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An evanescent field driven mono-molecular layer photoswitch: coordination and release of metallated macrocycles

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Photoswitching of 'on' and 'off' coordination sites in a self assembled monolayer containing the 4-(arylazo)pyridine chromophore has been achieved using the evanescent field and illustrated through coordination and photon induced release of zinc tetraphenylporphyrin.

Azobenzenes and related azo structures undergo wavelength dependent reversible photoisomerization between the more stable *trans*-form and the less stable *cis*-form, a phenomenon which has excited interest in view of potential applications in areas as diverse as liquid crystal alignment,[1] optical data storage,[2] non-linear optics[3] and photoswitching.[4] Formulations containing the chromophore that have attracted particular attention are Langmuir-Blodgett[4,5] and self-assembled monolayer (SAM) films.[6] These normally require specific functionalisation of the chromophore: in the case of SAMs deposited on a gold coated glass substrate[6,7] or on gold nanoparticles,[7,8] the chromophore has been derivatised with an alkoxy chain terminated with a thiol or disulfide to exploit S–Au binding. Photoswitching of the N=N double bond is achieved by direct illumination of the film at appropriate wavelengths.

We now demonstrate photoswitching of the N=N moiety within a SAM using the evanescent field emanating from the substrate when it is used as a waveguide. The use of waveguided light should present opportunities for developing nano-sized optical switches based on fibre optic technology. We have applied this approach to the photoswitching of a SAM of the 4-(arylazo)pyridine chromophore, Fig. 1. This system was designed to provide a basic/coordinating external surface which can be switched 'on' (*trans*-isomer) and 'off' (*cis* -isomer) by light, a development illustrated here through binding and release of zinc tetraphenylporphyrin (ZnTPP).

Use of the mixed SAM shown in Fig. 1 followed preliminary studies on a mono-component SAM. The latter showed slower and incomplete photoisomerization of the 4-(arylazo)pyridine moiety, results consistent with data for the related azobenzene chromophore.[7] The mixed SAM was deposited using the unsymmetrical disulfide (**1**), prepared from di-8-hydroxyoctyldisulfide *via* mesylation and sequential displacements of one of the mesylate groups by 4-(4-hydroxyphenyl)azopyridine and the other by phenol.

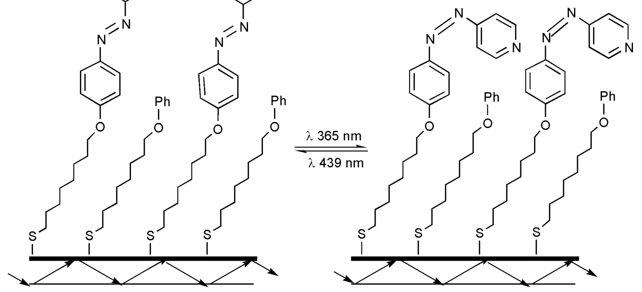
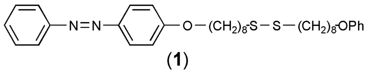


Fig. 1 A representation of the photoswitching of a SAM containing the 4-(arylazo)pyridine chromophore using waveguided light. Left, the pyridine coordinating sites are presented ('on'); right, sites withdrawn ('off').

To obtain the required SAM, compound (**1**), dissolved in ethyl ethanoate, was deposited onto an 8 nm thick film of gold supported on a substrate, a quartz glass slide. The latter was precoated with chromium (1 nm thick) to aid adhesion. The procedure adopted for substrate preparation and deposition was that described in earlier papers from our laboratories.[9]



(**1**)

Compound (**1**) in ethyl ethanoate (2.50×10^{-5}M) showed absorptions at 252 nm (ε 1.01×10^4 $M^{-1}cm^{-1}$), 352 nm (ε 2.10×10^4 $M^{-1}cm^{-1}$) and a weaker band at 437 nm (ε 1.08×10^3 $M^{-1}cm^{-1}$). The former two were assigned to π–π^* transitions, the third to an n–π^* absorption. After UV irradiation of the solution (λ 365 nm) the main band at 352 nm was replaced by one at 323 nm (ε 8.08×10^3 $M^{-1}cm^{-1}$) and the band centred at 437 nm became more intense (ε 2.76×10^3 $M^{-1}cm^{-1}$). These changes are consistent with photoisomerisation of the *trans* isomer of (**1**) into the *cis*-form. Further irradiation with 439 nm light effected the reverse (*cis*-to-*trans*) isomerisation, the absorption spectrum differing from that of the original solution by a small ($<5\%$) loss of the initial peak intensity at λ 352 nm.

