.angewandte.org or from the author.

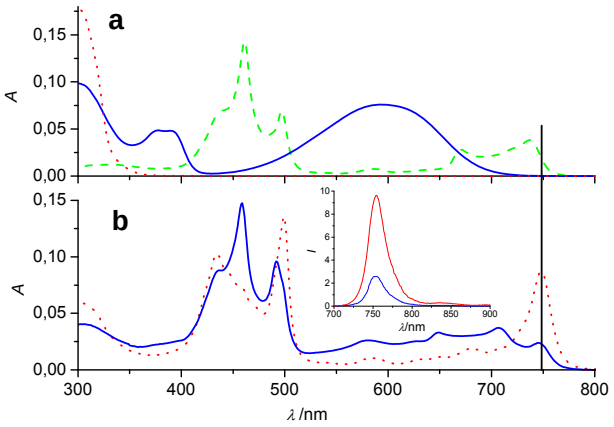

Figure 2. Absorption spectra in toluene of a) **DTEo** (·····), **DTEc** (——), **P_2** (– – –) and b) **DTEo-P_2** (·····), **DTEc-P_2** (——). In a) the **P_2** spectrum was recorded in the presence of 0.1 vol % pyridine, and the **DTE** absorbance have been multiplied by a factor 15 for ease of comparison. In b) the concentrations of **P_2** and **DTE** were ca 0.5 μM and 2 μM, respectively. Inset: Emission spectra of **P_2** in **DTEo-P_2** (——) and **DTEc-P_2** (——) after excitation at 748 nm (solid vertical line). It is clear that 748 nm light is well outside the absorption bands of **DTE** and that the overlap between **P_2** emission and **DTE** absorption is negligible.

Shown also in Figure 2a (green dashed line) is the absorption spectrum of the butadiyne-linked zinc porphyrin dimer **P_2**. The spectrum was recorded in toluene with 0.1 vol % pyridine and is characterized by absorption peaks in the Q-band region at 587 nm, 670 nm, and 737 nm. The very low rotational barrier imposed by the butadiyne link allows a broad distribution of conformations, and at room temperature all porphyrin-porphyrin dihedral angles are populated. It has been previously shown that when a bidentate dipyridyl pyrrole ligand is added, it will efficiently coordinate **P_2** to form a 1:1 complex in which the porphyrin macrocycles of the dimer are essentially co-planar.[21] This is manifested in substantial spectral changes. The most pronounced change is the intensification of the longest wavelength absorption band that has been shown to belong to the planar conformation.

Inspired by these observations, we investigated whether the formation of the bidentate planar 1:1 complex, and thus also the concomitant spectral changes, could be reversibly controlled by introducing the pyridine appended **DTE** derivative rather than the abovementioned "static" dipyridyl ligand. This idea is based on the fact that the open isomer possesses much more conformational flexibility than the closed form. **DTEo** should therefore be able to adopt a conformation well-suited for a chelated 1:1 complex with P_2, whereas **DTEc** cannot easily coordinate to both zinc centers of the same dimer molecule due to geometrical incompatibilities. In Figure 1, the postulated structures of the 1:1 **DTE-P_2** complexes for the open and the closed forms are shown. The formation of both complexes is supported by DFT optimizations (see Supporting Information for details), and the corresponding structures are shown in Figure 3. The binding constants for **DTEc-P_2** and **DTEo-P_2** in toluene were determined to 2.0×10^5 M^{-1} and 2.1×10^6 M^{-1}, respectively, i.e. the bidentate open form complex has a binding constant that is ca ten times higher than the mono-dentate closed form complex.[22]

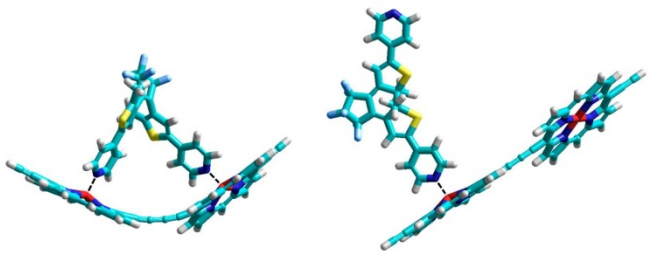

Figure 3. Geometry optimized structures of the **DTEo-P_2** (left) and **DTEc-P_2** (right) complexes, from DFT calculations on the molecules without *meso*-aryl or trihexyl silyl substituents.

