Synthesis and Characterization of New Monomeric and Polymeric Phthalocyanines

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ABSTRACT: Monomeric (M = 2Li or 2H) and polymeric (M = 2H, Zn, Cu, Co, or Ni), where M is metal or hydrogen, phthalocyanines were prepared by the tetramerization reaction of bisphthalonitrile monomer with appropriate materials. The electrical conductivities of the polymeric phthalocyanines, which were measured as gold sandwiches, were found to be 10^{-10}–10^{-7} S/cm *in vacuo* and in air. The binding property of a Co-containing polymeric phthalocyanine (**10**) toward alkali, alkaline-earth, and some heavy cations was studied in tetrahydrofuran. The extraction affinity of **10** for K$^+$ was found to be the highest in the heterogeneous phase extraction experiments. The disaggregation property of a Ni-containing polymeric phthalocyanine (**11**) was investigated with K$^+$, Na$^+$, and NH$_4^+$ cations. The intrinsic viscosities of all polymers were also measured by means of viscometry. All the novel compounds were characterized with elemental analysis, ultraviolet–visible, Fourier transform infrared, NMR, and mass spectrometry spectral data, and differential thermal analysis/thermogravimetry. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2115–2126, 2008

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INTRODUCTION

Phthalocyanines and related macrocycles have drawn considerable attention as molecular materials that give rise to outstanding electronic and optical properties. These properties arise from their electronic delocalization and make these compounds applicable in different fields of materials science; they are particularly promising as building blocks in nanotechnology. In fact, phthalocyanines have been successfully incorporated as active components of semiconductor and electrochromic devices, information storage systems, and liquid-crystal color displays, among other applications.[1]

Polymeric phthalocyanines are also very interesting because they belong to a class of π-conjugated semiconductor polymers that offer a unique combination of properties. Discovered in the 1950s, polymeric phthalocyanines remain enigmatic materials, and many of their intrinsic properties are known rather insufficiently.[2,3] Polymeric phthalocyanines have been mainly prepared through polycyclotetramerization reactions of bifunctional monomers such as aromatic tetracarbonitriles, various oxy-, arylene-dioxy-, and alkylenedioxy-bridged diphthalonitriles,

and other nitriles or tetracarboxylic acid derivatives in the presence of metal salts or metals.[2,4] The electrical properties of polymeric phthalocyanines are of interest because of their conjugated structure and stability against light, heat, moisture, and air. Hence, polymeric phthalocyanines are suitable candidates for use as environmentally stable electrically conductive materials.[4] On the other hand, macrocyclic compounds are known to extract specific metals or metal salts according to the specific cavity size of each macrocyclic compound.[5] The ion-binding ability of phthalocyanines containing homocrowns and heterocrowns is receiving considerable attention because of their effect on the aggregation of the molecules. After polymerization reactions, polymeric phthalocyanines have many macrocycle units and thus high metal-extraction affinities.

We recently outlined a concept for the synthesis of new types of monomeric and polymeric phthalocyanines with various functional groups. These phthalocyanines have N-, O-, and S-containing functionalities such as diazadioxa, cylindrical and spherical macrotricycles, crown ether fused diloops, and diazadithia macrocyclics with *tert*-butyl.[4,6,7]

We report here the synthesis and characterization of monomeric and polymeric phthalocyanines containing peripheral macrocyclic derivatives. This may allow the creation of novel functionalized materials as new kinds of alkali, alkaline-earth, and heavy-metal extraction agents in analytical chemistry. We examined the electrical conductivities of the

polymers as Au/MPc/Au sandwiches *in vacuo* and in an air atmosphere. The viscosity properties of all the polymers, the metal-extraction ability of a Co-containing polymeric phthalocyanine (**10**), and the disaggregation properties of a Ni-containing polymeric phthalocyanine (**11**) were also investigated.

EXPERIMENTAL

Materials

Acrylonitrile, sodium borohydride ($NaBH_4$), phosphorous pentoxide (P_2O_5), 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), ethanol, 1-pentanol, dimethylformamide (DMF), tetrahydrofuran (THF), chloroform, dichloromethane, petroleum ether, quinoline, sulfuric acid, hydrochloric acid, pyridine, acetone, 1,2-bis(2-iodoethoxy) ethane, sodium iodide, sodium thiosulfate, acetonitrile, sodium carbonate, dioxane, *n*-hexane, lithium, glacial acetic acid, silica gel, ammonia, $MgSO_4$, 4-toluenesulfonyl chloride, methanol, 1,2-(2-aminoethoxy)ethane, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $Cu(Ac)_2 \cdot H_2O$, and $Zn(Ac)_2 \cdot 2H_2O$ were obtained from Merck (Hohenbrunn, Germany) and used as received. Cesium carbonate (Cs_2CO_3) was received from Merck and used after drying in an oven at 250°C for 36 h. All organic solvents were dried and purified by the usual methods. 4-Nitrophthalonitrile was synthesized as described in the literature.[8] 1,10-Diaza-18-crown-6 was synthesized according to the literature.[9]

Measurement

Melting points of the compounds were determined with an electrothermal melting point apparatus and were uncorrected. ^{1}H-NMR spectra were recorded on a Varian Mercury Plus 300-MHz spectrometer (Oxford, UK) with $CDCl_3$ and dimethyl sulfoxide (DMSO)-d_6 as solvents and tetramethylsilane as an internal standard. ^{13}C-NMR spectra were recorded on a Varian Mercury Plus 75-MHz spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. Transmission IR spectra of samples were recorded on a Fourier transform infrared (FTIR) spectrophotometer (FT-IR-8201 PC, Shimadzu) with the samples in KBr pellets or NaCl disks. Optical spectra in the ultraviolet–visible (UV–vis) region were recorded with a Shimadzu model 1601 UV–vis spectrometer using 10-mm-path-length cuvettes at room temperature. The alternating-current conductivity was measured with an Autolab 30 Voltammetry-FRA 2 frequency analyzer. The frequency range was 100 Hz–1 MHz, and the applied amplitude (rms) was 10 mV. Mass spectra were measured on Varian MAT 711 and Micromass Quatro LC/Ultima LC-MS mass spectrometry (MS) spec-

trometers. The elemental analysis of the compounds was determined on a Leco CHNS-932 instrument. The metal contents of the metallophthalocyanine polymers were determined with a Unicam 929 AA spectrophotometer. Differential thermal analysis/thermogravimetry was performed on a Linseis L81 instrument under a nitrogen atmosphere at a heating rate of 10°C/min in a temperature range of 50–700°C. The intrinsic viscosities of freshly prepared dilute solutions of phthalocyanine polymers were measured in concentrated H_2SO_4 at 25°C with an Ubbelohde viscometer.

Preparation of N,N′-bis(3-cyanoethyl)-4,13-diaza-18-crown-6 (1)

1,10-Diaza-18-crown-6 (4.00 g, 15.20 mmol) and acrylonitrile (100 mL) were placed in a 250-mL, three-necked flask and refluxed under an inert nitrogen atmosphere for 70 h. Then, the reaction mixture was filtered, and the solvent was evaporated. The oily, viscous product was dried *in vacuo* and dissolved in THF, and after slow evaporation of the solvent, white crystals precipitated. The white crystals were filtered and dried *in vacuo* over P_2O_5 at room temperature. The final product (**1**) was soluble in common organic solvents such as chloroform, dichloromethane, DMF, pyridine, 1,2-dichloroethane, THF, and DMSO.

Yield: 51% (2.87 g). mp: 54–55°C. FTIR (KBr): 2980–2829 (—CH_2—), 2249 (C≡N), 1456, 1348, 1261, 1137–1047 (CH_2O—), 941, 825, 768 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ): 3.68 (s, 8H, OCH_2), 3.56 (t, 8H, OCH_2), 2.95 (t, 4H, NCH_2CH_2CN), 2.77 (t, 8H, NCH_2), 2.48 (t, 4H, CH_2CN). ^{13}C-NMR ($CDCl_3$, δ): 118.3 (CN), 70.3 (—OCH_2CH_2O), 69.1 (NCH_2CH_2O), 53.5, 53.2, 19.1 (NCH_2CH_2CN). ANAL. Calcd for $C_{18}H_{32}N_4O_4$ (368.03): C, 58.70%; H, 8.70%; N, 15.21%. Found: C, 58.32%; H, 8.87%; N, 14.98%. MS [electron impact (EI)] *m/z*: 369 [M + 1]$^+$, where M is molecular ion peak.

