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Highly Organosoluble Metal-Free Phthalocyanines and Metallophthalocyanines: Synthesis and Characterization

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The syntheses and characterization of metal-free and metal-containing (Zn and Ni) derivatives of a symmetrically octa-substituted phthalocyanine derived from 4,5:12,13-bis(4′-*tert*-butylbenzo)-8,9-(4′′,5′′-dicyanobenzo)-6,11-ditosyl-6,11-diaza-2,15-dithiacyclohexadeca-4,8,12-triene and CuPc from 4,5:12,13-bis(4′-*tert*-butylbenzo)-8,9-(4′′,5′′-dibromobenzo)-6,11-ditosyl-6,11-diaza-2,15-dithiacyclohexadeca-4,8,12-triene were carried out. Pentanuclear silver(I) and palladium(II) complexes have also been prepared from nickel(II) phthalocyaninate derivatives. The prepared phthalocyanines were semiconducting materials in the range of 10^{-5} to 10^{-10} S cm^{-1} in vacuo and under atmospheric pressure. The extraction abilities of NiPc and detosylated phthalocyanines were evaluated in chloroform/water by using several heavy-metal picrates such as Ag^{+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}, Pd^{2+}, and Zn^{2+}. The extraction affinities of NiPc and detosylated phthalocyanines for Ag^{+} were found to be the highest in solvent extraction experiments. The new compounds were characterized by using elemental analysis, UV/Vis, FTIR, NMR, MS spectroscopic data and DTA/TG.

Introduction

Phthalocyanines have been shown to have very interesting properties coupled with excellent stability to heat, light, and harsh chemical environments. Their optical and electronic properties have been exploited in various applications such as pigments in paints and printing inks, infrared security devices, information storage, and computer disk writing, conducting polymers and photoconductors, catalysts for oxidation of thiols, disulfides, chemical sensors, and in photodynamic therapy of cancer.[1,2] Transition-metal-based phthalocyanines have attracted attention in the areas of fuel cells, gas sensors, and biosensors.[1,2] Most of these applications require the use of phthalocyanines in the form of thin films. Further, it is desirable to have ordered, well-packed, and oriented molecular layers of phthalocyanines on various substrates.

Applications of peripherally unsubstituted phthalocyanines are restricted because of their insolubility in common solvents and water.[3,4] Phthalocyanines own an extended π-conjugated electron system which allows π stacking (aggregation) between planar macrocycles, provided the distance between the macrocycles is small.[5] By the peripheral attachment of bulky (e.g. *tert*-butyl),[6] long-chain groups (e.g. alkyl or alkoxy),[7] N-tosyl derivatives,[8] crown ether analogs[9–12] or macrobicyclic[13,14] and macrotricyclic[15] moieties to the macrocycles, transition-metal phthalocyanine complexes and their bridged systems can be made soluble in common organic solvents, for example chloroform or toluene,[4–6] because these substituents increase the distance between the stacked phthalocyanines and enable their solvation.[5,16] The *tert*-butyl group is especially suitable to increase the solubility of phthalocyanines in organic solvents.[5] Heteroatom-functionalized substituents were introduced onto the periphery of the phthalocyanine nucleus.[8–17] These peripheral groups are capable of binding alkali metal ions and provide donor sites for binding transition-metal ions, which leads to homo- and heteronuclear complexes.

Unfortunately, for many applications it is preferable to have both soluble and symmetric phthalocyanines. With this idea in mind, we set out to synthesize symmetrical di-*tert*-butylphtholonitrile and di-*tert*-butyl-*o*-dibromobenzene derivatives for condensation to very soluble symmetrical octa-*tert*-butyl-substituted phthalocyanines in this study. The electrical conductivities of the phthalocyanines as Au/MPc/Au sandwiches in vacuo and air atmosphere were examined. Additionally, the heavy metal extraction properties of **11** and **14** were investigated.

Results and Discussion

Synthetic Procedure and Characterization

The synthetic routes to **3**–**10** are summarized in Scheme 1 and **11**–**14** are summarized in Scheme 2. 1,2-Bis(4-*tert*-bu-

