

The First Synthesis of Covalently Linked Mixed Dimer Complexes containing Phthalocyanine and Porphyrin

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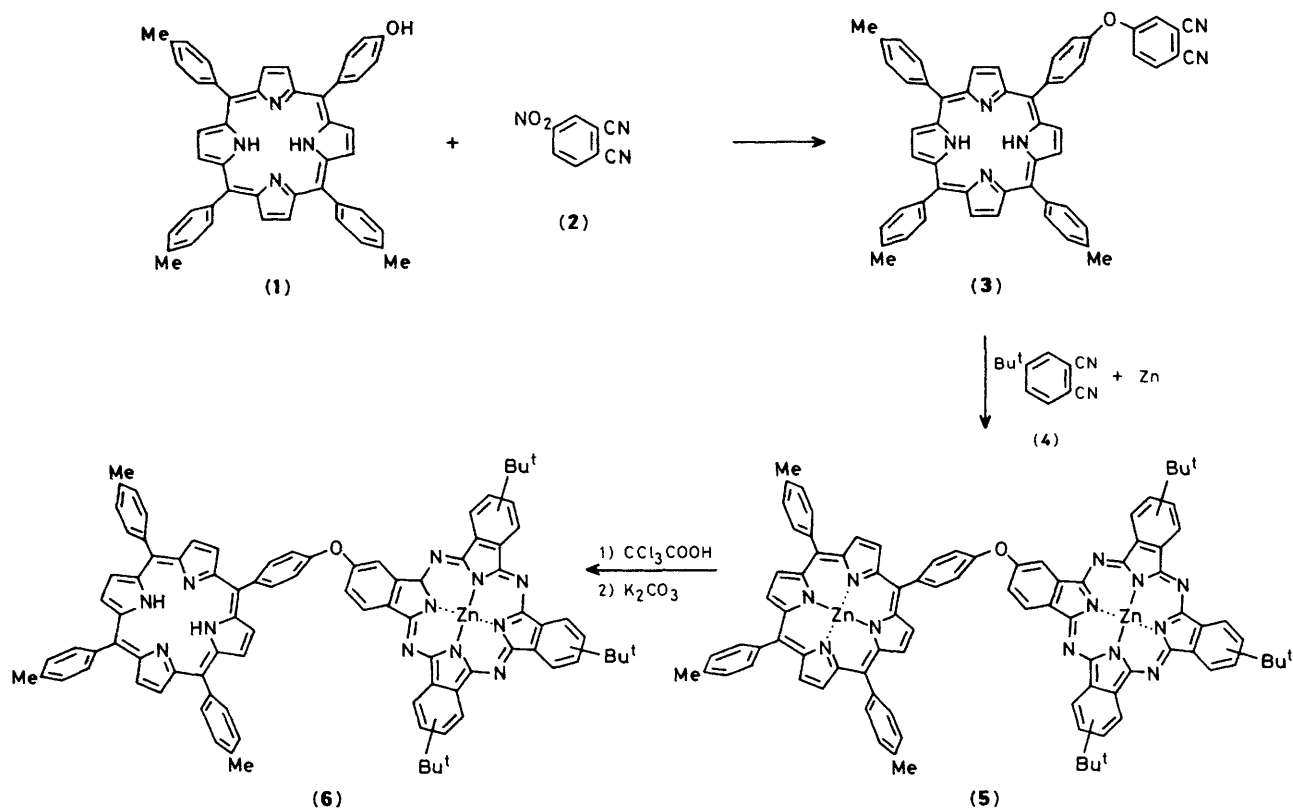
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The first synthesis of two covalently linked mixed phthalocyanine–porphyrin dimers especially designed for the study of photoelectron processes is presented along with the very efficient intramolecular energy transfer from the porphyrin toward the phthalocyanine moiety under light irradiation in one of these compounds.

Porphyrins,¹ phthalocyanines,¹ bismetalloporphyrins,^{2,3} and bismetallophthalocyanines^{4–8} have been used to investigate various biological processes such as enzymatic multielectron redox,⁹ reactions to control the energy and electron transfer of the 'special pair' in photosynthesis,¹⁰ and as molecular systems

for photochemical energy storage. The porphyrin and phthalocyanine complexes absorb respectively between 400–600 and 600–700 nm. A mixed system of both macrocycles should absorb over a large part of the solar spectrum.