Preparation of N,N′-bis(3-aminopropyl)-4,13-diaza-18-crown-6 (2)

Dinitrile (**1**; 3.68 g, 10 mmol) was dissolved in methanol (100 mL) at room temperature under N_2 gas, and $CoCl_2 \cdot 6H_2O$ (9.51 g, 40 mmol) was added to the solution and stirred for 30 min. $NaBH_4$ (15.08 g, 0.4 mol) was added to the solution in equal portions for 3 h. A violent gas evolution was observed during this step. The resultant mixture was stirred at room temperature for 5 h longer and then cautiously acidified with concentrated HCl (80 mL) while the reaction flask was cooled in an ice–water bath. The solvent was evaporated *in vacuo*, and the deep blue solid residue was placed in a concentrated ammonia

solution (100 mL) and chloroform (150 mL) and stirred for 1 h. The flesh-colored product was filtered off, and the aqueous phase was extracted with chloroform (6 × 50 mL). The combined organic phases were dried with $MgSO_4$, and then $MgSO_4$ was filtered and removed. The filtrate was evaporated *in vacuo*, and the obtained oily part was dissolved in anhydrous benzene and dried over a molecular sieve (3 Å; Merck) for 1 day.

Yield: 64% (2.41 g). FTIR (NaCl disk): 3354–3210 (NH_2), 2935–2784 (aliphatic CH_2), 1618 (NH_2), 1456, 1356, 1255, 1115–1009 (CH_2—O—CH_2), 945, 885, 731 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ): 3.56 (s, 8H, OCH_2), 3.42 (t, 8H, NCH_2CH_2O), 2.60–2.42 (m, 12H, NCH_2), 1.49–1.37 (m, 4H, $NCH_2CH_2CH_2NH_2$), 1.20 (s, 4H, NH_2). ^{13}C-NMR ($CDCl_3$, δ): 70.4 (—OCH_2CH_2O), 69.6 (NCH_2CH_2O), 54.6, 53.4, 40.1 (CH_2NH_2), 28.3 ($NCH_2CH_2CH_2NH_2$). ANAL. Calcd for $C_{18}H_{40}N_4O_4$ (376.04): C, 57.44%; H, 10.65%; N, 14.89%. Found: C, 57.64%; H, 10.32%; N, 14.65%. MS (EI) m/z: 377 $[M + 1]^+$.

Preparation of N,N'-bis(3-p-toluenesulfonylaminopropyl)-4,13-diaza-18-crown-6 (3)

A three-necked flask was charged with compound **2** (3.8 g, 10.1 mmol) and pyridine (15 mL). The mixture was stirred under an inert nitrogen atmosphere and cooled to −10°C. A solution of 4-toluenesulfonylchloride (3.81 g, 20 mmol) in pyridine (15 mL) was added dropwise to the reaction mixture for 45 min, and the reaction mixture was stirred at −10°C for 2 h longer. The temperature was increased up to 60°C, and the mixture was heated at the same temperature overnight. The reaction mixture was cooled to room temperature and then poured into ice-cooled hydrochloric acid (8 vol %, v/v) until the pH of the solution was about 5–6. The partly precipitated product was filtered. The filtrate was extracted with chloroform (5 × 50 mL). The combined organic phases were dried over $MgSO_4$. The mixture was filtered over a blue band, and then chloroform was removed. Ethanol (3–4 mL) was added to the residue, and then it was put into a refrigerator. The precipitated cream-colored product was filtered and dried *in vacuo* over P_2O_5.

Yield: 36% (2.50 g). mp: 187–190°C. FTIR (KBr): 3267 (N—H), 3078 (aromatic =CH), 2918–2850 (CH_2), 1610 (N—H), 1596 (aromatic —C=C—), 1491, 1448, 1360 (SO_2), 1340, 1175 (SO_2), 11140–1045 (CH_2—O—CH_2), 959, 887, 734, 704, 552 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ): 7.69 (d, 4H, ArH), 7.36 (d, 4H, ArH), 5.65 (s, broad, 2H, NHTs), 3.54 (s, 8H, OCH_2), 3.44 (t, 8H, NCH_2CH_2O), 3.18 (m, 4H, CH_2NHTs), 2.62–2.40 (m, 12H, NCH_2), 2.38 (s, 6H, CH_3), 1.67–1.59 (m, 4H, $NCH_2CH_2CH_2NHTs$). ^{13}C-NMR ($CDCl_3$, δ): 142.9, 137.4, 129.6, 127.2 (aromatic C), 70.2 (—OCH_2CH_2O), 69.1 (NCH_2CH_2O), 54.2, 51.8, 41.5 (CH_2NHTs), 29.1 ($NCH_2CH_2CH_2NHTs$). ANAL. Calcd for $C_{32}H_{52}N_4O_8S_2$ (684.12): C, 56.13%; H, 7.60%; N, 8.19%; S, 9.37%. Found: C, 56.42%; H, 7.45%; N, 8.47%; S, 9.60%. MS (EI) m/z: 684 $[M]^+$, 529 $[M − Ts]^+$, where Ts is p-$MeC_6H_4SO_2$.

Preparation of N,N'-bis (3-p-toluenesulfamido propylphthalonitrile)-4,13-diaza-18-crown-6 (4)

4-Nitrophthalonitrile (1.26 g, 7.30 mmol) and dry DMF (10 mL) were put in a three-necked flask and stirred at room temperature under an inert nitrogen atmosphere. Compound **3** (2.5 g, 3.65 mmol) was added to the reaction mixture, and the temperature was increased to 50°C. Powdered Cs_2CO_3 (3.64 g, 10.95 mmol) was added to the reaction mixture in eight equal portions at 30-min intervals with efficient stirring, and the reaction mixture was stirred at the same temperature for 6 days. Aliquots were taken periodically to check the completeness of the reactions and were observed with thin-layer chromatography (8 : 1.5 : 0.5 chloroform/methanol/ammonia). The reaction mixture was cooled, poured into an ice–water mixture, and stirred for 5 h. The mixture was extracted with chloroform (5 × 50 mL), and the organic phases was dried over $MgSO_4$. Chloroform was removed, and an oily, pale yellow product was obtained. The crude product was recrystallized from methanol and dried *in vacuo* over P_2O_5.

Yield: 77% (2.66 g). mp: 162–164°C. FTIR (KBr): 3066–3045 (aromatic =CH), 2926–2874 (aliphatic CH_2), 2235 (C≡N), 1610 (aromatic —C=C—), 1598, 1438, 1388 (SO_2), 1290, 1253, 1182 (SO_2), 1159–1020 (O—CH_2CH_2—O), 943, 817, 662, 552 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ): 7.80–7.31 (m, 14H, ArH), 3.58 (s, 8H, —OCH_2CH_2O), 3.49 (t, 4H, CH_2NTs), 3.40 (t, 8H, NCH_2CH_2O), 2.71–2.44 (m, 12H, NCH_2), 2.40 (s, 6H, CH_3), 1.91–1.82 (m, 4H, $NCH_2CH_2CH_2NTs$). ^{13}C-NMR ($CDCl_3$, δ): 148.6, 143.4, 136.8, 133.7, 129.3, 127.5, 119.8, 118.4, 116.2, 115.9–115.2 (CN), 108.6, 70.7, 68.3, 56.4, 53.9, 46.8 ($NCH_2CH_2CH_2NTs$), 29.6 ($NCH_2CH_2CH_2NTs$), 22.5 (Ar—CH_3). ANAL. Calcd for $C_{48}H_{56}N_8O_8S_2$ (936.12): C, 61.53%; H, 5.98%; N, 11.96%; S, 6.85%. Found: C, 61.34%; H, 6.26%; N, 12.15%; S, 7.08%. MS [fast atom bombardment (FAB)] m/z: 1070 $[M + Cs + 1]^+$, 937 $[M + 1]^+$, 936 $[M]^+$, 781 $[M − Ts]^+$, 626 $[M − 2Ts]^+$.