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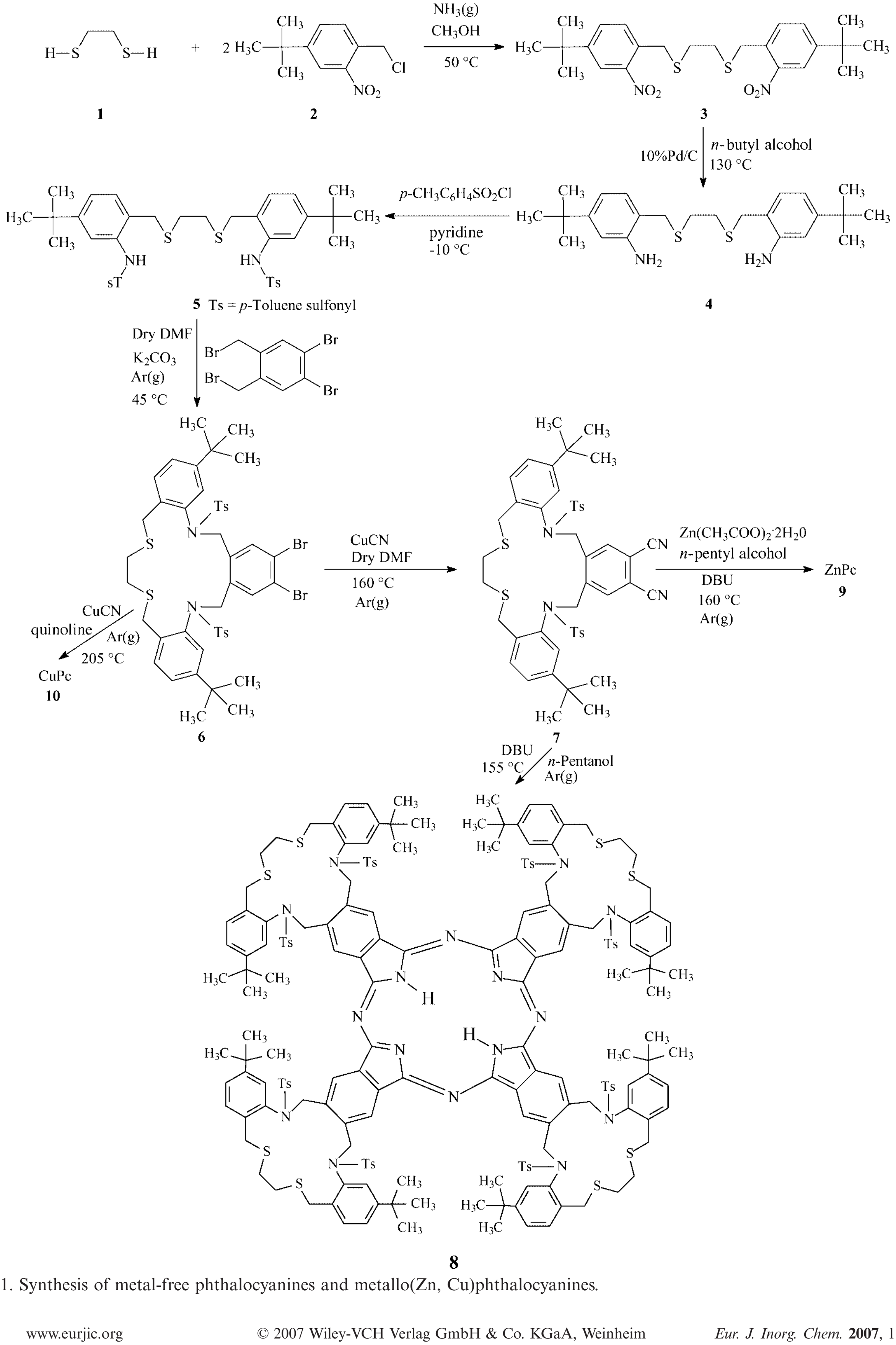
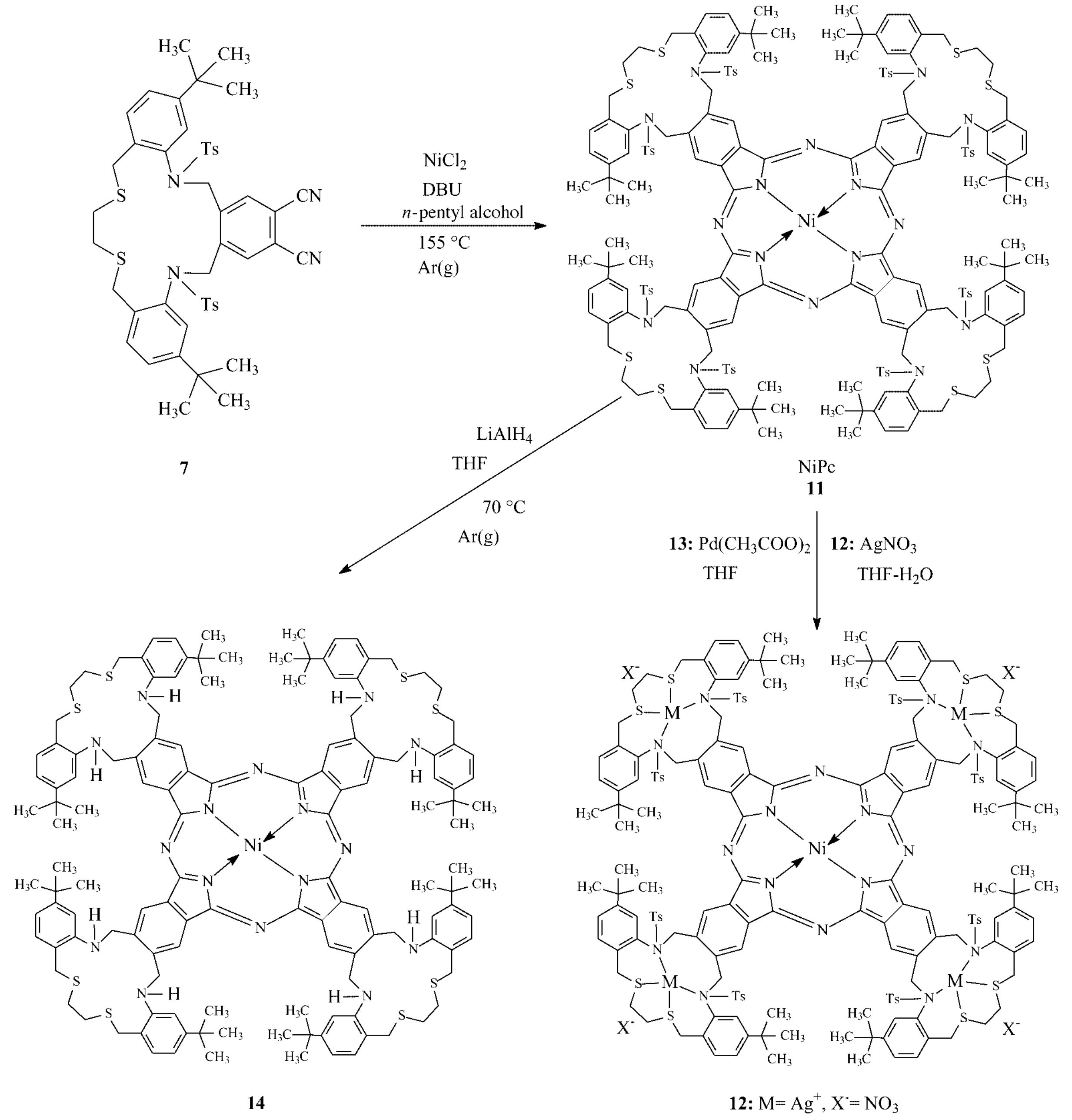
tyl-2-nitrobenzylthio)ethane (**3**) was prepared by a modified literature[18] procedure by the reaction of 1,2-ethandithiol (**1**) with 4-*tert*-butyl-2-nitrobenzyl chloride (**2**) in methanol in 62% yield. In this work, we were able to easily obtain nitro derivative **3** as a pure solid by simple crystallization, whereas Sakata and coworkers[18] obtained an oily product



Scheme 1. Synthesis of metal-free phthalocyanines and metallo(Zn, Cu)phthalocyanines.



Scheme 2. Synthesis of nickel phthalocyanine and its derivatives.

after a more exhausting and time consuming column chromatography method. This compound was characterized spectroscopically and analytically. The ^{1}H NMR spectrum of **3** showed characteristic signals for Ar–CH$_2$–S and SCH$_2$–CH$_2$S protons at δ = 4.20 and 2.70 ppm, respectively. The ^{13}C NMR spectrum of this compound also clearly indicates the presence of expected signals related to the above-mentioned groups at δ = 31.90 and 32.45 ppm, respectively. The IR spectrum featured a band at 684 cm^{-1}, which is attributable to the C–S bonds. The EI mass spectrum of this compound exhibited a molecular ion peak at *m*/*z* = 476.23 [M]$^+$, that also supports the structure.

Diamino derivative **4** was obtained by the reduction of **3** with 10%Pd/C (palladium activated charcoal), hydrazinium hydrate, and *n*-butyl alcohol in 78% overall yield. Because this method is more advantageous than the others, we preferred this one.[19] The disappearance of the signals for the NO$_2$ groups at 1543 and 1340 cm^{-1} and the appearance of the signals of the NH$_2$ groups at 3430–3320 cm^{-1} and bending signals at 1610 cm^{-1} in the IR spectrum confirmed the formation of amino derivative **4**. The ^{1}H and ^{13}C NMR spectra of **4** were very similar to those of precursor compound **3** except for the signals of the NH$_2$ groups at δ = 3.82 and 145.56 ppm, respectively. The EI mass spectrum displayed the $[M]^+$ parent ion peak at *m/z* = 416.09, which confirms the same structure.

Reaction of *p*-toluenesulfonyl chloride with compound **4** in dry pyridine[20] afforded compound **5** in 97.5% yield. The IR spectrum of compound **5** shows the signals related to the tosyl groups at 1343–1140 cm^{-1} and the N–H groups at 3270–1592 cm^{-1}, which indicates that the tosylation reaction was clearly achieved. A molecular ion peak at *m/z* = 724.19 $[M]^+$ in its mass spectrum together with elemental analysis data clearly supports the structure of compound **5**. The ^{1}H NMR spectrum of compound **5** exhibits signals for both the N–H and tosyl groups at δ = 8.29 ppm and δ = 7.85–7.35 (Tosyl–Ar–H) and 2.32 ppm (Tosyl–CH_3), respectively. The ^{13}C NMR spectrum shows the signals at δ = 148.56 ppm (Ar–C–NH) and 144.62, 135.32, 130.23, 127.44 ppm (Ts–Ar), and 21.34 (Tosyl–CH_3), respectively. All these spectroscopic data confirm the proposed structure.

Dibromobenzene derivative **6** was obtained from the reaction of compound **5** and α,α′-dibromomethyl-4,5-dibromobenzene in 36% yield as a pale brown solid. From the IR spectrum, the formation of the C–Br bond was confirmed by the presence of the peak at 632 cm^{-1}, and the signals for the N–H group of compound **5** at 3270–1592 cm^{-1} disappeared. Other IR peaks are similar to those of compound **5**. The N–H signals observed for compound **5** at δ = 8.29 ppm in the ^{1}H NMR spectrum disappeared and a new peak arose at δ = 7.75 ppm, which results from α,α′-dibromomethyl-4,5-dibromobenzene. The ^{13}C NMR spectra of **6** was very similar to that of the precursor compound **5** except for the carbon signal at δ = 149.41 ppm for the Ar–C–N– group. MS (FAB positive): *m/z* = 983.3 $[M]^+$ also confirmed the structure.