As part of our continuing interest in the studies of the



Scheme 1

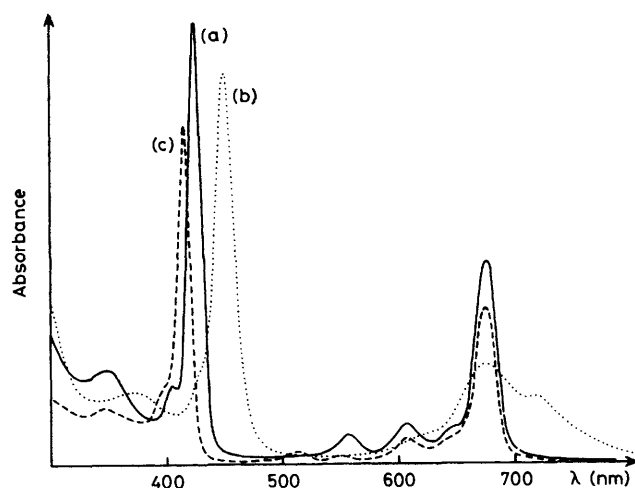


Figure 1. U.v.-visible spectra in toluene of: (a) (5), (b) (5) in acid medium, (c) (6) after neutralisation.

photochemistry of porphyrin dimers^{11,12} and phthalocyanines,¹³ we report here the synthesis of two covalently linked mixed dimers of porphyrin and phthalocyanine easily obtained by coupling of a meso-tetra-arylporphyrin substituted by a phthalonitrile group and *t*-butylphthalonitrile in the presence of zinc powder as a reducer. Furthermore this reaction offered a short general route to this new type of mixed dimeric compound.

The reaction of 5-(4-hydroxyphenyl)-10,15,20-tritolylporphyrin (1)¹⁴ with 4-nitrophthalonitrile (2)¹⁵ gave quantitatively 5-[4-(3,4-dicyanophenoxy)phenyl]-10,15,20-tritolylporphyrin (3)[†] (Scheme 1). Condensation of compound (3) and an excess of 4-*t*-butylphthalonitrile (4) with zinc powder at 213 °C for 4 hours gave the zinc mixed dimer complex (5) and a large amount of zinc tetra-*t*-butylphthalocyanine. The reaction mixture was washed with hot water, dried, and chromatographed on a silica gel column. Elution with toluene then a mixture of toluene and acetone gave three bands. The less polar compound was assigned as the zinc complex of porphyrin (3) (pink band), the second blue band was the zinc tetra-*t*-butylphthalocyanine, and the third green band was the dimer (5). This last compound was purified by preparative h.p.l.c.‡ Zinc was removed from the porphyrin moiety by treatment of the dimer (5) in toluene with an aqueous solution of dilute trichloroacetic acid (10%). The

† Spectroscopic data: i.r. (CHCl₃) ν(CN) 2220 cm⁻¹; u.v.-visible λ_{max} (nm), (ε dm³ mol⁻¹ cm⁻¹) in toluene: 420 (374 000), 515 (19 000), 550 (12 000), 592 (8 000), 648 (7 000); ¹H n.m.r. (100 MHz, CDCl₃) δ 8.85 (2H, d, H pyrrole), 8.80 (4H, s, H pyrrole), 8.75 (2H, d, H pyrrole), 8.22 (2H, d, H phenoxy), 8.05 (6H, d, H tolyl), 7.80 (1H, d, H phthalonitrile), 7.60 (1H, s, H phthalonitrile), 7.50 (7H, d, 6H tolyl + 1H phthalonitrile), 7.39 (2H, d, H phenoxy), 2.63 (9H, s, H tolyl), -2.84 (2H, s, NH).

‡ H.p.l.c. conditions: column Bondapack C18 (10 m), solvent mixture: toluene:acetone 100:1 (v/v), retention time: 3 min 40 s.

U.v.-visible λ_{max} (nm), (ε dm³ mol⁻¹ cm⁻¹) in toluene: 349 (74 000), 424 (398 000), 557 (20 000), 607 (34 000), 673 (189 000).

resulting compound (6) was then obtained by neutralization (10% aqueous K_2CO_3). This process can be monitored by u.v.-visible spectroscopy (Figure 1). Compounds (5) and (6) were identified by their fast atom bombardment (f.a.b.) mass spectra.¹⁶ Their molecular ions were observed at m/z 1480.5 (calculated 1480.3) and m/z 1417.8 (calculated 1417.0) respectively for compounds (5) and (6).

The electronic spectra in toluene of the two compounds (5) and (6) are very similar to those of an equimolar mixture of zinc complex or free base of tetratolylporphyrin and zinc tetra(t-butyl)phthalocyanine, indicating the lack of a strong intramolecular ground-state phthalocyanine-porphyrin interaction \ddagger (Figure 1).

Preliminary results on photolysis showed a very efficient intramolecular energy transfer from the zinc porphyrin ring to the zinc phthalocyanine chromophore in complex (5). The zinc porphyrin fluorescence at 600 and 644 nm was totally quenched whereas an enhanced fluorescence of the zinc phthalocyanine chromophore was observed at 690 nm. This behaviour was different to the fluorescence of an equimolar mixture of compound (3) and zinc tetra(t-butyl)phthalocyanine. Irradiation at 420 and (or) 680 nm of an aerated toluene solution of compound (5) results in the formation of singlet oxygen by intermolecular energy transfer.¹¹

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