Oxidation of Cobalt(II) Tetrapyrroles in the Presence of an Electron Acceptor†

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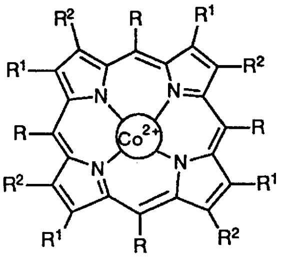
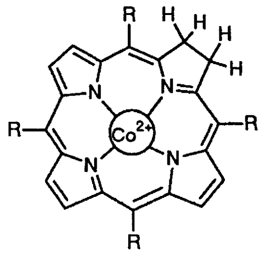
The interaction of cobalt(II) porphyrins and chlorin with 4,6-dinitrobenzofurazan 1-oxide (dnbfo) has been studied by spectroscopic methods. Initially all the cobalt(II) porphyrins form molecular complexes with the electron acceptor dnbfo, but with time a complete electron transfer is observed. This results in the formation of cobalt(III) porphyrins and the anion radical of dnbfo. The electron transfer is facilitated in the presence of molecular oxygen. The rate of oxidation is dependent on the porphyrin ring substituents as well as on the solvent mixture used. In the case of cobalt(II) 5,10,15,20-tetraphenylchlorin first oxidation occurs to cobalt(II) 5,10,15,20-tetraphenylporphyrin and this is followed by metal oxidation to give the cobalt(III) porphyrin. The oxidation of the cobalt(II) porphyrins and formation of the anion radical of dnbfo has been monitored by ESR spectroscopy. The *g* value and the linewidth of the radical compares well with that of the anion formed by chemical reduction. Proton and ^{19}F NMR data confirm the occurrence of the electron-transfer reaction.

Electron-transfer reactions of porphyrins and metalloporphyrins have been studied in great detail during the past decade because of their involvement as electron-transfer agents in many biological reactions involving haem proteins,[1,2] photosynthetic reaction centres[3–5] and artificial photocatalytic systems.[6–8] The addition or removal of an electron from metalloporphyrins could involve both the porphyrin π system and the central metal ion in the porphyrin core.[9,10] It is generally observed that for porphyrins containing metals like Zn, Cu and Cd the first electron addition or removal involves the porphyrin π system. Their redox chemistry has been the subject of numerous studies and the redox products have been characterised by spectroscopic,[11,12] electrochemical[13,14] and chemical methods.[15,16] On the other hand, with porphyrins containing metals like Co, Fe and Mn the metal ion participates in the redox chemistry.[17–19] In this regard cobalt(II) porphyrins have been widely studied and it has been shown that they undergo facile oxidation to cobalt(III) derivatives under a variety of conditions.[20,21] One such condition demands the presence of molecular oxygen and a donor axial ligand where the latter coordinates to the metal centre promoting electron transfer from cobalt to molecular oxygen.

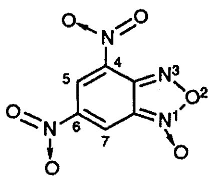
The present report describes studies of the oxidation of several cobalt(II) porphyrin derivatives in the presence of the electron acceptor 4,6-dinitrobenzofurazan 1-oxide (dnbfo). It is known that dnbfo forms highly coloured complexes with aromatic donors exhibiting a charge-transfer band in the visible region.[22] The π-acceptor behaviour of nitrobenzofuroxans with cobalt(II) derivatives of dimethyl 7,12-diethyl-3,8,13,17-tetramethylporphyrin-2,18-dipropanoate and etioporphyrin-(3,8,13,18-tetraethyl-2,7,12,17-tetramethylporphyrin) has also been reported.[23,24a] These studies are restricted to an evaluation of the binding constants and associated thermodynamic parameters for the charge-transfer complexes formed. In our study a complete electron transfer from the donor cobalt(II) porphyrins to the acceptor dnbfo has been observed and both the oxidised cobalt(III) derivative and the reduced dnbfo have been characterised using visible absorption, ^{1}H and ^{19}F NMR, ESR spectroscopic and cyclic voltammetric methods.



