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Mendeleev Commun., 1993, 3(3), 104–107

Mendeleev Communications

Synthesis of Chromophores Based on Porphyrins and Open-chain Polypyrroles

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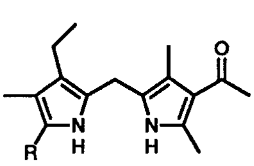
Two new cyclic polypyrrole pigments, porphyrin–dipyrrolylmethene and bis–porphyrin–biladiene, have been synthesised.

Modern photography and optical memory devices, up-to-date laser technologies and some other techniques are now in need of highly specialised pigments. A possible approach to the pigments in question is to combine different chromophores in one molecule. In fact, two such pigments have already been reported in the literature, these being bilindione and porphyrin in conjugation with non-porphyrinic chromophores.[1,2] It seemed to us that we could obtain products with very interesting spectral properties on binding porphyrin to compounds with strong absorption maxima, such as dipyrrolylmethane and biladiene.

We started the synthesis with meso-pyrrolylporphyrin **1**



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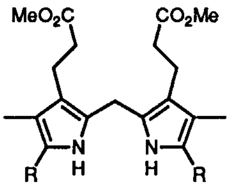

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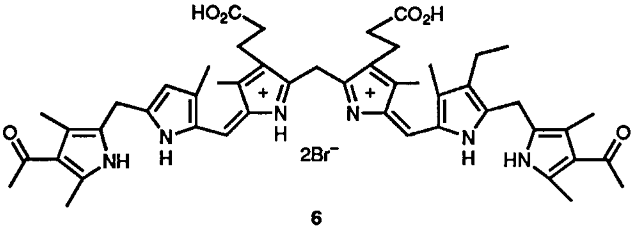

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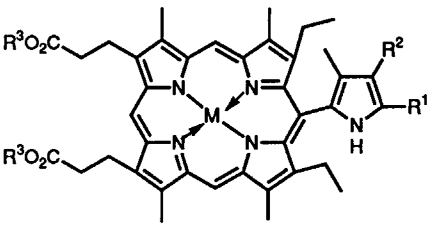

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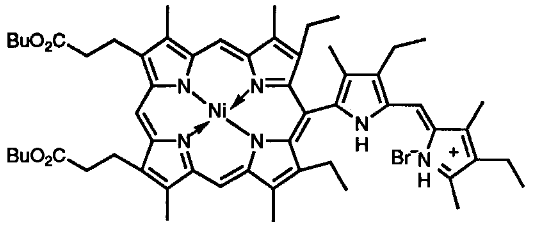

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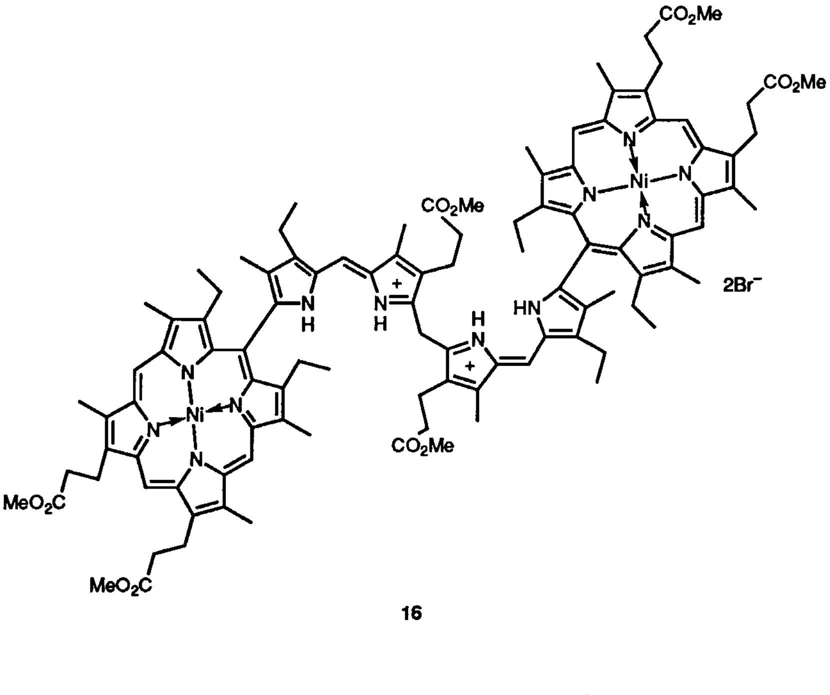