Preparation of monomeric dilithium phthalocyanine (5)

A three-necked flask was charged with compound **4** (0.36 g, 0.38 mmol) and dry 1-pentanol (100 mL). The reaction system was degassed several times and refluxed under an Ar atmosphere. Metallic Li (30 mg, 4.32 mmol) was dissolved in dry 1-pentanol (25 mL)

under an Ar atmosphere at 60°C and then added to the reaction mixture dropwise for over 15 min. The reaction mixture was refluxed for 2 days. The reaction was monitored with thin-layer chromatography (98 : 2 chloroform/methanol) on silica gel. The reaction mixture was filtered quickly to remove unreacted lithium salts and polymeric substances. After it cooled to room temperature, a small amount of a dark green, solid product precipitated, and it was collected by filtration. A semisolid product was obtained after evaporation of the filtrate. The semisolid product was dissolved in dichloromethane, and then n-hexane was added until the precipitation was completed. The dark green product was filtered. The solid products were combined and dried in a desiccator. The dried product was dissolved in a small amount of THF and then eluted on a neutral alumina column with a chloroform/methanol (98 : 2) solvent system. The solvent was evaporated, and the final dark green product was dried in vacuo over P_2O_5.

Yield: 25% (90 mg). mp: >300°C. FTIR (KBr): 3060–3045 (aromatic =CH), 2946–2870 (aliphatic CH_2), 2217 (C≡N), 1638 (C=N), 1600 (aromatic —C=C—), 1595, 1465, 1370 (SO_2), 1173 (SO_2), 1162–1012 (O—CH_2CH_2—O), 960, 672, 524 cm^{-1}. ^{1}H-NMR (CDCl$_3$, δ): 7.90–7.40 (m, br, 56H, ArH), 3.53 (s, 32H, —OCH_2CH_2O), 3.42 (t, 16H, CH_2NTs), 3.38 (t, 32H, NCH_2CH_2O), 2.80–2.47 (m, br, 48H, NCH_2), 2.42 (s, 24H, CH_3), 1.85–1.79 (m, br, 16H, N$CH_2CH_2CH_2$ NTs). ANAL. Calcd for $C_{192}H_{224}Li_2N_{32}O_{32}S_8$ (3759.50): C, 61.29%; H, 6.01%; N, 11.91%; S, 6.82%; Li, 0.37%. Found: C, 62.13%; H, 6.48%; N, 11.54%; S, 6.62%; Li, 0.54%. MS (FAB) m/z: 3753 $[M - Li]^+$, 3747 $[M - 2Li]^+$.

Preparation of monomeric metal-free phthalocyanine (6)

A three-necked flask was charged with compound **5** (0.188 g, 0.05 mmol) and an acetic acid/acetone (3.8 mL, v/v) solution, and they were stirred at room temperature for 30 min. An excess amount of ice was added to the reaction mixture, which was stirred for 45 min more. The obtained oily part was extracted with dichloromethane (4 × 25 mL). The organic phase was washed with an ammonia solution (20 mL, 10%, v/v), a saturated solution of NaCl (50 mL), and water. The organic phase was separated and dried over $MgSO_4$. The solvent was evaporated. The green residue was chromatographed on a silica column with chloroform/methanol (100 : 1). The solvent was evaporated to yield a dark green product.

Yield: 58% (0.108 g). mp: >300°C. FTIR (KBr): 3295 (N—H), 3052–3039 (aromatic =CH), 2960–2782 (aliphatic CH_2), 2224 (C≡N), 1635 (C=N), 1604 (aromatic —C=C—), 1590, 1480, 1375 (SO_2), 1180 (SO_2), 1140–1020 (O—CH_2CH_2—O), 950, 850, 654, 543 cm^{-1}.

^{1}H-NMR (CDCl$_3$, δ): 7.97–7.30 (m, br, 56H, ArH), 3.60 (s, 32H, —OCH_2CH_2O), 3.51 (t, 16H, CH_2NTs), 3.41 (t, 32H, NCH_2CH_2O), 2.78–2.45 (m, br, 48H, NCH_2), 2.35 (s, 24H, CH_3), 2.03–1.90 (m, br, 16H, N$CH_2CH_2CH_2$NTs), −3.40 (s, br, 2H). ANAL. Calcd for $C_{192}H_{226}N_{32}O_{32}S_8$ (3746.48): C, 61.50%; H, 6.03%; N, 11.96%; S, 6.85%. Found: C, 61.24%; H, 6.17%; N, 12.23%; S, 7.17%. MS (FAB) m/z: 3747 $[M + 1]^+$.

Preparation of polymeric metal-free phthalocyanine (7)

A mixture of compound **4** (0.468 g, 0.50 mmol), n-pentanol (2.5 mL), and DBU (0.08 g, 0.5 mmol) was placed in a standard Schlenk tube under a nitrogen atmosphere and degassed several times. The temperature was gradually increased to 145°C, and the mixture was degassed with nitrogen again. Then, the reaction mixture was refluxed at 145°C for 10 h. After the reaction mixture was cooled and decanted, the remaining part was stirred with 10 mL of a methanol/petroleum ether solution (1 : 1 v/v). The green product (**7**) was filtered off, washed with DMF, methanol, acetone, and diethyl ether, and dried at 60°C over P_2O_5.

Yield: 71.2% (0.39 g). mp: >300°C. FTIR (KBr): 3290 (N—H), 3064–3035 (aromatic =CH), 2980–2730 (CH_2), 2216 (C≡N), 1630 (—C=N—), 1600 (aromatic —C=C—), 1475, 1370, 1265, 1185, 1150–1045 (CH_2—O—CH_2), 1035, 976, 848, 652, 540 cm^{-1}. ANAL. Calcd for $(C_{192}H_{226}N_{32}O_{32}S_8)_n$ (3746.48): C, 61.50%; H, 6.03%; N, 11.96%; S, 6.85%. Found: C, 61.94%; H, 5.83%; N, 12.38%; S, 7.32%.

Preparation of Zn-(8) and Cu-(9) containing polymeric phthalocyanines

A mixture of bisphthalonitrile compound **4** (0.468 g, 0.50 mmol), zinc acetate dihydrate (0.056 g, 0.25 mmol) or cupric acetate monohydrate (0.050 g, 0.25 mmol), and amyl alcohol (5 mL) was put in a flask, and the temperature was increased to 160°C. DBU (0.04 mL, 0.04 g, 0.25 mmol) was added dropwise with a syringe to the system at the same temperature. The reaction was refluxed at 160°C for 10 h under a nitrogen atmosphere. After cooling, 10 mL of a methanol/water mixture (1 : 1 v/v) was added to the system, and it was stirred for 45 min longer. The crude product was collected by filtration and washed with methanol, DMF, water, petroleum ether, and acetone. The final green products (**8** and **9**) were dried in vacuo over P_2O_5 at 100°C.

Compound 8

Yield: 85.1% (0.48 g). mp: >300°C. FTIR (KBr): 3380 (imide N—H), 3060 (aromatic =CH), 2980–2870

(CH$_2$), 1775 (symmetric C=O), 1724 (asymmetric C=O), 1634 (—C=N—), 1602 (aromatic —C=C—), 1490, 1425, 1375, 1250, 1170, 1170–1020 (C—O—C), 950, 854, 720, 645 cm^{-1}. ANAL. Calcd for (C$_{192}$H$_{228}$N$_{28}$O$_{40}$S$_8$Zn)$_n$ (3885.86): C, 59.29%; H, 5.87%; N, 10.09%; S, 6.60%; Zn, 1.68%. Found: C, 59.07%; H, 6.24%; N, 9.76%; S, 7.06%; Zn, 1.42%.

Compound 9

Yield: 69.9% (0.39 g). mp: >300°C. FTIR (KBr): 3370 (imide N—H), 3050–3036 (aromatic =CH), 2970–2860 (CH$_2$), 1770 (symmetric C=O), 1716 (asymmetric C=O), 1630 (—C=N—), 1610 (aromatic —C=C—), 1596, 1470, 1441, 1380, 1256, 1165, 1145–1020 (C—O—C), 960, 870, 740, 556 cm^{-1}. ANAL. Calcd for (C$_{192}$H$_{228}$N$_{28}$O$_{40}$S$_8$Cu)$_n$ (3883.73): C, 59.32%; H, 5.87%; N, 10.09%; S, 6.60%; Cu, 1.64%. Found: C, 59.78%; H, 5.52%; N, 10.48%; S, 6.18%; Cu, 1.87%.

