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Laterally-extended porphyrin systems incorporating a switchable unit†

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p-Quinone units incorporated into the central portion of rigid π-systems linking either two porphyrin macrocycles or a porphyrin and a phenanthroline group have the potential to function as a chemically and electrochemically controllable switch, thus acting as a means of modulating electronic communication between the two end groups.

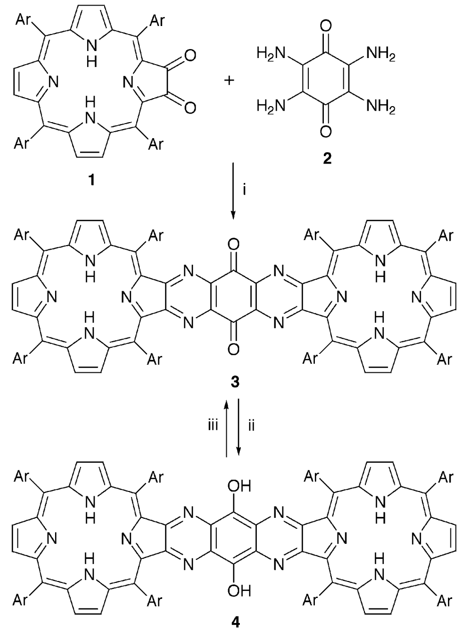
Switchable units can be used to regulate electronic communication between the components of a larger molecule.[1,2] Porphyrins are electron-rich aromatic systems with many oxidation states. The different oxidation levels of the porphyrin ring might be used to store information, for example, by equating the neutral macrocycle with binary 0 and a reduced species with binary 1. Switchable communication between otherwise-isolated porphyrin rings and between such a porphyrin and an input–output unit would allow construction of various electronic devices such as a 'molecular' shift register.[3] In other work we have demonstrated a means by which several porphyrins can be connected by π-conjugated bridges[4–7] and we have synthesised an extended system incorporating a phenanthroline end-group that allows connection of the extended π-pathway to an external redox centre.[8] Thus, synthesis of such systems that also incorporate a switchable unit that might be addressed by redox, photochemical or chemical means is of interest. We now report the synthesis and chemical and electrochemical switching of the extended systems **3** and **9** that have a quinonoid unit in the linker.

Bis-porphyrin **3** incorporating a quinonoid bridge was synthesised by heating 2 equiv. of 2,3-dioxo-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)chlorin[9,10] **1** with 1 equiv. of 2,3,5,6-tetraamino-1,4-benzoquinone[11] **2** in pyridine for 4 h (Scheme 1). Compound **3** was isolated in 80% yield by column chromatography. The electronic spectrum of the quinonoid bis-porphyrin system **3** [λ_{max} ($CHCl_3$)/nm 418 (log ε 5.40), 472 sh (5.11), 547 (4.61), 621 (4.29) and 675 (3.91); (CH_2Cl_2–MeOH; 9:1)/nm 414 (log ε 5.40), 467 sh (5.18), 547 (4.64), 621 (4.26) and 675 (3.94)] resembles more closely that of the model monoporphyrin-bridged system‡ **5** [λ_{max} ($CHCl_3$)/nm 426 (log ε 5.55), 473 sh (4.60), 542 (4.12), 577 sh (3.85), 613 (4.04) and 662 (3.36)] rather than that of the non-quinonoid bis-porphyrin system **6** [λ_{max} ($CHCl_3$)/nm 426 (log ε 5.54), 458 (5.51), 498 sh (4.96), 604 sh (4.27), 614 sh (4.30), 630 (4.34) and 677 (3.87)]. This indicates that incorporation of the quinonoid unit has been effective in reducing the extent of the π-conjugation in system **3**.

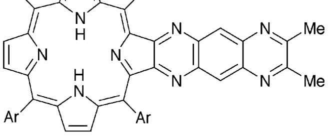
The quinonoid porphyrin–phenanthroline system **9** was prepared by the sequence outlined in Scheme 2. The diaminoquinoxalinoporphyrin **7**, generated by reaction of the porphyrin-dione **1** and 2,3,5,6-tetraamino-1,4-benzoquinone **2**, was condensed with 1,10-phenanthroline-5,6-dione **8** to give **9** [λ_{max} ($CHCl_3$)/nm 415 (log ε 5.26), 490 sh (4.49), 551 sh (4.23), 628 (3.91) and 682 sh (3.66)] in 91% overall yield.

