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Synthesis and characterization of homo-dimetallic ferrocendiynyl-bridged bis(ethenylphthalocyaninato complexes)

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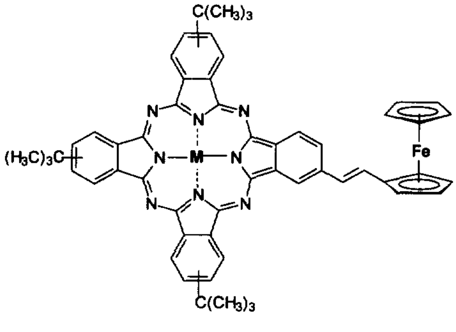
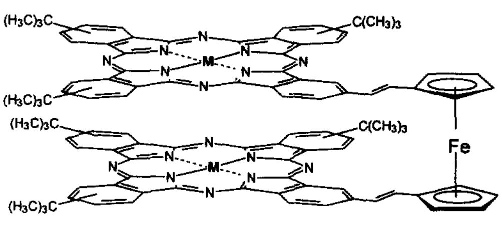
Abstract: Conjugated phthalocyanine-ferrocene systems **1** and **2** have been prepared. Homo-dimetallic ferrocendiynyl-bridged bismetallophthalocyanines **2** show a stacked conformation of the macrocycles in solution.

Phthalocyanines (Pcs)[1] have been a topic of increasing research interest due to their potential applicability in a variety of technological fields such as semiconductors,[2] nonlinear optics,[3] electrochromic display devices and liquid crystals, among others. Their chemical versatility and stability allow the tailoring of their physico-chemical parameters over a broad range. The intense color and rich redox properties of these compounds[4] are the basis of many of these applications.

The combination of two redox-active moieties, such as ferrocene and porphyrin, into one entity has been extensively studied in recent years.[5] Thus, dimeric porphyrins have attracted attention as models for electron transfer.[6] Despite the interest of this area, very few examples of mononuclear phthalocyanines covalently linked to one or more ferrocene moieties have been described.[7] However, binuclear phthalocyanine systems in which the macrocycles are bound together through a ferrocene subunit have not been reported so far.[8]



1a M = Zn
1b M = Co



2a M = Zn
2b M = Co

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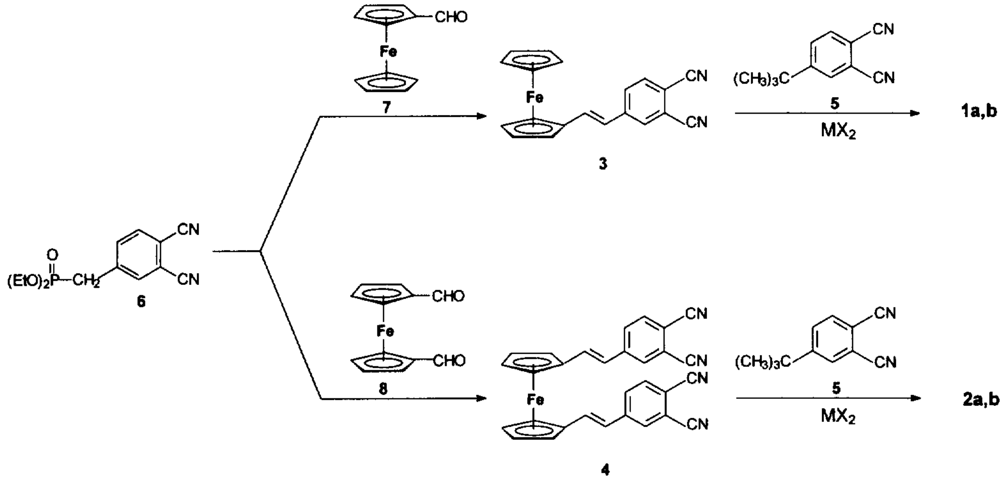
In the present paper, following our interest in phthalocyanine derivatives,[8,9] we describe for the first time homo-dimetallic ferrocendiynyl-bridged bisphthalocyaninato complexes **2** and conjugated Pc-ferrocene diads **1**. In the first case, the interplanar distance (*ca.* 3.3 Å) between the two cyclopentadiynyl rings and the rigid, stereochemically well defined, π-conjugated linkers between the ferrocene and the Pc-subunits provide an excellent situation for the cofacial stacking of the metallomacrocycles, thus allowing potential electronic, magnetic and photonic-based cooperation between the individual subunits of phthalocyanine.

