Molecular Devices

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Photochromic Supramolecular Memory With Nondestructive Readout**

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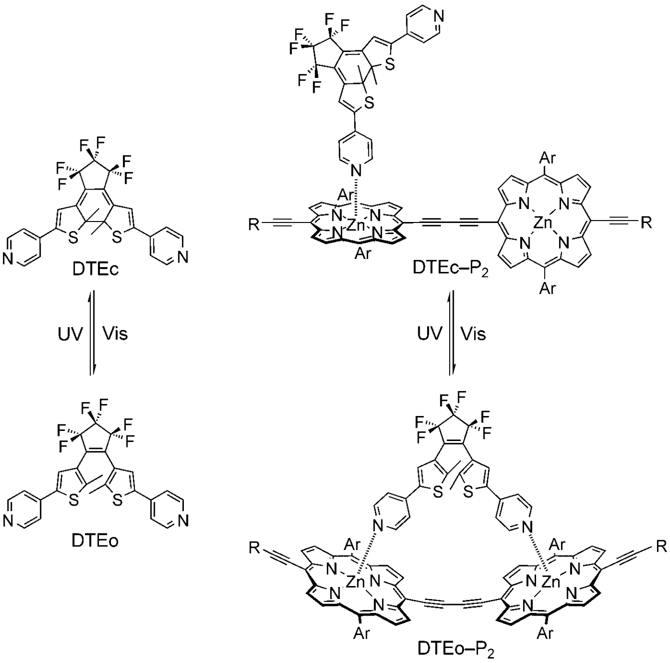
The use of molecules as elements for information processing and storage is a fast-developing research field.[1] Replacement of the materials traditionally used for such purposes by molecular entities implies a change of paradigm for miniaturization, power consumption, and so on. The light-induced color 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, that is, 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 can be retrieved optically without concomitant loss of data.[2–9] This process is referred to as nondestructive readout. 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. Herein we describe how a pyridine-appended photoswitch based on a dithienylethene (DTE) molecule is used together with a porphyrin dimer (P_2) to constitute a supramolecular memory with nondestructive readout capability. Porphyrins have been used as fluorescent reporters in various 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 unquenched). As described below, our approach harnesses the isomerization-induced structural changes of 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 that contain the DTE backbone have been extensively utilized for optically controlled molecular logic applications because of their excellent thermal stability and fatigue resistance.[15–19] The structures and isomerization of the DTE derivative used in this work are shown in Scheme 1. Several research groups have used the same pyridine-appended DTE derivative for applications such as nondestructive readout, although the functional principles used are different from the approach that we have taken.[3,4,10,20] The open form DTEo is isomerized to the closed form by using 302 nm UV light (ca. 1.5 mW cm^{-2}). ^{1}H NMR spectra show that the photostationary distribution is essentially 100 % of the closed form DTEc. When the reverse isomerization was triggered by broadband visible light ($\lambda >$ 450 nm, ca. 100 mW cm^{-2}), the sample was converted into 100% DTEo. 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



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

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solution have been reported to be 0.57 and 0.014, respectively.[20] Thermal interconversions were not observed over several weeks. As shown in Figure 1 a, DTEo absorbs exclusively in the UV region; the longest-wavelength absorption band is at 303 nm. DTEc displays absorption also in the visible region with a band centered around 594 nm. Neither form absorbs at wavelengths longer than approximately 725 nm.

