Synthesis and Characterization of Novel Octakis(2′-aminophenoxy and 2′-aminophenylsulfanyl)-Substituted Metallophthalocyanines

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Novel phthalocyanines (M = Ni, Zn, Co) bearing eight 2′-aminophenoxy and 2′-amino phenylsulfanyl substituents on peripheral positions have been prepared starting from 4,5-bis(2′-aminophenoxy)-1,2-dicyanobenzene or 4,5-bis(2′-aminophenyl sulfanyl)-1,2-dicyanobenzene and the corresponding anhydrous metal salts [$NiCl_2$, $Zn(O_2CMe)_2$, $CoCl_2$]. Complexation of octakis(2′-amino phenylsulfanyl)-substituted metallo phthalocyanines (**2b, 3b** and **4b**) with Pd^{II} to form the pentanuclear product was accomplished from their mixtures.

The diverse coordination chemistry of phthalocyanine complexes has encouraged researchers to 'tailor' quotation mark, right specific products with certain properties which are required for high-technology applications. For this broad range of applications, the stable phthalocyanine core should be amenable to modifications which can be accomplished either by changing the central metal ion or by adding functional groups to the periphery[1a][1b]. The importance of phthalocyanines in many fields including chemical sensors, solar cells, electrochromism, batteries, photodynamic therapy, semiconductive materials and liquid crystals is increasing rapidly as a result of newly-synthesized compounds[2-5]. Starting from simple mono-functional substituents, more complex structures such as crown ethers[6], tetraaza[7], diazatrioxa[8], diazadithia[9], tetraaza-crown ether double layer[10], and tetrathia macrocycles[11], which are capable of binding transition metal ions leading to homo- and heteropentanuclear complexes, have been introduced into the periphery of the phthalocyanines nucleus. As donors, thioether moieties can be placed between oxa and aza groups for their tendency to complex with alkali and transition-metal ions[12]. Thioether groups on the benzene rings of the phthalocyanine also proved to be effective, as shown by relatively few communications reporting alkylthio-substituted derivatives to shift the Q-band absorption of the phthalocyanine to a lower-energy region[13-15].

While the tetrasubstituted phthalocyanines obtained from 4-substituted phthalonitriles are a mixture of four isomers, 4,5-disubstituted starting materials give a single product. The interaction of *o*-bis(thioethers) with metal ions is naturally expected to be different from that of mono derivatives[14].

Phthalocyanines with sulfanyl substituents tend to exhibit stronger absorption bands at longer wavelengths in the near-IR than the unsubstituted or *O*-substituted ones[13][15][16], which is important in applications utilizing semiconductor lasers[18].

As part of our studies on phthalocyanines with multifunctional substituents, we report for the first time on the preparation and characterization of novel 4,5-disubstituted phthalonitrile derivatives as multifunctional ligands through base-catalysed nucleophilic aromatic displacement of 4,5-dichloro-1,2-dicyanobenzene with O- and S- nucleophiles (Scheme 1) and metal phthalocyanines (M = Ni, Zn, Co) derived from these disubstituted phthalonitriles, which carry two peripheral 2′-aminophenoxy or 2′-aminophenylsulfanyl substituents. However, we could isolate heteropolynuclear compounds, all having one metal ion for each dithio-substituted benzenoid group[13][14][15].

Results and Discussion

As in the case of most of the other substituted phthalocyanines, a rational method for the synthesis of this type of compound is to start with the dicyano derivative of the corresponding 4,5-disubstituted compound. The reaction to **1b**, starting from the corresponding 2-aminothiophenol and 4,5-dichloro-1,2-dicyanobenzene, in the presence of anhydrous K_2CO_3 in tetrahydrofuran (THF), gave rather high yields (73%). But for 4,5-bis(2′-aminophenoxy)-1,2-dicyanobenzene (**1a**), prepared from the corresponding 2-aminophenol and 4,5-dichloro-1,2-dicyanobenzene under similar conditions, the yield was rather low (20%). Compounds **1a** and **1b** were converted into the desired metal phthalocyaninates (**2a, 2b, 3a, 3b** and **4b**) by using anhydrous metal salts [$NiCl_2$, $Zn(O_2CMe)_2$, $CoCl_2$] in the presence of anhydrous solvents with high boiling points (i.e. quinoline or ethylene glycol)[1][8]. The crude dark-green cyclotetramerization product required final column chromatography with silica gel for purification.