[Co(tpp)]	R = Ph, $R^1 = R^2 = H$
[Co(tpdp)]	R = C_6D_5, $R^1 = R^2 = H$
[Co(tmop)]	R = C_6H_4OMe-*p*, $R^1 = R^2 = H$
[Co(tpfp)]	R = C_6F_5, $R^1 = R^2 = H$
[Co(tbtp)]	R = Ph, R^1 = Br, R^2 = H
[Co(oep)]	R = H, $R^1 = R^2$ = Et



[Co(tpc)] R = Ph



dnbfo

Results and Discussion

(*a*) *Optical Absorption Studies.—Cobalt*(II) *porphyrins.* The absorption spectra of various cobalt(II) porphyrins in organic solvents are well characterised.[11] Addition of increasing amounts of dnbfo to a $CHCl_3$ solution of various cobalt(II) porphyrins decreased the intensity of the Q-bands with the appearance of well defined isosbestic points, indicating the formation of a molecular complex in solution. The stoichiometry of the complexes determined as described earlier[24a] was found to be 1 : 1. However, with time, a red shift of the absorption bands (Q-bands, ≈14; Soret, ≈20 nm) was observed for all the cobalt(II) porphyrins studied. The absorption changes of a solution containing cobalt(II) 5,10,15,20-tetraphenylporphyrinate

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† *Non-SI unit employed:* G = 10^{-4} T.

Table 1 Optical absorption data for various cobalt(II) tetrapyrroles in the presence and absence of dnbfo

Complex	λ/nm Q-band(s)	λ/nm Soret band	Time taken for complete oxidation (min)
[Co(tpp)]	528.0	411	—
[Co(tpp)] + dnbfo	544.0, 584	430	330
[Co(tmop)]	530.0	414	—
[Co(tmop)] + dnbfo	543.0, 583	433	270
[Co(tbtp)]	545	424	—
[Co(tbtp)] + dnbfo	556, 586	453	600
[Co(tpfp)]	527	406	—
[Co(tpfp)] + dnbfo	539, 579	430	450
[Co(oep)]	521, 552.5	392	—
[Co(oep)] + dnbfo	527, 558.0	412	25
[Co(tpdp)]	528	411	—
[Co(tpdp)] + dnbfo	544, 583	430	300
[Co(tpc)]	528, 615	410	—
[Co(tpc)] + dnbfo	543.5, 584	437	200
[CoCl(tmop)]	546, 581	429	—
[CoCl(tpdp)]	549.5, 586	433.5	—
[Co(tmop)][a]	529	414	—
[Co(tmop)] + 2C_5H_5N[a]	553, 593	440	[b]
[Co(tmop)] + dnbfo[a]	543, 580	433	[b]
[Co(tmop)] + 2NaOMe[a]	545, 583.0	432	[b]

[a] In methanol–$CHCl_3$ (90:10). [b] The oxidation was instantaneous.

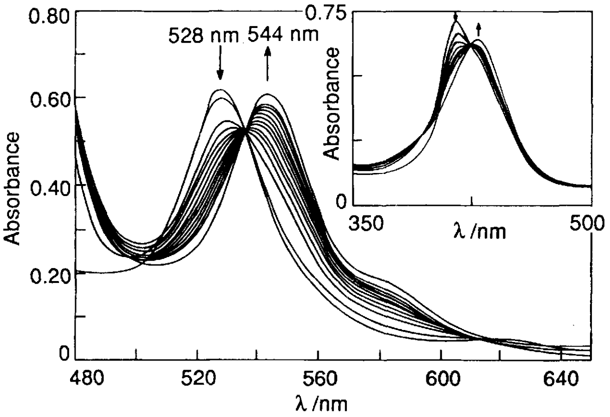

Fig. 1 Absorption changes of [Co(tpp)] (3.42 × 10^{-5} mol dm^{-3}) in the presence of dnbfo (1 × 10^{-3} mol dm^{-3}) in $CHCl_3$ with time (0–415 min at *ca.* 30 min intervals). The insert shows the absorption changes with time of [Co(tmop)] (5 × 10^{-6} mol dm^{-3}) with dnbfo (1 × 10^{-4} mol dm^{-3}) in CH_2Cl_2 in the absence of molecular oxygen