Substitution of the bromo groups in **6** with cyanide moieties by a Rosenmund–von Braun reaction with cuprous cyanide[21] afforded corresponding phthalonitrile **7** in 58% yield. In the IR spectrum of **7**, the signal at 632 cm^{-1} for the C–Br bond vanished and a new peak at 2224 cm^{-1} appeared which was attributed to the dicyano groups. In the ^{13}C NMR spectrum of this compound, the presence of the signal at δ = 115.62 ppm, attributable to the nitrile carbon atom, indicated that the conversion had taken place; the ^{1}H NMR spectrum displayed similarities with that of precursor compound **6**. The mass spectrum of compound **7** should a peak at *m/z* = 876.29 $[M]^+$ and this is in a good accord with the suggested structure.

Because of the eight *tert*-butyl and eight tosyl peripheral groups, all phthalocyanines except for **12** and **13** possess good solubility in common organic solvents and they can be purified by column chromatography by using appropriate solvent systems as coeluents that break up the molecular aggregation and increase the mobility of these compounds on silica gel or neutral alumina columns.

Metal-free phthalocyanine **8** was synthesized from the reaction of phthalonitrile derivative **7**, dry *n*-pentyl alcohol, and a catalytic amount of DBU. According to the IR spectrum of **8**, the signals for the C≡N groups at 2224 cm^{-1} for compound **7** disappeared and new peaks appeared at 3320–1040 cm^{-1} and 1630 cm^{-1} that are dedicated to the N–H and C=N bonds in the phthalocyanine core of **8**, respectively. In the ^{1}H NMR spectrum, a peak at δ = –5.24 ppm, which is very characteristic for metal-free phthalocyanines, was detected and confirmed the suggested structure. The peak related to the C≡N groups in the ^{13}C NMR spectrum of **7** vanished in the case of metal-free phthalocyanine **8**. Other ^{1}H- and ^{13}C NMR spectra peaks resembled those of precursor compound **7**. The mass spectrum of **8** was measured as *m/z* = 3507.45 $[M]^+$ and is in good accord with the suggested structure.

Cyclization of **7** with zinc(II) acetate or nickel(II) chloride in the presence of DBU in *n*-pentyl alcohol then furnished the corresponding (phthalocyaninato)metal complexes **9** or **11**. The elemental analysis and mass spectroscopic data of **9** (*m/z* = 3570.31 $[M]^+$) and **11** (*m/z* = 3563.15 $[M]^+$) are consistent with their calculated values. The ^{1}H NMR spectra of these compounds were almost identical to those of metal-free phthalocyanine **8**. The differences in the ^{1}H NMR spectra of H_2Pc, ZnPc, and NiPc were the broad signals encountered in the case of compound **9** and **11** as a result of the aggregation of phthalocyanine cores at the considerable high concentration used for the NMR measurements.[22] The other characteristics of these compounds were quite similar to those of **7** and **8**. Cyclotetramerization of **7** was confirmed by the disappearance of the sharp C≡N stretching vibration at 2224 cm^{-1} in the IR spectrum. The IR spectra of NiPc and ZnPc are also very similar to that of the precursor H_2Pc except for the disappearance of the N–H vibration of the phthalocyanine core.

Copper(II) phthalocyanine (**10**) was synthesized directly from dibromo derivative **6**, CuCN, and quinoline in 42% yield. The comparison of the IR spectra obtained from **6** and **10** confirmed the conversion of the bromo groups into the characteristic skeleton moiety of phthalocyanine. In this case, the C–Br band at 632 cm^{-1} disappeared and a C=N stretching vibration at 1642 cm^{-1} appeared. The mass spectrum of **10** showed a peak corresponding to $[M + 1]^+$ at *m/z* = 3568.15.

Metal-free phthalocyanine **8** and metallophthalocyanines **9**–**11** and **14** displayed typical UV/Vis electronic spectra with two significant absorption bands, one of them in the visible region at about 710–600 nm corresponding to the Q band, and the other in the UV, approximately at 300 nm. The Q band absorptions of **8** in chloroform at $\lambda_{\max}$ = 710, 672, and 656 nm and the other absorption at 376 and 310 nm are consistent with the results obtained previously for similar phthalocyanines (Figure 1A).[23] The Q band absorption present in **8** can be attributed to the fact that the symmetry of the metal-free phthalocyanine is nondegenerate (D_{2h}) and is split in a Q_x and a Q_y peak as shown in the spectrum.[24] The bands between 300–500 nm show superimposed bands of phthalocyanine due to the existence of the Soret band of phthalocyanine (Pc).

The UV/Vis absorption spectra of metallophthalocyanines **9** and **10** are given in Figure 1A and **11** and **14** are given in Figure 2 in chloroform at room temperature. These compounds showed the expected absorptions at the main

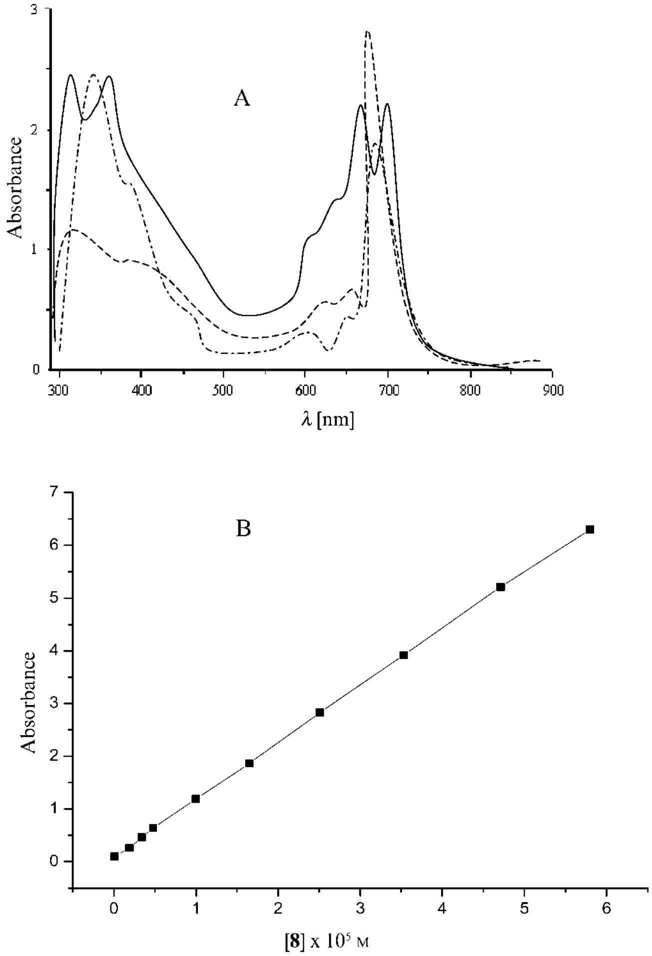


Figure 1. A) UV/Vis spectra of **8** (——), **9** (----) and **10** (-·-·-·) in chloroform (1×10^{-5} M). B) Plot of the Q-band (624 nm) absorbance versus concentration (from 2.5×10^{-7} to 5.80×10^{-5} M) in chloroform.

peaks of the Q- and B bands appearing at λ_{max} = 690, 692, 694, 683 nm and 330, 355, 341, 332 nm, respectively. This result is typical of metal complexes of substituted and unsubstituted Pc with D_{4h} symmetry.[2,25] Although ZnPc (**9**), CuPc (**10**), and NiPc (**11**) have a typical spectral pattern in the UV/Vis region for metallophthalocyanines, CuPc, NiPc, and detosylated **14** showed the new absorption bands at around 400 nm (466, 419, and 460 nm, respectively) in addition to the B band.[26] These new bands are sometimes observed, which can be ascribed to metal-to-ligand charge-transfer or ligand-to-metal charge-transfer transitions because metal ions have partially filled d orbitals. Alternatively, when the UV/Vis spectra data of **11** and **14** are compared, the Q bands in the UV/Vis spectra of **14** are shifted to shorter wavelengths with a decrease in the molar absorption coefficient as a result of the tendency to undergo aggregation.