The as-deposited SAM film from (**1**) shows the same strong absorption assigned to the *trans*-isomer but now observed at 354 nm. Photoisomerisation using light of 365 nm was achieved

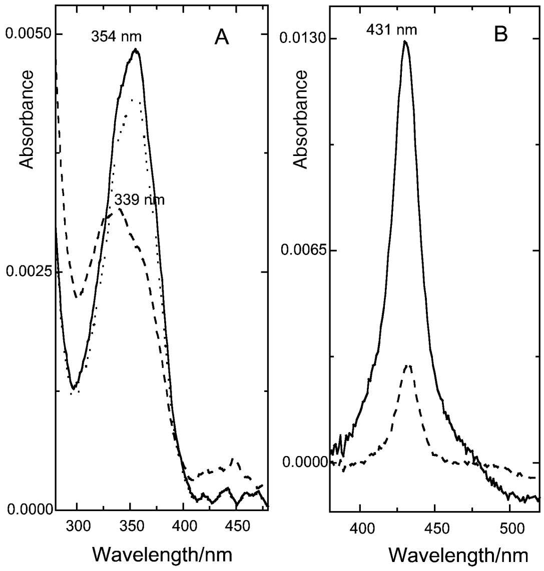


Fig. 2 A. 250–500 nm region of the UV-visible spectra of the SAM film. Solid line, as-deposited film; broken line (– – – –), after irradiation at 365 nm; and dotted line (· · · · ·) after further irradiation at 439 nm. Spectra are shown for a film illuminated using the evanescent field. B. The solid line shows the Soret band of ZnTPP from the macrocycle when complexed to the as-deposited SAM film. The broken line (– – – –) shows the much lower intensity of the band when the photoisomerised (*cis*-form) film is exposed to ZnTPP.

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by direct illumination and by using waveguided light. In the latter experiment, light was delivered to the edge of the shorter side of the glass substrate. The two techniques gave similar results, *viz* a diminution of the intensity of absorbance at 354 nm, and the appearance of a weak band at 339 nm (Fig. 2A). No further shoulder or shorter wavelength band appeared at 323 nm as observed upon irradiation of (**1**) in solution, implying that λ_{max} for the *cis*-form had shifted to longer wavelength in the film formulation. Irradiation of the photoisomerised SAM with 439 nm light led to $>95\%$ recovery of the original band intensity at λ 354 nm. The same restoration of band intensity occurred on storing the film in the dark for two weeks.

Investigation of coordination sites in the as-deposited (*trans*) film and the photoisomerised (*cis*) film was undertaken using ZnTPP to exploit the potential of the zinc to bind at a pyridine nitrogen atom. The films were immersed in a solution of ZnTPP in chloroform for 12 h, withdrawn, rinsed with toluene (5×2 ml) and investigated by UV-vis spectroscopy. The spectra (Fig. 2B) show the Soret band of ZnTPP at 431 nm, shifted from 424 nm in the solution phase. Significantly, it is 7 times more intense in the spectrum of the *trans*-form film than in that of the photoisomerised film. This demonstrates that in the latter the binding sites are largely withdrawn, thus confirming that the film contains predominantly the *cis*-form of the chromophore.

Fig. 3 depicts a cycle of three steps, for which the feasibility of (a) and (c) has been established above. We therefore sought to test step (b), the photon promoted release of ZnTPP from the *trans*-form. Accordingly, a substrate bearing the *trans*-form film coordinated with ZnTPP was placed vertically in a 60 ml jar containing toluene. One end of the substrate was above the level of the solvent and available to receive and waveguide 365 nm light along its long axis. The UV-vis spectrum of the film was monitored over a period of 3 hours irradiation during which time the intensity of the Soret band of SAM bound ZnTPP decreased by 69%. Over 10 h the intensity had decreased by 80%.