[Co(tpp)] (3.42 × 10^{-5} mol dm^{-3}) and dnbfo (1 × 10^{-3} mol dm^{-3}) with time in the presence of molecular oxygen are shown in Fig. 1. This complex in $CHCl_3$ shows a strong Q_{0-1} band at 528 nm which completely obscures the very weak Q_{0-0} component and an intense Soret band at 411 nm. In the presence of dnbfo, with time, the following changes were observed: (*i*) disappearance of the Q_{0-1} band at 528 nm, (*ii*) appearance of a new Q_{0-1} band at 544 nm and Q_{0-0} band at 584 nm and (*iii*) disappearance of the Soret band at 411 nm and appearance of a new Soret band at 430 nm. These changes are consistent[10] with oxidation to $[Co^{III}(tpp)]^+$. The band positions match well those in the absorption spectrum of [CoCl(tpp)].[25] All the cobalt(II) porphyrins illustrated show similar behaviour upon interaction with dnbfo, but the times required for complete oxidation were different depending on the substituents present. The absorption spectroscopic data for all these cobalt(II) porphyrins before and after interaction with dnbfo are listed in Table 1.

It is seen from Table 1 that the rate of oxidation of the cobalt(II) porphyrin to its cobalt(III) derivative depends on the porphyrin ring substituents. The presence of electron-withdrawing substituents (Br, F) reduces the basicity of the macrocycle, while the presence of electron-donating (Et, OMe) groups increases the basicity.[26] It has been shown that the metal–ligand bond strength as well as the spin state of the metal ion is critically dependent on the basicity of the macrocycle. Hence the reduced basicity of the macrocycle reduces the rate of oxidation in 5,10,15,20-tetrakis(pentafluorophenyl)- and 2,7,12,-17-tetrabromo-5,10,15,20-tetraphenyl-porphyrinatocobalt(II), [Co(tpfp)] and [Co(tbtp)], while the increased basicity of 5,10,15,20-tetra(*p*-methoxyphenyl)- and 2,3,7,8,12,13,17,18-octaethyl-porphyrinatocobalt(II), [Co(tmop)] and [Co(oep)], accounts for the observed increased rate of oxidation.

The oxidation was also followed in the absence of oxygen. Samples were prepared on a high-vacuum line. After several freeze–thaw cycles the solutions of dnbfo and cobalt(II) porphyrins were mixed and the optical cell was vacuum sealed. The spectrum recorded as a function of time (insert, Fig. 1) shows the existence of both cobalt-(II) and -(III) species in solution. However, the oxidation was not complete even after 24 h. The presence of one isosbestic point at 424 nm suggests that only two species are present in solution. When the solution is exposed to air a complete conversion into the cobalt(III) species is achieved within 1 h. It is known that the co-ordination of a ligand in the axial position of cobalt(II) is very unfavourable,[27,28] whereas molecular oxygen can co-ordinate with a tendency to accept electrons which leads to partial oxidation of cobalt and gives the oxygen superoxide character.[29] The amount of electron transfer to O_2 depends on the nature of the ligands co-ordinated to cobalt, solvent acidity and solvent polarity.[30] In the present study, when the solvent was changed from $CHCl_3$ to $CHCl_3$–MeOH (1:9 v/v), and with methoxide as axial ligand, the oxidation was instantaneous due to formation of an intermediate of the type $[L^{\delta+}Co^{II}P(O_2)^{\delta-}]$ (P = porphyrinate).[20] However, in the absence of a co-ordinating solvent or the ligand the mechanism of electron transfer is not understood at this time.