Because of the eight bulky *tert*-butyl and eight tosyl substituents, these phthalocyanines are expected to be relatively nonaggregated in solution. This was confirmed by variable-concentration UV/Vis studies of compounds **8**–**11** in $CHCl_3$. For these four compounds, plots of the Q-band absorbance versus concentration (from 2.50×10^{-7} to 5.80×10^{-5} mol L^{-1}) gave nearly straight lines, which shows that the compounds follow the Beer–Lambert law. This observation indicates that the compounds mainly exist in the monomeric form under the conditions employed. Complex **14**, however, is slightly aggregated at higher concentrations (ca. 10^{-4} mol L^{-1}). This situation can be attributed to an increase in the intermolecular interaction between the phthalocyanine units after removing the bulky tosyl groups in **11**.

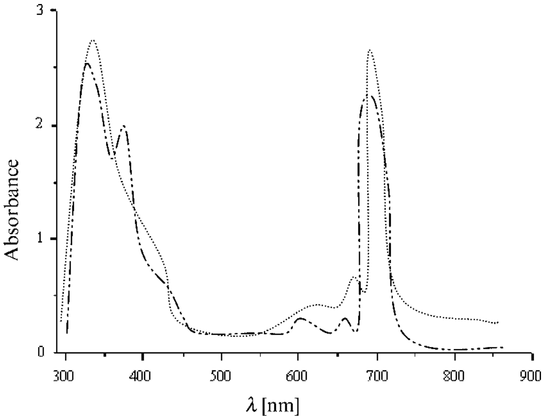


Figure 2. UV/Vis spectra of **11** (···) (1×10^{-5} M) and **14** (–··–··) in chloroform (1×10^{-5} M).

Nickel(II) phthalocyaninate derivatives of pentanuclear silver(I) complex **12** and palladium(II) complex **13** were prepared by treatment of **11** with $AgNO_3$ or $Pd(CH_3COO)_2$, respectively. From the IR spectra of products **12** and **13**, the vibrations belonging to the NO_3^- groups are observed at 1382 cm^{-1} and also symmetrical and asymmetrical vibrations of the CH_3COO^- groups are observed at 1580 and 1420 cm^{-1}, respectively, which confirmed the complexation of silver(I) or palladium(II) cations. The ^1H NMR spectra of **12** and **13** show downfield changes in all the chemical shifts of the protons in the macrocyclic rings upon complex formation. This can be attributed to the fact that the silver(I) and palladium(II) cations are strongly coordinated to the N and S atoms in the macrocyclic rings. The chemical shifts assigned to the acetate groups, which were observed at δ = 2.39 ppm, also confirmed the formation of target pentanuclear complex **13**. The FAB mass spectra of products **12** and **13**, which were recorded in a triflouroacetic acid/*m*-nitrobenzyl alcohol matrix, show peaks at *m*/*z* 4244.92 $[M + 2]^+$ and 4242.56 $[M]^+$, and 4461.50 $[M + 1]^+$, 4460.02 $[M]^+$, respectively. Elemental analyses of **12** and **13** also confirmed the formation of complexes with silver(I) or palladium(II) ions.

The tosyl groups in **11** were removed by treatment with excess $LiAlH_4$ in THF to give complex **14** containing free amino groups. Comparison of the IR data gives sufficient support for the proposed structure. The difference between the spectra of tosylated and free amino groups is clear from the presence of SO_2 vibrations in **11** at 1140 and 1343 cm^{-1} and the free N–H stretching vibrations for **14** at 3290 cm^{-1}.

The tosyl groups' signals observed for compound **11** in the ^{1}H NMR spectrum disappeared and a new peak appeared at δ = 3.21 ppm belonging to the N–H signals in **14**. After detosylation, the tosyl groups' signals in the ^{13}C NMR spectrum of **14** disappeared. The mass spectrum of compound **14** was 2338.08 $[M + Li]^+$and 2332.14 $[M + 1]^+$. All these spectroscopic data confirm the proposed structure.

The structures of the obtained phthalocyanines were an Au/MPc/Au sandwich in the configuration commonly used for the electrical conductivity measurements.[27] To prepare the samples, powdered materials were pressed at a load of 4 tons for 5 min into disk-shaped compacts with a thickness of 0.55–0.62 mm. The a.c. conductivity and parallel capacitance were measured with an Autolab 30 Voltammetry-FRA 2 impedance analyzer. The frequency range was 100 Hz to 1 MHz and the applied amplitude (rms) was 10 mV. The electrical conductivities of the obtained phthalocyanines were measured in a vacuum and under atmospheric pressure. Table 1 shows the a.c. electrical conductivities of phthalocyanines **8**–**14**. The conductivity values obtained under atmospheric pressure were higher than those under vacuum for all phthalocyanines probably because of absorbed oxygen.[27] These values correspond with those for semiconductive materials as encountered in a number of substituted phthalocyanine derivatives.[28] Relative to the conductivities of **11** and **14**, detosylated **14** shows a partial increase in the conductivity that is due to the removal of the bulky tosyl groups, which prevent the interaction of delocalized π-electrons on the phthalocyanine planes. Sixteen-membered diazadithiamacrocyclic substituents are expected to provide new chances to enhance the stacking of phthalocyanine units whereas their size and donor atoms are extremely harmonius to bond with transition metal cations in a 1:1 (metal/macrocycle ring) ratio.[29] Similar to the alkali metal complexes of analogous crown ether substituted phthalocyanines, planarity of the phthalocyanine nucleus will be extended. As a result, interaction of π-electrons will be achieved to realize charge transport. A.c. conductivities of nickel(II) phthalocyanine with four silver(I) or palladium(II) cations in the diazadithiamacrocyclic rings indicate a clear increase in the case of nitrate or acetate counterions.

The thermal properties of the synthesized macrocyclic compounds were investigated by DTA/TG.[30] Phthalocyanines are resistant to thermal oxidation. The DTA curves exhibited exothermic changes for all phthalocyanines **8**–**14** in the region investigated.[31] The initial decomposition temperature decreased in the order **9** > **7** > **11** > **8** > **13** > **14** > **6** > **10** > **12** (Table 2). Cu-containing phthalocyanine **10** was the most rapidly degrading metallophthalocyanine whereas Zn- and Ni-containing metallophthalocyanine showed good thermal stability under the working conditions. These results are in good agreement with the literature.[32] The DTA thermogram of **12** showed an endothermic peak at 230 °C, which is due to the dissociation of the nitrate groups. The thermal stabilities of **12** and **13** were lower than that of compound **11**. The thermal stabilities of **12** and **13** indicate that the dopants are rather weakly bound in the macrocyclic cavities because the bulky tosyl and *tert*-butyl groups in the macrocyclic ring have a steric effect.

The heavy metal binding ability of N–S-macrocyclic units is a well-known property. The binding abilities of the heavy metal ions in the N–S-macrocyclic units were esti-

Table 2. Thermal properties of the polymeric phthalocyanines.

Compound	Dissociation of NO_3 T_{max} [°C]	Initial decomposition temp. [°C]	Main decomposition temp. [°C]
6	–	331	387
7		348	415
8	–	337	425
9	–	376	494
10		324	428
11		345	454
12	230	320	430
13		350	443
14	–	335	438

Table 3. Heavy metal picrate extractions for **11**[a] and **14**[a] under liquid–liquid phase conditions.

Metal ion	Extractabilities of **11** and **14** [%][b]		λ_{max} of metal picrate
	11	**14**	[nm]
Ag^+	55.62 ± 0.01	86.23 ± 0.01	350
Cd^{2+}	35.41 ± 0.01	54.36 ± 0.01	362
Cu^{2+}	23.48 ± 0.01	48.54 ± 0.01	355
Hg^{2+}	16.33 ± 0.01	42.27 ± 0.01	360
Pb^{2+}	12.46 ± 0.01	35.67 ± 0.01	354
Pd^{2+}	39.80 ± 0.01	68.98 ± 0.01	360
Zn^{2+}	9.54 ± 0.01	31.73 ± 0.01	349

[a] Temperature 25 ± 1 °C; aqueous phase (10 mL), [picrate] = 3.0×10^{-3} M; organic phase (chloroform, 10 mL), [host molecule] = 3.0×10^{-3} M. [b] Average and standard deviation for three independent measurements.

