"Catch-and-release" of porphyrins by photoswitchable self-assembled monolayers

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A novel cationic, photoresponsive azobenzene derivative with the characteristic of self-assembly, 2-{4-[(*E*)-(4-{[11-(dodecylthio)undecyl]oxy}phenyl)diazenyl]phenoxy}-*N*,*N*,*N*-trimethylethanaminium bromide (**1**), has been synthesized. Self-assembled monolayers (SAMs) of **1** on ultrathin, transparent platinum electrodes have been fabricated and the reversible *trans* ⇆ *cis* interconversion has been demonstrated by absorption spectroscopy in transmission mode and contact angle measurements. It is shown that such photoresponsive SAMs promote the binding of anionic porphyrins at the metal surface and trigger their release upon light excitation exploiting the different *light-controlled* electrostatic interactions with the two isomeric forms of **1**.

Introduction

The fabrication of self-assembled monolayers (SAMs) on noble metal substrates constitutes one of the most active areas of modern materials science.[1] In this widely explored arena, the design of SAMs performing specific functions under the input of external stimuli is one of the most exciting goals in the perspective of "smart" nanocomposite devices.[2] Light is a very appealing trigger. Its easy availability and manipulation associated with the fast response of many photochemical reactions make light-controlled systems relatively simple and particularly attractive.

Porphyrins and their metal complexes represent a family of massively investigated molecules by virtue of their excellent spectroscopic, photochemical and electrochemical properties.[3] Organization of these macrocycles onto solid substrates has been extensively studied aiming to develop a variety of optoelectronic, photonic, photosynthetic, and sensing materials.[4] On these grounds, the design of SAMs able to control the porphyrin assembly and disassembly on two-dimensional (2D) surfaces under the input of photons represents a valuable objective to pursue. In this context, Cook *et al.* have recently reported the immobilization and release of zinc tetraphenylporphyrin on 2D surfaces exploiting the "on–off" metal–ligand coordination of an arylazopyridine self-assembled on gold surfaces.[5] Inspired by this work and stimulated by the recent results concerning the ability of cationic amphiphile monolayers to trap anionic hydrophilic 5,10,15,20-tetrakis(4-sulfonatophenyl)-21*H*,23*H*-porphyrin (TPPS) mainly *via* electrostatic interactions,[6] we have explored the possibility to achieve the "catch-and-release" of porphyrins on 2D surfaces simply by exploiting the Coulombic interactions between a cationic, photoresponsive SAM and the anionic TPPS. To this end, we have designed and synthesized the azobenzene derivative **1** (Fig. 1). This compound offers a combination of suitable prerequisites for the achievement of the above goal. In fact: i) the thioether group allows facile chemisorption on noble metal surfaces, ii) the quaternary ammonium group terminal group should encourage binding with the anionic TPPS through favorable electrostatic interaction, iii) the photoresponsive azobenzene moiety is expected to change the extent of such interactions, in view of its reversible *trans* ⇆ *cis* interconversion controlled by UV-Vis light,[7] iv) the unsubstituted alkyl chain provides the sweep volume for feasible photoisomerization within the SAM.[8]

Experimental

Materials and general procedures

4-Aminophenol, phenol, 11-bromo-1-undecene, 1-dodecanethiol, 9-borabicyclo[3.3.1]nonane (9-BBN), trimethylamine, sodium nitrite and sodium carbonate were purchased from Sigma-Aldrich (Milan) and used as received. All solvents used (from Carlo Erba, Milan) were analytical grade. Syntheses were carried out under a low intensity level of light.

Synthesis. 2-{4-[(*E*)-(4-{[11-(Dodecylthio)undecyl]oxy}phenyl)diazenyl]phenoxy}-*N*,*N*,*N*-trimethylethanaminium bromide (**1**) was synthesized according to the steps reported in Scheme 1.