Cobalt(II) *chlorins*. The effect of the interaction with dnbfo on the optical absorption spectrum of cobalt(II) chlorin is shown in Fig. 2. The absorption spectrum of 5,10,15,20-tetraphenylchlorinatocobalt(II) [Co(tpc)] in $CHCl_3$ is characterised by two Q-bands, a strong band at 615 nm and a weak band at 528 nm, and a Soret band at 410 nm. The changes observed upon interaction with dnbfo are (*i*) a gradual decrease in the absorbance at 615 nm, (*ii*) an increase in the intensity at 528 nm

Table 2 ESR parameters for cobalt porphyrin–dnbfo complexes and free radicals

Compound	$g_{\parallel}$	$g_{\perp}$	g_{iso} (radical)	$10^4 A_{\parallel}^{Co}$/cm^{-1}	$10^4 A_{\perp}^{Co}$/cm^{-1}	Linewidth (G)
[Co(tmop)]	2.057	3.277	—	245.0	95.0	—
[Co(tmop)] + dnbfo[a]	2.062	3.291	—	247.7	95.0	—
[Co(tmop)] + dnbfo[b]	—	—	2.0434	—	—	20.33
[Co(tpp)] + dnbfo[b]	—	—	2.0032	—	—	21.00
[Co(oep)] + dnbfo[b]	—	—	2.0042	—	—	21.89
dnbfo$^-$ [c]	—	—	2.0043	—	—	23.07

[a] Immediately after mixing. [b] After 24 h of mixing. [c] Chemically reduced anion of dnbfo.

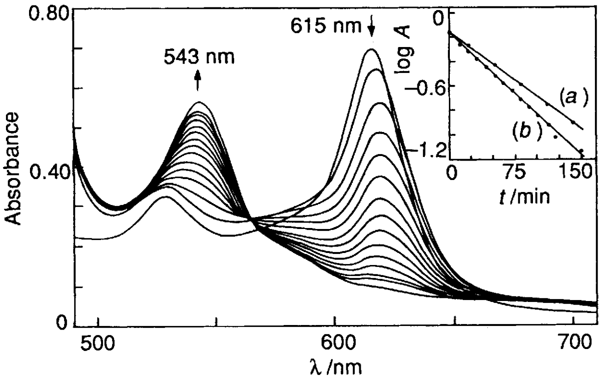

Fig. 2 Absorption changes of [Co(tpc)] (5.05×10^{-5} mol dm^{-3}) in the presence of dnbfo (3.86×10^{-3} mol dm^{-3}) in $CHCl_3$ with time (0–150 min at *ca.* 10 min intervals). The insert shows a plot of log *A vs.* time at [Co(tpc)]:dnbfo = 1:50 and 1:75 (*b*)

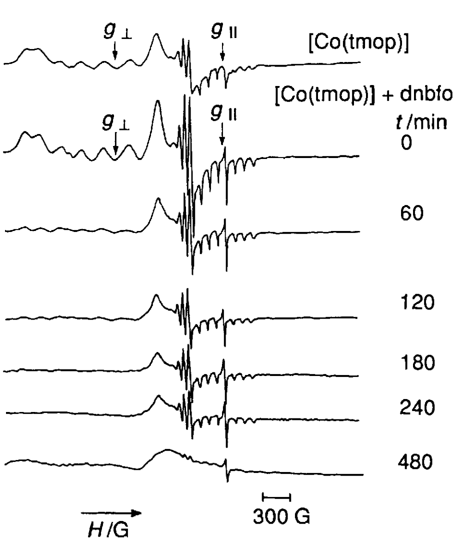

Fig. 3 ESR spectral changes of [Co(tmop)] (*ca.* 1×10^{-3} mol dm^{-3}) in the presence of excess of dnbfo with time