The interaction of palladium(II) ions with the peripheral thioether groups of the phthalocyanines gave products with

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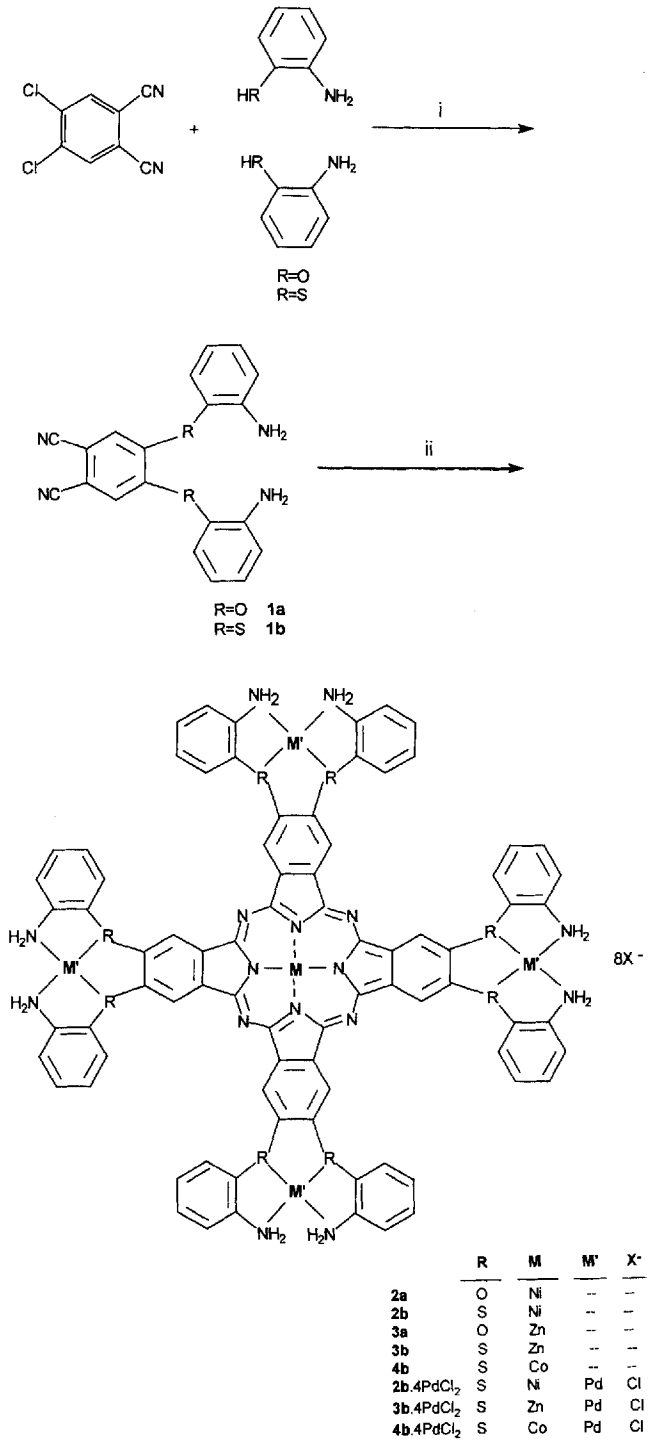
Scheme 1. i. 2-Aminophenol, 2-aminothiophenol, THF, K_2CO_3; ii. Quinoline, anhydrous $NiCl_2$, $Zn(O_2CMe)_2$, $CoCl_2$