Table 1. Electrical conductivity of the phthalocyanines at room temperature.

Compound	M	Conductivity [S cm^{-1}] in air	Conductivity [S cm^{-1}] in vacuo	Pellet thickness [mm]
8	2H	7.75×10^{-9}	6.23×10^{-10}	0.60
9	Zn	3.53×10^{-8}	1.64×10^{-9}	0.55
10	Cu	2.74×10^{-7}	2.36×10^{-8}	0.65
11	Ni	1.58×10^{-7}	3.47×10^{-8}	0.60
12	$Ni{\cdot}4AgNO_3$	2.42×10^{-5}	3.15×10^{-6}	0.62
13	$Ni{\cdot}4Pd(CH_3COO)_2$	3.50×10^{-6}	3.97×10^{-7}	0.56
14	Ni-8Ts	6.72×10^{-7}	4.95×10^{-8}	0.60

mated by solvent extraction of heavy metal picrates from the aqueous phase to an organic phase (Table 3). Picrate was used as the counter anion for all compounds. As depicted in Table 3, the highest extraction affinities of **11** and **14** were determined as 55.62 and 86.23% for Ag^+, respectively. The extraction affinity of **14** was more than that of **11** for all working cations. This indicates that cations are able to bind to **14** easier than they can to **11** after the bulky tosyl groups were removed.

Conclusions

In this paper, we have described the synthesis and characterization of new very soluble octa-substituted metal-free phthalocyanines and metallophthalocyanines (M = 2 H, Zn, Cu, and Ni) by using proper materials. Zn- and Ni-containing phthalocyanines showed good thermal stability whereas Cu-containing phthalocyanine degraded the most rapidly. The DTA thermogram of **12** showed an endothermic peak at 230 °C, which is due to the dissociation of the nitrate groups. Also, the thermal stabilities of **12** and **13** were lower than that of compound **11**. The electrical conductivities of the obtained phthalocyanines were found to be 10^{-10}–10^{-5} $S\,cm^{-1}$ in vacuo and air. The extraction abilities of **11** and **14** were evaluated by using a solvent extraction technique and the highest extraction affinities were observed for Ag^+ for all working conditions. The extraction affinity of **14** was more than that of **11** for all working cations.

Experimental Section

Materials: Reactions were performed under an atmosphere of argon. 4-*tert*-Butyl-2-nitrobenzyl chloride (**2**) was prepared according to the literature.[18] All other reagents and solvents were of reagent grade quality, purchased from commercial suppliers, and they were dried before use as described in the literature.[33] Silica gel (70–230 mesh) and Merck 90 active neutral alumina were used for chromatographic separations.

Measurements: Melting points were determined with an electrothermal apparatus and are uncorrected. ^1H and ^{13}C NMR spectroscopic data were recorded with a Varian XL-200 spectrometer and IR spectra were obtained with a Perkin–Elmer Spectrum One spectrometer. Optical spectra in the UV/Vis region were recorded with a model Shimadzu 1601 UV/Vis spectrometer with the use of 1-cm pathlength cuvettes at room temperature. The a.c. conductivity was measured with an Autolab 30 Voltammetry-FRA 2 frequency analyzer. The frequency range was 100 Hz to1 MHz and the applied amplitude (rms) was 10 mV. Mass spectra were measured with a Varian MAT 711 or a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer by using triflouroacetic acid/*m*-nitrobenzyl alcohol as the matrix. Elemental analyses were determined with a CHNS-932 LECO instrument. The metal content of the metallophthalocyanines was determined with a Unicam 929 AA spectrophotometer.

1,2-Bis(4-*tert*-butyl-2-nitrobenzylthio)ethane (3): 1,2-ethandithiol (2 mL, 60 mmol), 4-*tert*-butyl-2-nitrobenzyl chloride (11.35 g, 50 mmol), and methanol (10 mL) were stirred inside a washing bottle at 50 °C while ammonia gas was bubbled through the solution for 2 h. The mixture was then cooled down to room temperature, benzene (100 mL) was added, and the salt was removed by filtration. The solvent was evaporated and methanol (15 mL) was added to the residue, which was then kept inside the refrigerator overnight. The yellow crystals were separated by filtration, dried in vacuo, and then recrystallized from *n*-butyl alcohol. Yield: 7.3 g (62%). M.p. 139–142 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.01–7.48 (m, 6 H, Ar-H), 4.20 (s, 4 H, Ar-CH_2-S), 2.70 (t, 4 H, -SCH_2-CH_2S-), 1.32 [s, 18 H, $(CH_3)_3C$-] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 149.5 (Ar-C-NO_2), 147.2, 128.2, 124.3, 119.3, 117.2, 34.1 [Ar-C-$(CH_3)_3$], 32.5 (S-CH_2-CH_2-S), 31.9 (Ar-CH_2-S), 30.6 [(-$CH_3)_3$] ppm. IR (KBr): $\tilde{\nu}$ = 3043 (CH aromatic), 2954–2849(CH_2 aliphatic), 1543, 1340 (NO_2), 684 (C–S) cm^{-1}. MS (EI): *m*/*z* = 477.01 $[M + 1]^+$, 476.23 $[M]^+$, 475.30, 285.12, 284.07, 193.24, 192.15 $[M - C_{13}H_{18}NO_2S_2]^+$. $C_{24}H_{32}N_2O_4S_2$ (476.12): calcd. C 60.49, H 6.72, N 5.88, S 13.47; found C 60.32, H 6.92, N 5.69, S 13.62.

1,2-Bis(4-*tert*-butyl-2-aminobenzylthio)ethane (4): 1,2-Bis(4-*tert*-butyl-2-nitrobenzylthio)ethane (7.3 g, 153 mmol) was dissolved in *n*-butyl alcohol (200 mL) and heated at 80 °C. The temperature was then adjusted to 60 °C and 10%Pd/C (0.91 g) was added, and the reaction mixture was heated at reflux. Hydrazinium hydrate (30.6 mL) was added dropwise to the reaction mixture over a period of 30 min. After the addition, the mixture was heated at reflux for 10 h, and then the reaction was filtered over celite while it was hot. *n*-Butyl alcohol was removed under reduced pressure, and methanol (25 mL) was added to the residue, which was then kept in the refrigerator overnight. The precipitated white crystals were filtered off and washed several times with petroleum ether and dried in vacuo. Yield 3.5 g (78%). M.p. 106–108 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.29–6.56 (m, 6 H, Ar-H), 3.82 (br. s, 4 H, -NH_2), 3.62 (s, 4 H, Ar-CH_2-S), 2.91 (t, 4 H, -SCH_2-CH_2S-), 1.29 [s, 18 H, $(CH_3)_3C$-] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 145.6 (Ar-C-NH_2), 143.2, 127.1, 123.3, 118.8, 116.5, 34.0 [Ar-C-$(CH_3)_3$], 31.6 (S-CH_2-CH_2-S), 30.8 (Ar-CH_2-S), 30.2 [(-$CH_3)_3$] ppm. IR (KBr): $\tilde{\nu}$ = 3430–3320 (NH_2), 3025 (C–H aromatic), 2965–2864 (CH_2 aliphatic), 1610 (NH_2, bending), 1512, 1450, 1234 and 670 (C–S) cm^{-1}. MS (EI): *m*/*z* = 417.23 $[M + 1]^+$, 416.09 $[M]^+$, 254.15, 163.17 $[M + 1 - C_{13}H_{20}NS_2]^+$, 162.08 $[M - C_{13}H_{20}NS_2]^+$. $C_{24}H_{36}N_2S_2$ (416.12): calcd. C 69.21, H 8.65, N 6.73, S 15.40; found C 68.97, H 8.54, N 6.86, S 15.65.