and (*iii*) a red shift of the band at 528 nm to 543 nm with time. These changes were monitored by use of various amounts of dnbfo since effect (*iii*) was dependent on the amount of dnbfo present in solution. When the ratio of [Co(tpc)]:dnbfo is 1:10 effects (*i*) and (*ii*) are dominant, while (*i*) and (*iii*) are dominant when the ratio is increased to 1:50 and 1:75. The intensity decrease at 615 nm and simultaneous increase in the intensity of the band at 528 nm is consistent with oxidation of the chlorin ring, [Co^{II}(tpc)] being transformed into [Co^{II}(tpp)]. A further red shift of the band at 528 nm to 543 nm reflects metal-ion oxidation from [Co^{II}(tpp)] to [Co^{III}(tpp)]$^+$. The rates of oxidation derived from a plot of the change in optical density with time (Fig. 2, insert) are 6.44×10^{-5} (1:10), 1.95×10^{-4} (1:50) and 2.43×10^{-4} s^{-1} (1:75). These values are consistent with those reported previously for similar systems.[20] It is known that the oxidation of the porphyrin ring becomes progressively easier as the macrocycle becomes more saturated since the energy of the highest-occupied π orbital increases with saturation of the porphyrin skeleton.[31] The oxidation of the chlorin ring prior to the metal oxidation in the present study is consistent with the above observation.

(*b*) *ESR Studies.*—The changes in the ESR spectrum of [Co(tmop)] with time on interaction with dnbfo are shown in Fig. 3, and parameters derived from the spectra are listed in Table 2. The changes observed immediately following mixing with dnbfo are (*i*) the spectrum becomes better resolved, (*ii*) $g_{\parallel}$ and $g_{\perp}$ values change slightly giving a small increase in magnetic anisotropy ($g_{\parallel}^2 - g_{\perp}^2$), and (*iii*) a marginal increase in the $A_{\perp}^{Co}$ value. These changes are consistent with the formation of a molecular complex.[32] However with time the eight-line pattern due to the cobalt(II) ($I = \frac{7}{2}$) complex is reduced in intensity by about 80% upon interaction with dnbfo and a weak free-radical signal in the $g = 2$ region is generated. In the presence of air there is a drastic reduction in *g* and *A* values and the ESR spectrum is typical of a cobalt(II) porphyrin–O_2 adduct.[33] Addition of dnbfo to this solution results in gradual loss of the ESR signal due to the adduct and the appearance of a weak free-radical signal in the $g = 2$ region. The radical signal is weak probably due to decomposition of the dnbfo$^-$ formed. When the solvent was changed from $CHCl_3$ to $CHCl_3$–MeOH (1:9) the ESR signal due to the cobalt(II)–O_2 adduct was lost immediately after addition of dnbfo indicating that the cobalt(II) species has been oxidised to its cobalt(III) derivative, consistent with the absorption data. To make sure that the free-radical signal observed was due to the anion radical of the acceptor, dnbfo was chemically reduced with potassium metal in 1,2-dimethoxyethane. At room temperature, the ESR signal is well resolved with 15 hyperfine lines due to two nitrogens and two protons ($a_N = 8.5$ and $a_H = 3.1$ G). However, at low temperature these lines merge to give a single broad line. The *g* values and the linewidths of the radical signals obtained with the cobalt(II) porphyrin–dnbfo complex compare well with the free-radical signal (Table 2), supporting the conclusion that the dnbfo$^-$ radical is formed. Furthermore, a cyclic voltammogram of dnbfo in CH_2Cl_2 shows one irreversible reduction wave at $E_{\frac{1}{2}} = -0.070$ V. This value compares well with those of conventional aromatic π-electron acceptors known to form molecular complexes.[34]

(*c*) *NMR Studies.*—The ^1H NMR data for the cobalt(II) porphyrins and their complexes with dnbfo are listed in Table 3. The resonances of paramagnetic cobalt(II) porphyrins are expected to be broad and shifted downfield because of the presence of the odd electron in the d_{z^2} orbital with a $^2A_1$ ground state.[32] The resonances of the oxidised product are expected to be sharp, consistent with the formation of low-spin cobalt(III) derivatives. The ^1H NMR spectrum of dnbfo in $CDCl_3$ consists of resonances centred around δ 9.15 and 8.85 corresponding to the protons H^7 and H^5, respectively. In the presence of cobalt(II) porphyrins, these resonances become broad and experience a downfield shift consistent with the formation of molecular com-