*4,4′-Dihydroxyazobenzene (**A**) and 1-(11-bromo-undecylsulfanyl)dodecane (**C**).* Compounds **A** and **C** were prepared according to the methods described in the literature.[9,10]

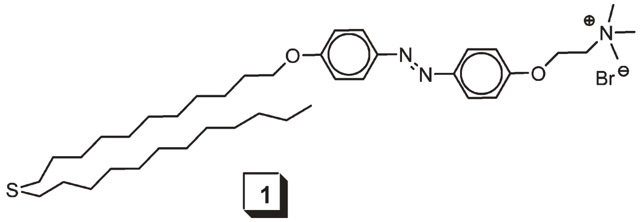

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Fig. 1 The chemical structure of **1**.

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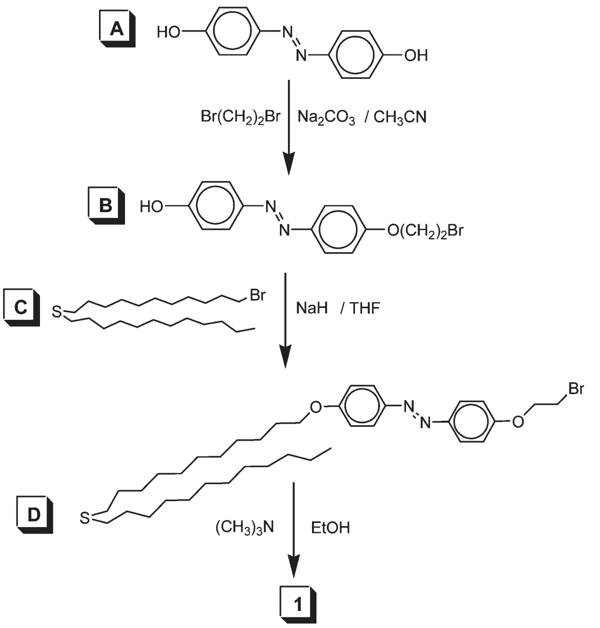

Scheme 1

*4-{(E)-[4-(2-Bromoethoxy)phenyl]diazenyl}phenol (**B**).* A mixture of **A** (2.6 g, 12 mmol), 1,2-dibromoethane (1 mL, 12 mmol) and sodium carbonate (18 g, 170 mmol) was refluxed in 100 ml of acetonitrile for 5 days. After cooling to ambient temperature the resulting suspension was filtered. The organic solution was concentrated under reduced pressure and purified by column chromatography (dichloromethane 100%) to give **B** (yield 20%) as a yellowish powder. Anal. Calcd (%) for $C_{14}H_{13}Br_1N_2O_2$: C, 52.36; H, 4.08; N, 8.72; found: C, 49.21; H, 3.95; N, 8.37. ESI-MS *m/z*: $[M]^+$ 321 (100%). H^1 NMR CDCl$_3$ (200 MHz) δ 7.9 (dd, 4H, J = 5 Hz, 4 Hz), 7 (dd, 4H, J = 7 Hz, 5 Hz), 5.6 (br, 1H), 4.4 (t, 2H, J = 6.2 Hz), 3.7 (t, 2H, J = 5.5 Hz).

*(E)-1-[4-(2-Bromoethoxy)phenyl]-2-(4-{[11-(dodecylthio)undecyl]oxy}phenyl)diazene (**D**).* A mixture of **B** (0.124 g, 0.4 mmol), **C** (0.8 g, 1.9 mmol) and sodium hydride (0.02 g, 0.8 mM) was refluxed in 50 ml of THF for 5 days. After cooling to ambient temperature, the resulting suspension was filtered and washed with THF. The organic residues were dried under reduced pressure and purified by column chromatography (dichloromethane–cyclohexane 6 : 4) to give **D** (yield 18%) as a yellowish powder. Anal. Calcd (%) for $C_{37}H_{59}Br_1N_2O_2S_1$: C, 65.75, H, 8.80, N, 4.14, S, 4.74; found: C, 67.85; H, 9.23; N, 3.97, S, 4.55. ESI-MS *m/z*: $[M]^+$ 675.4 (100%). ^{1}H NMR (CDCl$_3$): δ 7.9 (dd, 4H, J = 5 Hz, 4 Hz), 7.0 (dd, 4H, J = 7 Hz, 5 Hz), 4.4 (t, 2H, J = 6.2 Hz), 3.7 (t, 2H, J = 5.5 Hz). 4.0 (2H, t, J = 7.3 Hz), 2.4 (4H, t, J = 7.4 Hz), 1.7 (2H, t, J = 7.5 Hz), 1.5 (4H, q, J = 7.4 Hz), 1.2 (34H, broad s), 0.8 (3H, t, J = 7.5 Hz).

