



Thiophene-Appended Porphyrin Systems

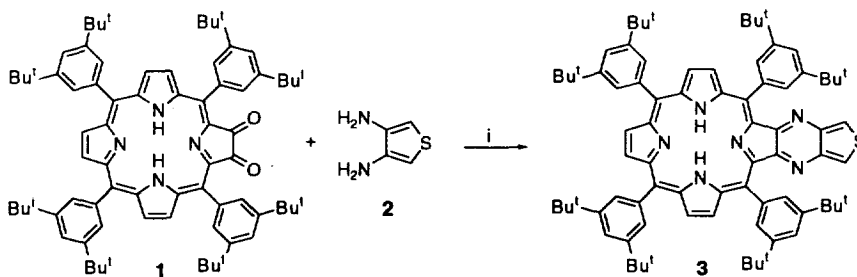
Maxwell J. Crossley* and Jognandan K. Prashar

School of Chemistry and Co-operative Research Centre for Molecular Engineering & Technology,
The University of Sydney, NSW 2006, Australia

Abstract: Condensation of porphyrin-2,3-diones with 3,4-diaminothiophene generate conjugated thiophene-appended porphyrin systems that bind directly to a gold [Au(111)] surface to form a monolayer. © 1997 Elsevier Science Ltd.

Recently thiophene has been shown to bond to Au(111) through the sulfur atom.¹ Thin films of poly(3-hexylthiophene) have also been found to interact with several other metals.² To study the self-assembly and molecular electronic properties of porphyrin-based monolayers and thin films, we sought to prepare thiophene-appended porphyrins which had full π -conjugation between the sulfur and the porphyrin ring. Recently we have reported the design and synthesis of laterally conjugated porphyrin oligomers and some of their properties as molecular wires.³⁻⁵ These compounds were prepared efficiently by sequential condensation of a porphyrin-2,3-dione with 1,2,4,5-benzenetetramine to generate a diamino-quinoxalinoporphyrin which was subsequently condensed with further porphyrin-2,3-dione and/or porphyrin-2,3,12,13-tetraone to give the extended porphyrin systems.⁶ Using a similar methodology we have synthesised a variety of thiophene-appended porphyrin systems by reacting 3,4-diaminothiophene **2** with compounds **1**, **4**, **6**, **9** and **11**.

5,10,15,20-Tetrakis(3,5-di-*tert*-butylphenyl)porphyrin-2,3-dione⁷ **1** in chloroform was heated at reflux with 3,4-diaminothiophene^{8,9} **2** (2 equivalents) for 2 hours to give the thiophene-appended porphyrin **3** in 76% yield (Scheme 1).

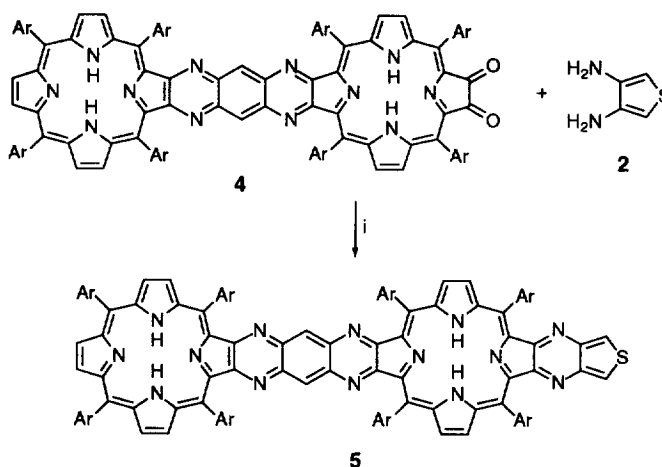


i) CHCl₃, reflux, 2 h.

Scheme 1

Compared with that of 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin, the visible spectrum of thiophene-appended porphyrin 3 is significantly red-shifted reflecting its extended π -conjugation.¹⁰ The ¹H n.m.r. spectrum of 3 shows the expected C_{2v} symmetry and molecular modelling showed that the sulfur atom of the thiophene ring protrudes from the envelope of the methyl groups of the *tert*-butyls by at least 0.5 Å, sufficient to allow unencumbered complexation at a metal surface.

