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Azobenzene-Porphyrins

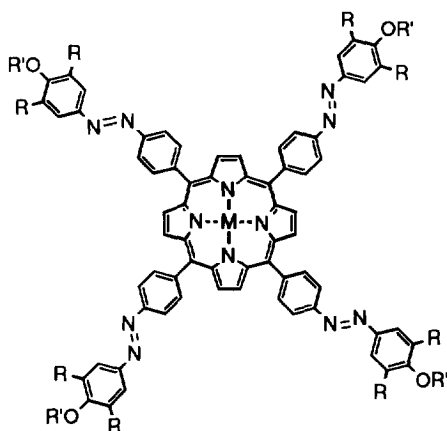
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Abstract: A series of covalently-connected azobenzene-porphyrin derivatives have been synthesised and their photochemical properties investigated. The photochemistry of the porphyrin components is essentially unaltered, but photochemical isomerisation of the azobenzene components can not be detected.

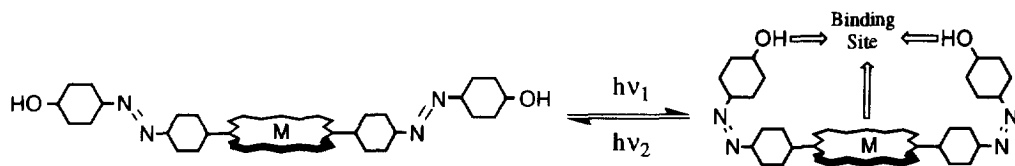
The potential for molecules to function as components in information processing systems is attracting increasing attention.¹ In principle, well-designed molecules or supramolecular assemblies could perform switching and gating functions in place of conventional silicon circuitry.² Progress in this field requires the synthesis of compounds which can process electronic or optical inputs and generate a usable output. We have therefore investigated the properties of covalently-connected azobenzene-porphyrin conjugates, 1-3.³



- M1a** R = H, R' = Me
M1b R = iPr, R' = Me
M2b R = iPr, R' = H
M3b R = iPr, R' = (CH₂)₁₅CH₃

M = H₂ or Zn

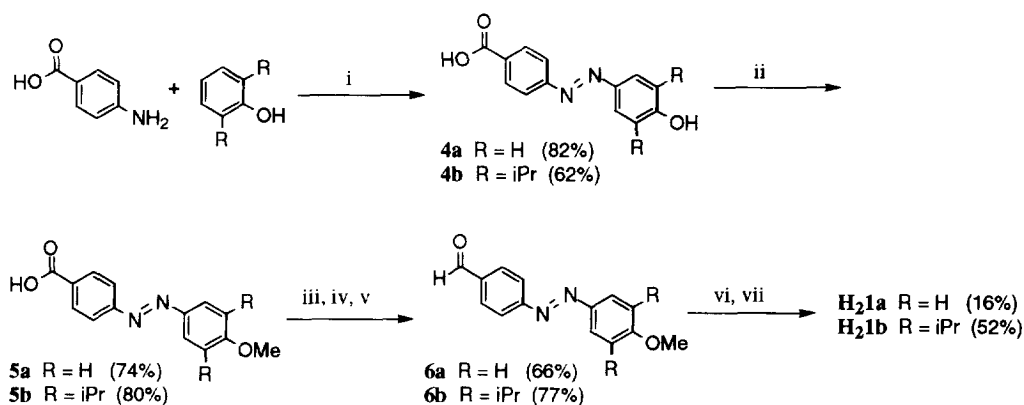
Azobenzenes and porphyrins absorb in different regions of the visible spectrum, and hence the two chromophores should be independently addressable. In addition, **2** contains hydrogen-bonding sites which should confer molecular recognition properties on the system, and the long alkyl chains on **3** may lead to mesomorphism. Irradiation of the azobenzene chromophore should induce a photochemical isomerisation of the N-N double bond, which would modulate the photophysical, molecular recognition or phase properties of these compounds (Scheme 1), i.e. these are potential molecular logic gates.



Scheme 1 Schematic illustration of the proposed photochemical switching of the molecular recognition properties of **M2**. This would in turn affect the photochemical properties of the porphyrin chromophore.