1,2-Bis(4-*tert*-butyl-2-tosylaminobenzylthio)ethane (5): *p*-Toluenesulfonyl chloride (1.233 g, 6.47 mmol) in pyridine (2.5 mL) was added dropwise over a period of 2 h to a –10 °C solution of 1,2-bis(4-*tert*-butyl-2-aminobenzylthio)ethane (**3**; 1.344 g, 3.23 mmol) in pyridine (2.5 mL). The reaction was stirred overnight at –10 °C and then stirred at room temperature for 15 h under a nitrogen atmosphere. The reaction mixture was gently poured into ice (50–100 g), conc. HCl (6 mL) was added, and the mixture stirred for 24 h. The precipitated solid was filtered off and washed several times with deionized water until the washing solvent was neutral. The pale yellow solid product was then dried in vacuo and recrystallized from acetone. Yield 2.28 g (97.5%). M.p. 220–222 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.29 (s, 2 H, N-H), 7.85 (d, 4 H, Tosyl-Ar-H), 7.35 (d, 4 H, Tosyl-Ar-H), 6.40–6.98 (m, 6 H, Ar-H), 3.67 (s, 4 H, Ar-CH_2-S), 2.73 (t, 4 H, -SCH_2-CH_2S-), 2.32 (s, 6 H, Tosyl-CH_3), 1.27 [s, 18 H, $(CH_3)_3C$-] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 148.6 (Ar-C-NH), 144.6 (Ts-Ar), 143.4, 135.3 (Ts-Ar), 130.2 (Ts-Ar), 127.4 (Ts-Ar), 127.2, 123.4, 118.9, 116.2, 34.1 [Ar-C-$(CH_3)_3$], 31.3 (S-CH_2-CH_2-S), 30.6 (Ar-CH_2-S), 30.2 [(-$CH_3)_3$], 21.5 (Ar-CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3270 (N–H), 3050 (CH aromatic), 2990–2835(CH_2 aliphatic), 1592 (N–H bending), 1343 and 1140 (SO_2), 674 (C–S) cm^{-1}. MS (FAB+): *m*/*z*: = 725.30 $[M + 1]^+$, 724.19 $[M]^+$, 570.42 $[M + 1 – Ts]^+$, 471.41, 470.12, 415.08 $[M + 1 – 2Ts]^+$, 414.14$[M – 2Ts]^+$. $C_{38}H_{48}N_2O_4S_4$ (724.24): calcd. C 62.96, H 6.62, N 3.87, S 17.71; found C 62.74, H 6.40, N 3.73, S 17.85.

4,5:12,13-Bis(4′-*tert*-butylbenzo)-8,9-(4′′,5′′-dibromobenzo)-6,11-ditosyl-6,11-diaza-2,15-dithiacyclohexadeca-4,8,12-triene (6): A 500-mL three-necked round-bottomed flask containing anhydrous DMF (100 mL) and fitted with a condenser was evacuated, refilled three times with argon gas and connected to a vacuum line. Under an argon atmosphere, the flask was charged with **5** (2.28 g, 3.15 mmol) and finely ground anhydrous K_2CO_3 (2.174 g, 15.75 mmol). The reaction mixture was stirred for 1 h at 45 °C. α,α′-Dibromomethyl-4,5-dibromobenzene (1.349 g, 3.15 mmol) in anhydrous DMF (50 mL) was added dropwise to the reaction mixture over a period of 6 h, and the reaction mixture was heated at reflux under an argon atmosphere for 6 d. The reaction was monitored by thin layer chromatography [chloroform/petroleum ether (7:3)]. At the end of this period, the mixture was cooled to room temperature, filtered, and washed with dry DMF and dichloromethane. The filtrate and the washing solvents were combined and the solvents evaporated to dryness under reduced pressure. The residue was added to ice (100 g) and stirred for 1 d. Thus, a pale brown solid was obtained and washed with deionized water (50 mL) and then dried in vacuo. The final purification of the product was carried out by column chromatography on silica gel (chloroform) to give a pale brown solid. Yield 1.12 g (36%). M.p. 264–265 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.75 (s, 2 H, Ar-H), 7.57 (d, 4 H, Tosyl-Ar-H), 7.30 (d, 4 H, Tosyl-Ar-H), 6.51–6.78 (m, 6 H, Ar-H), 4.92 (s, 4 H Ar-CH_2-N), 3.71 (s, 4 H, Ar-CH_2-S), 2.70 (t, 4 H, -SCH_2-CH_2S-), 2.40 (s, 6 H, Tosyl-CH_3), 1.22 [s, 18 H, $(CH_3)_3C$-] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 149.4 (Ar-C-N-), 144.9 (Ts-Ar), 142.7, 139.4, 134.7, 130.5, 127.5, 127.0, 125.5, 124.4, 119.7, 117.5, 49.7 (Ar-CH_2-N-Ar), 34.3 [Ar-C-$(CH_3)_3$], 31.7 (S-CH_2-CH_2-S), 31.7 (Ar-CH_2-S), 29.3 [(-$CH_3)_3$], 21.8 (Ar-CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3048 (CH aromatic), 2995–2865(CH_2 aliphatic), 1340 and 1145 (SO_2), 676 (C–S), 632 (C–Br) cm^{-1}. MS (FAB+): *m*/*z* = 982.23 $[M]^+$. $C_{46}H_{52}Br_2N_2O_4S_4$ (984.05): calcd. C 56.09, H 5.28, N 2.85, S 13.03; found C 56.39, H 5.47, N 2.63, S 13.41.

4,5:12,13-Bis(4′-tert-butylbenzo)-8,9-(4′′,5′′-dicyanobenzo)-6,11-ditosyl-6,11-diaza-2,15-dithiacyclohexadeca-4,8,12-triene (7): Compound **6** (3.05 g, 3.1 mmol) in anhydrous DMF (30 mL) and CuCN (0.95 g, 10.66 mmol) were added to a 250-mL round-bottomed flask. Under an argon atmosphere, the reaction mixture was gently heated to 160 °C and stirred for 24 h. The reaction mixture was then cooled to room temperature, a 25% NH_3 solution (150 mL) was added, and oxygen gas was bubbled through the reaction mixture for 24 h. The precipitated solid was then filtered off and washed several times with deionized water until the filtrate was neutral. The pale brown product was dried in vacuo over P_2O_5. The crude product was purified by column chromatography on silica gel [chloroform/petroleum ether/methanol (6:3:1)] to give a pale brown solid. Yield: 1.58 g (58%). M.p. 208–210 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.90 (s, 2 H, Ar-H), 7.60 (d, 4 H, Tosyl-Ar-H), 7.35 (d, 4 H, Tosyl-Ar-H), 6.56–6.79 (m, 6 H, Ar-H), 4.98 (s, 4 H Ar-CH_2-N), 3.75 (s, 4 H, Ar-CH_2-S), 2.74 (t, 4 H, -SCH_2-CH_2S-), 2.42 (s, 6 H, Tosyl-CH_3), 1.24 [s, 18 H, $(CH_3)_3C$-] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 147.2 (Ar-C-N-), 144.4, 142.2, 140.7, 133.7, 130.3, 127.5, 127.0, 124.0, 118.7, 116.3, 115.6 (C≡N), 114.1, 51.1 (Ar-CH_2-N-Ar), 35.0 [Ar-C-$(CH_3)_3$], 32.9 (S-CH_2-CH_2-S), 32.5 (Ar-CH_2-S), 30.1 [(-$CH_3)_3$], 20.9 (Ar-CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3045 (CH aromatic), 2980–2854(CH_2 aliphatic), 2224 (C≡N), 1500, 1460, 1343 and 1148 (SO_2), 675 (C–S) cm^{-1}. MS (FAB+): *m*/*z* = 876.32 $[M]^+$. $C_{48}H_{52}N_4O_4S_4$ (876.24): calcd. C 65.74, H 5.93, N 6.39, S 14.64; found C 65.44, H 5.68, N 6.64, S 14.02.