Preparation of 10 and 11

A mixture of bisphthalonitrile compound 4 (0.936 g, 1 mmol), dry quinoline (5 mL), and CoCl$_2$·6H$_2$O (0.120 g, 0.5 mmol) or NiCl$_2$·6H$_2$O (0.122 g, 0.5 mmol) was placed in a flask and degassed three times with nitrogen. The reaction mixture was refluxed at 220–230°C for 12 h (20 h for 11) under an inert nitrogen atmosphere. After refluxing, the reaction mixture was cooled, and then 25 mL of diethyl ether (10 mL of a methanol/water solution, 1/1 v/v) was added. The reaction was filtered after 1 h of stirring. The crude product was washed with a methanol/diethyl ether solution (20 mL, 1/1 v/v), DMF, hot ethanol, and acetone. The final products (10 and 11) were dried in vacuo over P$_2$O$_5$ at 100°C.

Compound 10

Yield: 80.5% (0.85 g). mp: >300°C. FTIR (KBr): 3405 (imide N—H), 3060–3048 (aromatic =CH), 2930–2784 (CH$_2$), 1775 (symmetric C=O), 1715 (asymmetric C=O), 1638 (—C=N—), 1600 (aromatic —C=C—), 1598, 1442, 1383, 1260, 1176, 1150–1020 (C—O—C), 980, 860, 714, 525 cm^{-1}. ANAL. Calcd for (C$_{192}$H$_{228}$N$_{28}$O$_{40}$S$_8$Co)$_n$ (3879.41): C, 59.39%; H, 5.88%; N, 10.10%; S, 6.61%; Co, 1.52%. Found: C, 59.09%; H, 6.16%; N, 10.54%; S, 6.23%; Co, 1.92%.

Compound 11

Yield: 88.8% (0.94 g). mp: >300°C. FTIR (KBr): 3390 (imide N—H), 3070–3050 (aromatic =CH), 2965–2807 (CH$_2$), 1770 (symmetric C=O), 1724 (asymmetric C=O), 1645 (—C=N—), 1610 (aromatic —C=C—), 1595, 1460, 1385,1264, 1180, 1165–1030 (C—O—C), 965, 850, 740, 590 cm^{-1}. ANAL. Calcd for

(C$_{192}$H$_{228}$N$_{28}$O$_{40}$S$_8$Ni)$_n$ (3879.18): C, 59.39%; H, 5.88%; N, 10.11%; S, 6.61%; Ni, 1.51%. Found: C, 59.75%; H, 5.57%; N, 10.52%; S, 7.10%; Ni, 1.75%.

Conversion of cyano end groups of 6 into imino groups (6a) and conversion of cyano end groups of 7 into imido groups (7a)

A sample of compound 6 (150 mg) or compound 7 (100 mg) was dissolved in a minimum volume of H$_2$SO$_4$ (96 wt %) at room temperature. After 3–4 h of stirring, the reaction mixture was filtered. The filtered part was poured into an excess amount of an ice–water mixture. The dark green crude product was washed with distilled water until the residue washing water was neutral. Then, the final products (6a and 7a) were washed with ethanol and diethyl ether and dried in vacuo over P$_2$O$_5$ at 100°C.

Compound 6a

Yield: 82% (126 mg). mp: >300°C. FTIR (KBr): 3375 (imide N—H), 3274 (N—H), 3055–3040 (aromatic =CH), 2965–2800 (aliphatic CH$_2$), 1770 (symmetric C=O), 1712 (asymmetric C=O), 1630 (—C=N—), 1595 (aromatic —C=C—), 1565, 1470, 1364, 1254, 1170, 1130–1025 (C—O—C), 956, 840, 724, 532 cm^{-1}. ^{1}H-NMR (DMSO-d_6, δ): 10.90 (s, 4H, imide NH), 8.01–7.35 (m, br, 56H, ArH), 3.66 (s, 32H, —OCH$_2$CH$_2$O), 3.48 (t, 16H, CH$_2$NTs), 3.37 (t, 32H, NCH$_2$CH$_2$O), 2.80–2.46 (m, br, 48H, NCH$_2$), 2.36 (s, 24H, CH$_3$), 1.98–1.87 (m, br, 16H, NCH$_2$CH$_2$CH$_2$NTs), −3.46 (s, br, 2H, NH). ANAL. Calcd for C$_{192}$H$_{230}$N$_{28}$O$_{40}$S$_8$ (3822.48): C, 60.28%; H, 6.02%; N, 10.26%; S, 6.70%. Found: C, 60.72%; H, 5.83%; N, 10.57%; S, 7.08%. MS (FAB) m/z: 3823 [M + 1]$^+$.

Compound 7a

Yield: 75% (75 mg). mp: >300°C. FTIR (KBr): 3370 (imide N—H), 3280 (N—H), 3065–3040 (aromatic =CH), 2970–2786 (CH$_2$), 1775 (symmetric C=O), 1718 (asymmetric C=O), 1625 (—C=N—), 1598 (aromatic —C=C—), 1560, 1475, 1370, 1260, 1180, 1145–1020 (C—O—C), 962, 826, 745, 516 cm^{-1}. ANAL. Calcd for (C$_{192}$H$_{230}$N$_{28}$O$_{40}$S$_8$)$_n$ (3822.48; for imide end groups): C, 60.28%; H, 6.02%; N, 10.26%; S, 6.70%. Found: C, 60.04%; H, 6.32%; N, 10.62%; S, 7.04%.

Measurement of the alkali, alkaline-earth, and heavy-metal binding properties of 10

The extraction properties of 10 were investigated under solid–liquid phase conditions with alkaline (Li$^+$, Na$^+$, K$^+$, and Cs$^+$), alkaline-earth (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}), and heavy-metal picrates (Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}) as substrates and by UV–vis measurements of the amounts of picrate in

Alkaline, Alkaline Earth, and Heavy-Metal Picrate Extractions for Compound 10[a] Under Solid–Liquid Two-Phase Conditions

Metal ion	Extractability of compound 10 (%)[b]	λ_{max} (nm) of metal picrate
Li$^+$	2.8 ± 0.1	358
Na$^+$	65.2 ± 0.1	360
K$^+$	96.4 ± 0.1	364
Cs$^+$	32.5 ± 0.1	355
Mg^{2+}	14.9 ± 0.1	354
Ca^{2+}	47.1 ± 0.1	360
Sr^{2+}	52.3 ± 0.1	364
Ba^{2+}	84.2 ± 0.1	354
Ni^{2+}	22.6 ± 0.1	355
Cu^{2+}	49.7 ± 0.1	349
Zn^{2+}	51.2 ± 0.1	364
Cd^{2+}	67.5 ± 0.1	360
Pb^{2+}	78.6 ± 0.1	364

[a] Temperature = 25 ±1°C; THF phase = 10 mL; [picrate] = 3.0 × 10^{-3} M; host molecule = 20 mg.
[b] Average and standard deviation for three independent measurements.

the THF phase before and after the treatment with polymers in suspension. Suspensions were prepared through the mixing of 20 mg of **10**, which was ground in a ball mill for 3 h to ensure the same par-ticle size, and the metal picrate solutions [the picrate solutions were prepared in 10 mL of THF through the reaction of equivalent amounts of each metal nitrate (Mg^{2+}, Ca^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}) or metal hydroxide (Li$^+$, Na$^+$, K$^+$, Cs$^+$, Sr^{2+}, Ba^{2+}) and picric acid in 10 mL of 10^{-3} M THF]. The prepared suspensions were placed in plastic bottles and shaken vigorously for 24 h at 25°C. The results and experimental conditions are reported in Table I. In the absence of the host **10** (i.e., a blank experiment), no metal-ion picrate extraction was detected. The extractability was determined on the basis of the absorbance of the picrate ion in the THF suspensions. The extractability (E) was calculated with Eq. (1):

$$E(\%) = [(A_{before} - A_{after})/A_{before}] \times 100 \qquad (1)$$

where A_{before} is the absorbance in the absence of a ligand and A_{after} is the absorbance in the THF suspension phase after extraction.

