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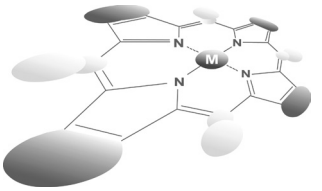

Unsymmetrical phthalocyanines with cyclopalladated azo functions

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Dedicated to Professor Michael Hanack on the occasion of his 80th birthday

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ABSTRACT: In this study, a synthetic procedure for unsymmetrical metallophthalocyanines of the form M[Pc(AB_3)], where A and B refer to two different types of peripheral functionality, has been developed and the new compounds have been converted to monomeric and dimeric palladium complexes. Asymmetrically substituted phthalocyanines were synthesized with the well-known statistical condensation method, by using two differently substituted precursors, namely 4-(2-ethoxyethoxy)-1-2-dicyanobenzene (**1**) and 4-{4-[Z/E]-phenylazo]-1-naphthyl}oxy-1,2-dicyanobenzene (**2**). Consequently, electron-donating 2-ethoxyethoxy groups and electron-withdrawing palladium complex are present in the same structure. Cyclopalladation was performed with [$Pd(PhCN)_2Cl_2$] to yield the bis-μ-chloro-bridged dimers and subsequently, the corresponding monomers were obtained by refluxing with three equivalents of potassium acetylacetonate. The resulting products were purified by column chromatography and characterized by several chemical and spectroscopic analysis methods. All compounds have very high solubility in organic solvents due to the presence of 2-ethoxyethoxy moiety.

KEYWORDS: phthalocyanine, azobenzene, 1-naphthol, 2-ethoxyethanol, cyclopalladation.

INTRODUCTION

Phthalocyanines (Pcs) have attracted great research attention for many years because of their two-dimensional π-electron conjugation, great structural variety, high thermal and chemical stability, and unique electrical, optical, magnetic, catalytic, mesogenic and film-formation properties for various applications [1, 2]. MPcs have low solubility in most organic solvents and they form aggregates. The solubility can be increased by introducing alkyl or alkoxy groups into the peripheral and non-peripheral positions of the phthalocyanine framework [3, 4]. Tetra-substituted Pcs show better solubility than the corresponding octa-substituted phthalocyanines due to the formation of constitutional isomers and the high dipole moment resulting from the unsymmetrical arrangement of the substituents at the periphery [5].

While the synthesis of symmetrically substituted phthalocyanines has been largely investigated, only minor attention has been devoted to the synthesis of unsymmetrical substituted phthalocyanines, owing to the problems associated with the low reaction yields and the mixtures of differently substituted products which render their isolation a difficult step. Usually the strategies to synthesize unsymmetrical substituted phthalocyanines are: (a) statistical condensation of two differently substituted precursors; (b) the sub-phthalocyanine approach and, (c) the polymeric support method [6–8]. The most practical and swift method is the statistical condensation approach; therefore we decided to synthesize the described compounds according to the statistical approach, which is the most useful method for the synthesis of A_3B structures according to a previously reported procedure [9].

There are different methods for synthesis of asymmetric phthalocyanines. In sub-phthalocyanine approach, a phthalonitrile is allowed to react with a sub-phthalocyanine to give an asymmetric phthalocyanine.

