

Peripherally tetra-palladated phthalocyanines

H. Yasemin Yenilmez, Ali İhsan Okur, Ahmet Gül *

Chemistry Department, Technical University of Istanbul, 34469, Maslak, Istanbul, Turkey

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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.

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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 PdCl₂ or Pd(OAc)₂, respectively. Acetato bridged cyclopalladated dimers exist in a folded anti-symmetric form with C₂-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);

* Corresponding author. Tel.: +90 212 285 6827; fax: +90 212 285 6386.
E-mail address: ahmetg@itu.edu.tr (A. Gül).

(*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.

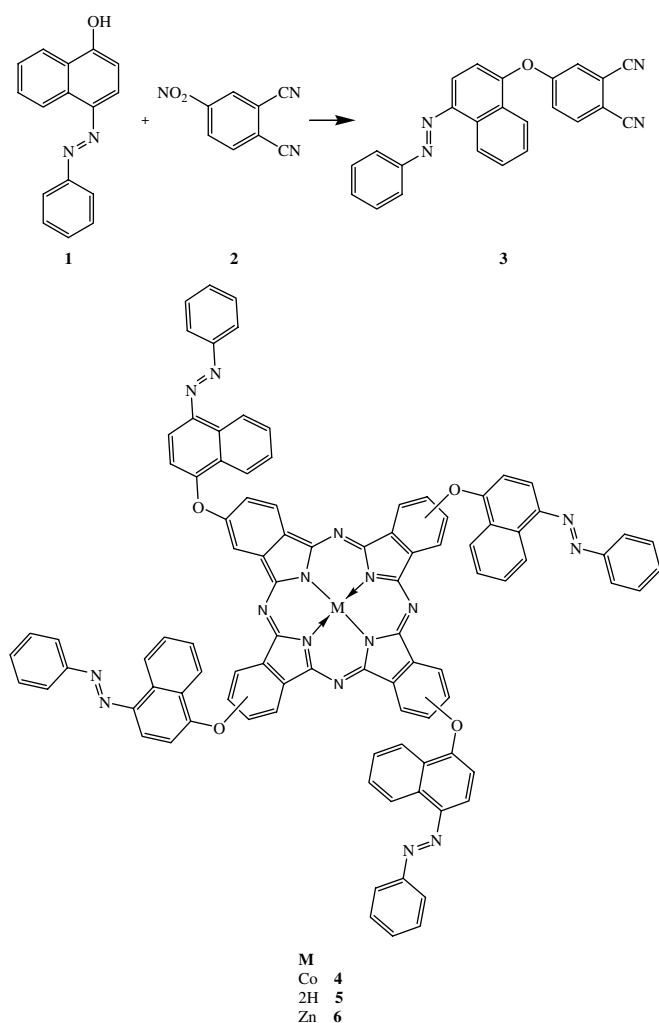
2. Results and discussion

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-nitrophenol **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.