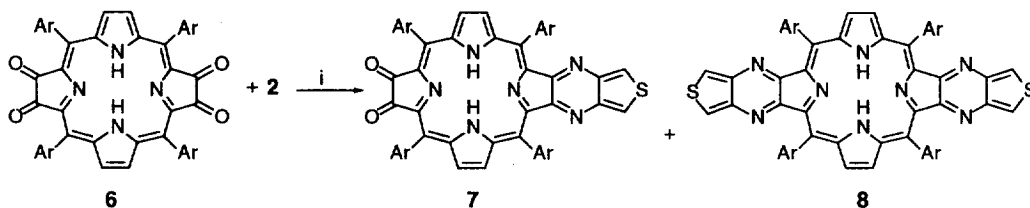
Bis-porphyrin-dione 4 similarly treated with 2 equivalents of 2 gave bis-porphyrin-thiophene 5 in 83% yield after purification of the product by column chromatography over silica (dichloromethane-light petroleum: 2:3) (Scheme 2).



i) CHCl_3 , reflux, 2 h (Ar = 3,5-Bu^t₂C₆H₃).

Scheme 2

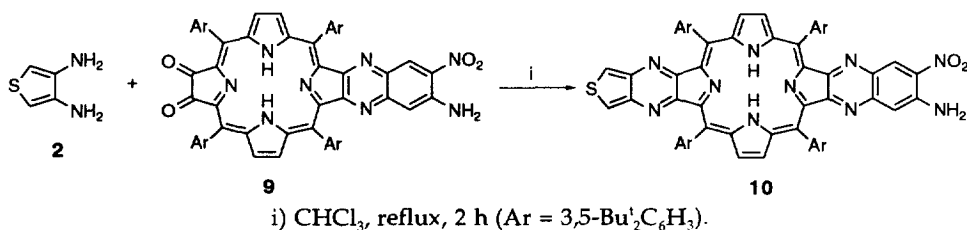
Reaction of 2 with porphyrin-2,3,12,13-tetraone 6 was also facile. Thus tetraone 6 was treated with 2.8 equivalents of 2 to give the bis-thiophene-appended porphyrin 8 in 80% yield. When only 0.7 equivalents of 2 was reacted with 6 a mixture of products was obtained. After purification of the products by column chromatography over silica (dichloromethane-light petroleum: 2:3) the mono-thiophenoporphyrin-dione 7 was obtained in 55% yield, small amounts (< 10%) of the bis-thiopheno-porphyrin 8 and recovered starting porphyrin-tetraone 6 were also isolated (Scheme 3).



i) CHCl_3 , reflux, 2 h (Ar = 3,5-Bu^t₂C₆H₃).

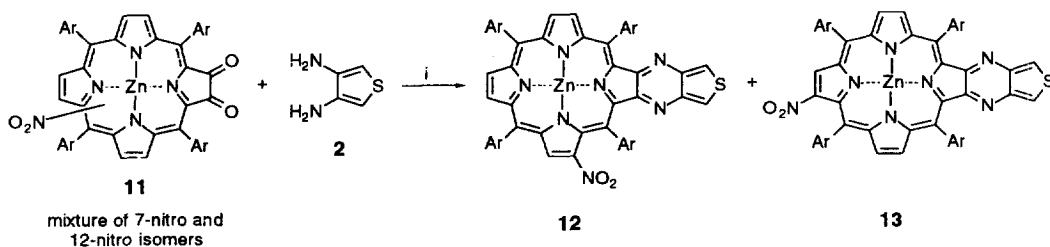
Scheme 3

The methodology for attaching the thiophene unit was also applied to amino-nitro-quinoxalino-porphyrin-dione¹¹ **9** which was converted to the corresponding substituted porphyrin **10** in 89% yield after purification by column chromatography over silica (dichloromethane-light petroleum: 2:3) (Scheme 4). Both **7** and **10** are potential precursors to further elaborated/extended thiophene-phenanthroline-appended porphyrin systems.