Table 3 Proton NMR chemical shifts (δ) and linewidths (Hz) of cobalt porphyrins in the presence and absence of dnbfo

	Phenyl			
Complex	*Meta*	*Ortho*	β-Pyrrole	OCH_3
[Co(tmop)]	9.43(s) (18.6)	13.07(s) (58.8)	15.96(s) (74.3)	5.25(s)(10.8)
[Co(tmop)] + dnbfo	7.19(m)	7.65(m)	9.37(s) (5.0)	3.99(s) (7.4)
[Co(tmop)] + C_5H_5N	7.17(m)	7.694(m)	9.48(s) (6.0)	4.03(s) (6.0)
[CoCl(tmop)]	7.41(d) J_{AB} = 8.5 Hz	8.17(d) J_{AB} = 8.5 Hz	9.35(s) (5.5)	4.11(s) (5.5)
[Co(tpdp)]	—	—	15.8(s) (173.4)	—
[Co(tpdp)] + dnbfo	—	—	9.39(s) (5.6)	—
[Co(tpdp)] + C_5H_5N	—	—	9.12(s) (5.6)	—
[CoCl(tpdp)] *	—	—	9.32(s) (6.2)	—
[Co(tpfp)]	—	—	15.31(s) (179.0)	—
[Co(tpfp)] + dnbfo	—	—	9.04(s) (6.0)	—

The numbers in parentheses correspond to linewidths in Hz. * In CD_3OD.

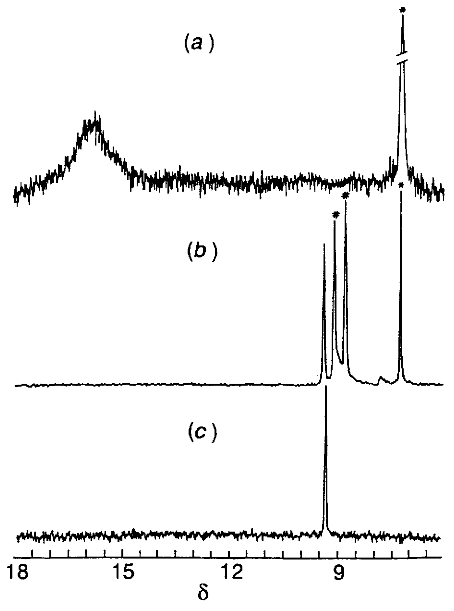

Fig. 4 Proton NMR spectra of (*a*) [Co(tpdp)], (*b*) [Co(tpdp)] containing excess of dnbfo (after 24 h of mixing) in $CDCl_3$ and (*c*) [CoCl(tpdp)] in CD_3OD (complex concentration *ca.* 1 × 10^{-3} mol dm^{-3}). The asterisk corresponds to a $CDCl_3$ signal and # to dnbfo protons (see text)

plexes.[33] From the concentration dependence of these shifts equilibrium constants have been calculated.[24] The effect of the interaction with dnbfo on the ^1H NMR resonances of 5,10,15,20-tetrakis(pentadeuteriophenyl)porphyrinatocobalt [Co(tpdp)] is shown in Fig. 4. For comparison the ^1H NMR spectrum of [CoCl(tpdp)] in CD_3OD is also included. It is apparent that the broad resonance of [Co(tpdp)] is lost upon interaction with dnbfo and is replaced by a sharp upfield resonance. The chemical shift and linewidth of the [Co(tpdp)]–dnbfo complex are in good agreement with that of [CoCl(tpdp)] consistent with the oxidation of a Co^{II} to Co^{III}. These data also compare well with those of cobalt(II) porphyrin–pyridine complexes where it is known that the presence of an axial base facilitates oxidation.[20]