*2-{4-[(E)-(4-{[11-(dodecylthio)undecyl]oxy}phenyl)diazenyl]phenoxy}-N,N,N-trimethylethanaminium bromide (**1**).* Compound **D** (0.02 g, 0.03 mmol) was dissolved in ethanol and was allowed to react with an excess of trimethylamine at 60 °C for one week. After cooling to room temperature, the mixture was concentrated under reduced pressure to afford **1** (yield 95%) as a yellowish powder. Anal. Calcd (%) for $C_{40}H_{68}Br_1N_3O_2S_1$: C, 65.37, H, 9.33, N, 5.72, S, 4.36; found: C, 66.33, H, 8.88, N, 6.05, S, 4.64. ESI-MS *m/z*: $[M]^+$ 654.5 (100%). ^{1}H NMR (CDCl$_3$): δ 7.8 (dd, 4H, J = 5 Hz, 4 Hz), 7.0 (dd, 4H, J = 7 Hz, 5 Hz), 4.6 (t, 2H, J = 6.2 Hz), 3.8 (t, 2H, J = 5.5 Hz), 3.3 (s, 9H), 4.1 (2H, t, J = 7.3 Hz), 2.5 (4H, t, J = 7.4 Hz), 1.8 (2H, t, J = 7.5 Hz), 1.5 (4H, q, J = 7.4 Hz), 1.2 (34H, broad s), 0.8 (3H, t, J = 7.5 Hz).

Instrumentation

^{1}H NMR spectra were recorded on a VARIAN INOVA 200 spectrometer, using TMS as internal standard. ESI-MS spectra were recorded on an Agilent 1100 Series ESI/MSD spectrometer. Experimental conditions were as follows: capillary voltage, 3.5 kV; fragmentor, 100 V; source temperature, 350 °C; drying gas, N$_2$ (10 l min^{-1}), carrier solvent, methanol (0.4 ml min^{-1}). The samples were dissolved in methanol containing trifluoroacetic acid. UV/vis absorption spectra were recorded with a Jasco V-560 spectrophotometer. Aqueous contact angles were measured using a goniometer (KERNCO) under ambient conditions.

UV-Vis irradiation was performed, under ambient conditions, by using the monochromatic radiation of a fluorimeter Fluorolog-2 (mod. F-111).

Results

Firstly, we tested the photobehavior of **1** in solution. As shown in Fig. 2A, irradiation of a CH$_2$Cl$_2$ solution of **1** with UV light

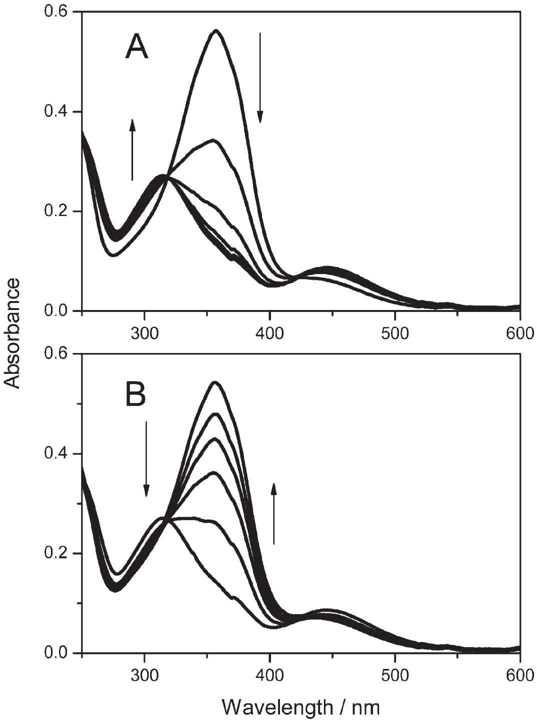

Fig. 2 Absorption spectra of a 18 μM CH$_2$Cl$_2$ solution of **1** recorded after intervals of irradiation with 360 nm light (A) and afterwards with 450 nm light. The spectra were recorded under ambient conditions using a quartz cell with an optical pathlength of 10 mm.

