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(18-CROWN-6)-LINKED BINUCLEAR PHTHALOCYANINES

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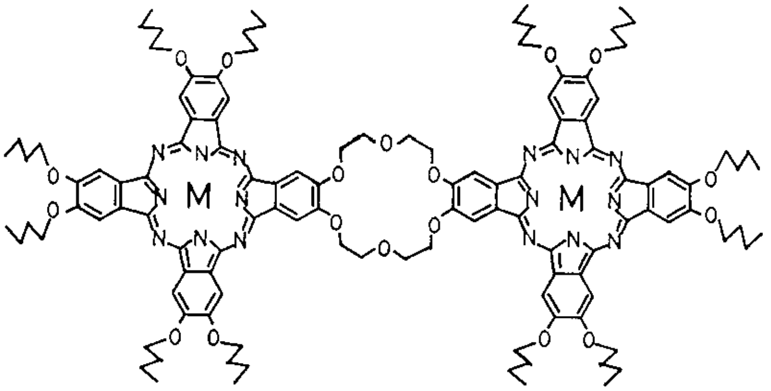
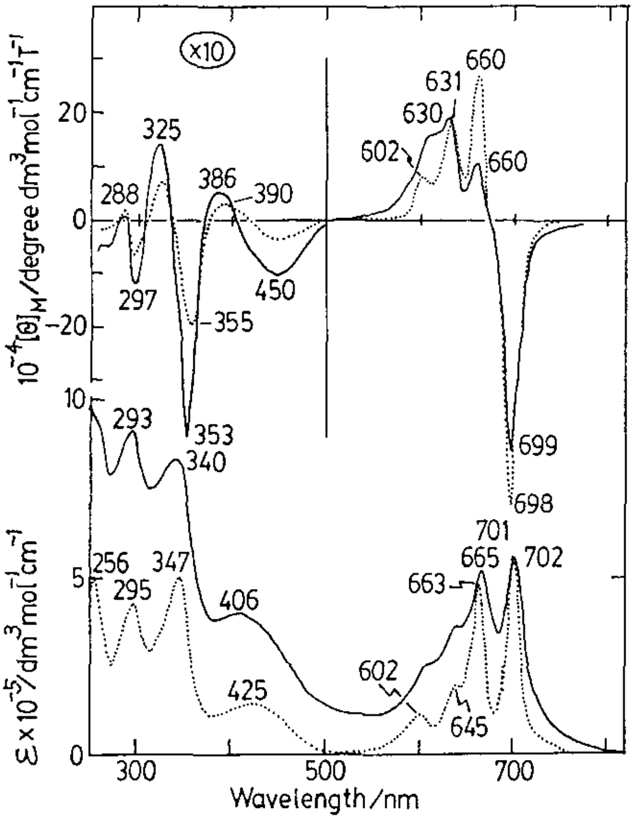
Abstract —— (18-Crown-6)-linked binuclear phthalocyanines have been synthesized and their electronic absorption and magnetic circular dichroism spectra have been recorded. Neither alkaline nor alkaline earth metals have affected the spectra.

Binuclear phthalocyanines covalently linked by five,[1,2] four,[3] two,[3] one,[4] zero,[5] and "-1"[6] atom bridges have been recently described, in addition to cofacial binuclear phthalocyanines.[5,7] We now report new relatively planar binuclear phthalocyanines, i.e. (18-crown-6)-linked phthalocyanines shown below. These compounds can be regarded as intermediate compounds between "-1" phthalocyanines and other binuclear phthalocyanines from the standpoint of constraints of bridges between two phthalocyanine units. That is to say, two phthalocyanine units in "-1" phthalocyanines do not rotate because of their rigid structure, while those in phthalocyanine binuclears linked by single alkyl bonding can take various conformations. (18-Crown-6)-linked phthalocyanines are not rigid as "-1" phthalocyanines, but still have some flexibility especially in the plane connecting two phthalocyanine units.



