Intramolecular Fluorescence Quenching in Azobenzene-substituted Porphyrins

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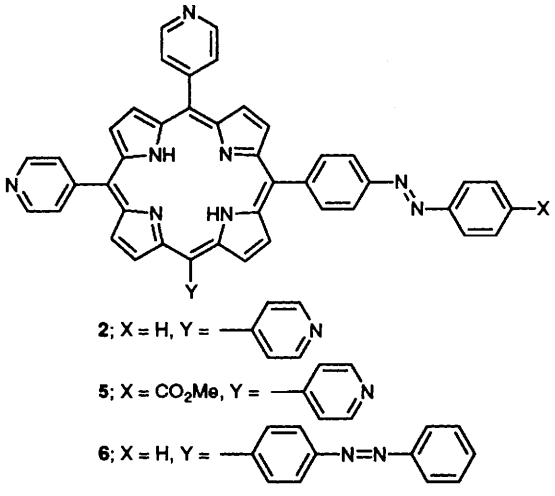
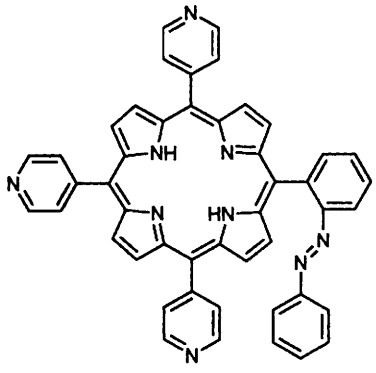
Azobenzene-substituted porphyrins have been synthesised by condensation of aminophenylporphyrins and nitrosophenyl derivatives; intramolecular fluorescence quenching is detected in the *ortho* position.

Because of the key role of porphyrin derivatives in natural photophysical and redox processes, the design and synthesis of new porphyrin models continue to attract considerable attention. However, most of these models have quinone groups as electron acceptors.[1] We are particularly interested in the determination of the advantages and limitations of the azophenyl group in this field. Though the azo group may behave as an electron-attracting group,[2] there is no report in the literature of using this group as an electron-acceptor group with porphyrin models. Moreover azobenzene derivatives undergo *cis–trans* isomerization under photochemical reactions and energy transfer may also be possible. We recently reported the electrosynthesis of nitroso and amino compounds from the familiar series of tetraphenylporphyrin derivatives.[3] We report here the preparation and the fluorescence studies of azophenylporphyrins. The observation of quenching of the fluorescence with *ortho*-azophenylporphyrin is unprecedented, to our knowledge.





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The well-known condensation of anilines and nitrosobenzenes in acetic acid to form azobenzenes[4] has been extended to the porphyrin series. Typically, the acetic acid-catalysed condensation of 5-(4-nitrosophenyl)-10,15,20-tris(4-pyridyl)-porphyrin **1**[3] with aniline (8 equiv., 3 h, 25° C) gave the expected azophenyl compound **2** in good yield (80%). **2** can be also obtained by coupling nitrosobenzene with the corresponding 5-(4-aminophenyl)-10,15,20-tris(4-pyridyl)porphyrin **3**[3,5] with a similar yield (78%). Condensation of **3** with methyl 4-nitrosobenzoate and condensation of two molecules of nitrosobenzene with 5,10-bis(4-aminophenyl)-15,20-bis-(4-pyridyl)porphyrin **4**[3] also gave the expected azophenyl derivatives **5** and **6**, in 82 and 68% yields, respectively. Starting with 5-(2-aminophenyl)-10,15,20-tris(4-pyridyl) porphyrin **7**,[3] the condensation also gave the expected *ortho*-azophenylporphyrin **8** but with a lower yield (35%), due to steric constraint. Condensation of aminophenylporphyrin **3** with nitrosophenylporphyrin **1** gave the expected dimer **9** (yield 39%). The electronic spectrum of the tetraazophenylporphyrin **10**, easily prepared by condensation of four molecules of nitrosobenzene with tetra(4-aminophenyl) porphyrin **11**, exhibits a strong peak at 320 nm (ε = 14 050 dm^3 mol^{-1} cm^{-1}, $CHCl_3$) associated with a probable azobenzene π–π^* transition,[6] thus the stereochemistry of this azo compound is mainly (*E*) [or totally (*E*)] and, by analogy, we propose that the (*E*)-isomer is also formed with the other porphyrins. The present synthesis of azophenyl-substituted porphyrins has several advantages:[7,8] (*i*) porphyrin monomers and dimers can be easily synthesised in a one-pot reaction, (*ii*) a variety of azophenyl derivatives having a wide range of electrochemical and stereochemical properties can be prepared.