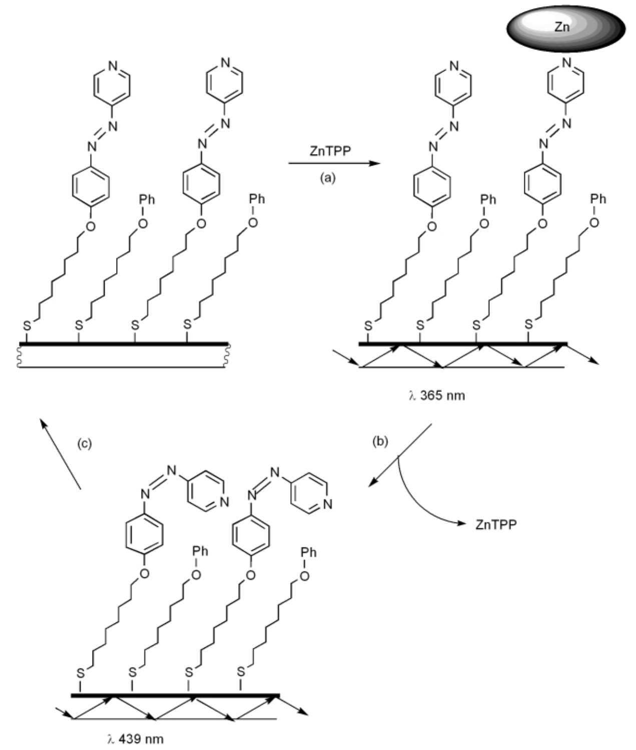

Fig. 3 An application of the SAM depicted in Fig. 1 showing a coordination–release cycle, utilising ZnTPP coordination at the surface as an illustration.

A second sample, maintained over 3 hours under the same conditions but without irradiation, showed a 15% decrease in absorption. We attribute the latter to slow release of the ZnTPP into the solvent. Evidently, the much greater reduction in intensity of the Soret band in the irradiation experiment is attributable to other molecular events. These would include *trans*-to-*cis* isomerism of either or both uncoordinated and ZnTPP-coordinated units within the film. The first would reduce the number of ‘on’ sites in the film and could be significant in terms of an equilibrium between bound and unbound ZnTPP when the film is immersed in solvent. The second would be important if the change of geometry about the double bond is the key to de-coordination of ZnTPP. Investigation of these processes is in hand.

We conclude that photoswitching of the arylazopyridine chromophore within a SAM provides for ‘on’/‘off’ coordination sites. This has been demonstrated for ZnTPP coordination and should be equally applicable to certain other metallomacrocycles. Furthermore, the novel use of the evanescent wave for photoisomerisation within a SAM would appear to present opportunities for developing miniaturised optical switches driven by waveguided light.

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Notes and references

1 T. Seki, T. Tamaki, Y. Suzuki, Y. Kawanishi and K. Ichimura, *Macromolecules*, 1989, **22**, 3505.
2 Z. F. Liu, K. Hashimoto and A. Fujishima, *Nature*, 1990, **347**, 658.
3 W. Lin, W. Lin, G. K. Wong and T. J. Marks, *J. Am. Chem. Soc.*, 1996, **118**, 8034.
4 H. Tachibana, T. Nakamura, M. Matsumoto, H. Komizu, E. Manda, H. Niino, A. Yabe and Y. Kawabata, *J. Am. Chem. Soc.*, 1989, **111**, 3080.
5 R. Wang, L. Jiang, T. Iyoda, D. A. Tryk, K. Hashimoto and A. Fujishima, *Langmuir*, 1996, **12**, 2052; M. Vélez, S. Mukhopadhyay, I. Muzikante, G. Matisova and S. Vieria, *Langmuir*, 1997, **13**, 870; M. Matsumoto, D. Miyazaki, M. Tanaka, R. Azumi, E. Manda, Y. Kondo, N. Yoshino and H. Tachibana, *J. Am. Chem. Soc.*, 1998, **120**, 1479; A. Wu and D. R. Talham, *Langmuir*, 2000, **16**, 7449.
6 W. B. Caldwell, D. J. Campbell, K. Chen, B. R. Herr, C. A. Mirkin, A. Malik, M. K. Durbin, P. Dutta and K. G. Huang, *J. Am. Chem. Soc.*, 1995, **117**, 6071; Y-Q. Wang, H-Z. Yu, J-Z. Cheng, J-W. Zhao, S-M. Cai and Z-F. Liu, *Langmuir*, 1996, **12**, 5466; R. Wang, T. Iyoda, D. A. Tryk, K. Hashimoto and A. Fujishima, *Langmuir*, 1997, **13**, 4644; R. Wang, T. Iyoda, L. Jiang, D. A. Tryk, K. Hashimoto and A. Fujishima, *J. Electroanal. Chem.*, 1997, **438**, 213; H.-Z. Yu, S. Ye, H.-L. Zhang, K. Uosaki and Z.-F. Liu, *Langmuir*, 2000, **16**, 6948; T. Kondo, T. Kanai and K. Uosaki, *Langmuir*, 2001, **17**, 6317.
7 S. D. Evans, S. R. Johnson, H. Ringsdorf, L. M. Williams and H. Wolf, *Langmuir*, 1998, **14**, 6436.
8 J. Zhang, J. K. Whitesell and M. A. Fox, *Chem. Mater.*, 2001, **13**, 2323.
9 D. J. Revell, I. Chambrier, M. J. Cook and D. A. Russell, *J. Mater. Chem.*, 2000, **10**, 31; T. R. E. Simpson, D. A. Revell, M. J. Cook and D. A. Russell, *Langmuir*, 1997, **13**, 460.