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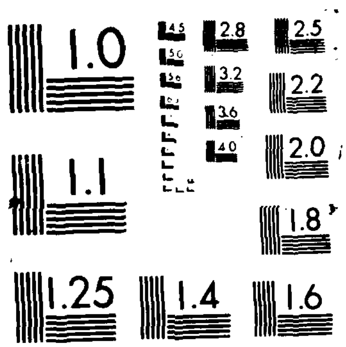
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1,8-Naphthalene Linked Cofacial Binuclear Phthalocyanines

By

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in

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Cofacial binuclear phthalocyanines linked by a three atom bridge are described, utilising the 1,8-position of the naphthalene nucleus. Electrochemical and uv/vis/nmr data are reported for the metal-free and cobalt derivatives in various oxidation states. Mixed valence cobalt species are discussed.

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1,8-Naphthalene Linked Cofacial Binuclear Phthalocyanines*

By Prof.Clifford C.Leznoff, Herman Lam, Dr.W.Andrew Nevin, Prof.Nagao Kobayashi,[+] Dr.Pavel Janda[++] and Prof.A.B.P.Lever

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Binuclear phthalocyanines covalently linked by 5[1,2], 4[3], 2[3], 1[4] and -1[5] atom bridges have been recently described. We now report new cofacial binuclear phthalocyanines 1a-d linked by a 3 atom bridge on a rigid naphthalene framework. These compounds complement 1,8-anthracene bridged porphines[6,7], and provide entry to a new class of pillared phthalocyanines. They should prove of value in the photo- or electro-activation of small molecules, such as di-oxygen, carbon or sulphur dioxide.

Treatment of 4-iodophthalonitrile (2) (4.0g, 16mmol) and 1,8-diiodonaphthalene (3) (2.0g, 5.3mmol) in a mixed coupling reaction, in the presence of elementary nickel powder under conditions described for homocoupling reactions[8,9] led to 1,8-bis(3,4-dicyanophenyl)naphthalene (4) (310mg, 15.5% yield) as a mixture of syn and anti isomers due to restricted rotation about the 1,8-positions of the naphthalene nucleus (Scheme I). Conversion of 4 (380mg, 1mmol) into its isoindoline 5 and a mixed condensation of 5 with the isoindoline 6 prepared from 4-neopentoxyphthalonitrile (6.0g, 28mmol) gave, following standard reaction conditions and chromatography[1-5] the desired 1,8-bis-2'-(9',16',23'-trineopentoxyphthalocyaninyl)naphthalene (1a) in 15.5% yield. The di-cobalt, di-copper and di-zinc derivatives (1b-d) of 1a were prepared by refluxing 1a with $CoCl_2$, $Cu(OAc)_2$ and $Zn(OAc)_2$ respectively, as previously described.[1-5]

Scheme I Synthesis of 1,8-bis-2'-(9',16',23'-trineopentoxyphthalocaninyl)-naphthalene 1a

The species 1a-d and 4 have been fully characterised.[10] The fast atom bombardment[11] (FAB) mass spectra of all the binuclear phthalocyanines 1a-d were most informative exhibiting parent ions as the base peak in the high mass region above 500 AMU. Furthermore no evidence of partially or half-metallated derivatives of **1b-d** were detected in their mass spectra. The ^{1}H nmr of **1a** exhibited the upfield shifted NH protons which were absent in the zinc derivative **1d**.

Electrochemical and spectroelectrochemical results show that the rigid geometry of the naphthalene bridge induces important changes in the cofacial dicobalt derivative **1b**, compared with previously studied mononuclear and "clamshell" binuclear cobalt phthalocyanines.[1-4,12] The halves of the molecule of **1b** do not oxidise and reduce at the same potential, resulting in clear splitting of the redox couples.