	R	M	M'	X⁻
2a	O	Ni	--	--
2b	S	Ni	--	--
3a	O	Zn	--	--
3b	S	Zn	--	--
4b	S	Co	--	--
2b.4PdCl$_2$	S	Ni	Pd	Cl
3b.4PdCl$_2$	S	Zn	Pd	Cl
4b.4PdCl$_2$	S	Co	Pd	Cl

a phthalocyanine:metal ratio of 1:4. They can be easily differentiated from the non-metallated derivatives by their bluish colour and lower solubility, even in high boiling point solvents such as DMF. In contrast to the tetraoxa or tetraaza anologues, the low solubility of these new pentanuclear compounds is an obstacle for further investigations. We could thus isolate Pd^{II} complexes of the phthalocyanines **2b**, **3b** and **4b**, all having one metal ion for each dithio-substituted benzenoid group.

Elemental analysis, IR, ^{1}H-NMR and UV/vis spectra confirm the proposed structures all of the new compounds. A diagnostic feature of the phthalocyanine formation from the cyano derivative **1a** or **1b** is the disapperance of sharp intense CN vibration bands at 2200 cm^{-1} of the reactants in the IR spectrum. The rest of the spectrum closely resembles that of **1a** and **1b** including the characteristic vibrations of aromatic (CH), ether (R–O–R, R–S–R) and other groups. The spectra of the phthalacyanines **2a**, **2b**, **3a**, **3b** and **4b** are very similar to each other. The IR absorption patterns of the pentanuclear compounds **2b**·4PdCl$_2$, **3b**·4PdCl$_2$, and **4b**·4PdCl$_2$, were similar, with virtually only minor changes in the stretching (3450–3350 cm^{-1}) and bending (1620 cm^{-1}) vibrations of the amino groups upon complexation.

A close investigation of the mass spectra of phthalonitrile derivatives **1a** and **1b** confirmed the proposed structures. In addition to the M^+ peaks at 341.1 (**1a**) and 374 (**1b**), the major fragment ions were easily identified and showed good agreement with the proposed structure in both cases.

The ^{1}H-NMR spectra of **1a** and **1b** are almost identical, with only small changes in shifts. In addition to the signals for the aromatic protons at around 6.6–7.36 ppm, the signals for Ar-NH_2 of **1a** and **1b** appear as slightly broad peaks at 5.21 ppm and 5.63 ppm, respectively. A common feature of the ^{1}H-NMR spectra of the phthalocyanines **2a**, **2b**, **3a** and **3b** is the broad absorptions probably caused by the aggregation of the phthalocyanines, which is frequently encountered at the concentrations used for NMR measurements[1][19]. The ^{1}H-NMR spectra of phthalocyanines **2a**, **2b**, **3a** and **3b**, when compared to macrocycle-substituted ones, show sharp peaks which indicate a lower tendency to aggregate, even at concentrations used for NMR measurement[8][19][20a][20b][20c]. ^{1}H-NMR spectra of the pentanuclear phthalocyanines show very small downfield shifts when compared to the nickel(II) and zinc(II) phthalocyaninates(**2a**, **2b** and **3a**, **3b**). The only difference between mononuclear phthalocyanines **2b**, **3b** and pentanuclear derivatives **2b**·4PdCl$_2$, **3b**·4PdCl$_2$ are the polar dichloropalladium groups attached to S-donors which probably enhance the broadening. The signals for the aromatic protons of the phthalocyanine core in **2a**, **2b**, **3a** and **3b** appear as expected at 8.1, 8.2, 8.1 and 8.2 ppm, respectively as singlets, and those for the phenyl substituents at 6.95–7.9, 7.2–7.87, 7.1–7.9 and 6.9–7.9 ppm, respectively as multiplets. The signals for the Ar-NH_2 protons of the 2-aminothiophenol or 2-aminophenol moiety appear at 5.3–5.63 ppm in all the phthalocyanines **2a**, **2b**, **3a**, **3b**, respectively; these chemical shifts disappear after deuterium exchange with addition of D_2O.