Metal-Free Phthalocyanine 8: Under a dry argon atmosphere, a standard Schlenk tube was charged with phthalonitrile derivative **7** (150 mg, 0.171 mmol), dry *n*-pentyl alcohol (1.5 mL), and 3–4 drops of DBU, and the mixture was degassed several times. The reaction mixture was heated at reflux (155 °C) for 16 h, cooled to room temperature, and diethyl ether (2–3 mL) was added. The precipitated light green solid product was filtered off and dried. This product was purified by column chromatography on silica gel [dichloromethane/methanol (100:1)]. The combined solvents were evaporated and light green metal-free phthalocyanine **8** was obtained and then dried in vacuo. Yield: 42 mg (28%). M.p. >300 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 8.06 (s, 8 H, Ar-H), 7.72–6.72 (m, 56 H, Ar-H), 4.78 (s, 16 H, Ar-CH_2-N), 3.69 (s, 16 H, Ar-CH_2-S), 2.80 (t, 16 H, -SCH_2-CH_2S-), 2.48 (s, 24 H, Tosyl-CH_3), 1.27 [s, 72 H, $(CH_3)_3C$-], –5.24 (br. s, 2 H, N-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 156.3, 146.4, 143.9, 141.6, 141.0, 137.1, 131.5, 129.4, 128.1, 126.8, 122.2, 119.8, 112.7, 53.1, 34.1, 31.8, 30.3, 29.5, 22.2 ppm. IR (KBr): $\tilde{\nu}$ = 3320 (N–H), 3054 (CH aromatic), 2963–2874 (CH_2 aliphatic), 1630 (C=N), 1510, 1480, 1340 and 1150 (SO_2), 1040 (N–H), 750, 680 (C–S) cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (logε) = 710 (5.34), 672 (5.35), 656 (5.19), 624 (5.08), 376 (5.38), 310 (5.39) nm. MS (FAB+): *m*/*z* = 3507.45 $[M]^+$. $C_{192}H_{210}N_{16}O_{16}S_{16}$ (3506.96): calcd. C 65.70, H 5.99, N 6.39, S 14.63; found C 65.96, H 5.90, N 6.57, S 14.97.

Phthalocyaninato Zinc(II) (9): Under a dry argon atmosphere, a standard Schlenk tube was charged with phthalonitrile derivative **7** (100 mg, 0.114 mmol), dry *n*-pentyl alcohol (1.5 mL), $Zn(CH_3COO)_2 \cdot 2H_2O$ (6.4 mg, 0.029 mmol), and 3–4 drops of DBU, and the mixture was degassed several times. The reaction mixture was heated at reflux (160 °C) for 15 h, cooled to room temperature, and diethyl ether (2–3 mL) was added. The precipitated green solid product was filtered off, washed with ethanol, water, and diethyl ether, respectively, and then dried. The obtained light green product was purified by column chromatography on silica gel [dichloromethane/methanol (100:1)]. The collected solvents were evaporated and light green Zn^{II} phthalocyaninate **9** obtained and then dried in vacuo. Yield 38.7 mg (38%). M.p. > 300 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.90 (br. s, 8 H, Ar-H), 7.67–6.50 (m, 56 H, Ar-H), 4.70 (s, 16H Ar-CH_2-N), 3.63 (s, 16 H, Ar-CH_2-S), 2.73 (t, 16 H, -SCH_2-CH_2S-), 2.39 (s, 24 H, Tosyl-CH_3), 1.22 [s, 72 H, $(CH_3)_3C$-] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 153.1, 145.9, 142.4, 141.1, 139.6, 137.3, 130.5, 129.4, 128.3, 127.0, 122.1, 119.7, 110.6, 52.2, 34.9, 32.5, 31.3, 29.5, 22.0 ppm. IR (KBr): $\tilde{\nu}$ = 3050 (CH aromatic), 2990–2848 (CH_2 aliphatic), 1632 (C=N), 1512, 1485, 1341 and 1134 (SO_2), 756, 672 (C–S) cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (logε) = 690 (5.45), 665 (4.90), 627 (4.83), 390 (4.96), 330 (5.07) nm. MS (FAB+): *m*/*z* = 3571.54 $[M + 1]^+$, 3570.31 $[M]^+$, 3506.12 $[M + 1 – Zn]^+$. $C_{192}H_{208}N_{16}O_{16}S_{16}Zn$ (3570.34): calcd. C 64.53, H 5.83, N 6.27, S 14.37, Zn 1.83; found C 64.28, H 5.69, N 6.43, S 14.61, Zn 1.71.

Phthalocyaninato Copper(II) (10): A mixture of dibromo derivative **6** (250 mg, 0.254 mmol), CuCN (68.2 mg, 0.762 mmol), and quinoline (1 mL) was placed in a stoppered Schlenk tube under an argon atmosphere, gently heated to 205 °C and refluxed for 22 h. The reaction mixture was then cooled to room temperature, ethanol (10 mL) added, stirred for 15 min, and filtered. The solid product was heated with a 3 N NaCN solution (3 × 25 mL) in order to remove excess CuCN over a period of 5 h. The dark green residue was filtered off and dried. This product was charged into a Soxhlet extraction column and extracted with chloroform for 18 h. The solvent was removed and solid product obtained. This green Cu^{II} phthalocyanine derivative was purified by column chromatography on neutral alumina (chloroform) to give a dark green solid product.

Yield 95 mg (42%). M.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 3060 (CH aromatic), 2985–2862 (CH_2 aliphatic), 1642 (C=N), 1515, 1495, 1350 and 1138 (SO_2), 755, 673 (C–S) cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (logε) = 692 (5.26), 655 (4.73), 611 (4.66), 466 (4.75), 394 (5.20), 355 (5.38) nm. MS (FAB+): *m*/*z* = 3568.15 [M + 1]$^+$, 3504.72 [M + 1 – Cu]$^+$. $C_{192}H_{208}CuN_{16}O_{16}S_{16}$ (3568.42): calcd. C 64.57, H 5.83, N 6.28, S 14.37, Cu 1.78; found C 64.74, H 6.03, N 6.49, S 14.85, Cu 1.94.

Phthalocyaninato Nickel(II) (11): Dicyano derivative **7** (80 mg, 0.091 mmol), dry *n*-pentyl alcohol (1.5 mL), $NiCl_2$ (12 mg, 0.092 mmol), and 3–4 drops of DBU were placed into a standard Schlenk tube under a dry argon atmosphere, and reaction mixture was evacuated several times and refilled with dry argon. Under an argon atmosphere, the reaction mixture was heated at reflux (155 °C) for 18 h. The reaction mixture was then cooled to room temperature, filtered, and dried. The obtained product was purified by column chromatography on silica gel [chloroform/methanol (100:1)]. The combined solvents were evaporated and dark green Ni^{II} phthalocyaninate **9** was obtained and dried in vacuo. Yield 26.5 mg (32.6%). M.p. > 300 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.93 (br. s, 8 H, Ar-H), 7.68–6.54 (m, 56 H, Ar-H), 4.73 (s, 16H Ar-CH_2-N), 3.61 (s, 16 H, Ar-CH_2-S), 2.77 (t, 16 H, -SCH_2-CH_2S-), 2.42 (s, 24 H, Tosyl-CH_3), 1.20 [s, 72 H, $(CH_3)_3C$-] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 153.5, 145.6, 142.3, 140.2, 139.9, 137.2, 130.4, 129.3, 128.1, 127.9, 121.6, 119.5, 109.8, 51.2, 35.0, 32.5, 31.1, 29.0, 22.1 ppm. IR (KBr): $\tilde{\nu}$ = 3057 (CH aromatic), 2981–2856 (CH_2 aliphatic), 1645 (C=N), 1505, 1489, 1346 and 1130 (SO_2), 762, 678 (C–S) cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (logε) = 694 (5.38), 668 (4.85), 622 (4.59), 419 (4.90), 341 (5.41) nm. MS (FAB+): *m*/*z* = 3563.15 [M]$^+$, 3505.62 [M – Ni]$^+$. $C_{192}H_{208}N_{16}NiO_{16}S_{16}$ (3563.66): calcd. C 64.65, H 5.84, N 6.29, S 14.39, Ni 1.65; found C 64.49, H 6.14, N 6.11, S 14.56, Ni 1.79.