◊SPP full member in good standing

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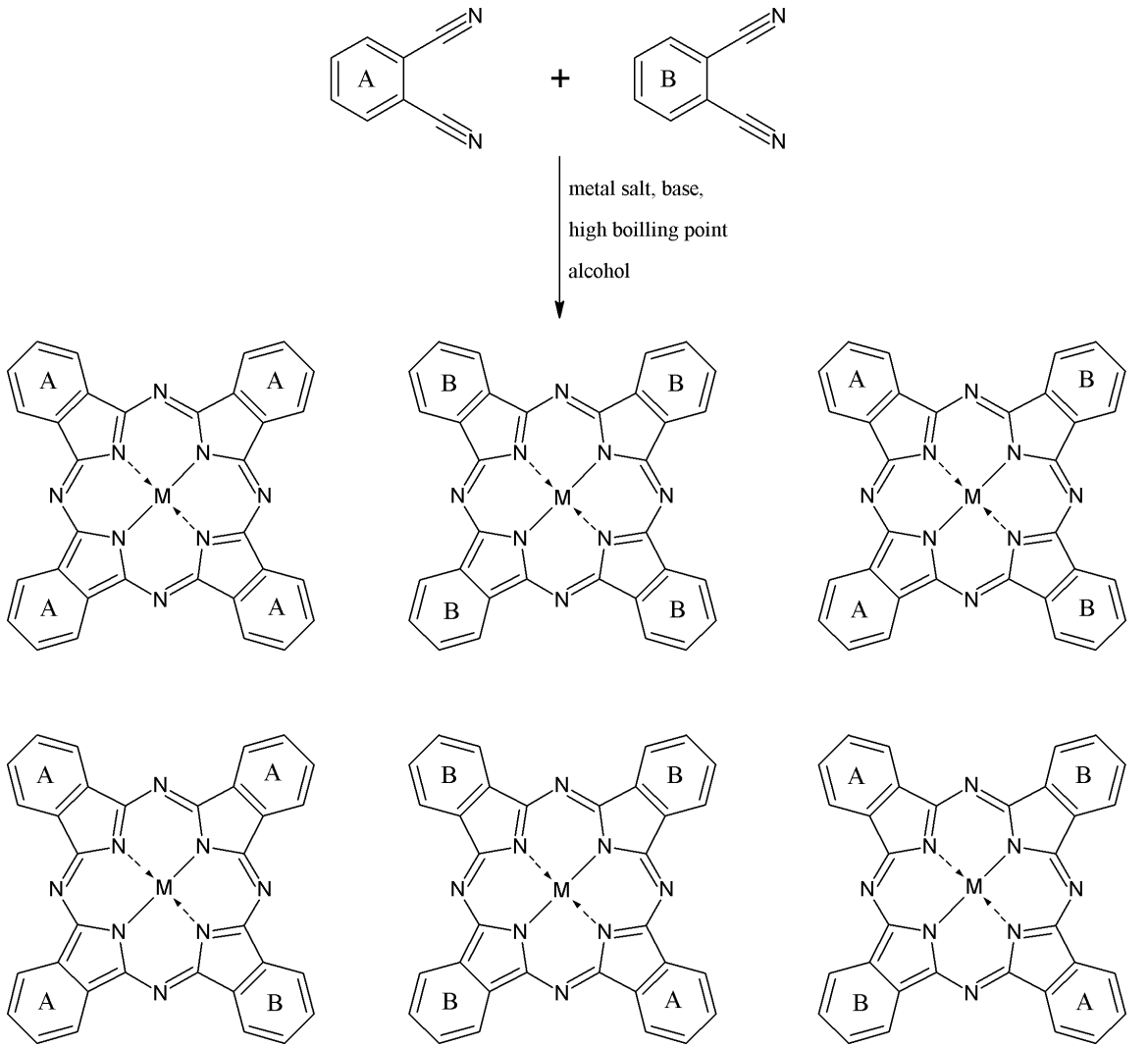
Statistical condensation approach in turn uses two phthalonitriles in different proportions to yield a mixture consisting of A_4, A_3B, A_2B_2, AB_3 and B_4 (Scheme 1). The ratio between the two phthalonitriles are determined according to their affinity to form macrocycles. When the reactivity of the two phthalonitriles is relatively similar, a 3:1 ratio has been preferred most of the time. In such a reaction, percentage formation of A_4, A_3B and other cross-condensation products has been given as 33%, 44% and 23%, respectively [10]. The most problematic part of asymmetric phthalocyanine synthesis is to isolate the desired phthalocyanine from the resultant mixture of macrocyclic products. To facilitate easy isolation, it is crucial to choose a suitable auxilary phthalonitrile derivative. The relative dissimilarity of the products in solubility or in chromatographic separation enables isolation more readily than in the other cases. Coordination compounds prepared from ligand systems capable of binding multiple metal ions are of importance in studies of electron transfer [11], magnetic interactions [12], optical phenomena [13], excited-state reactivity [14], biomimetic chemistry [15], mixed valency [16] and ionophoric activity [17]. One strategy for the design of multimetallic systems has involved the use of polynucleating macrocyclic ligands [18] and, in particular, much work has been devoted to the synthesis of porphyrins [19] and phthalocyanines [20] that have been functionalized with appendages that can coordinate metal ions as well. Several different approaches to designing polynucleating porphyrins and phthalocyanines have emerged. These include *meso* substitution with ferrocenes [21, 22] or crown ethers [23] as well as substitution with metal-ion-coordinating pendant-arms and basket-handles [24]. There are also examples of *meso*-tetrapyridylporphyrins that coordinate metal ions peripherally *via* the pyridyl groups [25]. However, for most of these complexes, the extent of electronic interaction between metal sites is quite low.

Dinuclear and mononuclear ortho-palladated compounds are one of the most widely studied classes of



Scheme 1. Statistical condensation method

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metallomesogens [26, 27]. Some pioneering discoveries in metallomesogens have been made with this kind of mesogenic materials. In dimeric molecules $[Pd_2(\mu\text{-}X)_2L_2]$ (L = orthopalladated imines and azines) the X-bridges determine the basic molecular shape, and consequently have a marked influence on the mesogenic or lack of mesogenic properties of the material [28, 29]. Thus, thiocyanato, chloro and bromo bridges produce planar dimeric structures prone to give mesomorphism [30, 31]. Carboxylato bridges force the molecule into a non-planar ridge-tent (or open-book) structure.