UV/vis absorption spectra of the phthalocyanine complexes exhibit characteristic Q and B bands. UV/vis spectra of phthalocyanines **2a**, **2b**, **3a**, **3b** and **4b** in DMF, show the intense Q-band absorptions of π-π^* transitions at 673, 711, 683, 699 and 694 nm, respectively. There is also a shoulder at slightly higher energy for all these products. B bands of all the phthalocyanines arising from the deeper π levels $\rightarrow$ LUMO transitions (Table 1) are observed in UV region at

about 300–425 nm. In order to test the effect of the central metal ion on the changes in the Q-band, the spectra of all phthalocyanines **2-4** in polar solvents have been carefully investigated (Table1).

Table 1. Electronic spectral data for the phthalocyanine complexes in *N,N*-dimethylformamide

Compound	λ_{max} / nm (10^{-4} ε / dm^3 mol^{-1} cm^{-1})
2a	673(7.96), 616(3.22), 425(2.84), 325(14.0)
2b	711(11.39), 639(3.68), 425(4.43), 325(12.65)
3a	683(8.53), 645(3.88), 390(8.17)
3b	699(9.44), 640(4.86), 365(6.12), 320(3.77)
4b	694(12.82), 630(6.86), 370(15.91), 340(4.06)
2b·4$PdCl_2$	695(6.66), 637(5.20), 302(14.22)
3b·4$PdCl_2$	691(8.75), 628(3.12), 367(3.87)
4b·4$PdCl_2$	687(7.84), 629(4.83), 330(10.06)

It was found that the wavelength of the maximum absorption follows the order Ni>Zn>Co for the phthalocyanines with S-substituents and Zn>Ni for those with O-substituents. Any increase in the concentration results in the aggregation of the phthalocyanine molecules, which is accompanied by a blue shift of the Q bands with a decrease in intensity. It has been concluded that aggregation is enhanced by solvent polarity[3][6a][21]. When the interaction of complexes **2b**, **3b**, and **4b** with Pd^{2+} ions in DMF/water in the ratio of 20:0.5 is studied spectrophotometrically with changes in the Q-band region, the result is the disappearance of the shoulder between 640–670 nm. The electronic configuration of the d^8 metal ion Pd^{2+} exhibits a preference for square-planar geometry also with some dithioether complexes[22]. While two of the coordination sites are saturated by thio groups, the other two are filled by chloride ions[23]. When the complexes obtained from 4,5-bis(2'-aminophenylsulfanyl)-1,2-dicyanobenzene with $PdCl_2$ is investigated as a model compound, it can be seen that the plane of the complex forms an angle with the plane of the benzene ring. Consequently, we should expect four PdS_2Cl_2 planes directed out of the plane of the phthalocyanines **2b**, **3b** or **4b**, which will cause the decomposition of aggregates of planar phthalocyanine molecules in solution.

In conclusion, 2-aminophenoxy and 2-aminosulfanyl substituents on the phthalocyanine periphery should be taken into account both as bathochromic shift agents and suitable donor sites for further complexation.

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Experimental Section

General: FT-IR (KBr): ATI Unicom–Mattson 1000 Spectrophotometer. – UV/vis: Varian DMS 90 (Table 1). – Elemental analysis: Instrumental Analysis Laboratory of TÜBİTAK Marmara Research Center. – ^{1}H NMR: Bruker (200 MHz) Spectrometer. MS: EI on VG Zabspec GS-MS Spectrometer. The metal contents of the complexes were determined with a Hitachi-180-80 atomic absorption spectrophotometer in solution prepared by decomposition of the compounds in conc. HCl and conc. HNO_3 (3:1) solution followed by dilution in water. The homogeneity of the products was tested in each step by TLC (SiO_2, Chloroform). 4,5-Dichloro-1,2-dicyanobenzene was synthesized according to the reported procedure[15].