The relative fluorescence quantum yields of azophenyl-substituted porphyrins are listed in Table 1. The positions of the absorption and fluorescence bands of the porphyrins are

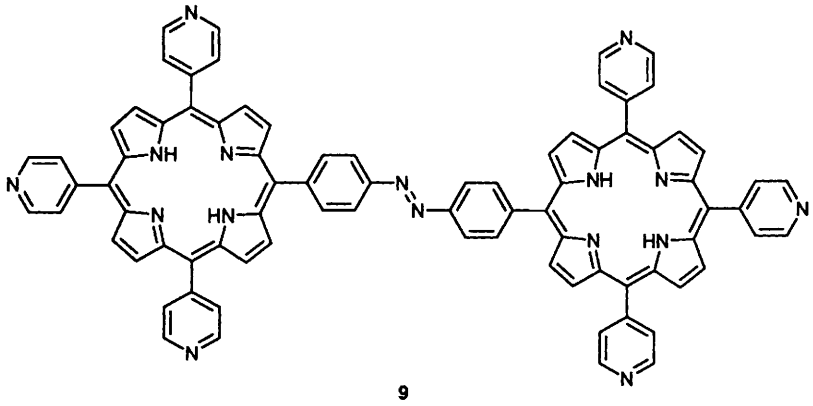

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Table 1 Relative fluorescence quantum yields from azophenylporphyrins

Compound	Φ_f[a]	Azophenyl–tpyp[b]
2	3.6	1.12
5	3.0	0.93
6	3.2	1
8	0.39	0.12
tpyr	3.2	1
HP	8.5	—

[a] The measured values are relative to the absolute value (0.085) of haematoporphyrin (HP) taken from ref. 9. All samples were 7×10^{-8} mol dm^{-3} in CH_2Cl_2 solution in 1 cm path-length cells under aerobic conditions. Excitations 418 nm. [b] Ratio of fluorescence yields of azophenylporphyrin to tpyp.

not greatly perturbed by the presence of the appended azophenyl groups and are almost identical with those of 5,10,15,20-tetrapyridylporphyrin (tpyp). The azophenylporphyrin derivatives show emissions at 651 and at 715 nm. However, the fluorescence of the porphyrin was greatly quenched by the presence of the azophenyl group when it was in the *ortho* position. In marked contrast, fluorescence was almost identical to that of tpyp or haematoporphyrin[9] when the azophenyl group was in the *para* position. Efficient fluorescence quenching is in accordance with the shorter donor–acceptor separation in **8**.

The *ortho* position presumably maximized the π–π electronic interaction between the porphyrin ring and the azophenyl group. In contrast, the *para*-azophenyl group is far away from the porphyrin ring. In the former case, the intramolecular fluorescence of the porphyrin by the azophenyl group may take place rapidly. A possible interaction porphyrin–*ortho*-azophenyl is also illustrated by its 300 MHz NMR spectrum; typically the *ortho*-azophenyl unit is greatly shielded and appears at δ 6.75(t) and 6.92(m) while the *para*-azophenyl group appears at δ 7.59 (m) and 8.07 (dd). A similar situation was previously reported by Maruyama *et al.*[10] with quinone-substituted porphyrins. In this case, when the *ortho*-quinone units can adopt a nearly coplanar orientation with the porphyrin ring, the intramolecular fluorescence quenching may take place very rapidly. The mechanism of quenching in this new system is uncertain, but may involve internal conversion due to either electron or energy transfer. The reduction of azobenzene to the radical anion occurs at a moderately negative potential (−1.38 V *vs.* SCE, solvent acetonitrile)[11] making electron transfer less favourable compared with quinone groups.

