Phthalocyanine-Modulated Isomerization Behaviour of an Azo-Based Photoswitch †

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A photoswitchable azobenzene-phthalocyanine-azobenzene triad has been synthesized and its electrochemical properties determined. Energy transfer among the subunits allows the modification of the *E*-*Z* ratio by selective excitation of the phthalocyanine moiety.

Phthalocyanines[1] (Pc’s) are specially well-suited building blocks for the preparation of a wide variety of materials with useful properties ranging from nonlinear optical applications to photoconductors or therapeutic agents.[2] These properties may be modulated by means of a wise selection of the central atom and/or the substituents. Among Pc's, the silicon ones are of great interest because of the possibility of axial substitution precluding aggregation in solution, and therefore, they could demonstrate appealing phenomena. Thus, substituents like dendritic structures, ferrocene, tetrathiafulvalene, carotenoids, among others, have been axially attached.[3] Here we report the synthesis, electrochemistry and the study of the isomerization of the silicon Pc-modulated azo-based photoswitch **1**. Compound **1** is the first example of a silicon Pc-azobenzene conjugate and, unlike other Pc-conjugate systems, the properties of both moieties in **1**, Pc and azoarene, can be mutually modulated by light. Thus, fluorescence emission of the phthalocyanine moiety is controlled by the isomerization state of the azo group, which in turn is regulated by irradiation on the absorption bands of the phthalocyanine.

Reaction of dichloro(phthalocyaninato)-silicon (**2**)[4] with 4-hydroxy-4′-nitroazobencene (**3**)[5] in the presence of sodium hydride using dry toluene as the solvent afforded **1** in 32% yield after purification by column chromatography.

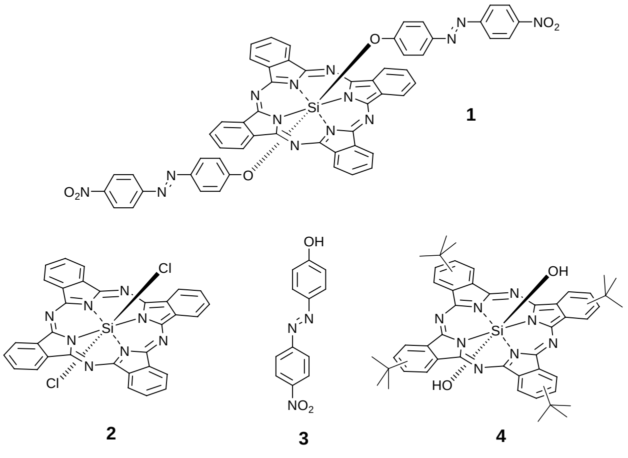

Chart 1 Drawing of compounds **1-4**.

†

The compound was fully characterized by ^{1}H NMR, FTIR, UV-vis and MALDI-TOF-MS.[6] Although MALDI-TOF experiments showed only a peak at m/z 782 corresponding to the silicon Pc with only one azo moiety attached, integration of the ^{1}H NMR signals clearly indicate the presence of two azo units linked to the Pc. The effect of the large ring current of the Pc on the protons of the azo moieties is noteworthy: the signals corresponding to the protons in the ortho position to the oxygen move from 6.99 ppm in **3** to 2.59 ppm in **1** (See Supplementary Material). The scarce solubility of the compound precluded ^{13}C NMR characterization.

The electrochemistry of **1**, **3** and **4** was performed in oxygen-free anhydrous THF (reductions of **1**, **3**, and **4**; oxidations of **1** and **4**) or MeCN (oxidations of **3**) using a standard three-electrode setup. **4** was used as a model compound for **Si(Pc)(OH)$_2$** because its higher solubility, lower tendency for aggregation and negligible electronic perturbation originated by t-butyl substituents. A set of three reductions waves were observed in THF for **3** and **4** whereas for **1** a more complex electrochemical profile was observed with a set of six reduction waves (Fig. 1). An important aspect in the reduction window for compound **1** is the fact that the second reductive wave is split into two waves, suggesting some degree of electronic delocalization over the two azoarene moieties, but it is difficult to assign which wave corresponds to the Pc and which to the coordinated azoarene. One oxidation wave was observed for **1,** two oxidations for **3**, and three oxidations for **4**.