4,5-Bis(2'-aminophenoxy)-1,2-dicyanobenzene and 4,5-bis(2'-aminophenyl sulfanyl)-1,2-dicyanobenzene (**1a** and **1b**): 2-aminophenol (0.553 g, 5.1 mmol) or 2-aminothiophenol (0.64 g, 5.1 mmol) and 4,5-dichloro-1,2-dicyano-benzene (0.5 g, 2.53 mmol) were dissolved in absolute tetrahydrofuran (60 ml) under nitrogen. After stirring for 20 min, finely ground anhydrous potassium carbonate (2.8 g, 20.3 mmol) was added portionwise over 30 min. with efficient stirring. The reaction mixture was stirred under nitrogen at reflux temperature for 24 h. Water(100 ml) was then added to separate any inorganic residues and the aqueous phase was extracted with chloroform (3 × 25 ml). The combined extracts were firstly treated with sodium carbonate solution (5%), then with water and finally dried over anhydrous sodium sulfate. The solvent was distilled off and the resulting yellow oily residue was crystallized from toluene. Both compound **1a** and **1b** were soluble in chloroform, dichloromethane, THF and DMF. Yield of compound **1a**: 0.15 g (17.33%); m.p.162–164 °C. – IR (KBr) $\tilde{\nu}$ = 3450–3350 cm^{-1}, 3100–3050, 2200, 1570, 1560, 1490, 1420, 1360, 1280, 1260, 1230, 1205, 1120, 980, 820, 710. – ^{1}H NMR ([D$_6$]-DMSO): δ = 7.36 (2 H, s, aromatic-H), 6.66–6.94 (8 H, m, Ar-H), 5.63 (s, 4 H, Ar-NH_2). – EI/MS (70eV), m/z (%): 341.1 (10) [M^+-1], 339.1, 311.2, 296.1, 294.1, 282.0, 269.0. – $C_{20}H_{14}N_4O_2$ (342): calcd. C 70.17, H 4.09, N 16.39; found C 69.33, H 3.78, N 15.95. Yield of compound **1b**: 0.70 g (73%); m.p. 182–184 °C. – IR (KBr) $\tilde{\nu}$ = 3450–3350 cm^{-1}, 3100, 2200, 1580, 1560, 1500, 1420, 1360, 1280, 1260, 1230, 1200, 1120, 980, 860, 710. – ^{1}H NMR ([D$_6$]-DMSO): δ = 7.45 (2 H, s, Ar-H), 6.6–6.9 (8 H, m, Ar-H), 5.21 (s, 4 H, Ar-NH_2). – EI/MS (70eV), m/z(%): 374 (90) [M^+], 341.1, 285, 249.1, 217.1, 187.0, 149.0, 125.0, 93, 80.0. – $C_{20}H_{14}N_4S_2$ (374): calcd. C 64.17, H 3.74, N 14.97; found C 64.96, H 4.18, N 14.37.

Nickel(II) Phthalocyaninates (**2a** and **2b**): A mixture of **1a** (0.17 g, 0.53 mmol), **1b** (0.2 g, 0.53 mmol), anhydrous $NiCl_2$ (0.012 g, 0.15 mmol) and quinoline (0.5 ml) was heated and stirred at 190–200 °C in a sealed glass tube for 5 h under nitrogen. After cooling to room temperature, the dark green mixture was diluted with ethanol (5 ml) and the crude product precipitated. This product was filtered off and washed with the same solvent, then with diethyl ether, acetone, ethyl acetate and chloroform to remove unreacted organic materials. The dark green metallophthalocyanine was then isolated by silica gel column chromatography with chloroform/DMF (100:1 v/v) as the eluent. The product was soluble in DMF, DMSO and quinoline. Yield of **2a**: 0.02 g (17.53%); m.p. >200 °C. – IR (KBr): $\tilde{\nu}$ = 3450–3350 cm^{-1}, 3040, 1600, 1480, 1430, 1400, 1285, 1130, 1100, 1080, 875, 790, 705. – ^{1}H NMR([D$_6$]-DMSO): δ = 8.1 (s, 8 H, Ar-H), 6.95–7.9 (m, 32 H, Ar-H), 5.55 (s, 16 H, Ar-NH_2). – $C_{80}H_{56}N_{16}NiO_8$ (1419): calcd. C 67.46, H 3.93, N 15.74; found C 67.07, H 3.63, N 15.52. Yield of **2b:** 0.04 g (19.31%); m.p. >200 °C. – IR (KBr): $\tilde{\nu}$ = 3350–3450 cm^{-1}, 3050, 1620, 1600, 1580, 1470, 1430, 1400, 1270, 1140, 1100, 1070, 910, 870, 710. – ^{1}H NMR ([D$_6$]-DMSO): δ = 8.2 (s, 8 H, Ar-H), 7.2-7.87 (m, 32 H, Ar-H), 5.3 (s, 16 H, Ar-NH_2). – $C_{80}H_{56}N_{16}NiS_8$ (1551): calcd.C 61.75, H 3.60, N 14.40; found C 61.16, H 3.17, N 14.08.