Scheme 4

Treatment of a mixture of zinc(II) 7- and 12-nitro-porphyrin-2,3-dione¹² **11** with 2 equivalents of 3,4-diaminothiophene **2** gave the zinc(II) 7- and 12-nitro-thiophenoporphyrins in 96% yield (Scheme 5). The two regioisomers were separated by column chromatography over silica (dichloromethane-light petroleum: 2:3) to give the 7-nitro-thiophenoporphyrin **12** in 67% yield and 12-nitro-thiophenoporphyrin **13** in 29% yield.



Scheme 5

Impedance spectroscopy, ellipsometry, grazing angle FTIR, and surface plasmon spectroscopy show that thiophene-appended porphyrins and phenanthroline-appended porphyrins¹¹ adsorb onto gold surfaces and form monolayer structures.¹³ These systems are currently undergoing further studies. In contrast, related porphyrins lacking these appendages do not bond directly to gold but can form monolayers when deposited with trigger molecules as Langmuir-Blodgett films at the air-water interface.¹⁴⁻¹⁶

The synthesis reported in this paper further illustrates the versatility of the porphyrin-2,3-dione **1** and porphyrin-2,3,12,13-tetraone **6** as key components in building interesting porphyrin arrays.^{3,6,7,11,17}

Acknowledgments

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References and Notes

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10. All new compounds have been fully characterised. Selected spectroscopic data: Compound 3: m/z (CI) 1172 ($M + 1$, 100%); ^1H n.m.r. (200 MHz, CDCl_3) δ -2.32 (2 H, s, inner NH), 1.50 (36 H, s, *t*-butyl H), 1.54 (36 H, s, *t*-butyl H), 7.76 (2 H, s, 2'- and 3'-H), 7.81 (2 H, t, J 1.9 Hz, *p*-ArH), 7.88 (2 H, t, J 1.9 Hz, *p*-ArH), 7.95 (4 H, d, J 1.9 Hz, *o*-ArH), 8.11 (4 H, d, J 1.9 Hz, *o*-ArH), 8.77 (2 H, s, 12- and 13-H), 8.97 and 8.98 (4 H, ABq, J_{AR} 5.1 Hz, 7-, 8-, 17- and 18-H); $\lambda_{\text{max}}(\text{CHCl}_3)$ 428 (log ϵ 5.12), 535 (4.17), 574sh (3.60), 604 (3.87), 659 nm (3.58). Compound 5: m/z (electrospray) 2362 ($M + 2$, 100%); $\lambda_{\text{max}}(\text{CHCl}_3)$ 427 (log ϵ 5.37), 464sh (5.26), 611 (4.25), 628 (4.28), 684 (3.79), 706 nm (4.02). Compound 7: m/z (CI) 1202 ($M + 1$, 100%); $\lambda_{\text{max}}(\text{CHCl}_3)$ 405 (log ϵ 5.20), 542sh (4.00), 618 (3.82), 696 nm (3.92). Compound 8: m/z (CI) 1280 ($M + 1$, 100%); $\lambda_{\text{max}}(\text{CHCl}_3)$ 457 (log ϵ 5.18), 545 (4.30), 614 (4.07), 670 (3.65), 696 nm (3.47). Compound 10: m/z (CI) 1334 ($M + 1$, 100%); $\lambda_{\text{max}}(\text{CHCl}_3)$ 423 (log ϵ 5.19), 547 (4.30), 636 (4.06), 692 nm (4.23). Compound 12 (7-nitro): m/z (CI) 1280 ($M + 2$, 100%), 1279 ($M + 1$, 99); $\lambda_{\text{max}}(\text{CHCl}_3)$ 436 (log ϵ 5.11), 552 (3.84), 591 (4.03), 643 nm (4.40). Compound 13 (12-nitro): m/z (CI) 1279 ($M + 1$, 100%); $\lambda_{\text{max}}(\text{CHCl}_3)$ 442 (log ϵ 5.00), 476sh (4.83), 506sh (4.53), 590 (4.20), 630 nm (3.99).
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