As the quinone unit is cross-conjugated and the various hydroquinone and semiquinone states derivable from it are through-conjugated,[12] there is a possibility that interconversion between these states in compounds **3**, **4**, **9** and **10** will act to switch the extent of π-conjugation between the end-groups, and thereby substantially alter the chromophore.

As expected, the quinonoid unit of compounds **3** and **9** can be readily switched to the corresponding hydroquinonoid forms **4** and **10** by chemical reduction. Thus, treatment of the bis-porphyrin **3** (υ_{max} 1701 cm^{-1}) with $NaBH_4$ in CH_2Cl_2–MeOH generated the analogue **4** (υ_{max} 3624 cm^{-1}), quantitatively (Scheme 1). The electronic spectrum showed that the Soret band of the reduced system **4** had been red-shifted by 22 nm (Fig. 1) and that its intensity had been greatly increased [λ_{max} (CH_2Cl_2–MeOH; 9:1)/nm 436 (log ε 5.89), 525 (4.59), 562 (4.15), 595 (4.23) and 652 (3.68)].[13] Under the same conditions the non-quinonoid bis-porphyrin **6** was left unchanged [λ_{max} (CH_2Cl_2–



Scheme 1 *Reagents and conditions*: i, pyridine, N_2, heat, 4 h; ii, $NaBH_4$, MeOH, CH_2Cl_2, N_2; iii, O_2 (Ar = 3,5-$Bu^t_2C_6H_3$).



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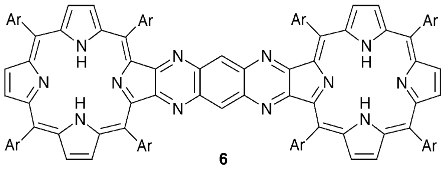

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† Electronic supplementary information (ESI) available: experimental procedures and characterization of compounds. See http://www.rsc.org/suppdata/cc/b1/b111655j/

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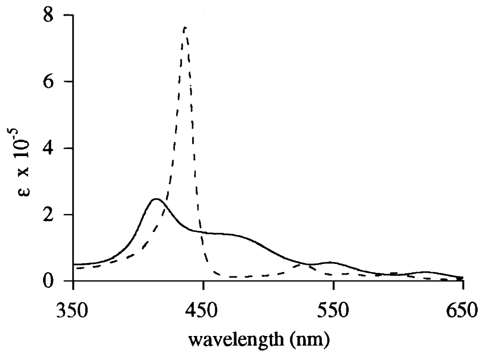


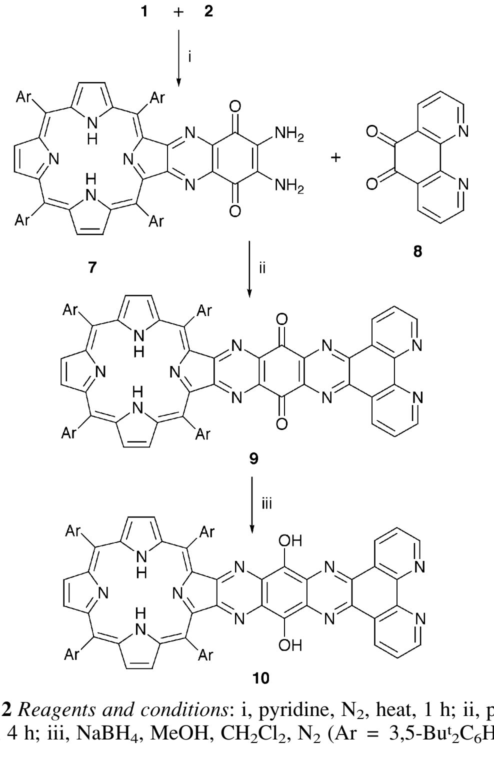
Fig. 1 Visible spectrum of quinonoid bis-porphyrin **3** (solid line) and its reduced hydroquinone form **4** (dashed line) in CH$_2$Cl$_2$–MeOH (9 : 1).