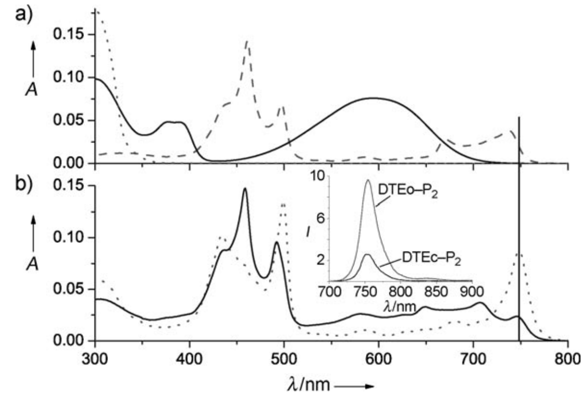

Figure 1. Absorption spectra in toluene of a) DTEo (dotted line), DTEc (solid line), and P_2 (dashed line), and b) DTEo–P_2 (dotted line) and DTEc–P_2 (solid line). In (a) the P_2 spectrum was recorded in the presence of 0.1 vol % pyridine, and the DTE absorbance has been multiplied by a factor of 15 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 lies outside the absorption bands of DTE and that the overlap between P_2 emission and DTE absorption is negligible.

The absorption spectrum of the butadiyne-linked zinc porphyrin dimer P_2 is also shown in Figure 1 a. 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 all the porphyrin–porphyrin dihedral angles are populated at room temperature. It has been previously shown that when a bidentate dipyridyl pyrrole ligand is added to P_2, it will efficiently coordinate to form a 1:1 complex in which the porphyrin macrocycles of the dimer are essentially coplanar.[21] Formation of the complex is manifested in substantial spectral changes. The most pronounced change is the intensification of the longest-wavelength absorption band that can be assigned to the planar conformation.

Encouraged 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 introduction of 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 that is 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 because of geometrical incompatibilities. The postulated structures of the 1:1 DTE–P_2 complexes for the open and the closed forms are shown in Scheme 1. The formation of both complexes is supported by DFT optimizations (see the Supporting Information for details), and the corresponding structures are shown in Figure 2. The binding constants for DTEc–P_2 and DTEo–P_2 in toluene were determined to $2.0\times10^{5}\,\text{M}^{-1}$ and $2.1\times10^{6}\,\text{M}^{-1}$, respectively; that is, the bidentate open-form complex has a binding constant that is approximately ten times higher than the monodentate closed-form complex.[22]

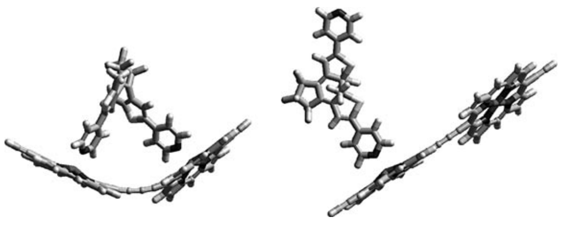

Figure 2. Geometry-optimized structures of the DTEo–P_2 (left) and DTEc–P_2 (right) complexes, from DFT calculations on the molecules without meso-aryl or trihexyl silyl substituents.

The absorption spectrum of DTEo–P_2 shown in Figure 1 b displays a very intense band at 748 nm, thus 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; this feature is also consistent 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 1 b. The spectral changes between 550 nm and 675 nm are mainly attributed to the absorption of DTEc that underlies the porphyrin bands. Furthermore, new spectral features are observed in regions where the absorption from the DTE photoswitch is zero or very low. Most importantly, the intensity of the band at 748 nm decreased by approximately 80 %, which clearly signals formation of the monodentate nonplanar DTEc–P_2 complex. Another observation to support this hypothesis is that the relative intensities of the absorption bands in the 400 nm and 500 nm regions are reversed.[21] Subsequent exposure to broadband visible light for 18 min restored the original absorption spectrum, thus showing that the process is fully reversible (see Figure 3 for extended photocycling). Note that the broadband visible light used in this step was chosen to induce the ring-opening reaction DTEc→DTEo, that is, 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 form, was exposed to extended irradiation at 748 nm for 64 h, thus showing that light of this wavelength does not interfere with the isomeric distribution DTEo–P_2/DTEc–P_2.[23] Thus, read-out of the isomeric state of DTE through observation of the absorption (or emission, see below) from the porphyrin dimer occurs in a fully nondestructive way as the probe wavelength, 748 nm, is outside the absorption bands of both forms of the