A few years ago we have reported the synthesis of phthalocyanines containing naphthyl-azobenzene moieties on the periphery and cyclopalladation of these azobenzene groups to reach binuclear and then mononuclear palladium(II) complexes [32]. In the present study, our first aim has been to extend the cyclopalladation reaction of azo groups to unsymmetrically substituted phthalocyanines, so the rather insoluble intermediate bridged polymeric structures obtained in the case of symmetrically substituted derivatives will be overcome. The original multimetallic compounds were purified and isolated by column chromatography and characterized by IR, UV-vis, ^{1}H NMR and MS.

RESULTS AND DISCUSSION

Our previous study about azobenzene-containing symmetrical phthalocyanines had some drawbacks like poor solubility and oligomer formation in palladium complexes [32] and it led us to synthesize asymmetrically substituted phthalocyanines. For this purpose, 2-ethoxyethoxy group which will enhance the solubility was used. Palladium complexes of asymmetric phthalocyanines have three electron-donating ethoxyethoxy groups and one electron-withdrawing palladium complex. This causes remarkable changes in the electronic distribution of phthalocyanine structure. We believe that this compound can be used in high-technology materials.

The phthalocyanines substituted by three 2-ethoxyethoxy and one azobenzene units were synthesized by a two-step procedure. First, the phthalonitrile derivative bearing a 2-ethoxy-ethoxy moiety was prepared by a nucleophilic ipso-nitro substitution reaction of 4-nitrophthalonitrile with 2-ethoxy-ethanol in the presence of K_2CO_3 (Scheme 2). This dinitrile derivative was isolated with 60% yield.

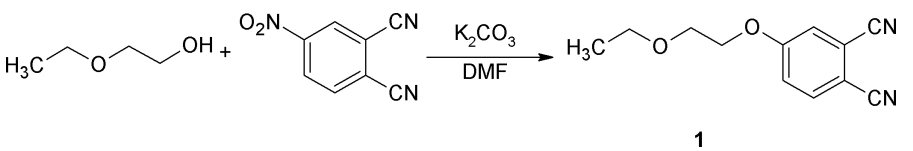
Since symmetrical phthalocyanines with all azobenzene (A) substituents lead to polymerization and subsequent insolubility after cyclopalladation reaction [32], we focused on the synthesis of an unsymmetrical phthalocyanine in AB_3 structure. The second unit (B) was 4-(2-ethoxyethoxy)phthalonitrile, which increased the solubility but did not undergo any complexation. Considering that tetra-substituted isomers are more soluble than octa-substituted ones, these two monosubstituted phthalonitrile precursors were utilized in asymmetric phthalocyanine synthesis.

During the synthesis of unsymmetrical phthalocyanines, the first step is generally to carry out the reaction of the precursors in the presence of metal salt in a high-boiling solvent. Since the reaction yields were pretty low, the lithium method (elemental lithium in pentanol) was tried and significant improvements in yield were observed.

Mixed condensation of 4-(2-ethoxyethoxy)phthalonitrile with 4-[(Z/E)-phenylazo]-1-naphthyl}oxyphthalonitrile in the presence of lithium was performed in *n*-pentanol (Scheme 3) [33]. After refluxing for 3 h, the reaction results with the formation of the corresponding Li_2Pc as expected mixtures of constitutional isomers. The crude product was precipitated with methanol-water mixture, filtered and then acidification with HCl resulted with the formation of metal-free phthalocyanine. The desired product with AB_3 structure was isolated by column chromatography. The metallo-phthalocyanines **4** and **5** were obtained by metalation of metal-free phthalocyanine **3** in dry DMF with cobalt chloride and zinc acetate, respectively (Scheme 3).

To form complexes through azobenzene functionalities, we have tried the reaction of $[Pd(PhCN)_2Cl_2]$ and metallophthalocyanines in equimolar amounts in MeOH/benzene at room temperature and the dimeric cyclopalladated phthalocyanine derivative was synthesized after 48 h (Scheme 4). The dimeric compounds can be transformed into monomeric ones by using O,O-, N,O- or S,S-chelators like acetylacetonato, 8-quinolinato, 2-picolinato, 2-quinaldato, dithiocarbamate and xanthate [28, 29]. In our case, we refluxed three equivalents of potassium acetylacetonate (Kacac) with the dimeric compound under nitrogen to obtain the monomeric derivative. The solubilities of both dimeric and monomeric compounds in chloroform, dichloromethane and tetrahydrofuran are at satisfactory level.