Cyclic and differential pulse voltammetry of **1b** in o-dichlorobenzene (DCB) with 0.2 M tetrabutylammonium perchlorate as supporting electrolyte revealed a series of three oxidation and four reduction waves with halfwave potentials of +0.53, +0.14, 0.00, -0.90, -1.29, -1.68, and -2.08 V vs Fc^{+}/Fc.[13,14] Comparison with the cyclic voltammogram of the mononuclear parent compound, CoTNPc, ($E_{1/2}$ = +0.59, +0.03, -0.91, and -2.07 V in DCB[12]) indicates splitting of the first oxidation (L^{+}/L), and first reduction (Co^{II}/Co^{I}) couples by 140 and 390 mV, respectively. This is the first example of clearly observed splitting of the redox waves in a ring bridged binuclear metal phthalocyanine and indicates a high degree of coupling between the halves of the molecule. Mixed valence L^{+}/L and Co(II)/Co(I) species are thus potentially available.

In contrast to **1b**, the splitting of the corresponding redox couple in the case of a so-called (-1) binuclear derivative (two phthalocyanine rings sharing a common benzene ring)[5] was less than 100mV (shoulder) in the mixed valence $Co^{II}-Co^{I}$ species. The reduction couples at -0.90 and -1.29 V were investigated by controlled potential electrolysis in an optically transparent thin layer electrode (OTTLE) cell utilising a gold minigrid or platinum mesh working electrode. Stepwise reduction across each of the couples in turn gives the spectroscopic changes shown in Fig.1. Reduction over the first wave gives a green solution, with isosbestic points occurring at 322, 348, 545, 642, 664 and 760 nm (Fig.1(a)). The spectrum is unlike any seen previously for a reduced cobalt phthalocyanine, having a Q band at 650 nm. It does however exhibit a new absorption band in the region of 450-470 nm associated with metal-to-ligand charge transfer (MLCT) in the transition $Co^{I}Pc[d(xz,yz)]$ - $\pi^{*}(1b_{1u})Pc$ of a $Co^{I}Pc$ species,[12,15,16] as well as a blue shift and increase in intensity of the Soret band.

The second reduction (Fig.1(b)) gives a yellow solution, with isosbestics at 332, 395, 566, 678 and 758 nm. The final spectrum is very similar to that of the mononuclear $Co^{I}TNPc$ species,[12] indicating that both cobalt atoms have been reduced to Co^{I}. The spectra are fully reversible by stepwise oxidation to the initial species.

Nernstian plots of the spectroelectrochemical data over each of the reductions give slopes approaching 59 mV, showing that each step involves a one-electron transfer. Thus the product of the reduction at -0.90 V must be a mixed valence species **1e**, of mainly [Co^{II}-Co^{I}] character. The intensity of the MLCT band is only 35% of that of the fully reduced [Co^{I}-Co^{I}] species, **1f** spectrum, so that some delocalisation of the added electron over the phthalocyanine ring system may be occurring. The presence of the well resolved Q band at 650 nm, rather than ca. 710nm, may also indicate extensive delocalisation throughout the molecule. A weak absorption occurs in **1e**, in the region of 800-900 nm (Fig. 1), absent from the spectra of both **1b** and **1f** and which may be an intervalence band.

The Q band region of the spectrum of **1e** mixed valence species is very different from that observed for the (-1) bridged mixed valence [Co^{II}-Co^{I}] compound,[5] which has a split Q band at 700 and 760 nm.

Neither of the species **1b** or **1f** exhibit esr absorption in DCB. Species **1e**, however, exhibits typical low spin $(d_{z^2})^1$ Co(II) esr absorption when 2-methylimidazole is added to the solution. The spectrum (g = 2.25) is very similar to that observed for the mixed valence Co(II)/Co(III) species of a cofacial dicobalt porphyrin[17] Co_2FTF_4, in the presence of N-methylimidazole.