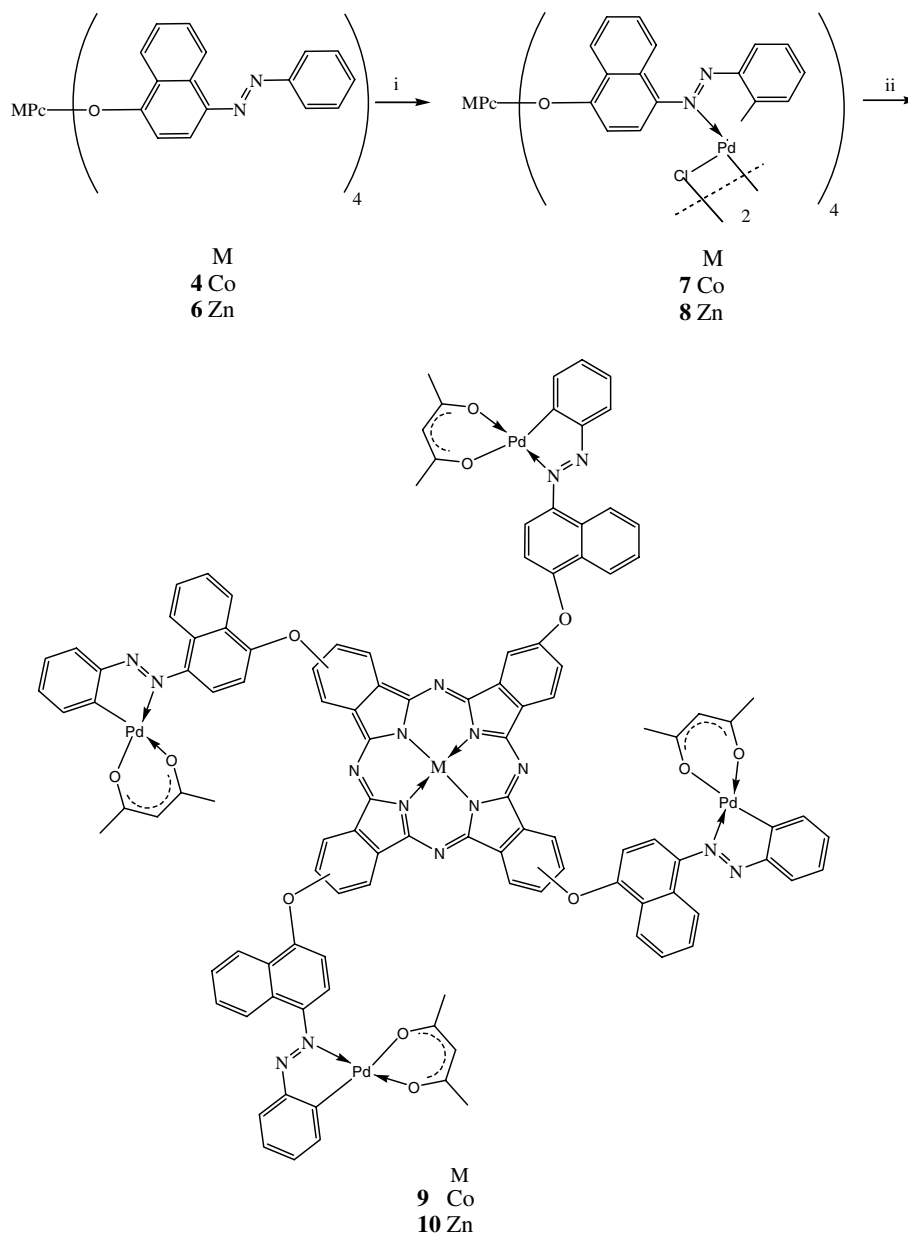
The second step in the study was the palladation of the azobenzene donor sites on the periphery. The metallo-phthalocyanines were treated with an equimolar amount of $[Pd(PhCN)_2Cl_2]$ in MeOH/benzene at room temperature to convert into a binuclear cyclopalladated oligomer. A suspension of binuclear 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 1H NMR, UV–Vis, IR and mass spectroscopy. The spectroscopic data of the new compounds were in accordance with the structures. In the 1H 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 1H 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 1H 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.



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



Scheme 2. Synthesis of palladated azobenzene complexes. (i) $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$, MeOH/benzene, 2 days r.t. (ii) Kcac (excess), absolute ethanol, under nitrogen, reflux, 3 h.

The UV–Vis spectra of the phthalocyanine core is dominated by two intense bands, the Q band around 680 nm and the B band in the near UV region, around 330 nm, both correlate to $\pi\text{--}\pi^*$ transitions [15,16]. A great deal of efforts have so far been made to shift the Q- and B-band of Pcs by extending the π system of Pc ring for matching wavelengths of the used light sources. We already know that the metal complex formation on chromophoric ligands generally causes a shift in the UV–Vis absorption spectrum, as accompanied by enhanced fastness of the dye and the absorption maxima of azobenzene complexes; the result is the outcome of visible absorption wavelengths mostly from yellow to orange. We aim to observe the effect of metal azobenzene complexes and its palladium complexes as substituents in UV–Vis absorption spectrum.

Electronic spectra are especially useful to establish the structure of all the phthalocyanines 4–10. The UV–Vis absorption spectra of the phthalocyanine system exhibit characteristic Q and B bands. UV–Vis spectra of metallo-phthalocyanines (4 and 6 in CHCl_3) exhibited intense single Q band absorption of the $\pi \rightarrow \pi^*$ transitions at 686 and 682 nm and B bands in the UV region at 327 and 336, respectively (Fig. 1). In the case of metal-free derivative 5 (in CHCl_3) splitted Q bands appeared at 670–705 nm and B band at 336 nm. An intense absorption due to the $\pi \rightarrow \pi^*$ transition of naphthalene groups appeared for all these phthalocyanine derivatives 4–6 in the UV region at ca. 290 nm [17–19]. The outcome of the presence of the diazo groups was an absorption band with a maximum at about 380 nm comparable in intensity with the B-bands

