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Peripherally tetra-palladated phthalocyanines

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Abstract

Phthalocyanines (M = Co, Zn or 2H) with four ({4-[(Z or E)-phenylazo]-1-naphthyl}oxy) substituents on the periphery have been synthesized to enlarge the absorbing range of the dyestuffs. Cyclopalladation of the azobenzene groups lead to network-type oligomeric products by formation of binuclear palladium (II) complexes and they have been further converted into monomeric species by treatment with acetylacetonate. The electronic spectra clearly indicate the absorptions resulting from phenylazo and naphthyl groups along with the Q and B bands of the phthalocyanines. The consequence of the palladation is a relatively intense broad absorption due to LMCT with maxima around 520 nm.

Keywords: Phthalocyanine; Azobenzene; 1-Naphthol; Cyclopalladation

1. Introduction

The physical and chemical properties of phthalocyanines (Pcs) have long attracted an interest owing to their intriguing electrical, optical, photochemical and catalytic properties [1–3]. A particularly attractive feature of Pcs is the dependence of the properties of the molecule on the nature of the peripheral functional groups, as well as the electronic properties of the central metal ion in the phthalocyanine ring [4]. The increasing importance and use of phthalocyanines as advanced materials have created an attractive force on chemists to play for designing variables of the central metal ion and the peripheral substituents to reach the planned interesting properties.

Azo dyes comprise an important class of chromophores. Azo dyes have been deeply investigated since antiquity and have been shown to be important colorants for yellow to orange dyes in industrial applications. These dyes have been applied as chelate indicators to detect metal ions, applying their color change by the complex formation. Many structural types of heterocyclic aromatic systems can be used as diazo components in azo dyes to enhance colour strength and brilliant shades for synthetic fabrics. Furthermore, it is well known that azo compounds usually show intense absorptions in the visible region (400–650 nm) in spite of very weak or even no absorption for the Pcs in this range.

Azobenzene derivatives are C, N donor ligands and are good candidates to synthesize cyclometallated compounds of transition and non-transition metals [5,6]. A majority of the reaction has been reported with palladium (II). Many reviews concerning their syntheses and reactivities appear in the literature [7–9]. Cyclopalladated compounds have found numerous applications in organic syntheses, material science, and biology and metallomesogenic fields. Azobenzenes yield chloro/acetato bridged dinuclear cyclopalladated compounds upon reaction with $PdCl_2$ or $Pd(OAc)_2$, respectively. Acetato bridged cyclopalladated dimers exist in a folded anti-symmetric form with C_2-symmetry. The bridge splitting reactions of the dimer with neutral and anionic ligands give mixed cyclopalladated complexes. For example, the reaction of $[Pd(A)Cl]_2$ [10] with monoanionic *N*,*O* and *S*,*S*-chelators (A = azobenzenes; *N*,*O* = 8-quinolinolato, 2-picolinato, 2-quinaldato);

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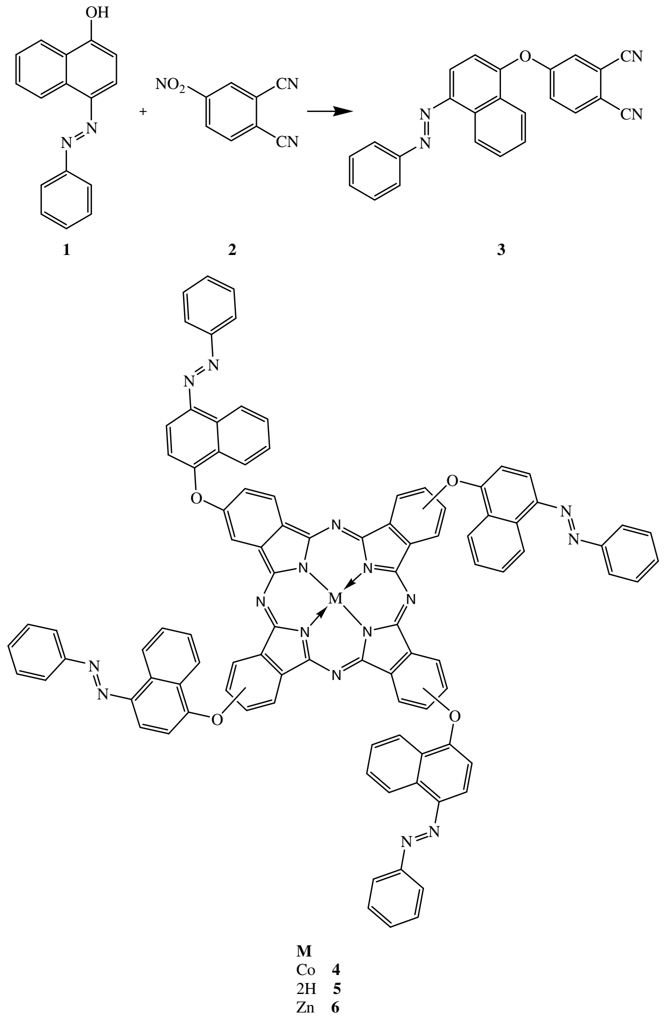
(*S*,*S* = dithiocarbamate, xanthate) gives monocyclopalladated mixed complex [Pd(A)(*N*,*O*)]-[Pd(A)](*S*,*S*)] [11,12].