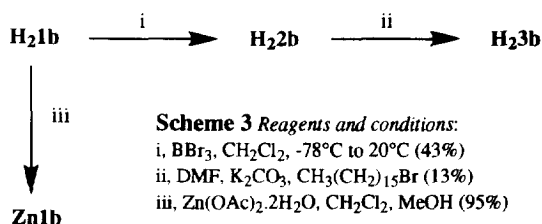
Synthesis

The porphyrins were synthesised from the corresponding azobenzene aldehydes using the Lindsey condensation procedure (Scheme 2).⁴ This route allowed the synthesis of gram quantities of the azobenzene-porphyrins **H₂1a** and **H₂1b**.⁵ The simple model chromophores **H₂7** and **8** were synthesised using similar procedures (see Figure 1).



Scheme 2 Reagents and conditions: i, NaNO_2 , HCl ; ii, Me_2SO , NaH , DMF ; iii, MeOH , H_2SO_4 ; iv, LiAlH_4 , ether; v, DMSO , $(\text{COCl})_2$, -78°C ; vi, CH_2Cl_2 , EtOH , $\text{BF}_3 \cdot \text{OEt}_2$; vii, DDQ , NEt_3

The subsequent derivatisation of **H₂1b** is outlined in Scheme 3. Cleavage of both tetramethyl ethers, **H₂1a** and **H₂1b**, was attempted with boron tribromide.⁶ However, **H₂1a** could not be cleanly demethylated due to the low solubility of the intermediate diol and triol. The use of isopropyl groups dramatically increased the solubility of the compounds so that even the fully demethylated tetraol **H₂2b** was readily soluble in non-polar organic solvents.



Scheme 3 Reagents and conditions:
i, BBR_3 , CH_2Cl_2 , -78°C to 20°C (43%)
ii, DMF , K_2CO_3 , $\text{CH}_3(\text{CH}_2)_{15}\text{Br}$ (13%)
iii, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, CH_2Cl_2 , MeOH (95%)

Photochemical Experiments

The UV/Visible absorption spectra of the azobenzene-porphyrins are almost a summation of the spectra of the component chromophores (Figure 1(a)), which suggests that there is little electronic communication between the azobenzene and the porphyrin components. Thus it is possible to address the two chromophores separately using different wavelength light (340 nm for the azobenzene and 430 nm for the porphyrin).

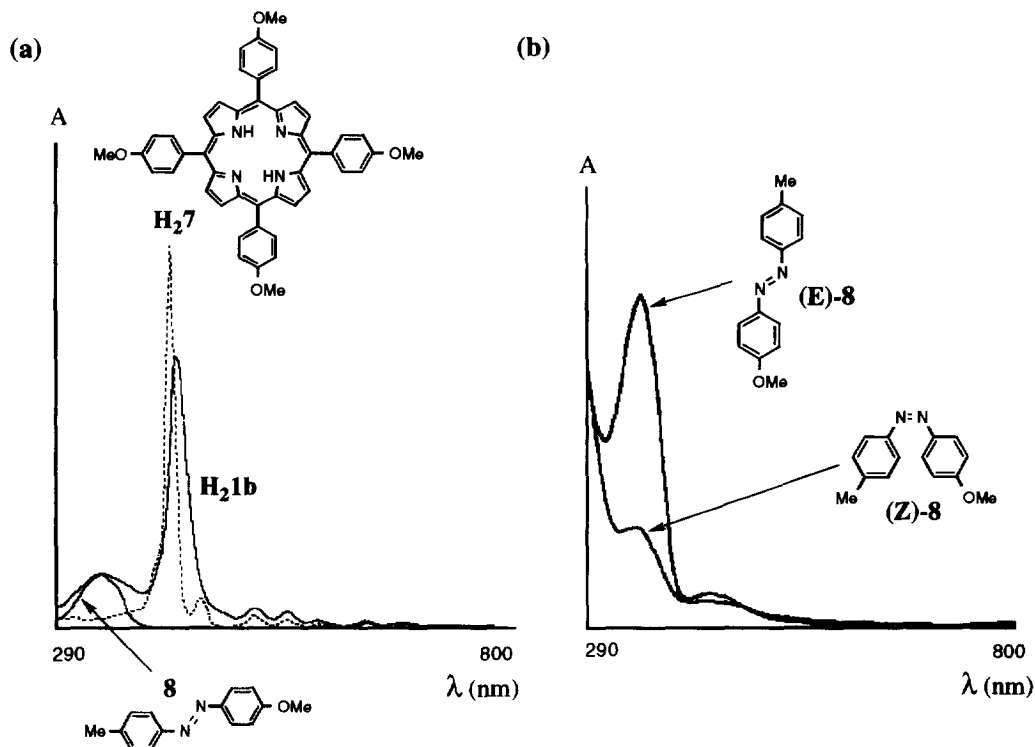


Figure 1 UV/Visible Absorption Spectra in CH_2Cl_2 (arbitrary absorption (A) scales)

- (a) The azobenzene-porphyrin **H₂1b** and the two model compounds **H₂7** and **8**
 (b) The change in the spectrum of **8** caused by photochemical isomerisation.