In comparing these data with those for the corresponding cofacial binuclear dicobalt porphyrins[17-20] note that the latter also show splitting of the Co^{II}/Co^{I} couple by up to 290 mV; however, unlike the phthalocyanines, no distinct changes in the electronic spectra were observed for the mixed valence species.[19]

Electrocatalytic reduction of oxygen was examined at electrodes (glassy carbon and ordinary pyrolytic graphite) covered with adsorbed **1b**. Oxygen reduction occurred at -0.34 V vs SCE in cyclic voltammetric curves through pH 1 to pH 13, and the limiting current corresponding to two electron reduction of oxygen to hydrogen peroxide was observed in rotating disc experiments. Logarithmic analysis of the wave yielded a Tafel plot of -120 mV/decade, which corresponds to a charge-transfer coefficient of 0.5 and a one-electron transfer rate-determining step.

Figure 1. Development of the electronic spectra with time, showing the formation in DCB solution, of (a) the mixed valence [Co^{II}-Co^{I}], **1e**, and (b) the doubly reduced [Co^{I}-Co^{I}], **1f** obtained by reduction of **1b** at potentials between -0.9 and -1.2V, and -1.3 and -1.6V vs Fc^{+}/Fc, respectively.

[**1b**] = 1 x 10^{-4}M, [TBAP] = 0.3M.

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uv/vis (o-dichlorobenzene): λ_{max} = 340 (ε = 79,500), 648 (ε = 77 600) nm; correct elemental analysis (C,H,N). - **1b**: MS(FAB) m/z 1784 (100%, M^{+}+1, molecular ion cluster); ir(KBr): ν = 2950, 1610, 1100, 740 cm^{-1}; uv/vis (o-dichlorobenzene): λ_{max} = 306(ε = 141 000), 638(ε = 123 000), 674(ε = 102 000) nm. - **1c**: MS(FAB): m/z 1793.6(100%, M^{+}+1, molecular ion cluster); ir(KBr): ν = 2950, 1610, 1100, 740 cm^{-1}; uv/vis (o-dichlorobenzene): λ_{max} = 300(ε =63,100), 338 (102 000), 640(ε = 95 500), 686(ε = 93 300), - **1d**: MS(FAB): m/z 1797.6 (100%, M^{+}+1, molecular ion cluster); ^{1}H nmr (300 MHz, $CDCl_3$: δ = 1.0 -1.6 (br.,36H,CH_3), 3.3-4.3 (br., 8H, OCH_2), 7.5 - 8.5 (br., aromatic); ir(KBr): ν = 2950, 1610, 1100, 740 cm^{-1}; uv/vis (o-dichlorobenzene): λ_{max} = 298(ε = 72 400), 340(ε = 112 000), 640(ε = 107 000), 686(ε = 93 300) nm