The absorption spectrum of **DTEo-P_2** shown in Figure 2b (red dotted line) displays a very intense band at 748 nm, strongly suggesting a structure where the porphyrin macrocycles adopt a mutually planar conformation. Furthermore, the absorption band at 499 nm is more intense than the band at 434 nm which is also in line with a planar arrangement. The band at 304 nm is the unperturbed absorption of **DTEo**. The spectrum recorded after 30 s irradiation at 302 nm is also shown in Figure 2b (blue solid line). The spectral changes between 550 nm and 675 nm are mainly attributed to the absorption of **DTEc** underlying the porphyrin bands. Furthermore, new spectral features are observed in regions where the absorption from the **DTE** photoswitch is zero or very low. Most important, the band at 748 nm has experienced a ca 80% decrease in intensity, clearly signaling formation of the mono-dentate non-planar **DTEc-P_2** complex. The relative intensities of the absorption bands in the 400 nm and 500 nm regions have been reversed which is another observation in favor of this notion.[21] Subsequent exposure to broadband visible light for 18 min restored the original absorption spectrum, showing that the process is fully reversible (see Figure 4 for extended photocycling).

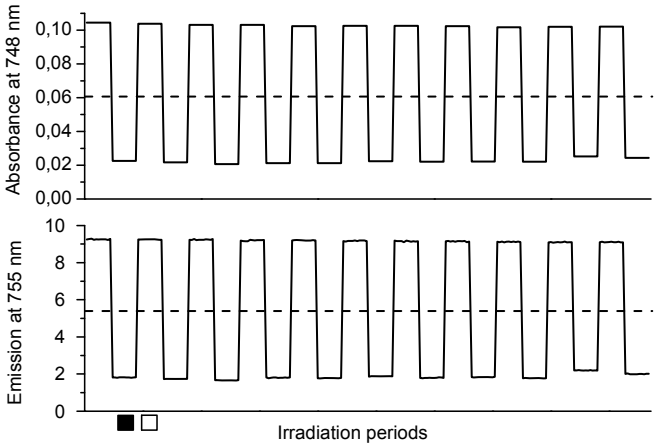

Figure 4. Photocycling of the **DTE-P_2** complex in toluene. The absorbance at λ = 748 nm (top panel) and emission intensity at λ = 755 nm upon excitation at λ = 748 nm (lower panel) measured for 5 s after each switching operation are shown: after UV irradiation for 30 s (■) and after broadband visible light irradiation for 18 min (□). The dashed horizontal lines represent arbitrarily set threshold levels, distinguishing a *low* value (0) from a *high* value (1). The traces are the actual measured signals, and therefore demonstrate the signal-to-noise levels present during the measurements.

Note that the broadband visible light used in this step was chosen to induce the ring-opening reaction **DTEc** → **DTEo**, i.e. by ensuring a significant spectral overlap with the photochromically active absorption of **DTEc**. In sharp contrast, no spectral changes were observed when the sample, in either isomeric forms, respectively, was exposed to extended irradiation for 64 h at 748 nm, showing that light of this wavelength does not interfere with the isomeric distribution **DTEo-P$_2$**/**DTEc-P$_2$**.[23] Thus, readout of the isomeric state of **DTE** through observation of the absorption (or emission, *vide infra*) from the porphyrin dimer is done in a fully non-destructive way. This is because the probe wavelength, 748 nm, is outside the absorption bands of both forms of the **DTE** photoswitch. Hence, the absorption at 748 nm may be reversibly switched between a *high* and a *low* state using broadband visible and UV light, respectively, and the absorption changes are conveniently monitored in a non-destructive manner. This photocycle was repeated ten times with no significant performance degradation (see Figure 4).

The readout process is not restricted to absorption measurements, but could equally well be replaced by fluorescence detection. This may be desirable for increasing the sensitivity in practical applications. Planar **P$_2$** displays moderately strong fluorescence upon excitation at 748 nm, and the changes in the emission intensity upon switching between the *high* and the *low* state shown in Figure 4 is exactly paralleling the corresponding absorption changes at 748 nm. The non-destructive nature of the readout process is preserved despite the fluorescent character of **P$_2$**, since the overlap of the **P$_2$** emission and the photochromically active absorption bands of **DTE** is negligible (see Figure 2).