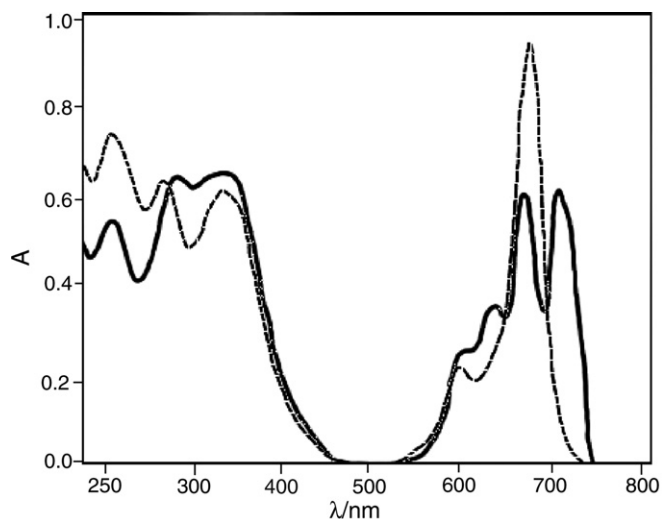


Fig. 1. UV–Vis spectra of metal-free phthalocyanine **5** (—), its cobalt phthalocyanine **4** (---).

of the phthalocyanine core. On the other hand, palladated azobenzene complexes exhibited a relatively intense absorption band, probably due to the ligand to metal charge transfer transition (LMCT), in the visible region at about 520 nm. All the phthalocyanine derivatives **7–10** have exhibited these properties.

Fig. 2 shows the electronic spectra of palladated **8** and **10** together with the parent zinc derivative **6** for a comparison. For all of them an intense single Q band absorption of the Pc core was observed at 682 nm. Complexation of azobenzene donors in **8** and **10** with palladium ions caused a hypsochromic shift for this chromophore. LMCT bands in palladated complexes **8** and **10** were evident with broad and relatively intense peaks with maxima around 518 and 521 nm, respectively.

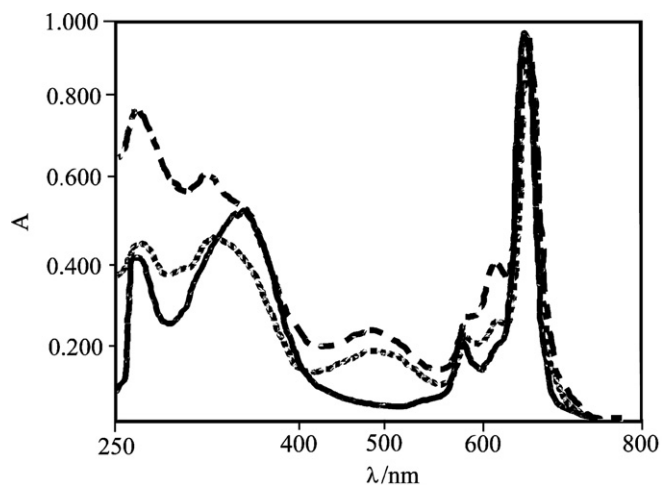


Fig. 2. UV–Vis spectra of zinc phthalocyanine **1** (—), its dimer complex **3** (····) and its monomer complex **5** (---).

3. Conclusions

Here the synthesis and characterization of phthalocyanines with four cyclopalladated phenylazo-substituents have been reported; these materials deserve further research on their catalytic and photoelectric properties.

4. Experimental

4.1. General techniques

IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer, electronic spectra on a Unicam UV2 spectrophotometer. ^1H NMR spectra were recorded on a Bruker 250 MHz spectrometer using TMS as internal reference. Mass Spectra were performed on Ultima Fourier Transform and Varian 711 mass spectrophotometer. 4-Nitrophthalonitrile **2** was synthesized according to published methods [20].

4.2. Synthesis

4.2.1. 4-({4-[(Z or E)-Phenylazo]-1-naphthyl}oxy)phthalonitrile (**3**)

4-Nitrophthalonitrile (**2**) (0.620 g, 0.0025 mol) was dissolved in dry DMF under N_2 atmosphere, and 4-[(Z or E)-phenylazo]-1-naphthol (**1**) (0.433 g, 0.0025 mol) was added and heated at 45 °C. After stirring for 15 min, anhydrous K_2CO_3 (0.483 g, 0.0035 mol) was added portion-wise during 2 h with efficient stirring. The reaction mixture was stirred under nitrogen for 48 h. Then the mixture was poured into ice-water. The resulting dark red solid was collected by filtration and washed with water until the washings were neutral. After drying in vacuo at 100 °C, the pure product was obtained by chromatography on silica gel using chloroform/methanol (100:1) mixture as eluent. The yield was 62.18% (0.582 g). M.p. 200 °C. Anal. Calc. for $\text{C}_{24}\text{H}_{14}\text{N}_4\text{O}$: C, 76.99; H, 3.77; N, 14.96. Found: C, 76.85; H, 3.63; N, 14.70%; ^1H NMR (CDCl_3): δ 7.17–9.04 (m, H–Ar); IR (ν_{CO} , cm^{-1}): 3078 (H–Ar), 2227 ($\text{C}\equiv\text{N}$), 1565 (Ar $\text{C}=\text{C}$), 1265, 1247 (Ar–O–Ar), 763.