The synthetic routes leading to ferrocene-functionalized metallophthalocyanines **1** and **2** are depicted in Scheme 1, and are based on the statistical condensation reaction between appropriately ferrocenyl substituted phthalonitriles **3** and **4** and phthalonitrile **5**.



Scheme 1

Compound **3** was prepared in 61% yield from 3,4-dicyanobenzylphosphonate **6**[10] and formylferrocene **7** under Wittig-Horner conditions (potassium *tert*-butoxide, toluene, 20h, Ar). The coupling constants (J = 16.2 Hz) for the olefinic protons (δ 7.13, 6.63), in the ^{1}H-NMR spectrum, enable unambiguous assignment of the *trans*-isomer. Treatment of **3** with *tert*-butylphthalonitrile **5** in a 1:4.5 ratio in the presence of the appropriate metal(II) salt (MX_2: anhydrous zinc chloride or cobalt chloride hexahydrate) using *N,N*-dimethylaminoethanol (DMAE) as solvent (145°C, 12 h) afforded the corresponding zinc or cobalt phthalocyaninates **1a,b** in *ca.* 25% yield, as a mixture of regioisomers, after separation by column chromatography on silica gel (dichloromethane-isopropanol 1:1).

In a similar way to that described above for the preparation of **3**, a mixture of the corresponding *cis-cis, cis-trans* and *trans-trans* isomers of **4** was obtained in 42 % yield, from **6** and 1,1′-diformylferrocene **7**,[11] using a 2.2:1 molar ratio of the reagents. The mixture of isomers of **4** was easily isomerized to ***(E,E)*-4** (iodine, toluene, reflux, 7 h, 90%). The preparation of *(E,E)*-**4** could be improved by using longer reaction times (60 h) and tetrahydrofuran as solvent. In these conditions, only the *trans-trans* isomer was obtained in 52% yield. The ^{1}H-NMR spectrum of **4** shows an AB system centered at *ca.* 6.8 ppm with coupling constant values between the olefinic protons of 16.2 Hz, and only two triplets corresponding to the H_α and H_β protons of the ferrocene subunit. The assignment of the ^{1}H and ^{13}C-NMR signals of the dicyano compound **4** was made on the basis of two-dimensional NMR experiments (HMQC).

The synthesis of compounds **2a,b** was carried out in a similar way as that of monomeric phthalocyanines **1a,b**, by statistical condensation of phthalonitriles **4** and **5** in the presence of the corresponding metallic salt. The mixture of products obtained was separated by chromatography on silica gel using hexane-tetrahydrofuran mixtures of increasing polarity, affording the corresponding bisphthalocyaninato in *ca.* 8% yield. It is noteworthy that compounds **1b** and **2b** (cobalt derivatives) are very sensitive to light exposure, especially in solution.

The UV-vis spectrum of compound **1a** in chloroform (Figure 1) shows a single Q-band at 691 nm, characteristic of monomeric metallophthalocyanines. Splitting of this band, usual for other unsymmetrically substituted alkenyl phthalocyanines[10] does not take place, even though compound **1a** is a mixture of several regioisomers. The electronic spectrum of the zinc dimer **2a** is depicted in Figure 1. The optical features of this compound differ remarkably from those of **1a**. The B-band is slightly shifted to shorter wavelength, whereas the Q-band is also blue-shifted and split in two main absorptions at 649 and 679 nm. The intensity of these bands is much lower than the Q-band of compound **1a**. This fact can be attributed to the cofacial arrangement of the two rings. It is well known that aggregation in phthalocyanines gives rise to effects in the UV-visible spectra similar to the one described above.[12] On the other hand aggregation phenomena in related Pc dimers have been already reported.[13] In our case the nature of Pc-Pc interaction is intramolecular rather than intermolecular since it is not affected by using different concentrations (10^{-5}-10^{-6} M). ^{1}H-NMR is not very informative because of the broadening of the signals of the aromatic protons of **2a**, which is actually a mixture of several isomers. A similar behaviour has been shown by compounds **1b** and **2b**. For this reason the same conclusions drafted above for compounds **1a** and **2a** can be applied to them.[14]