results in bleaching of the 356 nm band accompanied by the formation of new absorptions at 310 and 450 nm. A photostationary state (*ca.* 90% conversion of the *trans* isomer) was reached after 15 min irradiation.† Further irradiation of this solution with visible light led to the almost complete recovery (up to 95% of the initial value) of the original band at 356 nm (Fig. 2B). These results are in full agreement with the reversible *trans* ⇆ *cis* photoisomerization of the azobenzene moiety, suggesting that the functionalization of both the phenyl rings does not affect its photochromic properties.

In order to achieve SAMs of **1** (SAMs-**1**), we used our recently developed ultrathin Pt films[11] as suitable platforms. These metal substrates (thickness *ca.* 20 nm, roughness *ca.* 2 nm) exhibit a unique combination of excellent optical transparency, homogeneity, robustness, and conductivity features. As a result they offer the advantage to probe the spectroscopic properties of adsorbed chromophores simply by conventional spectrophotometry in transmission mode.[11] SAMs-**1** were obtained by immersion of the Pt substrates in a CH_2Cl_2 solution of **1** (0.5×10^{-3} M) for 20 h, at room temperature in the dark. The substrates were then rinsed several times with CH_2Cl_2 first and then methanol to remove any physisorbed material, and dried at room temperature.‡

Fig. 3A shows the absorption spectra of a typical SAM-**1** recorded before and after irradiation with UV light. The absorption spectrum of SAM-**1** before irradiation shows a main absorption band peaked at *ca.* 360 nm and safely assignable to the π–π* electronic transition of the *trans*-azobenzene moiety. The related absorbance value allows the estimation of a surface coverage of *ca.* 1 molecule per 100 $Å^2$.[12] This value is basically the same as we have obtained for a similar azo derivative not bearing the quaternary ammonium group and self-assembled on the same Pt substrate,[8f,11c] indicating that such chemical modification does not affect the packing process. UV irradiation of SAM-**1** results in significant bleaching of the 360 nm absorption band as well as a slight blue shift of λ_{max}, reaching a photostationary state after 5 min (Fig. 3A). This behavior fully agrees with that observed upon UV irradiation of **1** in CH_2Cl_2 solution (see Fig. 2A) and provides unambiguous, direct evidence for the *trans* to *cis* photoisomerization of SAM-**1**. Aqueous contact angle (θ_a) measurements give $\theta_a \approx 42°$, a value reflecting well the presence of both hydrophobic and hydrophilic end groups in the monolayer. In fact, such a value is around the average expected for typically hydrophobic (>100°) and hydrophilic (<10°) monolayers.[1a,b]

The reversible *trans* ⇆ *cis* photoswitching of the azobenzene-based SAMs was proven by alternate cycles of UV and visible irradiation in which the decrease and recovery of the 360 nm absorption band were monitored (Fig. 3B). Accordingly, similar behavior is also observed in θ_a changes upon UV-Vis irradiation. In particular, the increase of *ca.* 10° in the θ_a value after UV irradiation accounts for a reduced hydrophilicity of the *cis* isomer of **1**, probably due to reduced accessibility of the quaternary group to the water surface.