4.2.2. 2,9,16,23-Tetrakis({4-[(Z or E)-phenylazo]-1-naphthyl}oxy)-phthalocyaninatocobalt (II) (**4**)

A mixture of 0.25 mmol (0.0936 g) of compound **3** and 0.0625 mmol (0.008 g) of anhydrous CoCl_2 in 1.5 ml of hexanol was fused in a glass tube. The mixture was heated and stirred at 160 °C for 24 h under N_2 . The resulting green suspension was cooled to ambient temperature and the crude product was precipitated by addition of ethanol. It was filtered off. The precipitate was washed first with water, and ethanol, and then dried in vacuo. Finally, pure phthalocyanine derivatives were obtained by chromatography on silica gel using chloroform/methanol (100:1) mixture as eluent. The yield was 39.06% (38 mg). M.p. >200 °C. Anal. Calc. for $\text{C}_{96}\text{H}_{56}\text{CoN}_{16}\text{O}_4$: C, 74.08; H, 3.63; N, 14.40. Found: C, 74.18; H, 3.93; N, 14.32%; IR (ν_{CO} , cm^{-1}):

3063 (H–Ar), 1571 (Ar C=C), 1261, 1232 (Ar–O–Ar), 752; UV–Vis [in CHCl₃ λ_{max}/nm 10⁺⁴ ε (dm³ mol⁻¹ cm⁻¹): 278 (7.0), 327 (5.2), 387 (5.9), 617 (2.4), 686 (9.7); mass spectrum (FAB): *m/z* 1557.06 (M⁺).

4.2.3. 2,9,16,23-Tetrakis({4-[(Z or E)-phenylazo]-1-naphthyl}oxy)-phthalocyanine (5)

A mixture 0.25 mmol (0.0936 g) of phthalonitrile derivative **3** and 0.04 mmol of 1.8-diazabicyclo [5.4.0] undec-7-ene (DBU) (0.07 ml) in 1.5 ml of hexanol was heated and stirred at 160 °C for 24 h under N₂. The resulting green suspension was cooled to ambient temperature and the crude product was precipitated by addition of ethanol. It was filtered off. The precipitate was washed first with water and ethanol and then dried in vacuo. Finally, pure phthalocyanine derivatives were obtained by chromatography on silica gel using chloroform/methanol (100:1) mixture as eluent. The yield was 21.34% (20 mg). M.p. >200 °C. Anal. Calc. for C₉₆H₅₈N₁₆O₄: C, 76.89; H, 3.90; N, 14.94. Found: C, 77.11; H, 3.63; N, 14.42%; ¹H NMR (CDCl₃): 6.83–7.85 (m, H–Ar), –8.73 (br s, N–H); IR (ν_{CO}, cm⁻¹): 3286 (N–H), 3066 (H–Ar), 1571 (Ar C=C), 1229 (Ar–O–Ar), 754; UV–Vis [in CHCl₃ λ_{max}/nm 10⁺⁴ ε (dm³ mol⁻¹ cm⁻¹): 279 (5.8), 336 (7.1), 372 (7.3), 646 (3.9), 670 (8.2), 705 (9.4); mass spectrum (FAB): *m/z* 1501.19 (M⁺), 1499,75 (M).

4.2.4. 2,9,16,23-Tetrakis({4-[(Z or E)-phenylazo]-1-naphthyl}oxy)-phthalocyaninatozinc (II) (6)