The structures of newly synthesized ligand and its phthalocyanines were elucidated with elemental analsis and ESI-MS, ^{1}H NMR, IR and UV-vis spectra. The structures are in accordance with the spectral data. The sharp absorption band due to ν(C≡N) in the



Scheme 2. Synthesis of 4-(2-ethoxyethoxy)phthalonitrile

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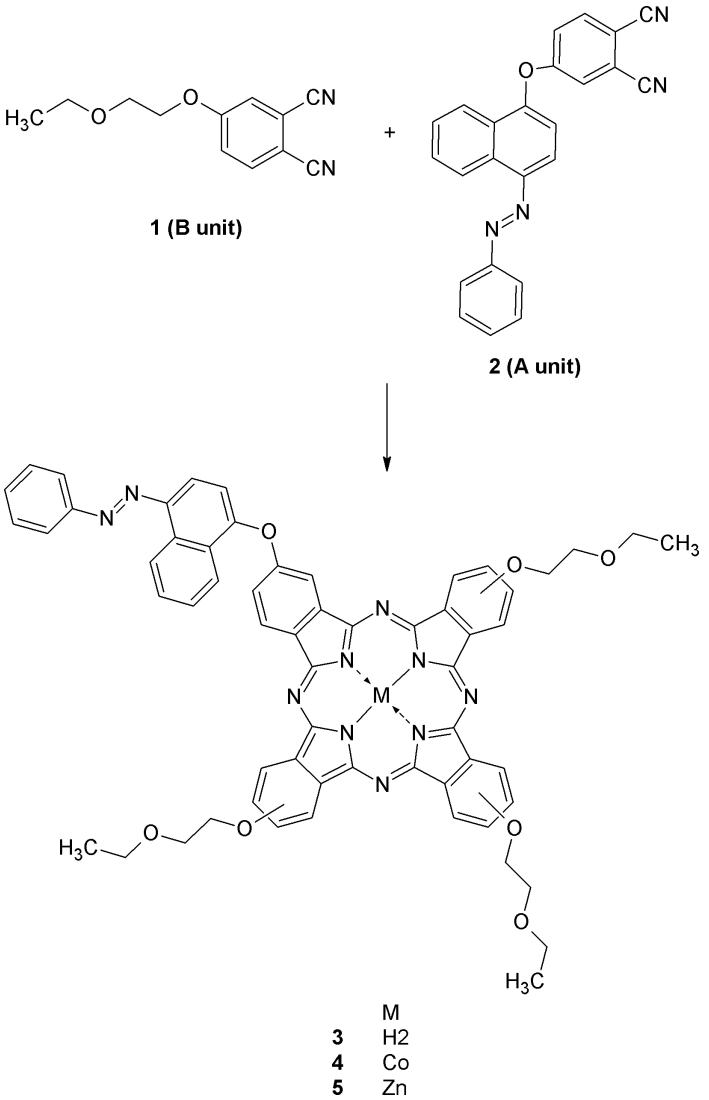

Scheme 3. Synthesis of metal-free and metallo-phthalocyanines

IR spectrum of the phthalonitriles about 2230 cm^{-1} disappeared after phthalocyanine formation. In the ^1H NMR spectrum of compound **1**, the terminal CH_3 and CH_2 protons were observed at $\delta = 1.25–1.19$ and $\delta = 3.62–3.53$ ppm as triplet and quintet, respectively. The internal O–CH_2–CH_2 moiety was present at $\delta = 4.21–4.18$ (near aromatic system) and $\delta = 3.82–3.78$ ppm (near aliphatic system). The aromatic protons were at $\delta = 7.71–7.19$ ppm. EI^+-GC-MS provided the molecular ion peak for **1** at $m/z = 216$.

In the IR spectra of novel asymmetrically substituted phthalocyanines, the peak due to ν(C≡N) is absent and aromatic CH, aliphatic CH and C–O–C vibrations were observed about 3060, 2955–2855 and 1231 cm^{-1}, respectively. The characteristic napthyl band was present around 745 cm^{-1}. ^1H NMR spectra showed the expected chemical shifts. Aromatic protons were observed as multiplets around $\delta = 6.6–7.7$ ppm for ZnPc and H_2Pc. The CH_2 moiety near ethereal bond was seen around $\delta = 3.4–4.10$ ppm. The terminal CH_3 was present about $\delta = 1.29$ ppm. The NH stretching absorption of the inner core of the metal-free phthalocyanines was observed at around 3289 cm^{-1}. The N–H protons of the metal-free phthalocyanine **3** was also identified in the ^1H NMR spectrum with a broad peak $\delta = -5.67$ ppm, which is a common feature of the ^1H NMR spectra of metal-free phthalocyanines [34].