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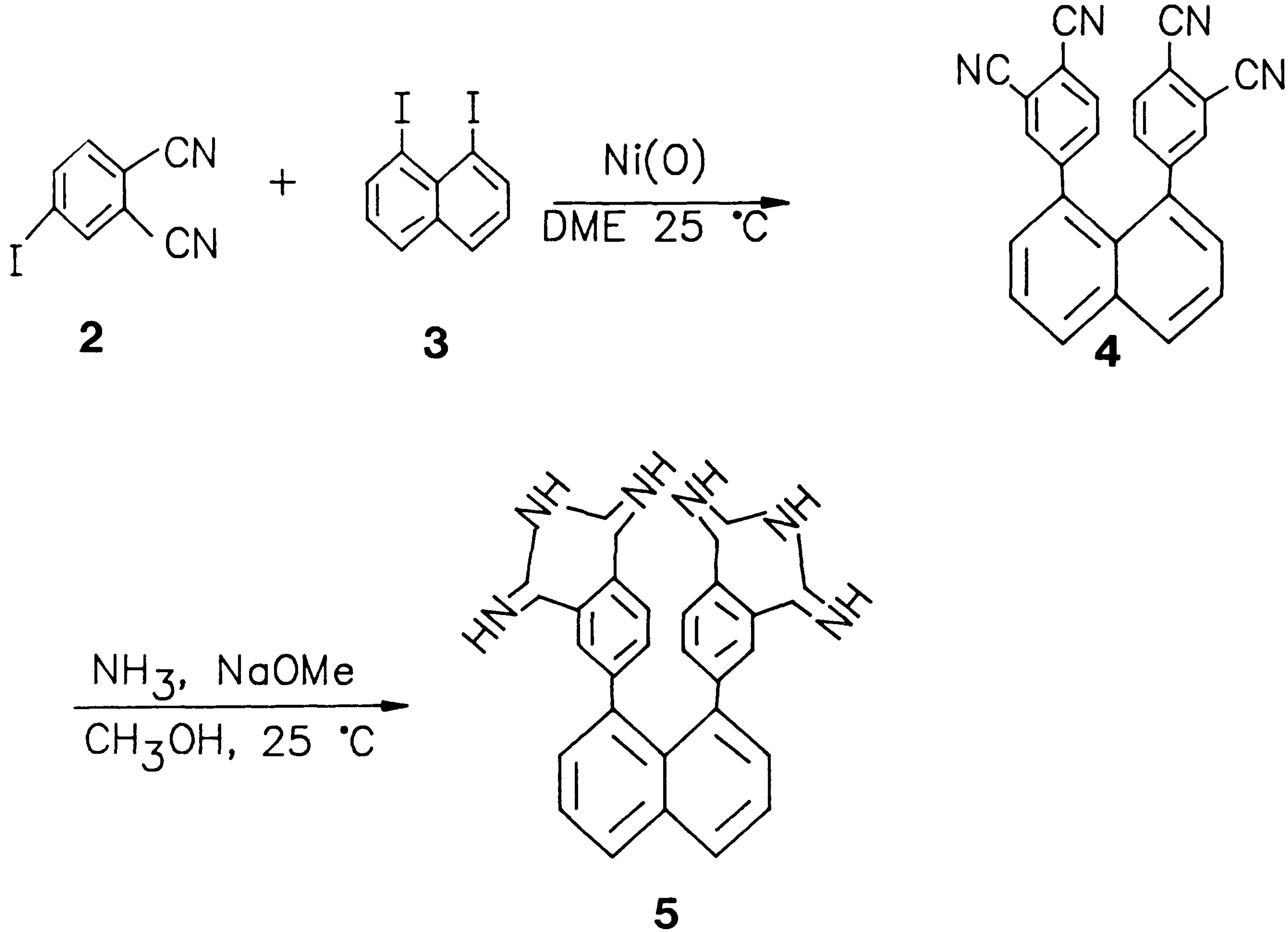
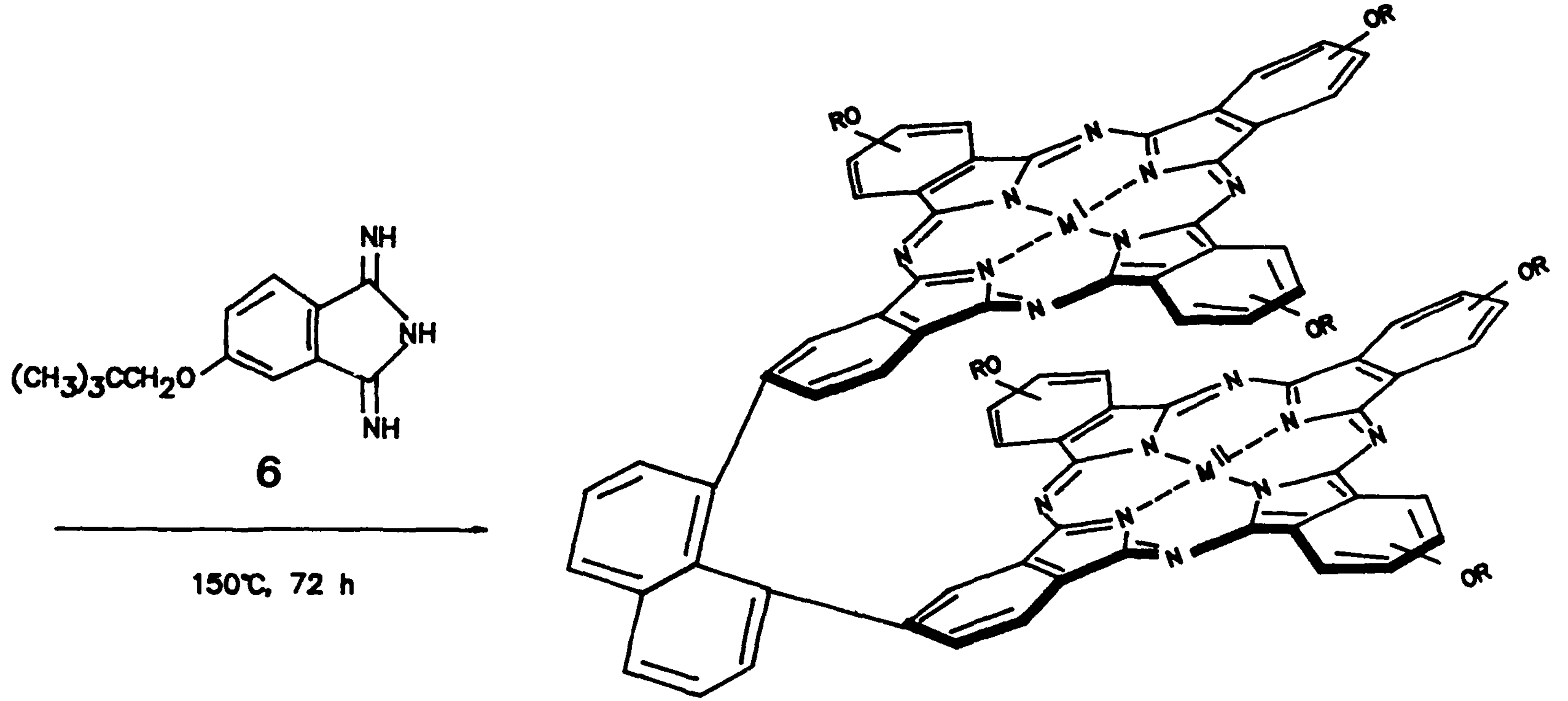