Further insights into the switching process are gained by comparing the absorption spectra of **P$_2$** in large excess of pyridine (green dashed line), **DTEc** (blue solid line), and **DTEo** (red dotted line) shown in Figure 5. The concentrations of the ligands were chosen high enough to ensure that virtually 100% of **P$_2$** was coordinated to the respective ligand, and the contribution from ligand absorption have been subtracted. The close resemblance between the spectra of **pyridine-P$_2$** and **DTEc-P$_2$** strongly supports the notion that **DTEc** forms the open 1:1 and 2:1 complexes with **P$_2$**, whereas **DTEo** forms a closed, chelated 1:1 complex, thereby planarizing **P$_2$**. The small differences between **pyridine-P$_2$** and **DTEc-P$_2$** may be accounted for by traces of **DTEo** in the solution, forming the stronger, planar 1:1 complex with **P$_2$**.[22]

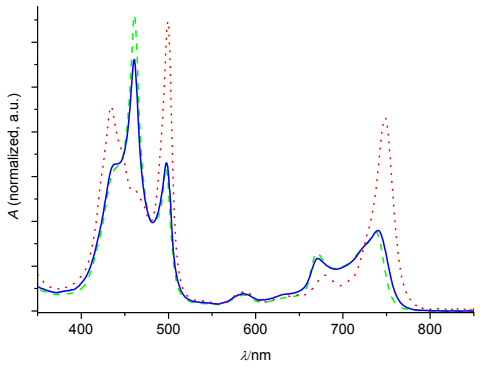

Figure 5. Absorption spectra in toluene of **P$_2$** (ca 1 μM) together with large excess of pyridine (ca 10 mM, – – –), **DTEc** (ca 0.1 mM, ——), and **DTEo** (ca 15 μM, ·····), respectively. The spectra are normalized at 480 nm, and the contribution from ligand absorption have been subtracted.

In terms of a molecular memory "write-read-erase" cycle, the system is initially set in the **DTEc-P$_2$** form using 302 nm UV light. The "write" process is chosen as broadband visible light irradiation, isomerizing the sample to the planar **DTEo-P$_2$** form, whereas the "read" process corresponds to monitoring either the **P$_2$** absorbance at 748 nm or the emission intensity at 755 nm after excitation at 748 nm. In this style, a *low* signal (0) may be converted to a *high* signal (1) in the writing process. The memory is then non-destructively read by monitoring either the absorbance or the emission intensity at the relevant wavelengths. Finally, the memory is erased by exposure to 302 nm UV light, resetting the system to the **DTEc-P$_2$** form.

In summary, we have shown that each of the two isomers of a pyridine-decorated **DTE** derivative forms a structurally and spectroscopically distinct complex with a porphyrin dimer. The major spectral shift occurs in a region outside the photochromically active absorption bands of **DTE**. Hence, the isomerization-induced absorption and emission changes are easily probed without affecting the state of the **DTE** derivative, allowing for a supramolecular optically controlled memory with a non-destructive readout process. We envision that the memory function is not the only interesting feature of this complex. It may also be used to control intermolecular interactions between **DTE-P$_2$** and other ligands in a reversible manner, or to control the rate of photoinduced electron transfer through porphyrin-based molecular wires.[24]

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[22] The binding constant determined for **DTEc-P_2** is a factor of five higher than for **pyridine-P_2** ($K = 4 \times 10^4\ M^{-1}$). This may be explained by traces of **DTEo** left in the sample after isomerization **DTEo** → **DTEc**. This fraction binds to **P_2** with a substantially higher binding constant, thereby increasing the apparent binding constant for **DTEc-P_2**. The UV-vis titration of **P_2** with **DTEc** is consistent with the statistical formation of the 1:1 **DTEc-P_2** complex and a 2:1 **$(DTEc)_2$-P_2** complex. There is no evidence for the formation of a cyclic 2:2 **$(DTEc)_2$-$(P_2)_2$** complex. Such a 2:2 complex would be expected to have a different distribution of torsional angles, and thus a significantly different absorption spectrum from the **pyridine-P_2** complex.

[23] The absorbance of the samples was monitored in the absorption spectrometer under continuous light exposure by the spectrometer lamp at 748 nm. After an initial equilibration phase corresponding to absorbance changes of ca 1% the signal leveled out at a constant value. This value was retained for more than two days. The corresponding experiment for **DTEc** alone at the 595 nm absorption maximum showed a 10% decrease in the absorption, showing that non-destructive readout is indeed promoted by formation of the **DTE-P_2** complexes.