RESULTS AND DISCUSSION

The synthesis of **1** was performed with 1,10-diaza-18-crown-6 and acrylonitrile (Scheme 1). Compound **1** was synthesized with a modification of the cited procedure[10] as described in the Experimental
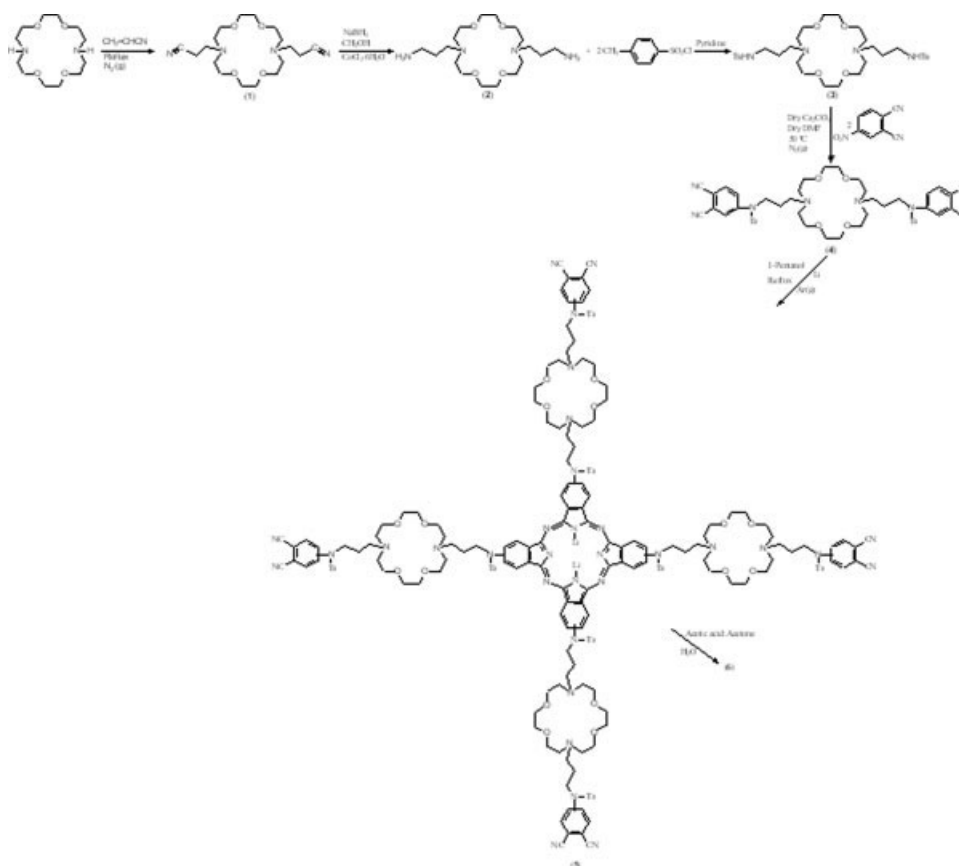
Scheme 1 Synthesis of monomeric lithium and metal-free phthalocyanines (**5** and **6**).

section. The elemental analysis and mass spectral data of **1** were satisfactory: 369 [M + 1]$^+$. Compound **1** was characterized with NMR and IR spectroscopy. In the ^{1}H-NMR (CDCl$_3$) spectrum of **1**, the NH group of 1,10-diaza-18-crown-6 disappeared as expected. The ^{1}H-NMR spectrum of **1** showed new signals at δ = 2.95 (t, 4H, NCH$_2$CH$_2$CN) and δ = 2.48 (t, 4H, CH$_2$CN), and the proton-decoupled ^{13}C-NMR spectrum of **1** indicated the presence of corresponding carbon atoms at δ = 118.3 (CN) and δ = 19.1 (NCH$_2$CH$_2$CN), respectively. The IR spectrum of **1** was easily verified with the disappearance of N—H and the presence of C≡N stretching vibrations at 2249 cm^{-1}. The difference between the IR spectra of 1,10-diaza-18-crown-6 and **1** was clear from the absence of characteristic vibrations such as N—H. Compound **1** was treated with CoCl$_2$·6H$_2$O in methanol in the presence of NaBH$_4$ to yield compound **2**. In the IR spectrum of **2**, stretching vibrations of NH$_2$ were observed at 3354–3210 cm^{-1}. The ^{1}H-NMR spectrum of **2** showed a new signal at δ = 1.20 (s, 4H, NH$_2$). The elemental analysis and mass spectral data of **2** were also satisfactory: 377 [M + 1]$^+$. The amino groups of **2** were protected by tosylation with *p*-toluenesulfonylchloride in pyridine to yield **3**. A comparison of the IR spectral data of **2** and **3** clearly indicated the conversion of primary amino groups into N—H groups with the disappearance of the NH$_2$ band at 3354–3210 cm^{-1} for **2** and the appearance of a new N—H band at 3267 cm^{-1} for **3**. The rest of the spectrum of **2** was very similar to that of **3**, including the characteristic vibrations of tosyl groups. The ^{1}H-NMR spectrum of **3** was also consistent with the proposed structure. In addition to the protons and carbon signals in **2**, new protons and carbons of tosyl groups appeared at δ values of 7.69 (d, 4H, ArH), 7.36 (d, 4H, ArH), 5.65 (s, broad, 2H, NHTs), and 2.38 (s, 6H, CH$_3$). The presence of the tosyl carbon atoms in the ^{13}C-NMR spectrum of **3** was consistent with the proposed structure. Compound **4** was prepared through the reaction of 4-nitrophthalonitrile and **3** in the presence of Cs$_2$CO$_3$ in DMF. Final purification of the tetranitrile derivative (**4**) by recrystallization afforded **4**, for which the elemental analysis and FAB mass spectral data were satisfactory: 1070 [M + Cs + 1]$^+$. In the ^{1}H and ^{13}C-NMR spectra of **4**, the NH group of compound **3** disappeared, and the nitrile carbon atom appeared as expected. The disappearance of N—H and the presence of the C≡N functional group at 2235 cm^{-1} in the IR spectrum of compound **4** confirmed the formation of **4**. Compound **5** was prepared through the reaction of **4** and metallic Li in dry 1-pentanol (Scheme 1). To prevent the formation of network polymers, the reaction was carried out under high-dilution conditions. The composition and structure of **5** were verified by elemental analysis and by FAB

mass, IR, and ^{1}H-NMR spectra. In the FAB mass spectrum of **5**, 3753 [M − Li]$^+$ and 3747 [M − 2Li]$^+$ were observed instead of the molecular ion peak. The synthesis of **6** from **5** was accomplished through a dilithium phthalocyanine intermediate followed by a proton-lithium exchange in an acetic acid/acetone solution. The presence of N—H vibrations at 3295 cm^{-1}, phthalocyanine inner proton atoms at δ = −3.40 (s, br, 2H, NH), and an MS (FAB) value of 3747 [M + 1]$^+$ were consistent with the proposed structure according to the IR, ^{1}H-NMR, and FAB mass spectral data, respectively. Model compound **6a**, containing a single phthalocyanine unit and suitable imido end groups, was prepared so that its characteristic data could be used for the analysis of the polymerization degree. The cyano end groups of **5** were converted into imido end groups by the treatment of **6** with concentrated H$_2$SO$_4$, and **6a** was obtained. Elemental analysis and UV–vis, IR, NMR, and mass spectral data of **5**, **6**, and **6a** confirmed the structures. The disappearance of C≡N and the presence of imido functional groups at 1770 and 1712 cm^{-1} in the IR spectrum of compound **6a** confirmed the formation of **6a**. The ^{1}H-NMR spectrum of **6a** revealed the presence of the aromatic structure (δ = 8.01 and 7.35) and the NH proton of the aromatic phthalocyanine ring (δ = −3.46). Also, a weak chemical shift, indicating the presence of imido end groups, was present at δ = 10.90.

The metal-free phthalocyanine polymer **7** was synthesized through the heating of a mixture of **4**, DBU, and amyl alcohol in a Schlenk tube. The transition-metal complexes were prepared from the tetracyano compound **4** and the corresponding metal salt in the proper solvent (Scheme 2).