UV-vis spectra of phthalocyanines are dominated by two intense bands, an ultraviolet Soret (B) band around 300–350 nm and a visible Q-band around 600–700 nm. The UV-vis spectra of **3**–**5** recorded in chloroform show the typical pattern of phthalocyaninato metal complexes. They are dominated by the π–π* transitions within the heteroaromatic 18-π-electron system [35–37]. The electronic absorption spectra of **3**–**5** exhibit a Q-band absorption at 668–704, 673, 674 nm, respectively. B-bands of these phthalocyanines appear in the UV region at about 335 nm (Fig. 1). An additional band was present due to the naphthyl system at 290 nm [38–40]. The intensity of this band was less when compared to the symmetric derivative [32]. The azobenzene moiety was observed as a small shoulder around 290 nm.

The IR spectra of dimeric complexes show some changes when converted into their monomeric ones. For example, the IR spectrum of monomeric Zn complex (**9**) shows new peaks at 686 and 3358 cm^{-1}. The bands at 770, 1058, 1273 and 1653 cm^{-1} in the dimeric complex (**7**) vanished in the monomeric derivative. There are also some minor shifts at 757 cm^{-1} from 744 cm^{-1}, 938 cm^{-1} from 942 cm^{-1}, but also a major shift like 1558 cm^{-1} from 1606 cm^{-1}.

As a result, unsymmetrical phthalocyanines bearing dimeric and monomeric azopalladium complexes as pendant groups were synthesized. Three 2-ethoxyethoxy groups served as electron donor as well as solubility enhancer.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with ATR capability, electronic spectra on a Scinco d-1000 spectrophotometer. ^1H NMR spectra were recorded on Bruker 250 MHz using TMS as the internal reference. Elemental analyzes were performed by the Instrumental Analysis Laboratory of the TUBITAK Marmara Research Centre. Mass spectra were performed on Bruker Micro TOF-LC/ESI/MS mass spectrometer. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. The homogeneity of the products was tested in each step by TLC. All solvents were dried and purified as described

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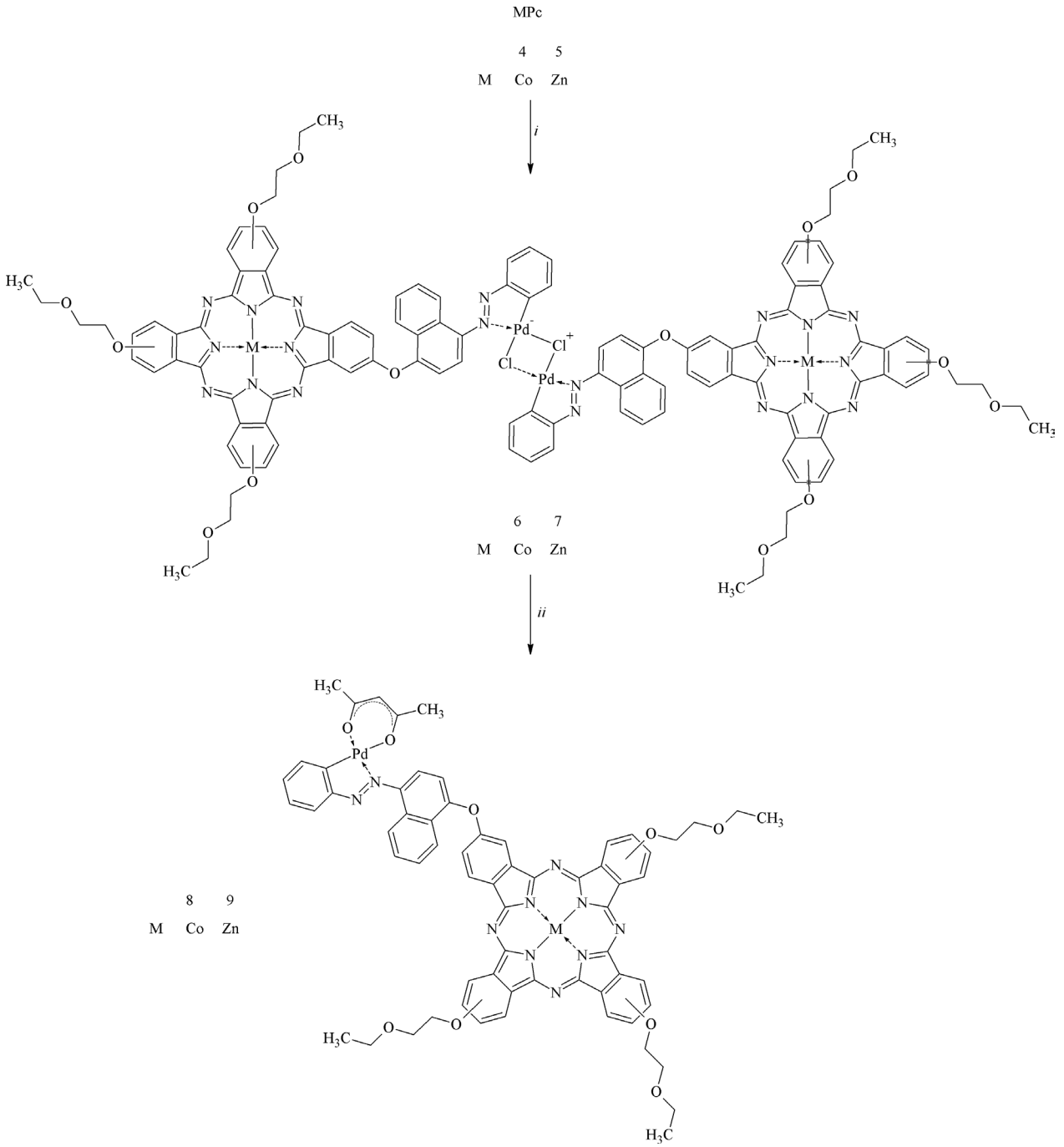