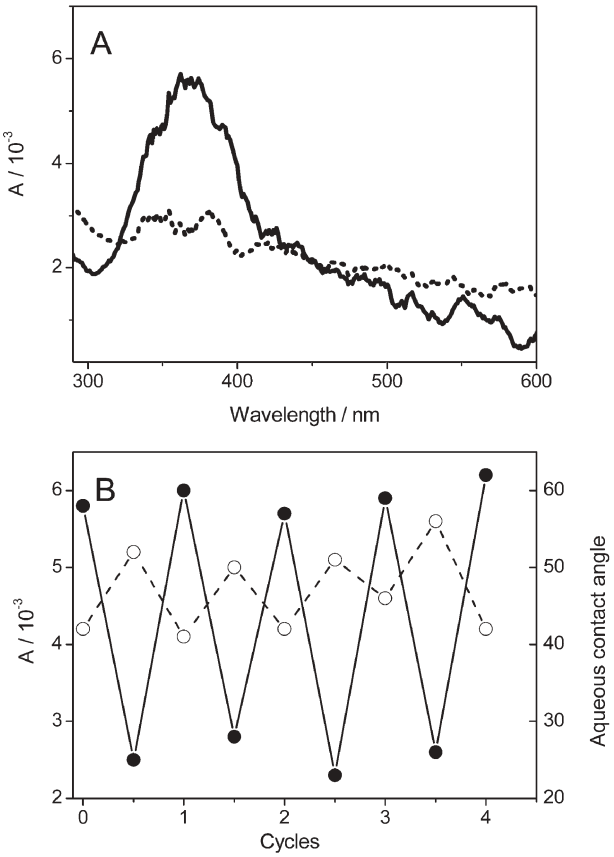

Fig. 3 (A) Absorption spectrum of SAM-**1** recorded before (—) and after (- - -) irradiation with UV (360 nm) light. (B) Switching of the absorbance maximum response (●) and aqueous contact angle (○) observed after alternate cycles of UV (360 nm, 5 min) and visible (450 nm, 20 min) light irradiation. The absorption spectra were recorded using as a reference sample the same ultrathin Pt substrate before chemisorption of **1**.

The suitability of SAM-**1** to immobilize TPPS was tested by soaking the film in an aqueous solution of porphyrin (0.1 mM) for 3 h.§ The substrate was then washed several times with water to remove the free TPPS and dried at room temperature. The absorption spectrum (Fig. 4A) shows clearly the presence of the typical Soret absorption of the TPPS at *ca.* 424 nm beside the absorption band of SAM-**1** at 360 nm.¶ By assuming that no significant differences in the molar absorptivity values of SAM-**1** and TPPS occur upon binding, we can roughly estimate the ratio **1** : TPPS to be *ca.* 7 : 1.

The sample was then placed in a spectrophotometric cell (10 mm pathlength) containing 3 ml of water and irradiated with 360 nm light at several interval times. After each step of irradiation the substrate was withdrawn, dried and

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† The percentage of the photostationary state was estimated on the basis of the extinction coefficients of the pure *trans* and *cis* isomers.[7b]

‡ Longer and shorter reaction times led to lower degrees of chemisorption of **1**, as determined from absorbance values at 360 nm (*vide infra*)

§ Longer reaction times and higher TPPS concentrations did not affect the amount of TPPS bound to the monolayer, as determined from the absorbance values at 424 nm (*vide infra*).

¶ That the immobilization of TPPS is strongly encouraged by electrostatic interactions was well-supported by control experiments carried out using the cationic *meso*-tetrakis(*N*-methylpyridyl)porphyrin, which did not show any significant porphyrin absorption in the SAM.