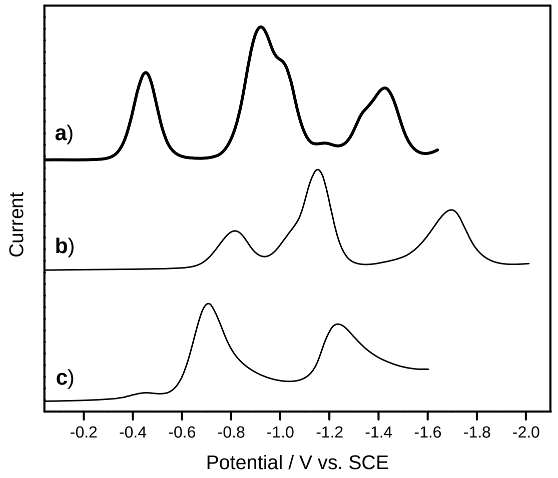

Fig. 1 Osteryoung square wave voltammetry (OSWV) for **1** (a), **3** (b) and **4** (c) in THF containing TBAPF$_6$ (0.1 mol dm^{-3}).

Compound	*E*/V *vs* Standard Calomel Electrode (SCE)
1	-0.45; -0.92*; -1.00*; -1.18*; -1.34; -1.42; 1.32
3	-0.82*; -1.15; -1.70*; 1.54; 1.77
4	-0.46; -0.71; -1.24; 1.00; 1.11; 1.38

* denotes a peak potential for an electrochemically irreversible wave.

Table 1 Electrochemical potentials.

[†] Electronic supplementary information (ESI) available: NMR spectrum and cyclic voltammetry of **1**. See http://www.rsc.org/suppdata/

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The electronic UV-vis spectrum of tryad **1** in benzene shows a typical (phthalocyaninato)silicon dihydroxyde (**Si(Pc)(OH)$_2$**) spectral profile[7] with a B band in the 300-400 region and a group of Q bands in the 600-700 nm region. The spectral profile featured by **1**, however, does not correspond to the simple summation of the individual spectra of **3** and **4** considering the 2:1 stoichiometry found in the complex **1**. Some particularities regarding the sum of the spectra of the separated constituents are found in the spectrum of **1** as a broadening of the B band with a shoulder in the 400-420 nm region, a red shift of 3-6 nm in the group of Q bands, and a decrease in the intensity expected for the longest wavelength Q band (Fig. 2). These spectral properties suggest some degree of intramolecular electronic interaction in the ground state among these subunits, reinforcing the observation concerning the electrochemical data.

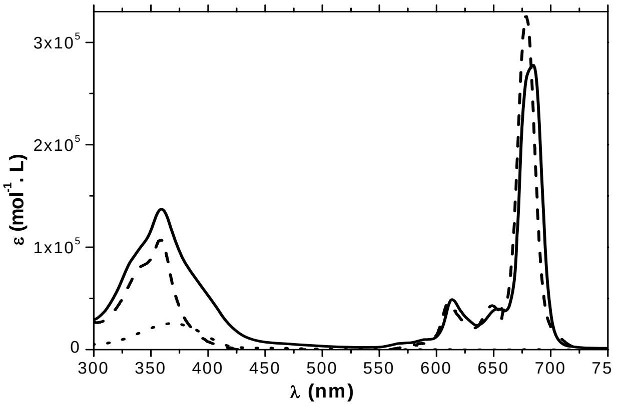


Fig. 2 Electronic absorption spectra in benzene solution of **1** (full line), **3** (dotted line) and **4** (broken line).

Irradiation of **1-*E*** in the spectral region corresponding to the π-π* (approx. 300-420 nm) or n-π* (approx. 450-500 nm) absorption bands of the free **3** caused a small decrease of the absorbance of the B band centered at 359 nm and a slight increase in the absorbance in the 400-500 nm region while the Q bands remained unchanged within experimental uncertainty. The spectrum of **1-*E*** was not affected when irradiation was performed with light of wavelengths longer than the region corresponding to the absorption of the n-π* band of the free azoarene **3**, as for example in the Q bands. Prolonged irradiation of benzene solutions of **4** did not cause any effect on the UV-vis spectrum. Thus, as the Pc B band and the azoarene π-π* band extensively overlap in **1** (see Fig. 2), the decrease in the absorbance observed for the B band and the increase in the region of 400-500 nm upon irradiation clearly indicate that the axial coordinated azoarene moieties undergo *E* to *Z* isomerization. The composition of the photostationary state (PS) in **1** is difficult to estimate considering the UV-vis data because of the competitive absorptions of the individual moieties in **1**, but considering the molar absortivities of Pc and azoarene components individually, the composition of the PS does not differ significantly from that obtained for **3**.[8] In the dark, the spectral features of **1-*E*** are recovered as a consequence of the thermal ***Z*** to ***E*** reaction. Both ***E*** to ***Z*** (photochemical) and ***Z*** to ***E*** (thermal) follow first-order kinetics as in **3**, but both processes are considerably slower (Tab. 2). Interestingly, irradiation of **1-*Z*** with light of 620 nm or 675 nm causes a fast recovery of the spectrum of **1-*E***. Therefore, this process can be attributed to a sensitized reaction, since the excitation is localized in the Q band region of the Pc moiety and any absorption from the axially coordinated azoarenes is excluded. The fast recovery of **1-*E***, as expected for a sensitized ***Z*** to ***E*** reaction, and the dependence on light intensity are additional evidences of a sensitized reaction.[9] No sensitized reaction is observed when mixtures of **4** and **3-*Z*** are irradiated in the Pc Q band, demonstrating that an intramolecular process is operating in the case of **1-*Z***.