Scheme 4. Synthesis of palladated azobenzene complexes

by Perrin and Armarego [41]. The solvents were stored over molecular sieves. 4-nitrophthalonitrile [42] and 4-({4-[(Z/E)-Phenylazo]-1-naphthyl}oxy)phthalonitrile (**2**) [32] were synthesized according to published methods.

4-(2-ethoxyethoxy)phthalonitrile (1). 4-nitrophthalonitrile (1 g, 0.8 mmol) and excess 2-ethoxyethanol (1 mL, 10 mmol) were dissolved in 10 mL of dry DMF. Anhydrous K_2CO_3 (1.57 g, 11.4 mmol) was added in portions over 2 h and the mixture was stirred vigorously at 50 °C under N_2 for 72 h. The reaction mixture was poured into saturated sodium chloride solution (100 mL). The precipitated solid was filtered, washed with water until the filtrate was neutral. The product was dissolved in $CHCl_3$ and dried over Na_2SO_4. The product was evaporated to dryness. Yield 0.75 g (60%), mp 43 °C. Anal. calcd. for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.90%. Found: C, 66.61; H, 5.64; N, 12.82. ^{1}H NMR (250 MHz; $CDCl_3$; Me_4Si): δ, ppm 7.71–7.67 (d, 1H, Ar–H), 7.30 (s, 1H, Ar–H), 7.25–7.19 (d, 1H, Ar–H),

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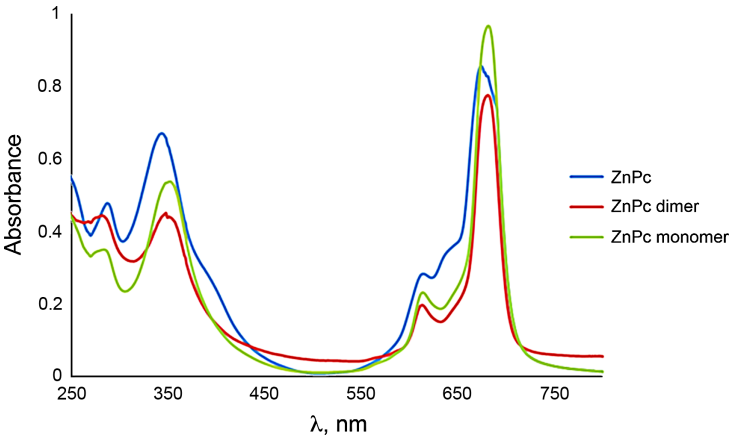

Fig. 1. UV-vis spectra of phthalocyanines **5**, **7** and **9** in $CHCl_3$

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4.21–4.18 (t, 2H, O–CH_2), 3.82–3.78 (t, 2H, CH_2–O), 3.62–3.53 (q, 2H, O–CH_2), 1.25–1.19 (t, 3H, –CH_3). IR: ν, cm^{-1} 3083 (Ar–H), 2975–2872 (alkyl CH), 2233 (CN), 1561 (C=C), 1255 (CH–O–CH). GC-MS (EI): *m/z* 216 (calcd. for $[M]^+$ 216).

