The Synthesis of Unsymmetrically Functionalized Platinum and Zinc Phthalocyanine Complexes

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The synthesis of platinum and zinc phthalocyanine complexes bearing three crown-ether macrocycles and one hexanoyloxy acid side-chain are described; such compounds can be used for the functionalization of polymeric chains or metal oxide surfaces. The detection of alkali- or alkaline-earth cations may then be envisaged.

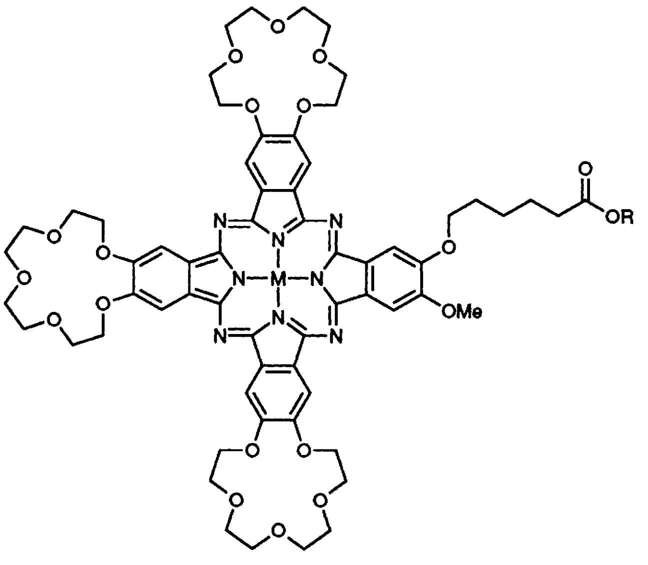
Metallo-organic complexes in which the chromophore is substituted with functional groups have been already described in the literature.[1–3] In this publication the synthesis of new phthalocyanine complexes is reported which possess a strong absorption band in the region 620–670 nm and a strongly shifted luminescence band relative to the absorption band (λ_{abs} + 300 nm). Furthermore the lifetime of the excited states (≈4 μs) of the newly prepared species should enable time-resolved luminescence experiments to be feasible.

In these dyes (Fig. 1) the chromophore is functionalized with a hexanoyloxy acid side-chain which should enable linking to various other moieties, while the crown-ether functionalities lead to increase in solubility in polar media in the presence of metal ions.

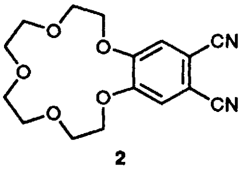
Symmetrically substituted crown-ether phthalocyanines have already been described in the literature.[4–6] Unsymmetrically substituted phthalocyanines have been the object of only a few publications.[7–12]

The new compounds **1** were obtained by reaction of benzo-15-crown-5 phthalonitrile **2**[13] and **3** in the presence of the appropriate metal salt.

Precursor **3** was obtained starting from commercially available 2-methoxyphenol and 6-bromohexanoic acid. This latter was first activated by conversion into the corresponding acid chloride which was treated with MeOH to yield the methyl ester derivative. 2-Methoxyphenol was reacted with Br_2 and protected with a benzyl group prior to treatment with CuCN to yield the corresponding dinitrile. After deprotection, the dinitrile was reacted with 6-bromomethylhexanoate to give **3**. The overall yield was of the order of 20%. All physico-chemical determinations (microanalysis, ^1H NMR, ^{13}C NMR, IR) were in agreement with the proposed structure.†



	M	R
1a	Zn	C_6H_{13}
1b	Zn	C_5H_{11}
1c	Zn	H
1d	Pt	C_6H_{13}
1e	Pt	Me



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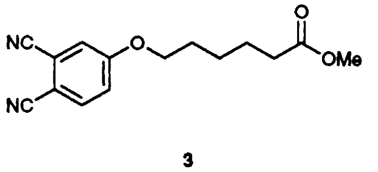

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The unsymmetrical zinc complex **1a** was obtained from the reaction of the phthalonitriles **2** (3 mmol) and **3** (1 mmol) in hexan-l-ol (10 ml) under reflux in the presence of a strong organic base [1,8-diazabicyclo[5.4.0]undec-7-ene, DBU (3 mmol)] and $ZnCl_2$ (1 mmol). During this reaction, trans-esterification occurs and the hexyl ester derivatives are formed. The derivatives with 0, 1, 2 or 3 ester groups were precipitated from the reaction medium with acetone, filtered off, and passed through an alumina plug [eluent $CHCl_3$–MeOH (9:1)] to eliminate the degradation products (yield 50% for the mixture of the products). The monoester phthalocyanine was purified from this mixture by preparative TLC [SiO_2; eluent CH_2Cl_2–MeOH–AcOH–H_2O (78:15:5:2)] followed by several precipitations with acetone of dichloromethane solutions of the product (yield: 25%). Identification is carried out by FAB mass spectrometry on the ester and on the corresponding acid **1c** after hydrolysis.‡ On the TLC plate, the following derivatives can also be detected: $R_f = 0$, degradation products; $R_f = 0.2$, tetra(crown ether) derivative; $R_f = 0.5$, **1a**; $R_f = 1$, mixture of other products. The *n*-pentyl derivative **1b** was obtained by use of pentan-1-ol in place of hexan-1-ol.

The platinum derivative **1d** was obtained in the same way; however the phthalonitriles were first converted into the corresponding diiminoisoindoline derivatives. The reaction is then carried out in hexan-1-ol in the absence of DBU, with $[PtCl_2(DMSO)_2]$ (1 mmol) and ammonia as previously described for symmetrically substituted aliphatic derivatives.[14] The purity of the *n*-hexyl ester and of the methyl ester **1e** (obtained by hydrolysis of **1d**, and subsequent reaction with methanol) has been checked by mass spectrometry and elemental analysis.§

Luminescence measurements have been carried out on the platinum and zinc phthalocyanine complexes. The zinc derivatives show a strong fluorescence (λ_{max} = 687 nm) comparable to that already described for related compounds.[15] The platinum complexes, owing to strong spin-orbit coupling, show only an emission peak around 965 nm with no detectable fluorescence.

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Footnotes

† Compound **2**: GC-MS M^+ = 302 (302.2); ^1H NMR ($CDCl_3$) 7.17 (s, 2H), 4.06 (t, 2H), 3.93 (s, 3H), 3.67 (s, 3H), 2.33 (t, 2H); IR (KBr disc, ν_{max}/cm^{-1}) 2229 (CN), 1728 (CO ester).

‡ FAB MS: **1a**, $M^+ = 1390.5$ (1391); **1b**, $M^+ = 1374$ (1377), **1c**, $M^+ = 1307$ (1306).

§ FAB MS: **1d**, $M^+ = 1521.54$ (1521); **1e**, $M^+ = 1451.46$ (1451).

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