16

1 R^1 = Me; R^2 = Ac; R^3 = Me; M = 2H
2 R = CHO
3 R = H
4 R = H
5 R = CO_2CH_2Ph
7 R = R^1 = Me; R^2 = Ac; R^3 = Me; M = Cu

8 R^1 = Me; R^2 = Ac; R^3 = Bu; M = 2H
9 R^1 = Me; R^2 = Et; R^3 = Bu; M = 2H
10 R^1 = CHO; R^2 = Et; R^3 = Bu; M = 2H
11 R^1 = CH_2OH, R^2 = Et; R^3 = Bu; M = 2H
12 R^1 = CH_2OEt; R^2 = Et; R^3 = Bu; M = 2H
13 R^1 = CHO; R^2 = Et; R^3 = Bu; M = Ni
14 R^1 = CHO, R^2 = Et; R^3 = Me; M = Ni

(Scheme 1), obtained by a well-known procedure.[3,4] This procedure included, however, some cumbersome and unpleasant stages such as purification of α-unsubstituted dipyrrolylmethane **3** and subsequent formylation of the purified **3** in HCN medium. We modified the route described in refs. 3 and 4 by omitting the purification step and formylating crude dipyrrolylmethane by Vilsmieer's technique.[5] Another unsubstituted dipyrrolylmethane **4** was prepared by treatment of the dibenzyl ester **5** with HBr–acetic acid (50%, w/w). This resulted in quantitative debenzylation and decarboxylation of **5** to give compound **4**.

Coupling of dipyrrolylmethanes **2** and **4** gave hexapyrrodiene **6** in 84% yield. This pyrrodiene **6** was heated with $Cu(OAc)_2$–NaOAc in a (1:1) mixture of MeOH and acetic acid to give a copper complex **7** in 77% yield. The copper atom was removed with concentrated H_2SO_4. For better solubility porphyrin **1** was esterified to its dibutyl ester **8**.[†]

To transform the *exo*-pyrrole substituent of porphyrin **8** into a polypyrrole chromophore of the dipyrrolylmethene or biladiene type we had to oxidise the CH_3-group in position 2 of the *exo*-pyrrole ring. This could be achieved only after reduction of the neighbouring acetyl function. Unfortunately, as we have earlier found, meso-pyrrolylporphyrins with no electron-accepting *exo*-substituents in the *exo*-pyrrolic ring are unstable.[6] Indeed, all attempts to selectively reduce the acetyl group of **8** by conventional methods[7,8] were unsuccessful. We finally circumvented these difficulties by using a reducing system B_2H_6/CF_3COOH in THF and succeeded in preparing porphyrin **9**[‡]. The yield of product was 94%. We then oxidised the 2′-CH_3 group with MnO_2/C in a C_6H_6–CF_3COOH mixture, thus obtaining porphyrin **10**[§] in 46% yield.

Porphyrin **10** reduction with $NaBH_4$ in a $CHCl_3$–MeOH mixture resulted in a very labile porphyrin **11**. A more stable derivative **12** was obtained by consecutive treatment of **11** with $(CH_3CO)_2O$ and EtOH. Spectral characteristics were recorded for both compounds; compound **12** was also subjected to elemental analysis. With porphyrin **10** we have prepared a nickel complex **13**; after transesterification in MeOH–H_2SO_4 we also obtained complex **14**. In the presence of 2–4 equivalents of HBr both these compounds successfully reacted with cryptopyrrole and dipyrrolylmethane **4**[¶] to give porphyrin–dipyrrolylmethene **15** and bis–porphyrin–biladiene **16**.

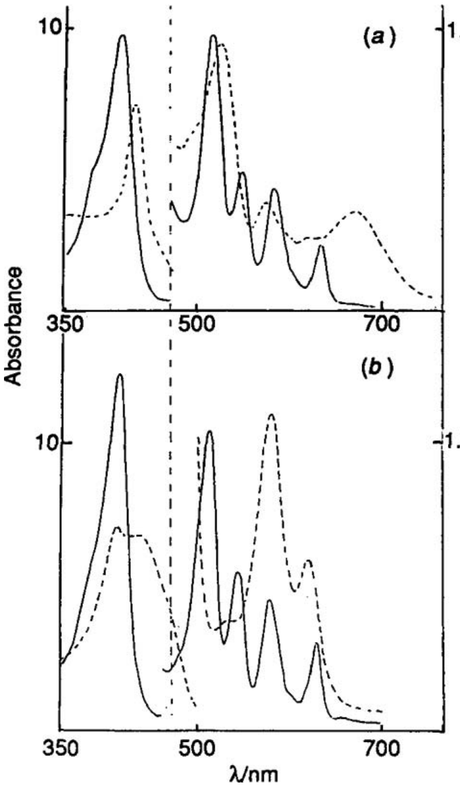

Fig. 1 Absorption spectra of porphyrin **9** (*a*) and porphyrin **10** (*b*) in $CHCl_3$ (solid line) and $CHCl_3 + 0.1\%$ CF_3COOH (dashed line)