	λ/nm (ε x10^4 /M^{-1}.cm^{-1})	**k$_{E\text{-}Z}$ x 10^{-3}(s^{-1})**	**k$_{Z\text{-}E}$ x10^{-3} (s^{-1})**
1	359(13.7); 613(4.9); 653(3.9); 684(27.7)	5.8	0.8; 13$^\#$
3	369(2.6); 456(1.3)	30	8.2
4	358(10.6); 610(4.6); 648(4.3); 678(32.5)	---	---

refers to the sensitized reaction.

Table 2 Absorption maxima data and first-order rate constants in benzene solution.

Compound **1** shows fluorescence emission at room temperature when excited in the B or Q bands. The emission spectral profile is very similar to that observed for the model compound **4**; however, the emission maxima are 8 nm red shifted if compared with the emission maxima of **4**. The fluorescence emission of **1** is also dependent on the isomerization state of the apendent azoarenes. A decrease in the fluorescence intensity is observed when **1-*E*** is converted into **1-*Z***; on the other hand, recovering **1-*E*** by means of the thermal or sensitized process brings back the initial fluorescence emission (Fig. 3). This behavior is observed for many cycles of **1-*E*** to **1-*Z*** conversion with no noticeable alteration in the initial or final fluorescence emission intensities, indicating a photoswitchable function dependent on the isomerization state of the coordinated azoarenes.

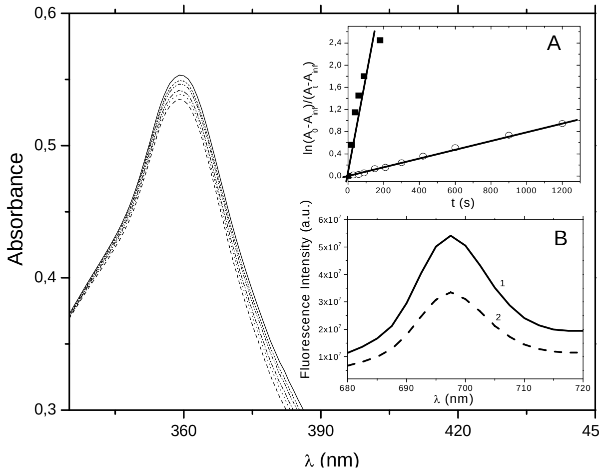
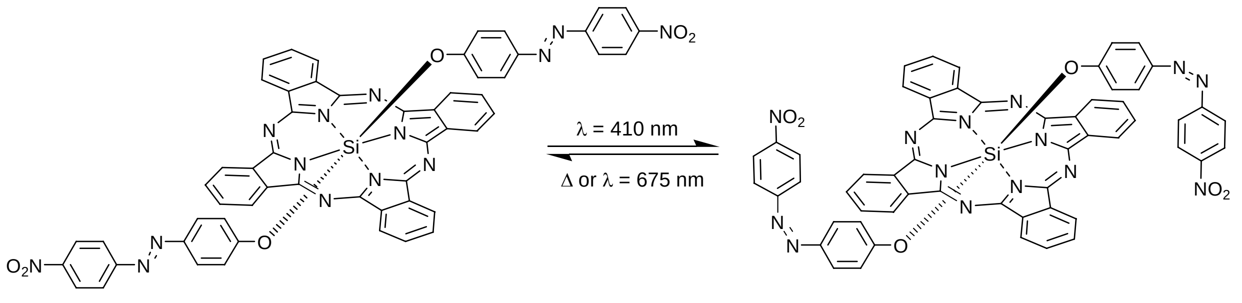


Fig. 3 Spectral changes for the B band of **1** during thermal *Z*-*E* reaction after attainment of the PS (lower curve). Inset A: First order plot for the thermal (open circles) and sensitized (bold squares) reaction for **1**. Inset B: Changes in the emission intensity for the Q$_{0\text{-}0}$ band upon photoisomerization; *E*-state (full line, 1) and *Z*-state (PS, broken line, 2).