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† *Selected spectroscopic data* for **2**, **5**, **6**, **8**, **9** and **10**. NMR spectra were recorded on a Bruker AC 300P spectrometer in $CDCl_3$ at 300 MHz. UV–VIS spectra were measured on a Uvikon 941 spectrometer in $CHCl_3$; ε/dm^3 $mmol^{-1}$ cm^{-1}. Fluorescence spectra were recorded on a SPEX instrument. Mass spectra were measured with a Finnigan-Matt 95Q instrument. Satisfactory analyses were obtained for the new compounds. **2**, ^{1}H: δ −2.86 (s, 2 H, NH), 7.59 [m, 3 H, Ph(azo)$_{m+p}$], 8.07 [dd, 2 H, Ph(azo)$_o$], 8.34 (m, 4 H, Ph); 8.15 (d, 6 H, pyr), 9.1 (m, 6 H, β-pyrrole), 8.87 (s, 2 H, β-pyrrole). VIS: λ_{max}/nm 420 (ε 317), 514 (ε 17), 553 (ε 6.8), 593 (ε 6.3), 656 (ε 1.4). FABMS: *m/z* 721.

5, ^{1}H: δ −3 (s, 2 H, NH), 3.99 (s, 3 H, OMe), 8.1 (d, 2 H, Ph azo), 8.26 (d, 2 H, Ph azo), 8.38 (s, 4 H, Ph), 8.80 (s, 6 H, pyr), 8.15 (d, 6 H, pyr), 8.95 (d, 2 H, β-pyrrole), 8.80 (s, 6 H, β-pyrrole). VIS: λ_{max}/nm 420 (ε 324), 515 (ε 6.7), 551 (ε 1.7), 591 (ε 1.7), 656 (ε 1.4).

6, ^{1}H: δ −2.8 (s, 2 H, NH), 7.58 [s, 2 H, Ph(azo)$_p$], 7.62 [dd, 4 H, Ph(azo)$_m$], 8.1 [dd, 4 H, Ph(azo)$_o$], 8.3 (m, 8 H, Ph), 9.05 (dd, 4 H, pyr), 8.15 (dd, 4 H, pyr), 8.96 (s, 2 H, β-pyrrole), 8.83 (s, 2 H, β-pyrrole), 8.97 (d, 2 H, β-pyrrole). VIS: λ_{max}/nm 423 (ε 324); 516 (ε 22), 553 (ε 12), 598 (ε 7.6), 648 (ε 7.2).

8, ^{1}H: δ −2.77 (s, 2 H, NH), 6.92 [t, 1 H, Ph(azo)$_p$], 6.75 [m, 4 H, Ph(azo)$_{m+o}$], 8.20 (dd, 2 H, Ph), 7.9 (dd, 2 H, Ph), 9.06 (d, 2 H, pyr), 8.13, (s, 6 H, pyr), 8.85 (s, 4 H, β-pyrrole), 8.84 (d, 2 H, β-pyrrole), 8.75 (d, 2 H, β-pyrrole). VIS: λ_{max}/nm 420 (ε 240), 516 (ε 13), 551 (ε 3.8), 593 (ε 3.2), 648 (ε 2.7).

9, ^{1}H: δ −2.95 (s, 2 H, NH), 8.48 (m, 8 H, Ph), 9.07 (s, 12 H, pyr), 8.2 (d, 12 H, pyr), 8.88 (s, 14 H, β-pyrrole), 8.98 (d, 2 H, β-pyrrole), 8.8 (d, 2 H, β-pyrrole). VIS: λ_{max}/nm 421, 515, 554, 594, 650, FABMS: *m/z* 1260.

10, ^{1}H: δ −2.68 (s, 2 H, NH), 7.61 [t, 12 H, Ph(azo)$_{m+p}$], 8.1 [d, 8 H, Ph(azo)$_o$], 8.34 (m, 16 H, Ph), 8.96 (s, 8 H, β-pyrrole). VIS: λ_{max}/nm 320 (ε 14), 428 (ε 220), 522 (ε 4.6), 559 (ε 3.7), 593 (ε 2.2), 652 (ε 3.1).

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