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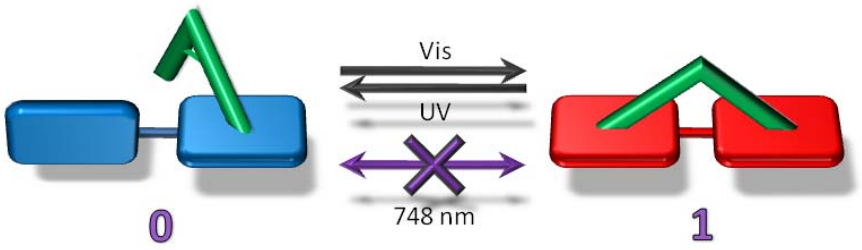

A supramolecular complex composed of a pyridine-appended dithienylethene (**DTE**) derivative and a porphyrin dimer ($\mathbf{P_2}$) functions as a molecular optically controlled memory with non-destructive readout capability. The light-controlled isomerization of **DTE** induces dramatic structural and spectral changes of $\mathbf{P_2}$. These changes are monitored in a region outside the photochromically active absorption bands of **DTE**, allowing for a non-destructive readout process.

Supporting Information

A Photochromic Supramolecular Memory With Non-Destructive Readout

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Synthesis

1,2-Bis(2′-methyl-5′-(pyrid-4″-yl)-thien-3′-yl)perfluorocyclopentene (DTE) was synthesized by the procedure reported by Gilat *et al*.[1]

Spectroscopic Measurements

All experiments were performed in toluene solution unless otherwise mentioned. Deoxygenation of the samples were not performed. The absorption measurements were performed using a CARY 4000 UV/Vis spectrometer. A SPEX Fluorolog-3 instrument was used for the emission measurements. The broadband visible light was generated by a 1000 W Xe/Hg lamp running at 450 W. The light from the Xe/Hg lamp was filtered by two hot mirrors (each with $A = 1.8$ at $\lambda = 900$ nm) to reduce the IR intensity. A yellow glass filter ($A > 1$at $\lambda < 415$ nm) was used to cut the shorter-wavelength light. The resulting light power density was ≈100 mWcm^{-2}. A UVP UV lamp (model UVM-57, ≈1.5 mWcm^{-2}) was used to provide the $\lambda = 302$ nm light. With the use of the broadband visible light, only one third of the sample volume was exposed to the light at any one time, whereas the whole sample volume was exposed to $\lambda = 302$ nm light. The samples were continously stirred during all irradiation processes.

DFT Optimizations

The Gaussian 03[2] program suite was used to geometry optimize $\mathbf{P_2}$ together with **DTE** in its open and closed form, using the B3LYP functional[3-5] and the 3-21(G) basis set.

Binding constants.

The binding constants for the **DTEo-P_2** and **DTEc-P_2** complexes were determined by titration of a stock solution of either **DTEo** or **DTEc** to **P_2** in toluene (see Figures S1-S4). The binding constants were then calculated to 2.1×10^6 M^{-1} and 2.0×10^5 M^{-1} for **DTEo-P_2** and **DTEc-P_2**, respectively, using SVD analysis in the spectral region 400 – 850 nm.[6] The overlapping absorption of **DTEc** was subtracted using a reference titration with equal **DTEc** concentrations. As the SVD-analysis still showed significant signs of more than two spectral components, the binding constant for **DTEc-P_2** was also determined with a single-wavelength binding isotherm at 742 nm which gave a similar result (1.6×10^5 M^{-1}). Two of the components detected in the titration of **P_2** with **DTEc** are probably the 1:1 **DTEc-P_2** complex and the 2:1 **(DTEc)$_2$-P_2** complex, formed in a statistical ratio.