CN
CN
I
+
I I
Ni(O)
DME 25 °C
NC
CN
CN
CN
2
3
4
NH$_3$, NaOMe
CH$_3$OH, 25 °C
HN
NH
NH
NH
NH
NH
5

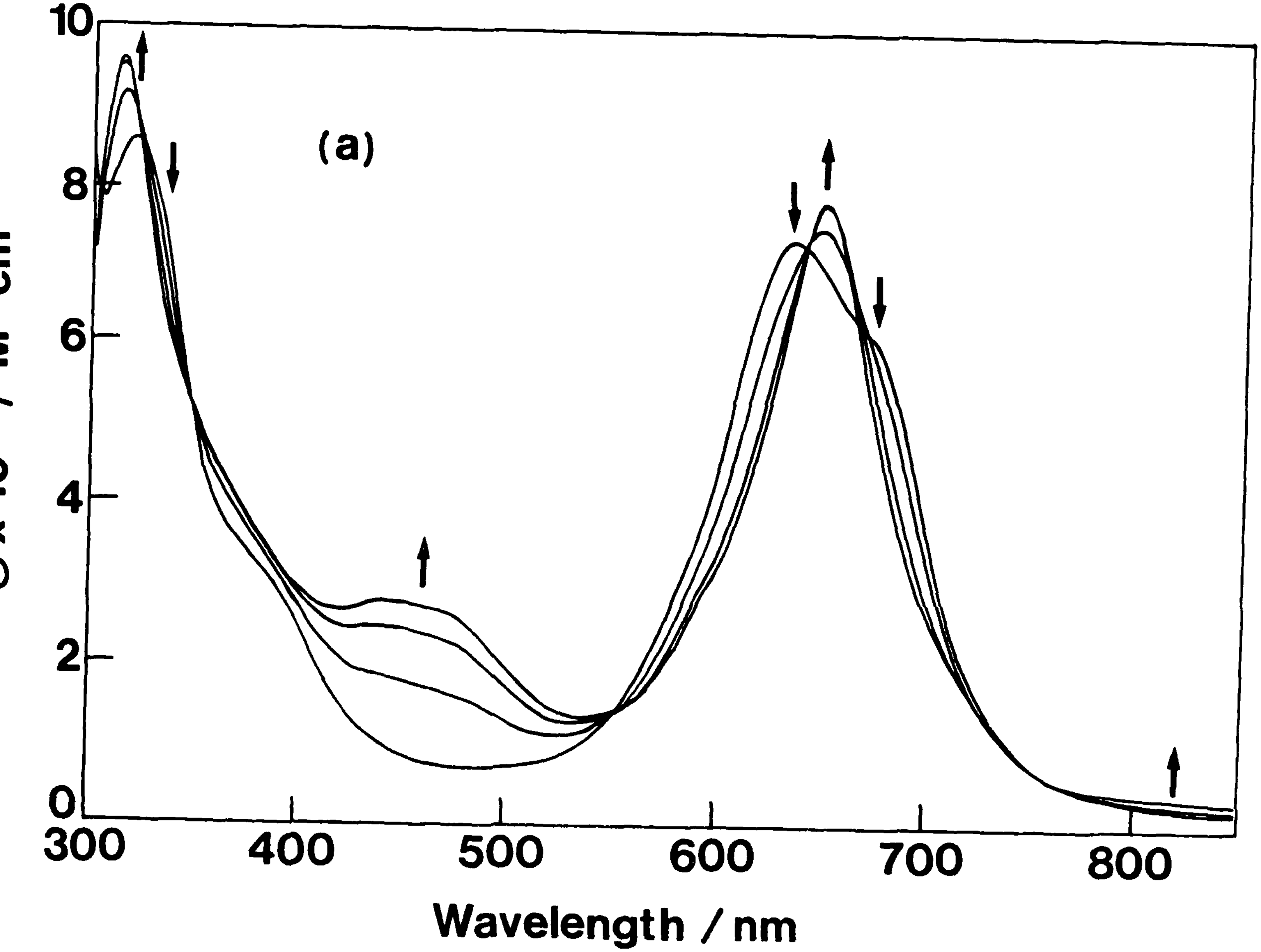
Scheme 1

PCD 3 ..