MeOH; 9 : 1)/nm 424 (log ε 5.56), 454 (5.49), 500 sh (4.94), 606 sh (4.25), 626 (4.31) and 670 sh (3.80)]. Prolonged exposure of a solution of the hydroquinone **4** to air resulted in its oxidation back to the quinone **3**.

Similar reduction of the quinonoid porphyrin–phenanthroline **9** with NaBH$_4$ was found to occur smoothly to give hydroquinone **10** [λ_{max} (CH$_2$Cl$_2$–MeOH; 9 : 1)/nm 430 (log ε 5.41), 526 (4.30), 560 sh (3.98), 596 (3.97) and 650 (3.62)], quantitatively (Scheme 2). A red-shift of the Soret band and a substantial increase in the extinction coefficient was observed in the electronic spectrum of **10**.

In organic solvents, electrochemical reduction of quinones first affords semiquinone radical anions and thence hydroquinone dianions which are readily protonated.[14] Porphyrins are also redox-active. It is thus of particular interest to see if the quinone bridge of **3** and **9** can function as a switch under electrochemical reduction conditions. Spectroelectrochemistry provides a convenient means of monitoring the site of reduction (porphyrin ring or quinone bridge). Reduction of a porphyrin ring generates a porphyrin π-anion radical, a species that lacks the intense, distinctive Soret band of a porphyrin[15,16] while the spectroscopy of the through-conjugated hydroquinone species **4** and **10** indicates that quinone reduction will result in an increase in intensity and a red-shift of the Soret band.

Controlled potential electrochemistry (just below the first reduction potential at −1.2 V§) of the symmetrical system **3** in CH$_2$Cl$_2$ under argon resulted in a steady and substantial decline in the intensity of the Soret band relative to other bands and no change in its position, indicative of reduction at a porphyrin ring. The non-quinonoid bis-porphyrin **6** showed the same behaviour under identical conditions. In contrast, controlled potential electrochemistry of the porphyrin–quinone–phenanthroline system **9** gave a species with an intense Soret band that had red-shifted from 413 to 429 nm, indicative of quinone reduction. Cyclic voltammetry experiments show that the electrochemistry of **9** is complex and may involve following chemistry. Studies are underway to explore the kinetics of these reductions and to fully characterise intermediates and the resultant thermodynamically favoured anions.



Scheme 2 *Reagents and conditions*: i, pyridine, N$_2$, heat, 1 h; ii, pyridine, N$_2$, heat, 4 h; iii, NaBH$_4$, MeOH, CH$_2$Cl$_2$, N$_2$ (Ar = 3,5-Bu$^t_2$C$_6$H$_3$).

Hydroquinone diradicals are produced from quinones as photochemical excited states,[17] but the possibility of switching these systems photochemically is yet to be explored.

In summary, laterally-extended porphyrin systems incorporating a quinonoid unit as a potential switch have been synthesised and can be reversibly reduced to hydroquinone analogues with modified chromophores. There is also clear evidence that the porphyrin–quinone–phenanthroline system **9** can be switched electrochemically between cross-conjugated and through-conjugated systems. Further studies on the switching and information storage properties of these very interesting compounds and their metallated derivatives are underway.

We thank the Australian Research Council for a research grant.

Notes and references

‡ Prepared by reaction of porphyrin-dione **1** with 1,2,4-triamino-5-nitrobenzene to give the aminonitroquinoxalinoporphyrin which was reduced with NaBH$_4$/Pd/C to give the diaminoquinoxalinoporphyrin and thence treated with 2,3-butanedione to give **5** in 77% overall yield.

§ Bulk electrolysis was performed with a PAR 273A potentiostat. The working electrode was a Hg pool, constantly stirred to maintain a fresh surface. The auxiliary electrode was Pt gauze and the reference electrode was a Ag/AgNO$_3$/CH$_3$CN non-aqueous electrode; both were isolated from the solution by a glass frit. Spectra were recorded by a CAREY 5E UV-Vis-NIR spectrophometer through a fibre-optic probe. Data were collected periodically until one Coulomb equiv. had been added.

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