The proton NMR spectrum of [Co(oep)] shows three resonances at δ 29.5 (s, 126), 8.79 (s, 35) and 6.1 (s, 22 Hz) due to *meso*-hydrogens, CH_2 protons and the CH_3 protons of the ethyl groups respectively. For the dnbfo complex all three resonances are shifted upfield to δ 9.3 (s, 7.4), 4.2 (m) and 1.93 (m) indicating oxidation. The ^1H NMR spectrum of [Co(tpc)] is characterised by a broad singlet due to pyrrole protons at δ 15.9 (117.7 Hz) while the *ortho*-hydrogens of the phenyl groups give a singlet at δ 13.07 (99 Hz). The *meta*- and *para*-hydrogens resonate at δ 9.68 (44 Hz) while the β-CH_2 of the saturated ring gives a singlet at δ 7.59 (43 Hz). The NMR spectrum was recorded as a function of time in the presence of dnbfo. After about 3 h of mixing it showed the absence of the β-CH_2 signal at δ 7.59, while after 10 h of mixing it showed a sharp singlet at δ 9.39 (6 Hz) and a multiplet centred around δ 7.6 for the phenyl protons. This is consistent with chlorin-ring oxidation followed by metal oxidation as observed from the optical absorption studies.

These conclusions are also supported by ^{19}F NMR studies on [Co(tpfp)], in the presence of dnbfo. The resonances were well resolved with the chemical shifts and coupling constants comparable to those of diamagnetic [Zn(tpfp)], indicating the formation of a diamagnetic cobalt(III) derivative.[24b]

In summary, the cobalt(II) porphyrins undergo metal-centred oxidation to cobalt(III) porphyrins in the presence of a π acceptor. The redox products have been characterised using various spectroscopic methods. The mechanism of electron transfer and the role of molecular oxygen in the electron-transfer process are not clear and further studies are in progress to clarify them.

Experimental

The porphyrins H_2tpp,[35] H_2tpdp,[36] H_2tmop [37] and H_2tbtp [38] were prepared by the literature procedures; H_2tpfp and H_2oep were obtained from Aldrich Chemicals. The cobalt(II) derivatives of all these macrocycles were prepared and purified using a reported procedure.[39] 5,10,15,20-Tetraphenylchlorin (H_2tpc) was prepared from H_2tpp using the procedure of Whitlock *et al.*[40] The purity was checked by visible absorption and NMR spectra: λ_{max}/nm(ε/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$) 651(41 × 10^3), 597(6 × 10^3), 546(11.5 × 10^3), 519.5(16 × 10^3) and 419(18 × 10^4); δ(^1H) −1.44 (2 H, s, NH), 4.16 (4 H, s, β-CH_2), 7.6–8.2 (20 H, m, phenyl) and 8.4–8.6 (6 H, m, pyrrole).

The complex [Co(tpc)] was prepared by refluxing H_2tpc (20 mg) and cobalt acetate (16 mg) in a mixture of freshly distilled dimethylformamide (10 cm^3) and acetic acid (10 cm^3) for 6 h under argon. Solvent was removed under reduced pressure and the solid residue was washed several times with water and dried. Recrystallisation from chloroform–light petroleum (1:1) afforded a pure crystalline solid (14 mg, 64% yield):[41] λ_{max}/nm(ε/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$) 615(14.07 × 10^3), 570(sh), 528(6.34 × 10^3) and 411(11.33 × 10^4).

The compound dnbfo was prepared following the procedure of Green and Row:[42] λ_{max}(CH_2Cl_2) 233, 261, 276, 333 and 422 (lit.,[42] 234, 260, 277, 330 and 420 nm).

Optical spectra were recorded on a Shimadzu UV-160 spectrophotometer, ^1H and ^{19}F NMR spectra on a JEOL FX 90 Q multinuclear spectrometer and ESR measurements on a Varian E-9 X-band spectrometer at liquid-nitrogen temperature. Cyclic voltammetric studies were made with a BAS model CV-27 polarographic analyser.

Acknowledgements

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