Zinc(II) Phthalocyaninates (**3a** and **3b**): A mixture of compound **1a** (0.18 g, 0.53 mmol), **1b** (0.2 g (0.53 mmol), anhydrous zinc acetate(0.0245 g, 0.70 mmol) and quinoline (0.7 ml) was heated and stirred at 180–190 °C for 2 h under nitrogen. The reaction was then continued for another 4 h at 195–205 °C. After cooling to room temperature, ethanol (5 ml) was added in order to precipitate the product. The dark green product was filtered off and then washed several times, firstly with the same hot solvent, then diethyl ether, acetone, ethyl acetate and chloroform to remove unreacted organic materials. It was isolated by silica gel column chromatography with chloroform/DMF (100:1 v/v) as a eluent. These products

are soluble in DMF, DMSO, and quinoline. Yield of **3a**: 0.035 g (18.27%) m.p. >200°C. – IR (KBr): $\tilde{\nu}$ = 3350–3450 cm^{-1}, 3050–3070, 1620, 1590, 1480, 1420, 1280, 1120, 1090, 1050, 890, 760, 710. – ^1H NMR ([D_6]-DMSO); δ = 8.1 (s, 8 H, Ar-H), 7.1–7.9 (m, 32 H, Ar-H), 5.56 (m, 16 H, Ar-NH_2 broad). – $C_{80}H_{56}N_{16}O_8Zn$ (1433): calcd. C 62.78, H 3.66, N 14.65; found C 61.34, H 3.04, N 13.53. Yield of **3b**: 0.04 g (19.19%); m.p. > 200 °C. – IR (KBr): $\tilde{\nu}$ = 3350–3450 cm^{-1}, 3100, 1610, 1500, 1470, 1450, 1410, 1270, 1120, 1100, 1060, 900, 770, 700. – ^1H NMR ([D_6]-DMSO): δ = 8.2 (s, 8 H, Ar-H), 6.90–7.90 (m, 32 H, Ar-H), 5.63 (s, 16 H, Ar-NH_2). – $C_{80}H_{56}N_{16}S_8Zn$ (1561): calcd. C 61.49, H 3.59, N 14.35; found C 60.74, H 3.60, N 13.99.

Cobalt(II) Phthalocyaninate (**4b**): A mixture of dicyano compound **1b** (0.250 g, 0.67 mmol), anhydrous $CoCl_2$ (0.0219 g, 0.17 mmol) and anhydrous ethylene glycol (13 ml) was heated and stirred at 190–200 °C for 8–9 h under nitrogen in a round-bottomed flask. The resulting dark green suspension was cooled to room temperature. The mixture was heated in ethanol to precipitate the dark green product, and then filtered. The product was dissolved in DMF (10ml), and the solution was added dropwise to warm ethyl acetate with stirring. The precipitate formed was filtered off, washed firstly with ethyl acetate, and then with diethyl ether, to remove the unreacted organic materials, and dried. The product was purified by column chromatography with silica gel [chloroform-DMF (100:1v/v) as the eluent]. The product is soluble in DMF, DMSO and quinoline. Yield: 0.03g, (11.55%); m.p >200 °C. – IR (KBr): $\tilde{\nu}$ = 3350–3450 cm^{-1}, 3050, 1610, 1500, 1470, 1420, 1400, 1270, 1120, 1100, 1070, 860, 700. – $C_{80}H_{56}CoN_{16}S_8$ (1555): calcd. C 61.73, H 3.60, N 14.40; found C 61.27, H 3.47, N 14.08.