The IR spectrum of **7** was slightly broadened and reduced in intensity. This could be attributed to the difficulty in grinding the sample to a small particle size and the polymeric structure. The peaks at 3290 and 1035 cm^{-1} were the characteristic metal-free phthalocyanine N—H stretching and pyrrole ring vibration bands. A weak —C=N— absorption at 1630 cm^{-1} was detected. Elemental analysis was satisfactory. In the IR spectra for **7a**, the disappearances of the peak at 2216 cm^{-1} due to cyano groups of **7** and the appearance of new peaks at ~1775–1718 cm^{-1} due to imido groups supported the conversion of cyano groups into imido groups.

IR spectra of the metallophthalocyanine polymers (**8–11**) were very similar, except for the metal-free phthalocyanine polymer **7**. **7** showed an N—H stretching band at 3290 and 1035 cm^{-1} due to the inner core.[11] These bands disappeared in the spectra of the metallophthalocyanine polymers. These bands are especially beneficial for the characterization of metal-free phthalocyanine polymers, as there is little frequency dependence on ring substitution and they

R: C≡N   (7)

R: (structure) N—H   (7a-11)

Compound	M
7, 7a	2H
8	Zn
9	Cu
10	Co
11	Ni
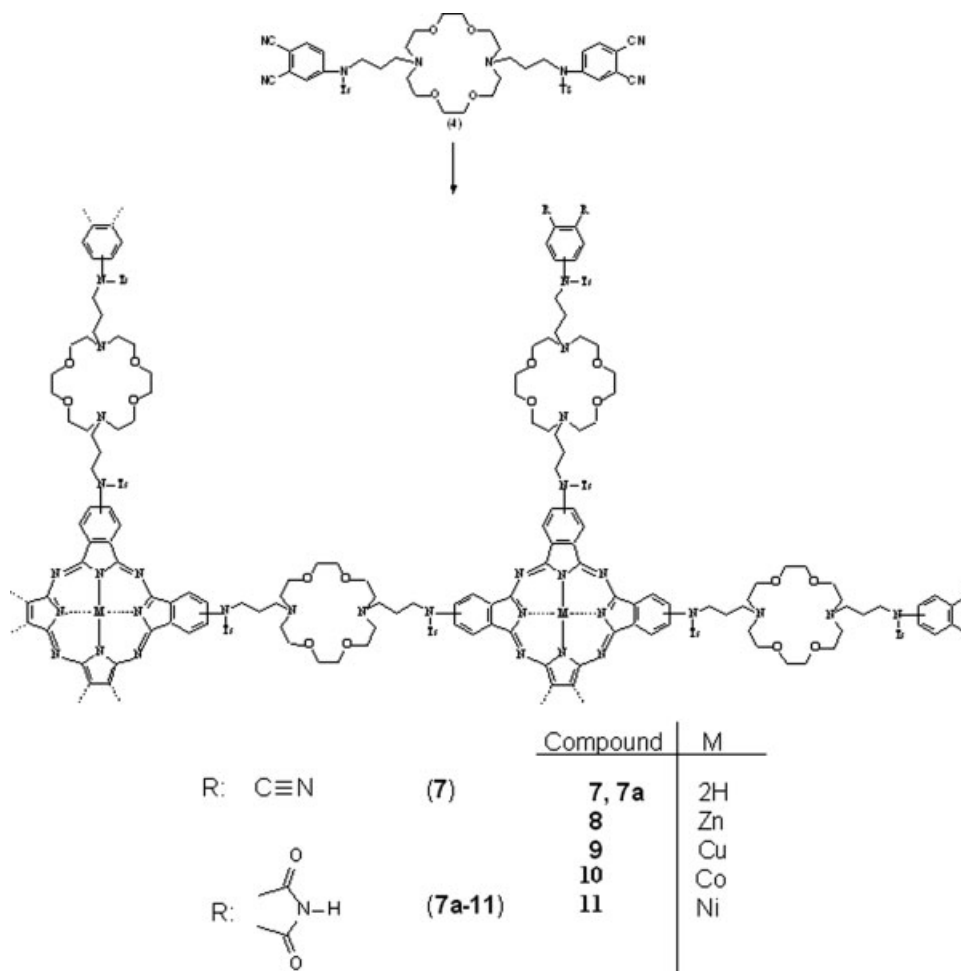
Scheme 2 Synthesis of the polymeric phthalocyanines (**7–11**).

are not overlapped by strong bisphthalonitrile monomer absorptions.[4] The end groups of the metal-free phthalocyanine polymer were cyano groups (2216 cm^{-1}), whereas the end groups of the metallophthalocyanine polymers were imido groups (∼ 1770 – 1716 cm^{-1}). The existence of imido groups in the case of metallophthalocyanine polymers was attributed to the presence of moisture during workup and the hydrated metal salts. There was little shifting to longer wavelength numbers in most of the IR bands of the metal complexes with respect to the metal-free analogues.[4,12] The spectra of the complexes were quite complex and revealed many metal-independent ligand absorptions, and metal–N vibrations were expected to appear at 400–100 cm^{-1}, but they were not detected in KBr pellets.[13]

It is very difficult to determine the molecular weights of polymeric phthalocyanines because of their poor solubility in common organic solvents. One possible procedure for determining the degree of polymerization is IR spectroscopy through a comparison of the intensities of the end cyano groups and other ring vibrations. This method has been applied in only a few cases.[14] We determined the degree of polymerization after converting cyano end groups of the metal-free phthalocyanine polymer into imido end groups because of the relatively good intensity of C=O imide groups with respect to nitrile groups. After this, the ratios of the absorption intensities of C—O—C ether groups of the polymers (∼ 1170 cm^{-1}) and asymmetric C=O groups of the imides (∼ 1716 cm^{-1}) were calculated [compound/ $\log_{10} I_{1170}/I_{1716}$: **6a**/0.04, **7a**/0.47, **8**/0.76, **9**/0.65, **10**/ 1.20, and **11**/0.86]. The polymerization degrees followed this order: **10** > **11** > **8** > **9** > **7a** > **6a**. On the other hand, the IR spectrum of **7** showed a low degree of polymerization because of the high intensity of the nitrile groups.

The elemental analyses of the metal-free and metallophthalocyanine polymers (**7**, **7a**, and **8–11**) were satisfactory.

The monomeric phthalocyanines (**5** and **6**) and polymeric phthalocyanines (**7–11**) gave UV–vis absorption spectra typical of phthalocyanines (Table II).

TABLE II
Wavelength and Absorption Coefficients of the UV–vis Spectra of the Monomeric and Polymeric Phthalocyanines

Compound	M	Solvent	λ (nm; log ε)	UV–vis ratio[a]
5	2H	Chloroform	680 (5.33), 620 (4.24), 395 (4.88), 344 (4.90), 312 (4.93)	0.92
6	2H	Chloroform	709 (5.32), 678 (5.31), 650 (4.75), 610 (4.33), 365 (5.20), 325 (5.30)	1.00
7	2H	Pyridine	704 (4.38), 676 (4.36), 644 (4.19), 608 (3.95), 356 (4.45), 338 (4.54), 321 (4.31), 295 (4.30)	0.98
		H_2SO_4	776 (4.01), 731[b] (3.75), 693 (3.28), 652 (2.96), 414 (3.40), 308 (4.22), 285 (4.27), 254 (4.26)	1.06
8	Zn	H_2SO_4	835 (3.73), 760[b] (3.60), 726 (3.34), 671 (2.78), 418 (3.30), 354 (3.42), 325 (3.25), 267 (4.35)	1.17
9	Cu	H_2SO_4	852 (3.90), 756[b] (3.98), 734 (3.81), 659 (2.75), 429 (3.91), 394 (4.06), 301 (4.49), 277 (4.58), 253 (4.60)	1.15
10	Co	H_2SO_4	820 (3.40), 759[b] (3.17), 715 (2.70), 654 (2.38), 379 (4.38), 354 (4.57), 314 (4.60), 267 (4.64)	1.36
11	Ni	H_2SO_4	857 (4.26), 807[b] (4.20), 731 (4.11), 651 (3.59), 512 (2.32), 416 (4.18), 397 (4.29), 315 (4.54), 277 (4.59)	1.08

ε, absorption coefficient.
[a] Intensity ratio of absorption B bands (or Soret band transition) at $\lambda = 253$–325 nm and Q bands at $\lambda = 697$–850 nm (concentrations = 1.0×10^{-5} g/L in chloroform, 1.0×10^{-4} g/L in H_2SO_4, and 1.0×10^{-4} g/L in pyridine).
[b] Shoulder.