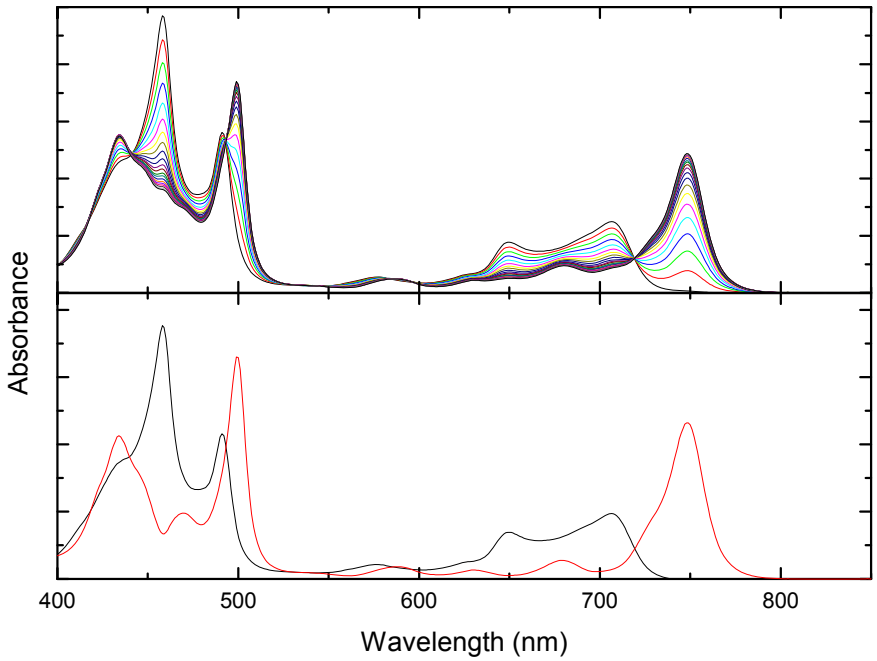

Figure S1. Top panel: Titration of **DTEo** to **P_2** in toluene. Lower panel: Spectral components of free **P_2** (black line) and the **DTEo-P_2** complex (red line) resolved from the SVD-analysis.

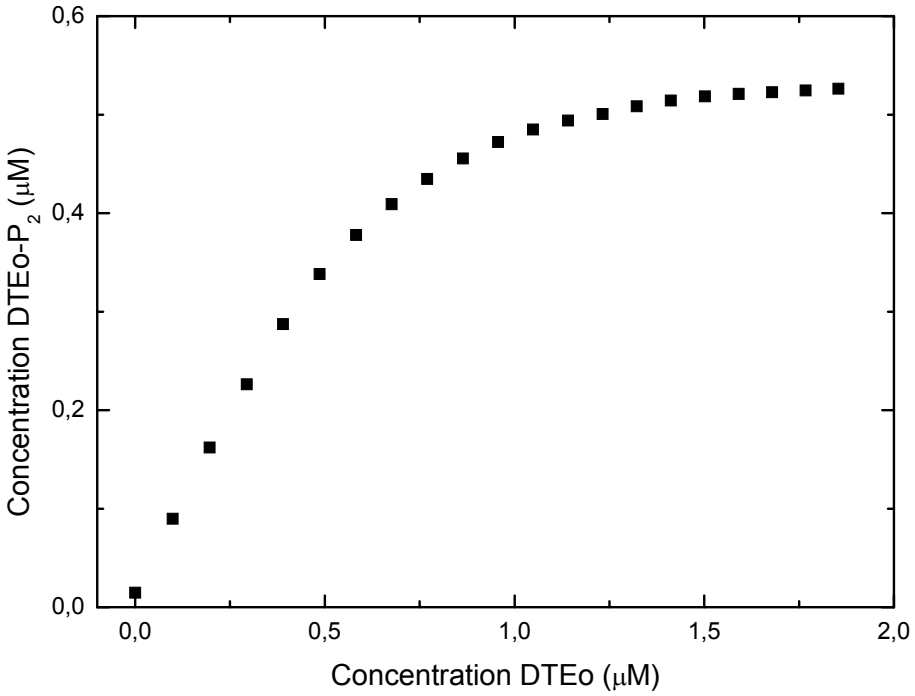

Figure S2. Concentration of the **DTEo-P_2** complex as a function added **DTEo** resolved from the SVD-analysis. The total concentration of **P_2** was 6.8×10^{-7} M.