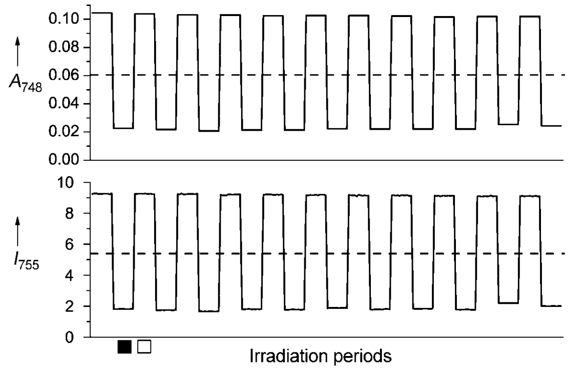

Figure 3. Photocycling of the DTE–P_2 complex in toluene. The absorbance at $\lambda = 748$ nm (top panel) and emission intensity at $\lambda = 755$ nm upon excitation at $\lambda = 748$ nm (lower panel) measured for 5 s after each switching operation are shown: after UV irradiation for 30 s (■) and after broadband visible light irradiation for 18 min (□). The dashed horizontal lines represent arbitrary threshold levels that distinguish 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.

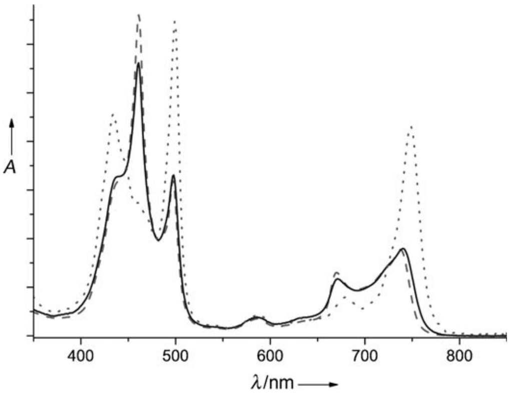

Figure 4. Absorption spectra in toluene of P_2 (ca. 1 μM) together with large excess of pyridine (ca. 10 mM, dashed line), DTEc (ca. 0.1 mM, solid line), and DTEo (ca. 15 μM, dotted line), respectively. The spectra are normalized at 480 nm, and the contribution from ligand absorption has been subtracted.

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 nondestructive manner. This photocycle was repeated ten times with no significant performance degradation (see Figure 3).

The readout process is not restricted to absorption measurements, but could equally well be replaced by fluorescence detection, which may be desirable for increased 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 3 exactly parallels the corresponding absorption changes at 748 nm. The nondestructive 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 1).

Further insights into the switching process are gained by comparing the absorption spectra of P_2 in a large excess of pyridine, DTEc, and DTEo shown in Figure 4. The concentrations of the ligands were high enough to ensure that virtually 100 % of P_2 was coordinated to the respective ligand. 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, which form the stronger, planar 1:1 complex with P_2.[22]

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 was carried out by irradiation with broadband visible light, which isomerizes 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 way, a low signal (0) may be converted to a high signal (1) in the writing process. The memory is then nondestructively 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, which resets the system to the DTEc–P_2 form.

In summary, we have shown that each of the two isomers of a pyridine-appended 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, thus allowing for a supramolecular optically controlled memory with a nondestructive 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 that of pyridine–P_2 ($K = 4 \times 10^4\,\text{M}^{-1}$). This result 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 $(\text{DTEc})_2$–P_2 complex. There is no evidence for the formation of a cyclic 2:2 $(\text{DTEc})_2$–$(P_2)_2$ complex. Such a 2:2 complex would be expected to have a different distribution of torsional angles, and thus a significantly different absorption spectrum to the pyridine–P_2 complex.

[23] The absorbance of the samples was monitored in an absorption spectrometer under continuous light exposure from 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 with DTEc alone at the 595 nm absorption maximum showed a 10% decrease in the absorption, thus showing that nondestructive readout is indeed promoted by formation of the DTE–P_2 complexes.

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