A mixture 0.25 mmol (0.0936 g) of compound **3** and 0.0625 mmol (0.008 g) of anhydrous Zn(OAc)₂ in 1.5 ml of hexanol was fused in a glass tube. The mixture was heated and stirred at 160 °C for 24 h under N₂. The resulting green suspension was cooled to ambient temperature and the crude product was precipitated by addition of ethanol. It was filtered off. The precipitate was washed first with water, and ethanol, and then dried in vacuo. Finally, pure phthalocyanine derivatives were obtained by chromatography on silica gel using chloroform/methanol (100:1) mixture as eluent. Yield was 22.524% (22 mg). M.p. >200 °C. Anal. Calc. for C₉₆H₅₆ZnN₁₆O₄: C, 73.77; H, 3.61; N, 14.34. Found: C, 73.95; H, 3.87; N, 14.05; ¹H NMR (CDCl₃): 7.14–8.03 (m, H–Ar); IR (ν_{CO}, cm⁻¹): 3053 (H–Ar), 1571 (Ar C=C), 1263, 1232 (Ar–O–Ar), 757; UV–Vis [in CHCl₃ λ_{max}/nm 10⁺⁴ ε (dm³ mol⁻¹ cm⁻¹): 275 (3.6), 336(3.2), 357 (4.7), 382 (4.8), 615 (1.5), 682 (8.9).

4.2.5. Synthesis of the binuclear complexes

In a typical preparation, 2,9,16,23-tetrakis({4-[(Z or E)-phenylazo]-1-naphthyl}oxy)-phthalocyaninatozinc **6** (0.02 g, 1.28 × 10⁻⁵ mmol) was suspended in MeOH (0.7 ml) and benzene (0.7 ml) under nitrogen. An equimolar amount of [Pd(PhCN)₂Cl₂] was added to the suspension and, a black precipitate formed after a few minutes. The suspension was stirred for 2 days at room temperature, and after this period the solid was filtered off, washed several times with diethyl ether and vacuum dried. A black solid was obtained.

Compound 8. 14 mg, 50%. Anal. Calc. for C₉₆H₅₅C₁₄ZnN₁₆O₄Pd₄: C, 54.15; H, 2.60; N, 10.52. Found: C, 53.67; H, 2.50; N, 10.06%; IR (ν_{CO}, cm⁻¹): 3058 (H–Ar), 1562 (C=C), 1235 (Ar–O–Ar), 758; UV–Vis [in DMF λ_{max}/nm 10⁺⁴ ε (dm³ mol⁻¹ cm⁻¹): 281 (4.6), 346 (5.0), 518 (1.9), 682 (9.3).

Compound 7. 18 mg, 65%. Anal. Calc. for C₉₆H₅₅C₁₄Co–N₁₆O₄Pd₄: C, 54.31; H, 2.61; N, 10.56. Found: C, 53.65; H, 2.38; N, 9.82%; IR (ν_{CO}, cm⁻¹): 3063 (H–Ar), 1561 (C=C), 1235 (Ar–O–Ar), 754; UV–Vis [in DMF λ_{max}/nm 10⁺⁴ ε (dm³ mol⁻¹ cm⁻¹): 275 (6.9), 394 (4.4), 537 (3.1), 667 (7.1).

4.2.6. Synthesis of the monomeric pentanuclear phthalocyanines

In a typical preparation, the binuclear complex **8** (0.02 g, 9.4 × 10⁻⁶ mol) was suspended in absolute ethanol and 3 equiv. of potassium acetylacetonate (0.008 g, 5.6 × 10⁻⁵ mmol) was added under nitrogen. The suspension was refluxed for 3 h, cooled to room temperature and filtered. The resulting dark black solid was filtered off, washed several times with diethyl ether and vacuum dried.

Compound 10. 15 mg, 66%. Anal. Calc. for C₁₁₆H₈₀N₁₆O₁₂Pd₄Zn: C, 58.51; H, 3.39, N, 9.41. Found: C, 58.35; H, 3.24; N, 9.62%; IR (ν_{CO}, cm⁻¹): 3063 (H–Ar), 2962 (CH₃), 2916 (CH), 1658 (C=O), 1562 (C=C), 1237 (Ar–O–Ar), 757; λ_{max}(DMF)/nm 267 (ε/dm³ mol⁻¹ cm⁻¹ 69350), 345 (52600), 521 (13520), 682 (43755).

Compound 9. 18 mg, 80%. Anal. Calc. for C₁₁₆H₈₀Co–N₁₆O₁₂Pd₄: C, 58.67; H, 3.40; N, 9.44. Found: C, 58.52; H, 3.43; N, 9.35%; IR (ν_{CO}, cm⁻¹): 3058 (H–Ar), 2922 (CH₃), 2845 (CH), 1658 (C=O), 1562 (C=C), 1236 (Ar–O–Ar), 752; UV–Vis [in DMF λ_{max}/nm 10⁺⁴ ε (dm³ mol⁻¹ cm⁻¹): 267 (5.5), 372 (3.7), 526 (4.6), 656 (5.6).

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