Thus, complex **14** (0.064 mmol) and dipyrrolylmethane **4** (0.032 mmol) in a mixture (5 ml; 3:2) of dichloroethane and MeOH after treatment with methanolic HBr (0.21 mmol HBr in 0.5 ml MeOH) resulted in product **16**. After crystallization from acetone–ethyl acetate the yield of **16** was 89%. ^{1}H NMR resonances, δ ($CDCl_3$): 14.69, 14.22 (2H, 2H, s, NH biladiene); 9.59 (4H, s, β,δ-meso-H); 9.54 (2H, s, γ-meso-H); 7.58 (2H, s, -CH = biladiene); 4.18 (8H, t, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CO}$); 3.67 (12H, s, OCH_3 porph.); 3.44 (6H, s, OCH_3 biladiene); 3.40 (12H, s, 1,4-CH_3 porph.); 3.31 (12H, s, 5,8-CH_3 porph.); 3.12 (8H, t, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CO}$); 2.96, 2.92 (4H, 4H, q, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$ porph.); 2.77 (8H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$ and $\mathrm{C}\mathit{H}_2\mathrm{CH_2CO}$ biladiene); 2.38 (6H, s, 2, 18-CH_3 biladiene); 2.18 (4H, t, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CO}$ biladiene); 2.02 (1H, d, $J_{\mathrm{A-B}}$ 1.5 Hz, -CH_2-biladiene); 1.70 (1H, d, $J_{\mathrm{A-B}}$ 1.5 Hz, -CH_2-biladiene); 1.41 (6H, s, 7,13-CH_3 biladiene); 1.37 (6H, t, $\mathrm{CH_2C}\mathit{H}_3$ biladiene); 1.19, 1.13 ppm (6H, 6H, 2t $\mathrm{CH_2C}\mathit{H}_3$ porph). The *m*/*z* peak 1883 in the mass spectrum[||] further confirmed the suggested structure **16**.

The meso-porphyrins obtained have certain very interesting properties, for example, the absorption spectra of compounds **9** and **10** in $CHCl_3$ are typical for porphyrins and seem quite similar, but on addition of acid they show considerable differences in behaviour (Fig. 1). This could be an indication of a porphyrin-pyrrole transition into phlorin-pyrrolene.

The spectra of compounds **15** and **16** exhibit absorption bands with maxima at 561 and 524 nm for porphyrin Ni-

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[†] The structure of porphyrin **8** (from heptane) was confirmed by elemental analysis data, UV and IR spectroscopy, mass spectrometry and ^{1}H NMR spectrometry using NOE techniques. The latter method allowed an unequivocal assignment of all ^{1}H NMR resonances, δ ($CDCl_3$): 9.86 (1H, s, NH pyrr.); 9.77(2H, s, β,δ-meso-H); 8.80(1H, s, γ-meso-H); 4.05(4H, t, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2CH_2CH_3}$); 3.58(6H, s, 1,4-ring CH_3); 3.54(4H, t, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CO}$); 3.08(6H, s, 5,8-ring CH_3); 2.97 (3H, s, 2-CH_3 pyrr.); 2.88(3H, s, 4-CH_3 pyrr.); 2.85(4H,t, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CO}$); 2.03(3H, s, $COCH_3$ pyrr.); 1.53–1.11(14H, m, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$ and $\mathrm{CH_2C}\mathit{H}_3$); 0.76(6H, t, $\mathrm{OCH_2CH_2CH_2C}\mathit{H}_3$); −3.51, −4.11 ppm(1H, 1H, s, NH).