$M = H_2$; H_4CrBPc
$M = Cu$; Cu_2CrBPc

One hundred mg (2.174×10^{-4} mol) of 4',5',4",5"-tetracyano-2,3,11,12-dibenzo-1,4,7,-10,13,16-hexaoxacyclooctadeca-2,11-diene (so called tetracyanodibenzo-18-crown-6)[8] and 2.0 g (7.353 x 10^{-3} mol) of 1,2-dibutoxy-4,5-dicyanobenzene[9)] were refluxed in dry 2-N,N-dimethylaminoethanol[10)] (10 ml) under stream of ammonia gas for 8 hours. After cooling, methanol was added, and the precipitate was filtered and washed thoroughly with methanol. The residue was imposed on an alumina column (act. III) using chloroform as eluant. The first dark band was non-metallated mononuclear 2,3,9,10,-16,17,23,24-octabutoxyphthalocyanine (H_2OBPc).[11)] Elution of the second band with chloroform-ethanol mixtures provided a small green band enriched with the aiming binuclear. This layer was further purified using Bio-beads SX-2 column and methylene chloride as eluant to give 30 mg (6.6% yield) of the product as a very dark blue shining solid. Anal. found: C 68.15, H 7.01, N 10.49%; calcd for $C_{120}H_{144}N_{16}O_{18}$: C 68.68, H 6.92, N 10.68%. Ms m/z: *2098*(M^+*+1, 100*), *2097*(M^+*, 70*); *ir*(*KBr*,cm^{-1}): *3300*(*NH*), *1620*, 1240, 1100, 1010(NH); ^{1}H nmr($CDCl_3$): δ 8.56(br s,16H), 0.5-5(m,124H), -3.43(br s,4H). Figure 1 demonstrates the uv-visible absorption and magnetic circular dichroism (MCD) spectra of mononuclear control molecule, H_2OBPc, and binuclear H_4CrBPc. The positions of electronic absorption peaks do not differ markedly between H_2OBPc and H_4CrBPc, however, intensity (absorption coefficient) differs significantly. Generally, the absorption coefficients in the Q band of pure mononuclear phthalocyanines are intensier than those in the Soret region.[12)] Just opposite relationship is observed for binuclear H_4-CrBPc. In addition, four Q band peaks of H_4CrBPc are not as sharp as those of H_2OBPc, suggesting the existence of long-range (through space) interactions between the two chlomophores. Broad bands at



Figire 1. Electronic absorption (bottom) and MCD (top) spectra for H_4CrBPc (solid lines) and H_2OBPc (dotted lines) in chloroform. [H_4CrBPc]/M = 1.21 x 10^{-5} and [H_2-OBPc]/M = 2.10 x 10^{-5}. Optical path/cm = 1.0. Magnetic field/T = 1.09.

ca. 380-500 nm are unusual[12)] for phthalocyanines, but discernible easily in phthalocyanines having alkoxy substituent groups[1-7)] and become prominent with the increase of alkoxy groups.[13)] Thus, these bands may be associated with the ether oxygen lone pairs. MCD spectra are also interpretable as those of non-metallated phthalocyanines. Since there is no degenerate excited state, zig-zag patterns are produced as superimposition of Faraday B-terms.[12)]

Figure 2 is the spectra for Cu_2CrBPc.[14)] By the introduction of metals into phthalocyanine core, its symmetry is heightened from D_{2h} to D_{4h}. Both the absorption and MCD spectra reflect this change. Four Q band peaks in H_4CrBPc reduce into two peaks and two dispersion type MCD curves (Faraday A terms) are observed in both the Q and Soret region. However, as for H_4CrBPc, the Soret band is intensier than the Q band. Since the shape of the absorption spectrum does not change even in highly dilute solutions (ca. 10^{-7} M), long-range intramolecular coupling of two phthalocyanine units is again suggested. This figure contains also the absorption spectra in chloroform-ethanol mixtures. As have been seen for several phthalocyanine systems,[15)] phthalocyanines are prone to aggregate in polar solvents. Extent of aggregation (in general that of card-packed fashion) has been judged by the intensity of "aggregated Q band peak"[15)] which appears at shorter wavelength of Q_{0-0} absorption of monomeric phthalocyanines. The lack of such a peak in ethanol-rich systems indicates the absence of such aggregation.

Since one of the notable fucntion of the crown ether family is a cation binding ability,[16)] the effect of several cations on the electronic absorption spectra of H_4- and Cu_2CrBPc have been examined in chloroform. However, Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} have not affected the spectra. Two phthalo-

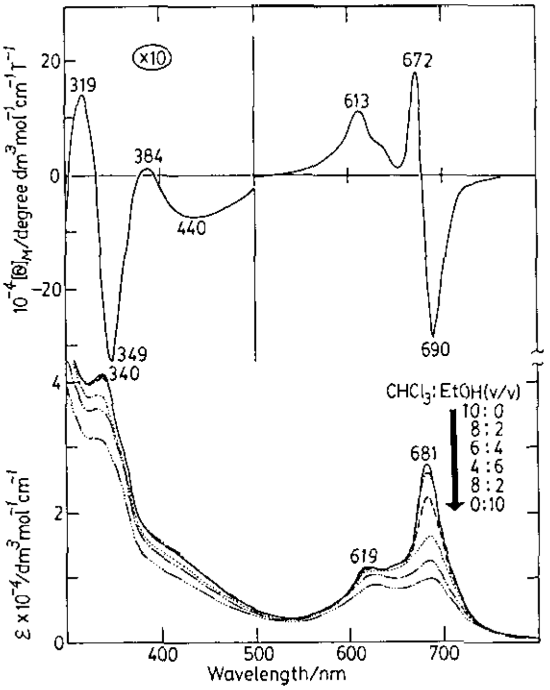


Figure 2. Electronic absorption (bottom) and MCD (top) spectra for Cu_2CrBPc in chloroform-ethanol mixtures or in chloroform. $[Cu_2CrBPc]/M = 2.78 \times 10^{-5}$. Optical path/cm = 1.0. Magnetic field/T = 1.09.

cyanine moieties in these binuclears may be too large for these cations to affect the spectra.

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