Palladium(II) Complexes of **2b, 3b** *and* **4b**: μ_5(Phthalocyaninato)-nickel(II)tetrapalladium(II) octachloride (**2b**·4$PdCl_2$), μ_5-(phthalocyaninato) tetrapalladium(II)zinc(II) octachloride (**3b**·4$PdCl_2$) and μ_5-(phthalocyaninato)cobalt(II) tetrapalladium(II) octachloride (**4b**·4$PdCl_2$): The metallophthalocyanines **2b** (0.01 g, 0.0064 mmol), **3b** (0.0106 g, 0.0064 mmol) and **4b** (0.01 g, 0.0064 mmol) were dissolved in DMF/water (20:0.5 ml) and a solution of $Na_2[PdCl_4].3H_2O$ (0.0152 g, 0.52 mmol) in the same solvent mixture (5 ml) was added and reluxed for 12 h with stirring. The colour became blue-green while refluxing, and precipitation occured. The dark green precipitate was separated by centrifuge, washed several times successively with H_2O, EtOH, and Et_2O, and dried in vacuo. Yield of **2b**·4$PdCl_2$: 0.0125 (85.4%); m.p. >300 °C. – IR (KBr): $\tilde{\nu}$ = 3350-3450 cm^{-1}, 3040, 1610, 1540, 1470, 1420, 1400, 1300, 1140, 1100, 1070, 960, 900, 870, 705, 660. – ^1H NMR ([D_6]-DMSO): δ = 8.4 (s, 8 H, Ar-H), 7.0–7.9 (m, 32 H, Ar-H), 5.56 (s, 16 H, Ar-NH_2). – $C_{80}H_{56}Cl_8N_{16}NiPd_4S_8$ (2262): calcd. C 42.47, H 2.47, N 9.91; Ni 2.56, Pd 18.75; found C 44.26, H 2.65, N 9.14, Ni 2.53, Pd 16.86. Yield of **3b** 4$PdCl_2$: 0.0130 g (88.82%); m.p >300 °C. – IR (KBr): $\tilde{\nu}$ = 3350-3450 cm^{-1}, 3080, 1610, 1500, 1450, 1400, 1380, 1130, 1100, 1050, 900, 840, 770, 700. – ^1H NMR ([D_6]-DMSO): δ = 8.15 (s, 8 H, Ar-H), 7.05–8.04 (m, 32 H, Ar-H), 5.54 (s br, 16 H, Ar-NH_2). – $C_{80}H_{56}Cl_8N_{16}Pd_4S_8Zn$ (2269): calcd. C 42.39, H 2.46, N 9.86, Zn 2.86, Pd 18.68; found C 43.54, H 2.63, N 9.95, Zn 2.79, Pd 18.51. Yield of **4b**·4$PdCl_2$: 0.0130 g (89%); m.p. >300 °C. – IR (KBr): $\tilde{\nu}$ = 3340–3450 cm^{-1}, 3070, 1620, 1545, 1420, 1390, 1360, 1110, 1100, 1070, 850, 785, 700. – $C_{80}H_{56}Cl_8CoN_{16}Pd_4S_8$ (2263): calcd. C 42.39, H 2.47, N 9.89, Co 2.60, Pd 18.72; found C 44.10, H 2.56, N 10.13, Co 2.58, Pd 17.97.

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