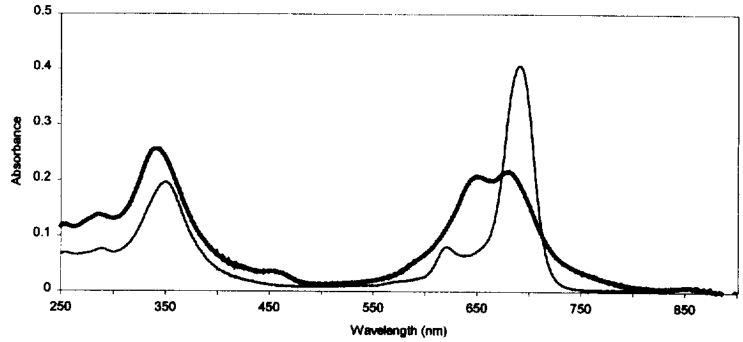


Figure 1: UV-visible spectra of phthalocyanines **1a** (thin line) and **2a** (bold line) in chloroform solution

In summary, conjugated phthalocyanine-ferrocene systems **1** and **2** have been prepared for the first time. Dimeric phthalocyanines are of interest as models for the study of electron and energy transfer, as well as electrochemically promoted switching processes.

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14. Selected spectroscopy data.

    1a: ^{1}H-NMR (300 MHz, CDCl$_3$) δ 8.8-7.8 (br. signals, aromatic and olefinic-H), 4.7 (2xm, H-2', H-5' ferrocene), 4.5 (2xm, H-3', H-4' ferrocene), 4.3 (5xs, Cp), 1.9-1.7 (27xm, C(CH$_3$)$_3$); FAB-MS (*m-NBA*) m/z 955 [(M+H)$^+$]; UV/vis (CHCl$_3$) (log ε/ dm^3 mol^{-1} cm^{-1}) λ_{max} 350 (4.97), 621 (4.59), 691 (5.29) nm; IR (KBr) ν 2955, 1608 (C=N, C=C), 1489, 1090. **1b**: FAB-MS (*m-NBA*) m/z 950 [(M+H)$^+$]; UV/vis (CHCl$_3$) (log ε/ dm^3 mol^{-1} cm^{-1}) λ_{max} 289 (4.86), 331 (4.97), 615 (4.60), 681 (5.18) nm; IR (KBr) ν 2953, 1609 (C=N, C=C), 1256, 1093. **2a**: FAB-MS (*m-NBA*) m/z 1727-1723 [(M+H)$^+$]; UV/vis (CHCl$_3$) (log ε/ dm^3 mol^{-1} cm^{-1}) λ_{max} 341 (5.00), 649 (4.92), 679 (4.93) nm; IR (KBr) ν 2955, 1604 (C=N, C=C), 1091. **2b**: FAB-MS (*m-NBA*) m/z 1713 [(M+H)$^+$]; UV/vis (CHCl$_3$) (log ε/ dm^3 mol^{-1} cm^{-1}) λ_{max} 292 (4.59), 325 (4.56), 643 (4.42), 672 (4.48). IR (KBr) ν 2962, 1261,1093. **3**: ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.80 (d, 1H, ArH$_2''$, J = 1.8 Hz), 7.71 (d, 1H, ArH$_5''$, J = 8.1 Hz), 7.67 (dd, 1H, ArH$_6''$, J = 1.8 Hz, 8.1 Hz), 7.13 (d, 1H, $J_{A\text{-}B}$ = 16.2 Hz,), 6.63 (d, 1H, J = 16.2 Hz,), 4.51 (t, 2H, J = 1.6 Hz, H-2, H-5, CpH), 4.42 (t, 2H, J = 1.6 Hz, H-3, H-4, CpH), 4,17 (s, 5H, CpH). EI-MS (%) m/z 338 (M$^+$, 100); IR (KBr) ν 2225 (C≡N), 1630, 1585, 1228, 817. **4**: ^{1}H-NMR (300 MHz, acetone-d_6) δ 8.14 (d, 2H, ArH$_2'''$, J = 1.8 Hz), 7.77 (d, 2H, ArH$_5'''$, J = 8.2 Hz), 7.64 (dd, 2H, ArH$_6'''$, J = 1.8 Hz, 8.2 Hz), 7.08 (d, 2H, $J_{A\text{-}B}$ = 16.2 Hz,), 6.65 (d, 2H, $J_{A\text{-}B}$ = 16.2 Hz,), 4.66 (t, 4H, J = 1.8 Hz, H-2, H-5, H-2', H-5', CpH), 4.46 (t, 4H, J = 1.8 Hz, H-3, H-4, H-3', H-4',Cp). FAB-MS (*m-NBA*) m/z 490 [(M+H)$^+$]; IR (KBr) ν 2232 (C≡N), 1635, 1590.