2-({4-[(Z/E)-phenylazo]-1-naphthyl}oxy)-9,16,23-tris (2-ethoxyethoxy)phthalocyanine(II) (3). A mixture of 0.26 g of **1** (1.2 mmol) and 0.15 g of 4-({4-[(Z/E)-Phenylazo]-1-naphthyl}oxy)phthalonitrile **2** (0.41 mmol) were dissolved in 6 mL of dry 1-pentanol and heated at 140 °C under N_2. After addition of elemental lithium (0.120 g, 17.29 mmol) a green color appeared in a few seconds. The suspension was stirred under reflux for 3 h. The mixture was then cooled to room temperature. The reaction mixture was poured into 1:1 water/methanol mixture. The mixture was acidified with HCl and the resulting precipitate was centrifuged. The precipitated green-colored solid was filtered and washed with water, and chromatographed over SiO_2 by eluting the main product with v/v 20:3 chloroform:tetrahydrofuran. The pure product was finally dried *in vacuo*. Yield 0.18 g (45%), mp > 200 °C. Anal. calcd. for $C_{60}H_{52}N_{10}O_7$: C, 70.30; H, 5.11; N, 13.66%. Found: C, 70.45; H, 5.22; N, 13.57. UV-vis ($CHCl_3$): λ, nm (log ε) 291 (4.04), 336 (4.32), 384 (3.95), 611 (3.91), 644 (4.09), 668 (4.25), 704 (4.25). ^1H NMR (250 MHz; $CDCl_3$; Me_4Si): δ, ppm 7.67–6.67 (m, Ar–H), 4.13–3.73 (m, CH_2), 1.41–1.22 (m, –CH_3), -5.67 (N–H). IR: ν, cm^{-1} 3289 (N–H), 3064 (Ar–H), 2956–2858 (alkyl CH), 1611 (C=C), 1231 (Ar–O–Ar), 1095–1065 (CH–O–CH), 744. MS (ES^+): *m/z* 1023.94 (calcd. for $[M]^+$ 1023).

2-({4-[(Z/E)-phenylazo]-1-naphthyl}oxy)-9,16,23-tris (2-ethoxyethoxy)phthalocyaninatocobalt(II) (4). The metal-free phthalocyanine **3** (0.20 g, 0.18 mmol) was dissolved in 20 mL of dry DMF and anhydrous cobalt(II) chloride (0.27 g, 2.1 mmol) was added and the mixture was heated under stirring for 24 h at 80 °C. After cooling to room temperature, the suspension was added to water (100 mL) and the precipitated blue solid was filtered and then dried *in vacuo*. Yield 0.13 g (65%), mp > 200 °C. Anal. calcd. for $C_{60}H_{50}CoN_{10}O_7$: C, 66.60; H, 4.66; N, 12.94%. Found: C, 66.78; H, 4.59; N, 12.83%. UV-vis ($CHCl_3$): λ, nm (log ε) 289 (4.22), 324 (4.13), 378 (3.78), 619 (3.98), 673 (4.17). IR: ν, cm^{-1} 3065 (Ar–H), 2970–2865 (alkyl CH), 1608 (C=C), 1232 (Ar–O–Ar), 1089–1065 (CH–O–CH), 749. MS (ESI^+): *m/z* 1081.4 (calcd. for $[M]^+$ 1081).

2-({4-[(Z/E)-phenylazo]-1-naphthyl}-oxy)-9,16,23-tris (2-ethoxyethoxy)phthalocyaninatozinc (5). The metal-free phthalocyanine **3** (0.20 g, 0.18 mmol) was dissolved in 20 mL of dry DMF and anhydrous zinc acetate (0.38 g, 2.1 mmol) was added and the mixture was heated under stirring for 24 h at 80 °C. After cooling to room temperature, the suspension was added to water (100 mL) and the precipitated green solid was filtered and then dried *in vacuo*. Yield 0.10 g (50%), mp > 200 °C. Anal. calcd. for $C_{60}H_{50}N_{10}O_7Zn$: C, 66.20; H, 4.63; N, 12.87%. Found: C, 66.12; H, 4.54; N, 12.95. UV-vis ($CHCl_3$): λ, nm (log ε) 289 (4.52), 342 (4.78), 614 (4.41), 674 (4.90). ^1H NMR (250 MHz; $CDCl_3$; Me_4Si): δ, ppm 7.61–6.82 (m, Ar–H), 3.84–3.42 (m, CH_2), 1.29–1.16 (m, –CH3). IR: ν, cm^{-1} 3058 (Ar–H), 2963–2866 (alkyl CH), 1607 (C=C), 1229 (Ar–O–Ar), 1090–1060 (CH–O–CH), 743. MS (ES^+): *m/z* 1178.5 [M + 92$^+$] (interpreted for the ZnPc molecule axially coordinated by a single 2-ethoxyethoxy moiety).

