Light-triggered Luminescence Modulation Using Labile Axial Coordination to Zinc–Porphyrin

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Modulation of luminescence intensity triggered by light input is demonstrated. The system consists of a Zn–porphyrin and an azopyridine derivative, which axially coordinates to Zn–porphyrin and quenches its fluorescence more efficiently in the *trans*-form than in the *cis*-form. Thus, light-induced isomerization of the azopyridine results in the increase/decrease of the porphyrin fluorescence.

Manipulating electrons and photons at the molecular or supramolecular level is the aim of our research, motivated by potential utility of molecule-based electronic and photonic devices.[1] External triggers that have been proved to work as a control element in photoswitches include electrons, protons, and metal ions.[2] Less developed are photon-triggered photoswitches, i.e., light in and light out, maintaining the signal homogeneity, which is a prerequisite to making logic devices.[3] Photoswitches consist of luminescent center and a control unit which is responsive to an external trigger. Noncovalent construction of these units have several advantages over covalent constructs, especially in building elaborate molecule-based architectures.[4]

We previously reported a noncovalent electron- and proton-responsive photoswitch wherein the fluorescence from Zn–tetraphenylporphyrin (ZnTPP) is switched on/off in response to external triggers.[5] We later extended this approach to construct a noncovalent switch for intramolecular energy transfer using a Zn–porphyrin/free-base porphyrin conjugate.[6] These switches operate in response to electrons, protons, and small molecules. We here report an exclusively photon-based luminescence intensity modulation, making use of the association/dissociation of azopyridine derivatives and Zn–porphyrin triggered by light illumination.

The strategy we employed is based on photoisomerization and consequent steric changes of an azopyridine derivative, resulting in the alteration in binding affinity with ZnTPP or Zn–tetramesitylporphyrin (ZnTMP).[7] In the *trans*-form, 3-phenylazopyridines can coordinate to Zn–porphyrin without any steric hindrance, while in the *cis*-form, they coordinate to Zn–porphyrin to a lesser extent due to the steric hindrance between the porphyrin macrocycle and the phenylazo moiety in the azo compound, which may point toward the porphyrin. Phenylazopyridines quench the fluorescence of porphyrins very effectively when axially bound,[5,6] but obviously not when detached from the porphyrin. This is the mode of operation we have envisioned, which is given in Figure 1, being proved with spectroscopic measurements as described below.

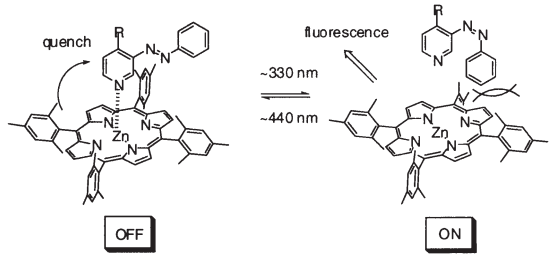

Figure 1. Mode of operation of light-driven photoswitch.

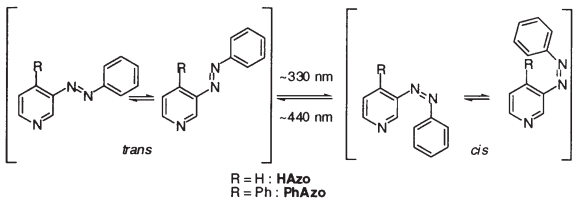

Figure 2. Photoisomerization of 3-(phenylazo)pyridines.

Two compounds were examined as candidates for a component in the photoswitch, 3-(phenylazo)pyridine (**HAzo**) and 4-phenyl-3-(phenylazo)pyridine (**PhAzo**).[8,9] These compounds in the *trans*-form have a large $\pi\pi^*$ absorption band at $\approx$330 nm and a small $n\pi^*$ band at $\approx$440 nm. An irradiation at the shorter wavelength band results in the formation of *cis*-forms accompanied by a decrease in the shorter wavelength absorption and an increase in the longer wavelength absorption. A phenyl group is introduced in **PhAzo** for the molecule to favor the conformation shown on the left in the *cis*-form in Figure 2, in which the phenylazo group points toward the porphyrin macrocycle when axially bound. The following description concerns the case involving **PhAzo** and ZnTMP, since this combination showed the most effective photomodulation.[10]

A solution of ZnTMP in toluene was titrated with ***trans*-PhAzo** to examine the axial coordination and resulting fluorescence quenching. Upon addition of ***trans*-PhAzo**, peaks in the Q-band and the Soret-band regions in the absorption spectrum of ZnTMP showed a red-shift by 10–15 nm, which is indicative of axial coordination.[11] It was revealed that the spectral changes follow a 1:1 binding isotherm, from which the association constant was calculated as $K_{trans} = 15900\ (\pm 200)\ M^{-1}$. This value allows one to estimate the ratio of free ZnTPP to the total ZnTPP concentration as a function of added ***trans*-PhAzo**, which is shown in Figure 3. The figure also includes intensity data for the fluorescence of ZnTMP, measured with excitation at 585 nm, one of the isosbestic points. The result that the relative fluorescence intensity is only slightly above the ratio of free ZnTMP indicates that the fluorescence from the bound species, ***trans*-PhAzo**·ZnTMP, is very weak ($\approx$7% of that of free ZnTMP), demonstrating that **PhAzo** quenches the fluorescence of ZnTMP very effectively, when axially bound.[12]