In principle, the observed fluorescence quenching can be attributed to three main pathways: energy transfer, electron transfer, and enhancing of the non-radiative transitions. Energy transfer seem implausible because the singlet energy of the azoarene moieties (*ca.* 3.3 eV) lies higher than the energy of the Pc singlet state (1.78 eV) and the calculated[10] free energy variations (Δ*G*) for both reductive (0.21 V) and oxidative (0.36 V) electron transfer processes have a positive value indicating a non-spontaneous process. Another possibility is that the quenching observed upon isomerization could be due to an increase in the non-radiative transitions induced by some degree of distortion of the macrocycle. The motion of the coordinated azoarenes when isomerization takes place, could originate a displacement of the Si (IV) from the plane of the Pc, or as the ***Z*** form is bent, the proximity between the bulky nitrophenyl residues and the Pc macrocycle becomes closer, causing a non-planar distortion[11] affecting mainly the excited state.



1-*E* **1-*Z***

Fig. 4 Interconversion between 1-*E* and 1-*Z*.

There are few examples concerning an effective photoswitchable function involving complexes of tetrapyrrolic compounds and isomerizable groups. The different coordination abilities found in the function of the ***E*** or ***Z*** isomerization states of some pyridilazoarenes toward metalloporphyrin and/or metallophthalocyanine coordination has been used for the modulation of the absorbance[12] or fluorescence emission[13] intensities. In the case of absorbance modulation, long irradiation times are needed for changing the isomerization state and a "weak" signal was obtained. The fluorescence modulation of a zinc porphyrin (ZnTPP) is dependent not only on the isomerization state but also on concentration, and no sensitized process is reported. Recently, a triad formed by covalently coordinated azoarenes to a phosphorous porphyrin has been reported by Maiya.[14] As in the present work, the fluorescence properties are dependent on the isomerization state of the axial ligands; nevertheless, no sensitized reaction was observed, meaning that the reestablishment of the initial state is restricted by the kinetics of the thermal reaction.

In conclusion, the emission properties of **1** can be modulated by the isomerization state of the axially coordinated azoarenes, creating an on-off (***E-Z*** states) fluorescence signal, and, unlike other reported systems, the recovery of the initial state does not depend only on the rate of the thermal reaction, since it can be controlled by a sensitized mechanism (Fig. 4). Moreover, the wavelength of the 'turning off' light is more than 250 nm away from the 'turning on' wavelength. This system seems promising taking into account the stability of the axially coordinated moieties, the greater versatility in the achievement of the desired isomerization state, and the broad spectral region considering both direct and sensitized excitation.

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6 Selected data for compound **1**: m.p. > 350 ºC (decomp). ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.68 (m, 8H), 8.41 (m, 8H), 8.14 (d, 4H, J = 9.1 Hz), 7.55 (d, 4H, J = 9.1 Hz), 6.31 (d, 4H, J = 8.9 Hz), 2.59 (d, 4H, J = 8.9 Hz). IR (ATR) 1589, 1520, 1490, 1338, 1293, 1253, 1125, 1082, 913, 866, 760, 735, 705, 689, 647, 636 cm^{-1}. EM (MALDI-TOF, Dithranol) *m/z*: 782 (M^+ - $C_{12}H_8N_3O_3$).

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8 Compound **3** has a peculiar isomerization behavior with a poor content of the *Z* form in the PS and after attainment of the PS no photochemical *Z* to *E* conversion was achieved by selective irradiation. This characteristic is probably due to the particular push-pull nature of **3** (M. Hagir, N. Ichinose, C. Zhao, H. Horiuchi, H. Hiratsuka and T. Nakayama, *Chem. Phys. Letters*, 2004, **391**, 297) and the existence of tautomeric structures that favor nitrogen-nitrogen single bond (G. Gabor, Y. F. Frei and E. Fisher, *J. Phys. Chem.*, 1968, **72**, 3266) that precludes in this case extensive *E* to *Z* isomerization.

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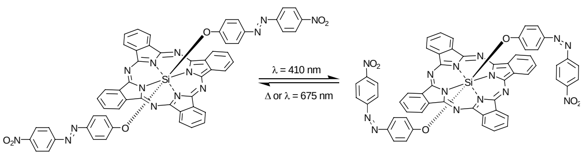
Graphical Abstract



1-*E* **1-*Z***

Short Text for Graphical Abstract

Selective excitation of the phthalocyanine moiety of a photoswitchable azobenzene-phthalocyanine-azobenzene triad allows the modification of the *E*-*Z* ratio, which in turn controls the emission intensity of the phthalocyanine.