Preparation of dimeric Pd complex of 4 and 5 (6 and 7). In a typical preparation, the phthalocyanine **4** (0.014 g, 1.29 × 10^{-5} mol) was dissolved in 1 mL of MeOH and 1 mL of benzene under nitrogen and equimolar amount of $[Pd(PhCN)_2Cl_2]$ was added to this mixture. After a short time, the color became dull. The solution was stirred for 2 days. After this period the solid was filtered off, washed several times with *n*-hexane and dried *in vacuo*. **Compound 6.** Yield 15 mg (48%). Anal. calcd. for $C_{120}H_{98}Cl_2Co_2N_{20}O_{14}Pd_2$: C, 58.93; H, 4.04; N, 11.45%. Found: C, 58.65; H, 4.19; N, 11.74. UV-vis ($CHCl_3$): λ, nm (log ε) 298 (4.76), 326 (4.78), 376 (4.43), 618 (4.55), 673 (4.93). IR: δ, cm^{-1} 3058 (Ar–H), 2969–2866 (alkyl CH), 1608 (C=C), 1231 (Ar–O–Ar), 1088–1064 (CH–O–CH), 750. MS (ES^+): *m/z* 2440.56 (calcd. for [M–2$^+$] 2440). **Compound 7.** Yield 16 mg (51%). Anal. calcd. for $C_{120}H_{98}Cl_2N_{20}O_{14}Pd_2Zn_2$: C, 58.62; H, 4.02; N, 11.39%. Found: C, 58.65; H, 4.23; N, 11.57. UV-vis ($CHCl_3$): λ, nm (log ε) 289 (4.05), 351 (4.46), 613 (4.08), 681 (4.65). ^1H NMR (250 MHz; DMSO-d_6; Me_4Si): δ, ppm 8.96–6.88 (m, Ar–H), 4.63–3.51 (m, CH_2), 0.90–0.88 (m, –CH_3). IR: δ, cm^{-1} 3053 (H–Ar), 2925–2865 (alkyl CH), 1606 (C=C), 1224 (Ar– O–Ar). MS (ES^+): *m/z* 2470.92 (calcd. for [M + H_2O^+] 2470).

Preparation of monomeric Pd complexes of 4 and 5 (8 and 9). In a typical preparation, the binuclear

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complex **6** (0.02 g, 8.2×10^{-6} mol) was suspended in absolute ethanol and 3 equiv. of Kacac (3.39 mg, 2.5×10^{-5} mol) was added under nitrogen. The suspension was refluxed for 3 h, cooled to room temperature and filtered. The resulting dark blue solid was filtered off, washed several times with diethyl ether and dried *in vacuo*. **Compound 8.** Yield 0.015 g (70%). Anal. calcd. for $C_{66}H_{59}CoN_{10}O_9Pd$: C, 60.54; H, 4.61; N, 10.86%. Found: C, 60.68; H, 4.59; N, 12.9. UV-vis ($CHCl_3$): λ, nm (log ε) 295 (4.80), 323 (4.79), 380 (4.33), 615 (4.52), 674 (4.86). IR: δ, cm^{-1} 3060 (H–Ar), 2963–2860 (alkyl CH), 1608 (C=C), 1238 (Ar– O–Ar), 751. MS (ES^+): *m/z* 1336.1 [M + 51^+] (interpreted for the monomeric molecule in which the cobalt ion is coordinated by an ethanol molecule, and the N=N bond of naphthylazo moiety and the double bond of acac ligand are reduced). **Compound 9.** Yield 18 mg (85%). Anal. calcd. for $C_{66}H_{59}N_{10}O_9PdZn$: C, 60.24; H, 4.59; N, 10.81%. Found: C, 60.35; H, 4.39; N, 12.62. UV-vis ($CHCl_3$): λ, nm (log ε) 288 (4.11), 347 (4.04), 614 (4.03), 680 (4.05). ^1H NMR (250 MHz; $CDCl_3$; Me_4Si): δ, ppm 7.66–6.83 (m, Ar–H), 3.65–3.42 (m, CH_2), 1.40–1.16 (m, $–CH_3$). IR: δ, cm^{-1} 3058 (H–Ar), 2969–2924 (alkyl CH), 1606 (C=C), 1237 (Ar– O–Ar), 757. MS (ES^+): *m/z* 1290.9 (calcd. for $[M]^+$ 1290).

CONCLUSION

In conclusion, synthesis and characterization of unsymmetrical phthalocyanines substituted with phenylazonaphthyloxy- and 2-ethoxyethoxy substituents were achived by mixed cyclotetramerization of corresponding two phthalonitrile derivatives. Cyclopalladation of phenylazonaphthyloxy groups with $[Pd(PhCN)_2Cl_2]$ gave the bis-μ-chloro-bridged dimers, which were converted to the corresponding monomers by refluxing with potassium acetylacetonate. Three 2-ethoxyethoxy substituents served as electron donors as well as solubility enhancers. The azobenzene moiety formed a complex with palladium(II) ion and this entity was added to the phthalocyanine molecule as an electron-withdrawing group. Since electron-donating and electron-withdrawing groups are brought together in the same molecule, a promising new family of phthalocyanines was synthesized with interesting optical and electrical properties.

Acknowledgements

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