Silver(I) Complex of 11 (12): Nickel(II) phthalocyanine derivative **11** (0.10 g, 0.028 mmol) was dissolved in tetrahydrofuran/water (5.1:0.1) in a 100-mL three-necked round-bottomed flask. Silver nitrate (0.038 g, 0.225 mmol) in the same solvent mixture (5.1:0.1) was added. The mixture was heated at reflux for 4 h, and a bluish–green product formed. The product was filtered off and washed with hot water, hot ethanol, and then diethyl ether. The deep blue product was then dried with P_2O_5 in vacuo. Yield: 0.069 g (58%). ^1H NMR (200 MHz, CF_3COOD): δ = 7.95 (br. s, 8 H, Ar-H), 7.70–6.52 (m, 56 H, Ar-H), 4.80 (s, 16 H, Ar-CH_2-N), 3.69 (s, 16 H, Ar-CH_2-S), 2.84 (t, 16 H, -SCH_2-CH_2S-), 2.41 (s, 24 H, Tosyl-CH_3), 1.21 [s, 72 H, $(CH_3)_3C$-] ppm. IR (KBr): $\tilde{\nu}$ = 3045, 2942, 1615, 1480, 1382 (NO_3), 1340, 1235, 1120, 1100, 1048, 1015, 840, 760, 681 cm^{-1}. MS (FAB+): *m*/*z* = 4244.92 [M + 2]$^+$, 4242.56 [M]$^+$, 4180.26 [M – NO_3]$^+$, 4118.17 [M – $2NO_3$]$^{2+}$, 4056.08 [M – $3NO_3$]$^{3+}$. $C_{192}H_{208}Ag_4N_{20}NiO_{28}S_{16}$ (4243.14): calcd. C 54.30, H 4.90, N 6.60, S 12.09, Ni 1.38, Ag 10.17; found C 54.16, H 4.67, N 6.86, S 12.31, Ni 1.54, Ag 10.42.

Palladium(II) Complex of 11 (13): Metallophthalocyanine **11** (0.10 g, 0.028 mmol) was dissolved in tetrahydrofuran (5 mL) and a solution of $Pd(CH_3COO)_2$ (0.0503 g, 0.2236 mmol) in THF (5 mL) was added. The color became bluish–green while heated at reflux for 5 h and then precipitation occurred. The product was separated by centrifugation and washed several times successively with hot water, hot ethanol, and then diethyl ether. The bluish–green product was filtered off and dried with P_2O_5 in vacuo. Yield: 0.081 g (65%). ^1H NMR (200 MHz, CF_3COOD): δ = 8.12 (br. s, 8 H, Ar-H), 7.75–6.50 (m, 56 H, Ar-H), 4.79 (s, 16H Ar-CH_2-N), 3.70 (s, 16 H, Ar-CH_2-S), 2.85 (t, 16 H, -SCH_2-CH_2S-), 2.43 (s, 24 H, Tosyl-CH_3), 2.39 (s, 24 H, CH_3COO), 1.21 [s, 72 H, $(CH_3)_3C$-] ppm. IR (KBr): $\tilde{\nu}$ = 3055, 2980, 1630, 1580 (asym.CH_3COO), 1503, 1470, 1420 (sym. CH_3COO), 1343, 1220, 1110, 1090, 1040, 1010, 740, 674 cm^{-1}. MS (FAB+): *m*/*z* = 4461.50 [M + 1]$^+$, 4460.02 [M]$^+$, 4400.13 [M – CH_3COOH]$^+$. $C_{208}H_{232}N_{16}NiO_{32}Pd_4S_{16}$ (4461.26): calcd. C 55.95, H 5.20, N 5.02, S 11.50, Ni 1.32, Pd 9.54; found C 56.14, H 5.32, N 4.87, S 11.65, Ni 1.49, Pd 9.75.

Detosylation of 11 with $LiAlH_4$ – Compound 14: A solution of **11** (0.100 g, 0.028 mmol) in dry THF (100 mL) was slowly added to a stirred suspension of $LiAlH_4$ (0.11 g, 2.8 mmol) in dry THF (100 mL) at room temperature under an argon atmosphere. The resulting mixture was stirred and heated at reflux for 5 d. A mixture of ethyl acetate and water was carefully added with stirring at 0 °C to decompose the excess $LiAlH_4$. The resulting precipitate was filtered and washed thoroughly with ethyl acetate and CH_2Cl_2. The combined filtrates were dried ($MgSO_4$) and the solvents evaporated. The residue was purified by chromatography on silica gel [CH_2Cl_2/CH_3OH/NH_4OH (98:1:1)]. Evaporation of the solvent gave **14** as a green solid. Yield: 0.016 g (25%). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.94 (br., 8 H, Ar-H), 7.17–6.59 (m, 24 H, Ar-H), 4.69 (s, 16H Ar-CH_2-N), 3.65 (s, 16 H, Ar-CH_2-S), 3.21 (br. s, 8 H, N-H, D_2O exchange), 2.78 (t, 16 H, -SCH_2-CH_2S-), 1.24 [s, 72 H, $(CH_3)_3C$-] ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 152.6, 150.1, 147.8, 139.4, 136.3, 127.8, 123.8, 122.6, 118.5, 112.3, 45.6, 34.0, 32.5, 31.1, 28.9 ppm. IR (KBr): $\tilde{\nu}$ = 3290 (N–H), 3040 (CH aromatic), 2960–2859 (CH_2 aliphatic), 1632 (C=N), 1500, 1490, 1240, 1120 (N–H), 760, 672 (C–S) cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (logε) = 683 (5.33), 658 (4.38), 606 (4.51), 460 (4.80), 379 (5.30), 332 (5.39) nm. MS (FAB+): *m*/*z* = 2338.08 [M + Li]$^+$, 2332.14 [M + 1]$^+$, 2331.16 [M – Li]$^+$. $C_{136}H_{160}N_{16}NiS_8$ (2331.18): calcd. C 70.01, H 6.86, N 9.61, S 11.00, Ni 2.52; found C 70.21, H 6.68, N 9.54, S 11.27, Ni 2.69.

Measurements of Heavy Metal-Binding Properties of 11 and 14: The extraction properties of **11** and **14** were investigated under liquid–liquid phase and neutral conditions by using heavy metal picrates (Ag^+, Cd^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}, Pd^{2+}, and Zn^{2+}) as substrates and by measuring with UV/Vis the amounts of metal picrate in the aqueous phase before and after treatment with the related compounds. Heavy metal picrates were prepared by the mixture of metal nitrates (4×10^{-2} M) and picric acid (1.5×10^{-2} M) in deionized water. We also prepared solutions (3×10^{-3} M) of related compounds **11** and **14** in dichloromethane. Equal volumes of both metal picrate solutions and compound solutions were then added into plastic bottles, kept closed, and shaken for 10 h by a shaker at 25 ± 1 °C. After shaking, the aqueous phases were separated and the percent of picrate salt extracted (*E*%) was determined by UV spectrophotometry. For each combination of host and metal picrate, the picrate extraction was conducted on three different samples and the average value of percent picrate extracted, with standard deviation, was calculated. The picrate extraction results are presented in Table 3. In the absence of host, blank experiment, no metal ion picrate extraction was detected. The extractability was determined on the basis of the absorbance of picrate ions in the aqueous solutions. The extractability was calculated by using the equation below:

$$E(\%) = [(A_{before} - A_{after})/A_{before}]\times100$$

where A_{before} is the absorbance in the absence of ligand. A_{after} denotes the absorbance in the aqueous solution phase after extraction.

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