The fluorescence spectra of the azobenzene-porphyrins (on irradiation at the Soret maximum at 430 nm) are similar to that of the model porphyrin **H₂7**. Thus covalent connection of the two chromophores does not greatly perturb the excited state properties of the porphyrin component. However, the same is not true of the azobenzene components where there is a significant change in the excited state properties. The simple model azobenzene **8** was readily converted from the thermodynamically more stable (E) isomer to the (Z) isomer by irradiation with a mercury-lamp at 313 nm. In the absence of visible light, the (Z) isomer was stable for hours, and Figure 1(b) shows the change in the UV/Visible absorption spectrum caused by photochemical isomerisation. Similar experiments with the azobenzene-porphyrins produced no detectable change in the UV/Visible absorption spectrum. Thus in these systems, either the azobenzene excited state decays via a process which is faster than the isomerisation reaction, or the thermal relaxation of the (Z) to the

(E) isomer is so fast that the (Z) isomer was not detected on the timescale at which we were working (minutes). Porphyrins have been reported to act as intermolecular sensitizers of the (E) to (Z) isomerisation of azobenzenes, but that does not appear to be the case in this system.⁷ When excited at the azobenzene absorption maximum at 340 nm, the fluorescence spectra of the azobenzene-porphyrins are essentially identical to those of the model compounds **H₂7** and **Zn7**, so the mechanism of relaxation is neither direct fluorescent emission nor energy transfer to the porphyrin. This behaviour was not substantially affected by metallation of the porphyrins with zinc, coordination of ligands (pyridine or quinuclidine) to the metal or changes in solvent polarity (dichloromethane or hexane).

In conclusion, we have shown that the two different chromophores in covalently-connected azobenzene-porphyrins can be separately addressed by different wavelengths of light. While the excited state properties of the porphyrin components are not affected by connection to the azobenzenes, the excited state properties of the azobenzene components are significantly perturbed in these compounds: they no longer undergo photochemical isomerisation. More detailed studies of the photochemistry of these compounds are in progress.

Acknowledgements

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- Data for **H₂1a**: ¹H NMR (CDCl₃): δ (ppm) = 8.96 (8H, s, pyrrolic H); 8.38 (8H, d, ArH); 8.29 (8H, d, ArH); 8.11 (8H, d, ArH); 7.12 (8H, d, ArH); 3.96 (12H, s, OCH₃); -2.68 (2H, s, broad, pyrrolic NH). UV/VIS (CH₂Cl₂): λ_{max} = 346 nm (ε: 1.0 × 10⁵); 430 nm (ε: 5.1 × 10⁵); 518 nm (ε: 4.0 × 10⁴); 558 nm (ε: 3.2 × 10⁴); 592 nm (ε: 1.6 × 10⁴); 630 nm (ε: 1.6 × 10⁴); 690 nm (ε: 1.2 × 10⁴). MS (+ve FAB): 1152 (M⁺). Mp: >400°C.
Data for **H₂1b**: ¹H NMR (CDCl₃): δ (ppm) = 8.98 (8H, s, pyrrolic H); 8.39 (8H, d, ArH); 8.30 (8H, d, ArH); 7.90 (8H, d, ArH); 3.86 (12H, s, OCH₃); 3.46 (8H, sept, CH(CH₃)₂); 1.40 (48H, d, CHCH₃); -2.67 (2H, s, pyrrolic NH). UV/VIS (CH₂Cl₂): λ_{max} = 338 nm (ε: 9.7 × 10⁴); 430 nm (ε: 5.0 × 10⁵); 521 nm (ε: 3.3 × 10⁴); 558 nm (ε: 2.8 × 10⁴); 592 nm (ε: 1.3 × 10⁴); 650 nm (ε: 1.2 × 10⁴). MS (+ve FAB): 1486 (M⁺). Mp: >400°C.
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