A solution of ***trans*-PhAzo** (0.25 mM) and ZnTMP (10 μM) in toluene was prepared, in which the amount of ***trans*-PhAzo**·ZnTMP is estimated to be 7.9 μM or 79% of total porphyrin molecules. This solution was illuminated by 326-nm light using

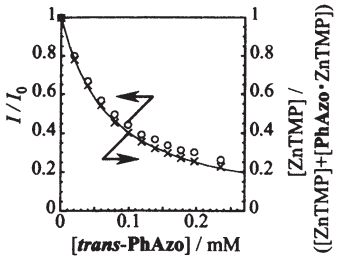

Figure 3. Ratios of free ZnTMP to total ZnTMP (10 μM) obtained from titration data (×) and the calculated association constant (–) as a function of added ***trans*-PhAzo** in toluene at 25 °C. Relative fluorescence intensities (○) are also shown (λ_{ex} = 585 nm).

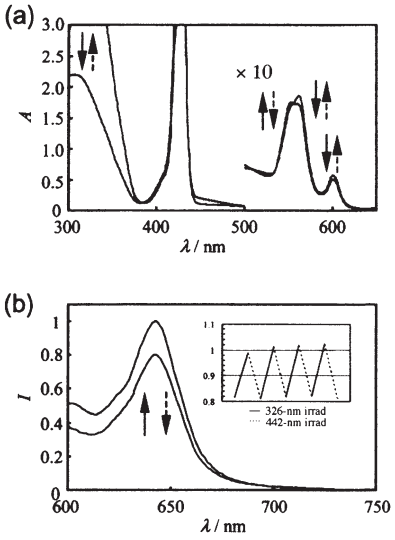

Figure 4. Illumination-induced spectral changes for a solution of **PhAzo** (0.25 mM) and ZnTMP (10 μM) in toluene at 25 °C. Solid arrows represent changes associated with *trans*-to-*cis* isomerization upon 326-nm irradiation, while dotted arrows represent the opposite process upon 442-nm irradiation. (a) Absorption spectra. (b) Fluorescence spectra (λ_{ex} = 585 nm). The inset shows the intensity variations on the repetition of alternate irradiation.

the light source of a fluorimeter (slit width 20 nm) until the spectrum became constant (20–30 min). A large decrease in absorbance around 300–380 nm and a slight increase around 400–500 in the UV–vis spectrum upon illumination showed that ***trans*-PhAzo** photoisomerized into the *cis*-form, see Figure 4a. The ratio of *trans*- and *cis*-forms in the photostationary state under these conditions was *trans*/*cis* = 33/67.[13] Concomitant with these spectral changes due to the azo compound, the Q-band of ZnTMP also exhibited changes in the direction indicative of the dissociation of axial ligand. The amount of complex, **PhAzo**·ZnTMP at this photostationary state was estimated from the shape of the spectrum to be ≈6.5 μM. The association constant between ***cis*-PhAzo** and ZnTMP was estimated as K_{cis} = 1600 (± 400) M^{-1}, using the value of K_{trans} and the known amounts of ***trans*-PhAzo**, ***cis*-PhAzo**, and **PhAzo**·ZnTMP. Thus, an order of magnitude decrease for K_{cis} from K_{trans} enables the dissociation of **PhAzo** from ZnTMP. Subsequent illumination at 442 nm reversed all changes described above, indicating *cis*-to-*trans* conversion of **PhAzo** and simultaneous increase of the bound species, **PhAzo**·ZnTMP.

The fluorescence from ZnTMP was monitored by excitation at 585 nm, which is one of the isosbestic points, during the cycle of irradiation and the results are shown in Figure 4b. The fluorescence was enhanced upon 326-nm illumination and diminished upon 442-nm illumination. The former process corresponds to *trans*-to-*cis* conversion and the related dissociation of **PhAzo** from ZnTMP, while the latter to exactly the opposite process. These changes were reasonably reversible as shown in the inset of Figure 4b. The on/off ratio under the experimental conditions is 1/0.8. Thus, a new mode of operation is demonstrated for light-responsive fluorescence modulation based on non-covalent assemblies.

In conclusion, the intensity of light output is modulated with a light trigger. The mode of operation is based on the association/dissociation of a light emitting unit and a control unit. Studies using 2-(phenylazo)pyridines, in place of 3-(phenylazo)pyridines, and attempts to improve the on/off ratio are underway in our laboratory.

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References and Notes

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8 **PhAzo** was prepared by the reaction of nitrosobenzene and 3-amino-4-phenylpyridine, which was obtained with a method developed by one of us (JMB): J. M. Bakke, E. Ranes, J. Riha, and H. Svensen, *Acta Chem. Scand.*, **53**, 141 (1999).
9 Data for **PhAzo**: ^{1}H NMR ($CDCl_3$) δ = 8.85 (1H, s), 8.72 (1H, d, J = 5.2 Hz), 7.96–7.82 (2H, m), 7.53–7.46 (9H, m). FAB–MS: m/z = 260 (MH^+). CHN analysis agreed within 0.25% with the structure.
10 The other systems will be reported in a full account later.
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12 The mechanism of the quenching is not clear at the moment, although electron transfer may be inferred, see ref. 6.
13 The absorption spectrum for ***cis*-PhAzo**, necessary for the evaluation of *trans*/*cis* ratio, was obtained from spectra for *trans*/*cis* mixed solutions, in which the amount of each component was known from ^{1}H NMR measurements.

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