As can be seen in Table II, there was a shoulder at the slightly higher energy sides for polymeric phthalocyanines. The presence of shoulders in the UV–vis spectra of the polymers corresponded to the aggregated or nonaggregated species in concentrated sulfuric acid. The metal-free phthalocyanine polymer (7) decomposed slowly by hydrolysis in concentrated H_2SO_4, and this was demonstrated by a decrease in the absorption coefficient at longer wavelengths. Metal-containing polymers (8–11), however, were stable. From organic solvents to concentrated H_2SO_4, the long-wave absorption band underwent a significant bathochromic shift, which was due to degradation and weak protonation of the phthalocyanine ring at the meso nitrogen atoms. The intensity of these absorptions also decreased. The UV–vis spectrum of 7 was obtained

in pyridine and concentrated H_2SO_4. The electronic absorption spectra of 5 and 6 in chloroform and of 7 in pyridine and H_2SO_4 at room temperature are shown in Figures 1 and 2. There was a single Q band (Q band transition) for 5, whereas a split Q band, as expected, and two strong bands were in the visible region for 6 and 7.[15] The split Q band, which is characteristic for metal-free phthalocyanines, was observed at λ_{max} values of 709 and 678 and 704 and 676 nm with shoulders at 650 and 644 nm for 6 and 7, respectively, which indicated the monomeric species; the monomeric species with D_{2h} symmetry showed two intense absorptions around 700 nm.[15,16] On the other hand, such split-Q band absorptions are due to the $\pi \rightarrow \pi^*$ transition of this fully conjugated 18π electron systems.[17] In the case of an H_2SO_4 solution of 7, the primary
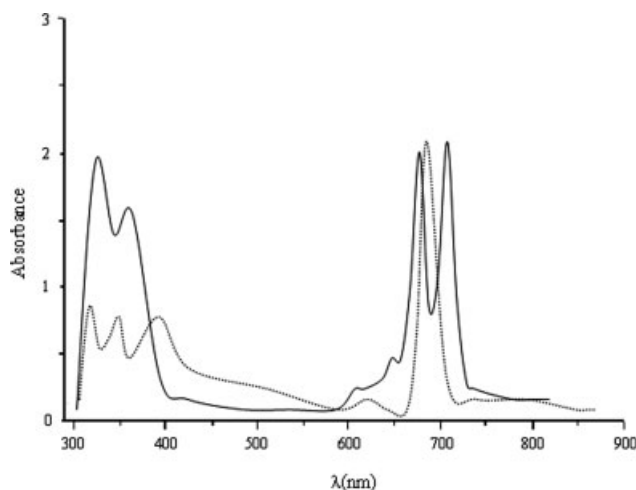

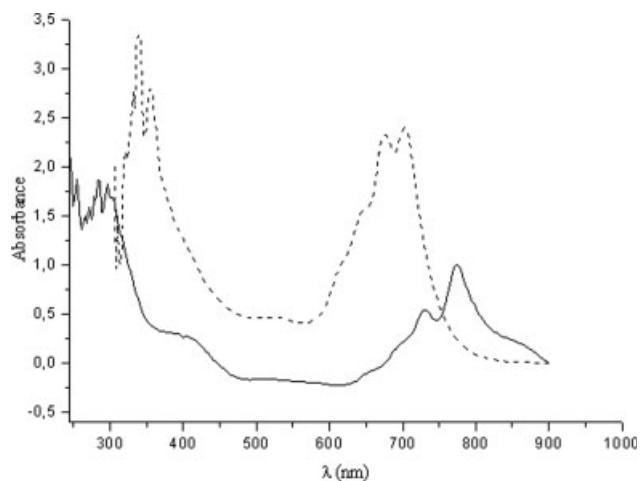Figure 1 UV–vis spectra of (···) 5 and (—) 6 in chloroform (concentration = 1.0×10^{-5} M).

Figure 2 UV–vis spectra of 7 in (---) pyridine (concentration = 1.0×10^{-4} g/L) and (—) H_2SO_4 (concentration = 1.0×10^{-4} g/L).
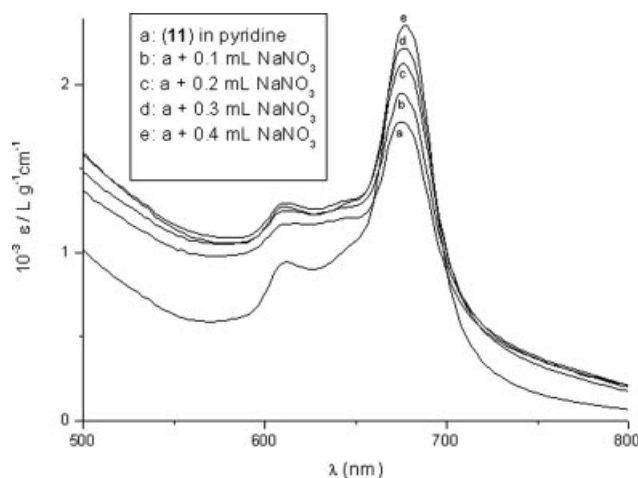
Figure 3 Changes in the visible spectra of **11** in pyridine (concentration $= 1.0 \times 10^{-3}$ g/L) after the addition of NaNO$_3$ solutions in methanol (concentration $= 1.0 \times 10^{-3}$ M). ε, absorption coefficient.

Figure 4 Changes in the visible spectra of **11** in pyridine (concentration $= 1.0 \times 10^{-3}$ g/L) after the addition of KNO$_3$ solutions in methanol (concentration $= 1.0 \times 10^{-3}$ M). ε, absorption coefficient.

band in the visible region was broadened and shifted to a longer wavelength (72 nm). In all cases, the ratios of the UV (Soret band transition) and visible intensities (Q band transition) were less than or equal to 1 (Table II). This result can be attributed to the absence of poly(isoindolinine) co-units in all of the polymeric phthalocyanines (**8–11**).