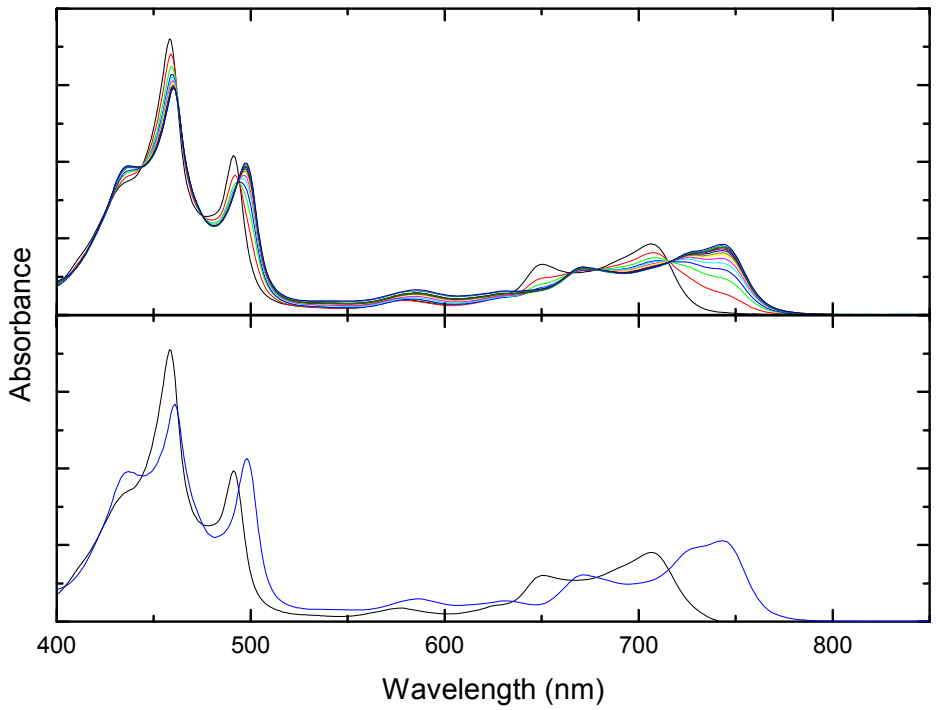

Figure S3. Top panel: Titration of **DTEc** to **P_2** in toluene. Lower panel: Spectral components of free **P_2** (black line) and the **DTEc-P_2** complex (blue line) resolved from the SVD-analysis.

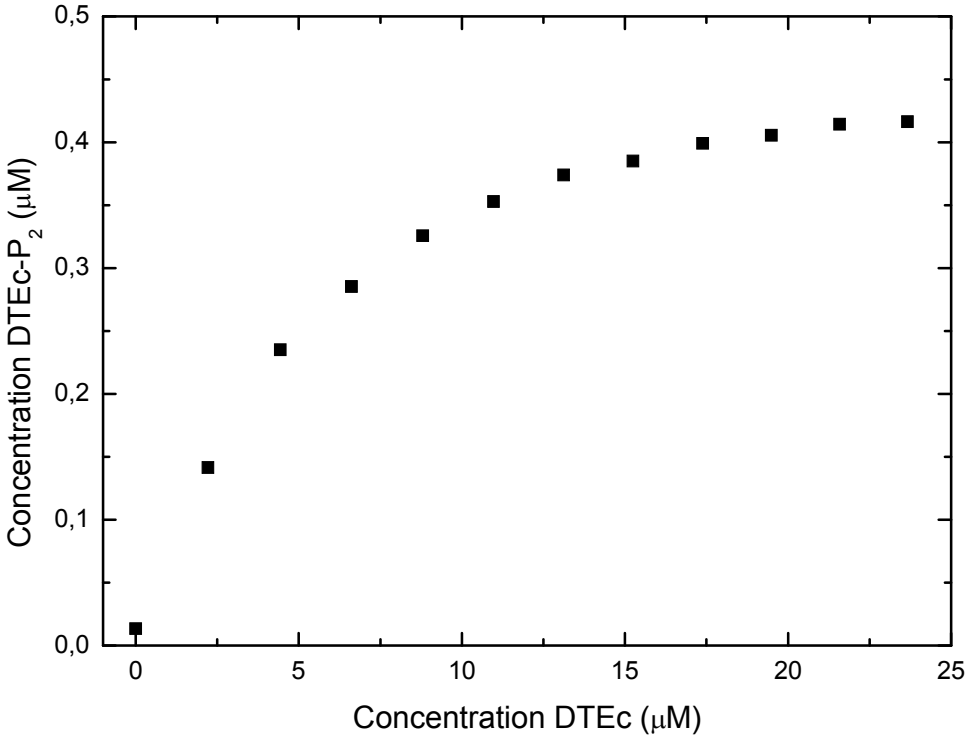

Figure S4. Concentration of the **DTEc-P_2** complex as a function added **DTEc** resolved from the SVD-analysis. The total concentration of P_2 was 5.1×10^{-7} M.

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