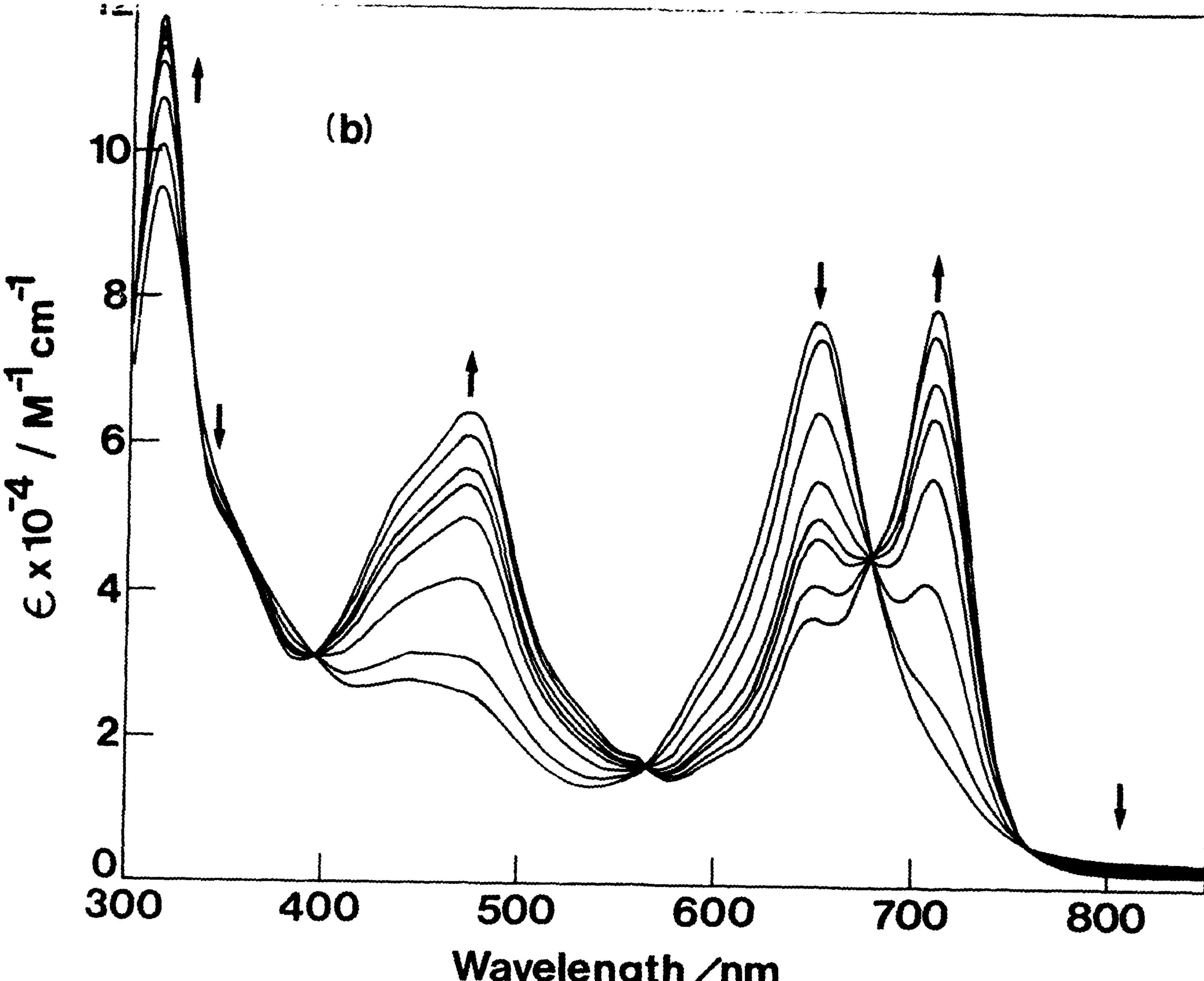


1a R = $CH_2C(CH_3)_3$, M^{I} = M^{II} = H_2
b R = $CH_2C(CH_3)_3$, M^{I} = M^{II} = Co^{II}
c R = $CH_2C(CH_3)_3$, M^{I} = M^{II} = Cu^{II}
d R = $CH_2C(CH_3)_3$, M^{I} = M^{II} = Zn^{II}
e R = $CH_2C(CH_3)_3$, M^{I} = Co^{I}, M^{II} = Co^{II}
f R = $CH_2C(CH_3)_3$, M^{I} = M^{II} = Co^{I}

scheme I



(a)
0
2
4
6
8
10
300
400
500
600
700
800
Wavelength / nm
∈ x 10⁻⁴ / M⁻¹cm⁻¹


(b)
ε x 10⁻⁴ / M⁻¹cm⁻¹
0
2
4
6
8
10
300
400
500
600
700
800
Wavelength /nm

END

12-87

DTIC