[‡] The spectral characteristics of porphyrin **9**. Absorption spectrum: λ_{max} ($\varepsilon \times 10^{-3}$) (in $CHCl_3$): 406(146); 507(14.6); 540(7.3); 575(6.4); 627 nm (3.4). (In $CHCl_3 + 0.1\%$ CF_3COOH): 422(216); 513(28.1); 565(11.2); 613(7.3); 663 nm (10.0). Mass spectrum, *m*/*z*: 800 (M^+, 60); 785(100); 770(33). ^{1}H NMR resonances, δ ($CDCl_3$): 10.4(2H, s, β, δ-meso-H); 9.89(1H, s, NH pyrr.); 8.38(1H, s, γ-meso-H); 4.34(4H, t, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CO}$); 4.28(4H, t, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2CH_2CH_3}$); 3.62, 3.56 (6H, 6H, s, ring-CH_3); 3.24(4H, t, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CO}$); 3.10, 2.93, 2.71(2H, 2H, 2H, q, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$, porph. and pyrr.); 2.54(3H, s, 2-CH_3 pyrr.); 1.78(3H, s, 4-CH_3 pyrr.); 1.62–1.39, 1.38–1.11(17H, m, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$ and $\mathrm{CH_2C}\mathit{H}_3$, porph. and pyrr.); 0.75(6H, t, $\mathrm{OCH_2CH_2CH_2C}\mathit{H}_3$); −3.25, −3.34 ppm(1H, 1H, s, NH).

[§] Porphyrin **10** was fully characterized by physico-chemical methods. Absorption spectrum: λ_{max} ($\varepsilon \times 10^{-3}$) (in $CHCl_3$): 407(193); 505(16.2); 539(8.5); 573(7.0); 626nm (4.7); (In $CHCl_3 + 0.1\%$ CF_3COOH): 407(108); 430 shoulder (105); 532(6.0); 570(17.3); 617 nm (9.3). Mass spectrum, *m*/*z* (FAB): 814 (M + 1). ^{1}H NMR resonances, δ ($CDCl_3$): 10.5(2H, s, β,δ-meso-H); 10.06(1H, s, NH pyrr.); 9.91 (1H, s, CHO); 9.85(1H, s, γ-meso-H); 4.26(4H, t, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CO}$); 4.07(4H, t, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2CH_2CH_3}$); 3.58, 3.57(6H, 6H, s, ring-CH_3); 3.20(4H, t, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CO}$); 3.07, 2.95, 2.92(2H, 2H, 2H, q, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$, porph. and pyrr.); 1.78(3H, s, 4-CH_3 pyrr.);1.54–1.40, 1.29(17H, m, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$ and $\mathrm{CH_2C}\mathit{H}_3$ porph. and pyrr.); 0.73(6H, t, $\mathrm{OCH_2CH_2CH_2C}\mathit{H}_3$); −3.27, −3.46 ppm(1H, 1H, s, NH).

[¶] Crystalline dipyrrolylmethane **4** was prepared according to the procedure described in ref. 10.

[||] The mass spectrum of bis-porphyrin–biladiene **16** was recorded on a Kratos MS–50 (FAB) mass spectrophotometer.

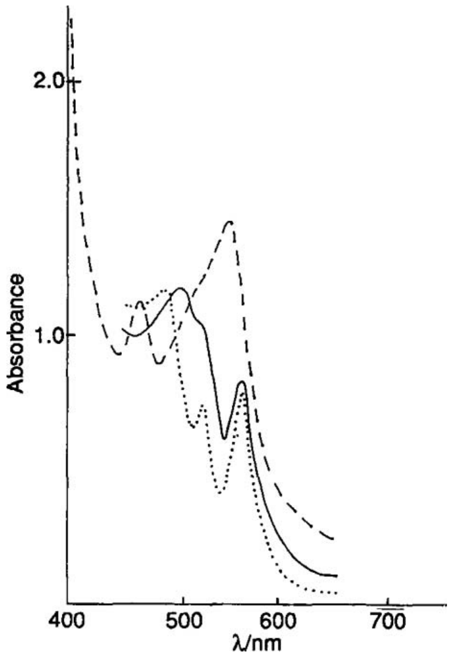

Fig. 2. Absorption spectra of porphyrin **16** in $CHCl_3$ (solid line), $CHCl_3$ with 1% Et_3N (dashed line), $CHCl_3$ with 0.01% bromide (dotted line)

complexes; they also show an intense band in the 500 nm region typical for non-cyclic polypyrrole chromophores. Addition of trace amounts of bromine to pigments **16** solution gave a band at 554 nm with $\varepsilon = 75\,000$ (Fig.2).

We continue further spectral and physico-chemical investigation of porphyrins bound to open-chain polypyrroles, and the results will be published separately.

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Received: Moscow, 6th January 1993
Cambridge, 8th February 1993; Com. 3/00390F