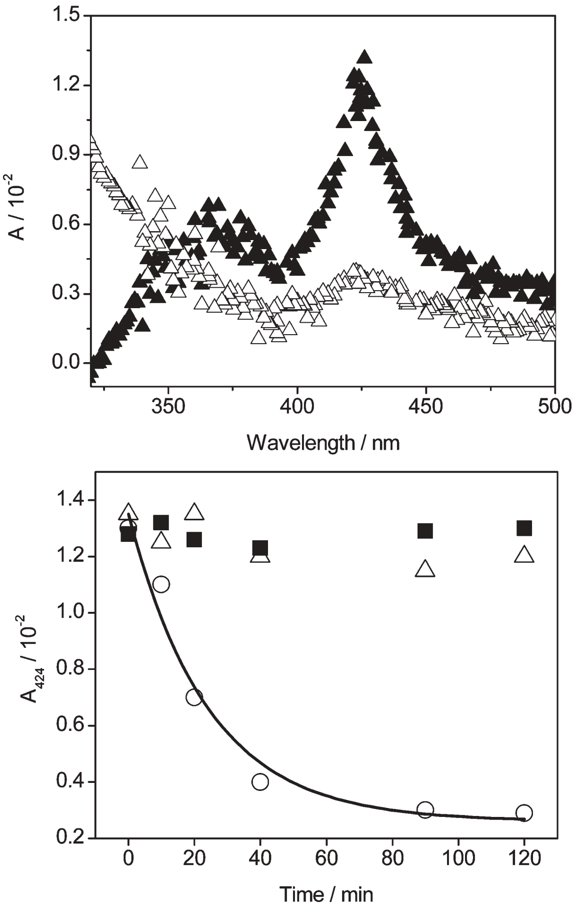
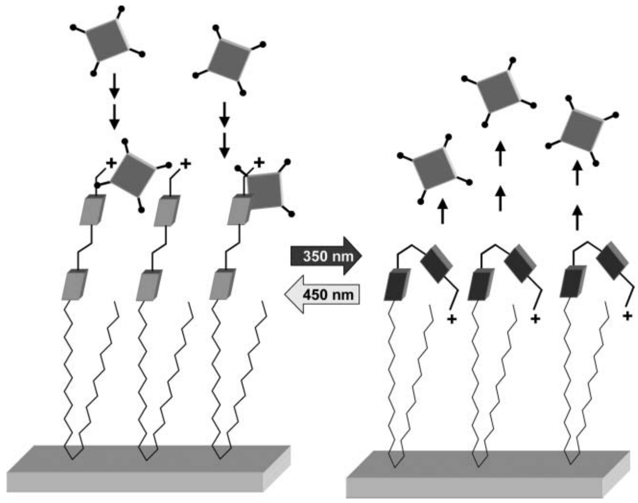


Fig. 4 (A) Absorption spectra of SAM-**1** after immersion for 3 h in a solution of TPPS and washing with water before (▲) and after (△) 2 h irradiation with UV (360 nm) light. (B) Absorbance changes of the Soret band in the case of the films non-irradiated (■), irradiated with 424 nm light (△) and irradiated with 360 nm light (○). The solid line represents the fitting of the data according to a first-order process.

investigated by UV-Vis spectroscopy. A photostationary state was reached after 2 hours of irradiation. As shown in Fig. 4A, the corresponding absorption spectrum reveals the occurrence of the *trans–cis* photoisomerization of SAM-**1** accompanied by *ca*. 80% decrease of the TPPS absorbance. According to what was expected for the photoisomerization process, the porphyrin photorelease resembles first-order kinetics (Fig. 4B) and is in line with the changes of the surface properties occurring upon UV irradiation of the SAM. In fact, the cationic end-groups switch to a conformation probably less favorable for effective electrostatic interactions with the anionic porphyrin. The reduced hydrophilicity observed in the case of the *cis* form of SAM-**1** (*vide supra*) supports well this hypothesis. That the release of TPPS is strictly related to the photoisomerization of the azo chromophore is further corroborated by two key control experiments in which similar samples were i) kept in the dark and ii) irradiated at the wavelength of the Soret absorption for the same interval times. As shown in Fig. 4B no significant release of porphyrin was observed in both cases.

In conclusion, as illustrated in Scheme 2, we have demonstrated that assembly and disassembly of porphyrins on a 2D surface can be achieved by exploiting the *light-controlled* electrostatic interactions with the two isomeric forms of a cationic azobenzene SAM. In view of the non-specific nature of the Coulombic interactions, we believe that such an approach is not limited to the example presented herein but may also be suitable for controlling the immobilization and release of molecules rich in negative charges such as polynucleotides and/or other biologically relevant targets. These studies are currently in progress in our laboratory and the results will appear in forthcoming papers.



Scheme 2 Idealized representation for the "catch and release" of TPPS by the photoswitchable SAM-**1**.

Acknowledgements

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