Inspired by the approaches mentioned above, we have planned to make an attempt to attach palladated azobenzene complexes onto the Pc ring to enlarge the absorbing range of Pcs. Addition of naphthyl substituents simultaneously takes the intensely absorbed range further to the UV region. Planar phthalocyanine groups provide an extremely suitable basis to attach four entities separated from each other. So far there has been no report about Pcs with palladated azobenzene complexes connected onto the pendant Pc rings. In the present study, we first report the synthesis of phthalocyanines containing naphthyl-azobenzene moieties on the periphery and then cyclopalladation of the azobenzene groups to lead to binuclear and then mononuclear palladium (II) complexes. The nine new compounds show wide absorption bands in the visible and UV region besides the intense Q-band.



Scheme 1. Synthesis of metal-free and metallo-phthalocyanines.

2. Results and discussion

Scheme 1 shows the synthesis of the target phthalocyanines **4**–**6**. The first step in the synthetic procedure was to obtain 4-({4-[(Z or E)-phenylazo]-1-naphthyl}oxy) phthalonitrile **3**. It was prepared from 4-nitrophtalonitrile **2** and 4-[(Z or E)-phenylazo]-1-naphthol **1** in DMF; K_2CO_3 was used as the base for this nucleophilic aromatic displacement. Cyclotetramerization of the dicyano-derivative **3** to the metal-free and metallo-phthalocyanines were accomplished in *n*-hexanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and/or metal salts.

The second step in the study was the palladation of the azobenzene donor sites on the periphery. The metallo-phthalocyanines were treated with an equimolar amount of $[Pd(PhCN)_2Cl_2]$ in MeOH/benzene at room temperature to convert into a binuclear cyclopalladated oligomer. A suspension of binuclear complex and 3 equiv. of potassium acetylacetonate were refluxed for 3 h under N_2 to obtain mononuclear palladium (II) complex (see Scheme 2).

Characterization of the products involved a combination of methods including ^{1}H NMR, UV–Vis, IR and mass spectroscopy. The spectroscopic data of the new compounds were in accordance with the structures. In the ^{1}H NMR spectrum of **3**, aromatic protons appeared at 7.17–9.04 ppm. In the IR spectrum of **3** the presence of $C\equiv N$ and Ar–O–Ar groups was indicated by the intense stretching bands at 2227 and 1265 cm^{-1}, respectively. Cyclotetramerization of the dinitrile to give phthalocyanines **4**–**6** was confirmed by the disappearance of the sharp $C\equiv N$ vibration of the precursor **3**. The IR spectra of metal-free **5** and metallo-phthalocyanines **4**, **6** are very similar. The significant difference is the presence of N–H stretching absorption (3286 cm^{-1}) of the inner core of metal-free phthalocyanine **5**. IR spectra of all these compounds **4**–**6** showed aromatic C–O–C peaks at ca. 1261 and 1232, and a characteristic substituted naphthalene peak at about 755 cm^{-1}. The N–H protons of the metal-free phthalocyanine **5** was also identified in the ^{1}H NMR spectrum with a broad peak at $\delta = -8.73$ ppm, presenting the typical shielding of inner core protons, which is a common feature of the ^{1}H NMR spectra of metal-free phthalocyanines [13,14].

A comparison of the IR spectra of oligomeric **6** and monomeric **8** ZnPc, it is seen that the main pattern remains unchanged, but some peaks either becomes weaker or disappears completely, when converting to the monomer. Peaks at 1413–1428 cm^{-1} from the oligomer are not present in the monomer's spectrum, where the peak group at 1450–1480 cm^{-1} becomes very weak. The sharp peak at 1610 cm^{-1} in oligomer's spectrum is a shoulder in the monomer. Similar statements can be made with CoPc oligomer and monomer. There are weak peaks at 1456–1480 cm^{-1} in the monomer, while they are sharp in the oligomer. The peak at 1638 cm^{-1} disappears in the monomer. Upon conversion to monomer, the peak at 1614 cm^{-1} weakens, and the one at 1522 cm^{-1} sharpens.