Disaggregation of **11**, followed by changes in the visible spectra after the addition of methanol, K$^+$, Na$^+$, and NH$_4^+$ cations, is an effective route for characterizing the complexation behavior of the diaza-18-crown-6 peripheral substituents. First, we clarified whether methanol had any effect on the visible spectrum of **11**. For this purpose, different amounts of methanol were added to a solution of **11** in pyridine. There was only a little change in the intensities of Q bands in the visible absorption spectrum of **11** with increasing amounts of methanol. Then, different concentrations of metal salt (e.g., NaNO$_3$, KNO$_3$, and NH$_4$NO$_3$) solutions in methanol (1.0×10^{-3} M) were added to a solution of polymer **11** in pyridine (1.0×10^{-3} g/L). When we added NaNO$_3$, KNO$_3$, and NH$_4$NO$_3$ solutions to the solution of polymer **11**, there was a dramatic change due to disaggregation in the visible spectrum of **11**. This observation could be attributed to the disaggregation of **11** by trapped Na$^+$, K$^+$, and NH$_4^+$ ions in the diaza-18-crown-6 units. In other words, the cavity radius of diaza-18-crown-6 is harmonious with these ions, and there is no intermolecular complexation between the phthalocyanine units (Figs. 3–5).[18] This nonaggregative behavior could have important advantages not only for studying intramolecular processes in compounds such as **11** but also for applying these compounds in photodynamic therapy.[19]
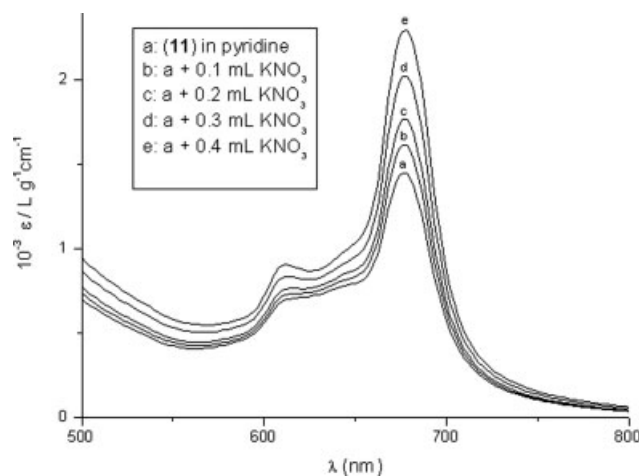
The intrinsic viscosities of dilute solutions of the polymers were measured with an Ubbelohde viscometer. The intrinsic viscosities of all the polymers were similar (Table III). Figure 6 shows the viscosities of the polymers as a function of the polymer concentration and indicates that the viscosities decreased, depending on the polymer concentration. This behavior can be explained by two effects: (1) degradation of the polymers and (2) weak protonation of the four bridging nitrogen atoms in the core of each phthalocyanine and the nitrogen atoms of the peripheral substituents. On the other hand, there were almost linear decreases for all the polymers (Fig. 6).
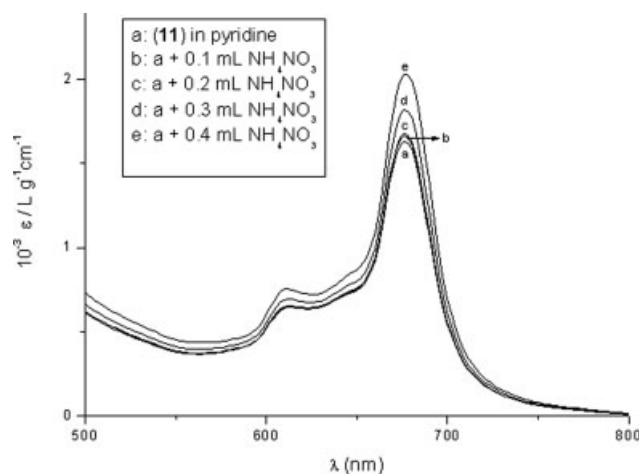

Figure 5 Changes in the visible spectra of **11** in pyridine (concentration $= 1.0 \times 10^{-3}$ g/L) after the addition of NH$_4$NO$_3$ solutions in methanol (concentration $= 1.0 \times 10^{-3}$ M). ε, absorption coefficient.

TABLE III
Electrical Conductivity and Intrinsic Viscosities of the Polymeric Phthalocyanines at Room Temperature

Compound	M	Conductivity (S/cm) in air	in vacuo	Pellet thickness (mm)	Intrinsic viscosity (H_2SO_4)
7	2H	2.65×10^{-9}	4.43×10^{-10}	0.60	2.46
7a	2H	3.30×10^{-9}	6.20×10^{-10}	0.55	—
8	Zn	2.25×10^{-7}	4.14×10^{-8}	0.55	1.47
9	Cu	4.16×10^{-8}	8.90×10^{-9}	0.60	1.87
10	Co	6.27×10^{-7}	3.29×10^{-8}	0.65	2.32
11	Ni	3.67×10^{-8}	1.08×10^{-8}	0.60	1.69

The structure of the polymers was an Au/MPc/ Au sandwich in the configuration commonly used for electrical conductivity measurements.[20] To prepare the samples, powdered materials were pressed at a load of 3 tons/cm^2 for 3 min into compact disks with a thickness of 0.55–0.65 mm and a diameter of 13 mm. The electrical conductivities of the polymers were measured in vacuo and in air. Table III shows the alternating-current electrical conductivities of polymers **7**, **7a**, and **8–11**. These values correspond to those of semiconductive materials encountered in most of the substituted phthalocyanine derivatives.[21] The conductivity values obtained under an air atmosphere were higher than those obtained in vacuo for all the polymers, probably because of absorbed oxygen in air.[22]

The thermal stability of the phthalocyanine polymers (**7–11**) was determined by thermal analysis. Because of the high thermal stability of the phthalocyanine core, cleavage of the substituent macrocycles takes place first, and then the main decomposition occurs above 400°C.[23] However, the crown ether units are not stable at temperatures above 300°C even under inert conditions.[6] The initial decomposition temperature decreased in the order of **8** > **10** > **11** > **9** > **7** (Table IV). Cu-containing polymer **9** was the most rapidly degraded metallophthalocyanine, whereas the Zn-containing metallophthalocyanine polymer showed the highest thermal stability under the working conditions.
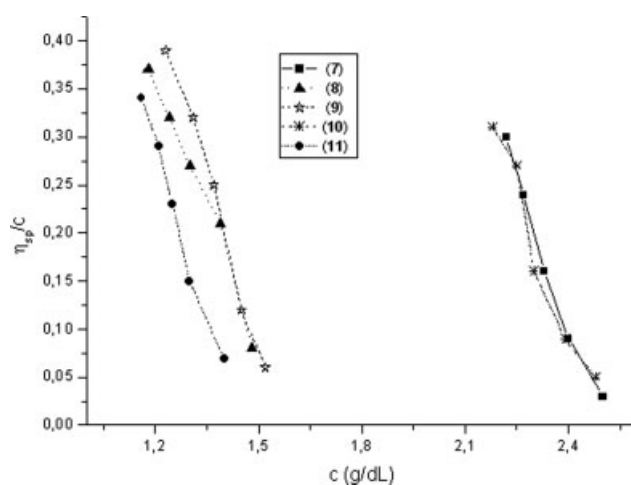
The binding property of **10** toward alkali, alkaline-earth, and some transition cations was studied in THF. Because of their insolubility, heterogeneous phase extraction of the metal picrates from THF solutions to the solid Co-containing polymer was investigated. Picrate was used as a counteranion for all compounds. The results can be seen in Table I. An examination of the data revealed the following results: (1) the tendency of binding all metal picrates paralleled the increase in the ionic diameter, except for Cs$^+$, and (2) the highest extraction affinities of **10** were determined to be 96.4 and 84.2% for K$^+$ and Ba^{2+}. The highest extraction affinities in the case of K$^+$ and Ba^{2+} were probably due to the greater compatibility of K$^+$ and Ba^{2+} with the macrocyclic unit in comparison with the other ions. In addition, according to the data in Table I, the abilities of diaza-18-crown-6 to extract potassium and barium picrate were very close. This could be attributed to the similarity in the diameters of K$^+$ and Ba^{2+} cations. The extraction affinities of the heavy-metal picrates were determined to be 22.6, 49.7, 51.2, 67.5, and 78.6% for Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}, respectively. The lowest extraction affinity of Ni^{2+} was probably due to the smallest ion diameter in comparison with those of the other heavy-metal ions. The ability of diaza-18-crown-6 to extract other heavy-metal-ion picrates was closely parallel because of the similarity in the diameters of these cations.

Figure 6 Viscosity curves of the metal-free and metallophthalocyanine polymers. η_{sp}, specific viscosity.

TABLE IV
Thermal Properties of the Polymeric Phthalocyanines

Polymer	M	Initial decomposition temperature (°C)	Main decomposition temperature (°C)
7	2H	320	445
8	Zn	390	587
9	Cu	326	518
10	Co	360	547
11	Ni	344	532

CONCLUSIONS

We have presented the synthesis and characterization of new monomeric and polymeric phthalocyanines with diaza-18-crown-6 units. The monomeric phthalocyanines (**5** and **6**) and polymeric phthalocyanines (**7–11**) were prepared with a tetranitrile monomer and proper precursors. Zn-, Ni-, and Co-containing polymers showed good thermal stability, whereas Cu-containing and metal-free polymers were the most rapidly degraded. The electrical conductivities of the polymeric phthalocyanines, which were measured as gold sandwiches, were found to be 10^{-10}–10^{-7} S/cm *in vacuo* and in air. The extraction ability of **10** was evaluated in THF with several alkali, alkaline-earth, and heavy-metal picrates, and the highest extraction affinity was observed for K^+ and Ba^{2+}. The intrinsic viscosities of the metal-free polymer and metallophthalocyanine polymers were similar. Compound **11** had a clear disaggregation tendency with the addition of KNO_3, $NaNO_3$, and NH_4NO_3.

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