Synthesis and characterization of new polymeric phthalocyanines substituted with diaza-18-crown-6 macrocycles through ethyleneoxy bridges

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Abstract

A tetranitrile monomer was synthesized by nucleophilic aromatic substitution of N,N'-bis(2-hydroxyethyl)-4,13-diaza-18-crown-6 onto 4-nitrophthalonitrile. A series of polymeric metal-free and metallophthalocyanine (M = 2H, Zn, Cu, Co and Ni) polymers was prepared by polymeric tetramerization reaction of the tetranitrile monomer with proper materials. The electrical conductivities of the polymeric phthalocyanines measured as gold sandwiches were found to be ~10^{-9}-10^{-4} S cm^{-1} in a vacuum and in argon. The extraction ability of the metal-free polymeric phthalocyanine was evaluated in tetrahydrofuran using several alkali metal picrates such as Li^+, Na^+, K^+ and Cs^+. The extraction affinity of the metal-free polymeric phthalocyanine for K^+ was found to be highest in the heterogeneous solid-liquid phase extraction experiments. The disaggregation property of the metal-free polymeric phthalocyanine was investigated with sodium, potassium and ammonium ions and methanol. All the novel compounds were characterized by using elemental analysis, UV–Vis, FT-IR, NMR and MS spectral data and DTA/TG.

Keywords: Bisphthalonitrile; Diaza-18-crown-6; Electrical conductivity; Extraction; Polymeric phthalocyanine

1. Introduction

Phthalocyanines have found practical applications in a wide range of high technology fields such as nonlinear optics, photosensitizers, gas sensors, catalysts, liquid crystals, optical data storage, sensitizers for photodynamic therapy of cancer, electrodes in fuel cell, photoelectric conversion materials in solar cells, and laser service substances, among others [1–3]. A great number of remarkable applications of phthalocyanines arise from their unique 18π electron conjugated aromatic cloud, which makes them present high thermal and chemical stability and remarkable photoelectric properties [4].

A combination of a phthalocyanine with a polymer or incorporation of a phthalocyanine into a polymer is a powerful tool for designing materials with interesting properties [5]. Polymeric phthalocyanines were mainly prepared via polycyclotetramerization reactions of bifunctional monomers such as various nitriles [6–21] or tetracarboxylic acid derivatives [22–25] in the presence of metal salts or metals. We have previously synthesized novel phthalocyanines carrying various macrocyclic groups and polymeric phthalocyanines [26].

In the present work, metal-free and metallophthalocyanine polymers which contain ethyleneoxy diaza-18-crown-6 moieties were synthesized and characterized. The electrical conductivities of the polymers as Au/MPC/Au sandwiches in a vacuum and in argon atmosphere were examined. The viscosity properties of all the polymers and alkali...
metal extraction ability and disaggregation property of the metal-free polymeric phthalocyanine were investigated.

2. Experimental

2.1. Materials

Phosphorus pentoxide (P₂O₅), 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), ethyl alcohol, n-pentanol, dimethylformamide (DMF), tetrahydrofuran (THF), chloroform, dichloromethane, petroleum ether, quinoline, sulphuric acid, hydrochloric acid, pyridine, acetone, 1,2-bis(2-iodoxyethoxy)ethane, sodium iodide, sodium thiosulfate, acetonitrile, sodium carbonate, dioxane, ethylene oxide, methanol, 1,2-(2-aminoethoxy)ethane were received from Merck and used as supplied. Cesium carbonate (Cs₂CO₃) was received from Merck and used after drying in oven at 200–210 °C for 20 min. Some part of the product was precipitated as white crystals. They were mechanically separated from the mother liquor; m.p., 49–51 °C.

Compound 3: yield, 2.88 g (72%). Anal. Calc. for C₁₁₆H₁₄₅N₂O₆: C, 54.84; H, 9.78; N, 7.99. Found: C, 55.01; H, 9.64; N, 8.12%. IR (KBr): v_max (cm⁻¹): 3327 (s, OH), 2955–2810 (–CH₂–), 1483, 1477, 1442, 1361, 1353, 1255, 1126–1045 (s, CH₂O–), 954, 875. H NMR (CDCl₃): δ = 4.43 (s, broad, 2H, D₂O exchangeable, OH), 3.69 (q, J = 6.44 Hz, 8H, NCH₂C₂H₃OH), 5.69 (NCH₂H₂O), 60.14 (NCH₂H₂O), 56.43 (NCH₂CH₂-OH), 54.15 (NCH₂CH₂OH), MS (Electron impact, EI), m/z (%): 369.08 (3.12) [M + H₂O⁺]⁺, 352.22 (1.23) [M + 2]⁺, 351.25 (1.90) [M + 1]⁺, 350.25 (1.8) [M⁺], 349.11 (1.02) [M – 1]⁺, 333.31 (1.24) [M – OH]⁺, 319.36 (100.00) [M – CH₂O⁺], 289.17 (23.36) [M + 1 – 2CH₂OH]⁺, 275.42 (20.13) [M + 1 – C₅H₅O₂]⁺, 188.32 (10.29), 176.20 (10.81), 162.45 (25.52), 146.43 (20.73), 132.09 (18.32), 114.28 (35.67), 100.39 (40.56).

2.2. Measurements

Melting points of the compounds were determined with an electrothermal melting point apparatus and were uncorrected. 1H NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer with CDCl₃ as solvent and tetramethylsilane as the internal standard. 13C NMR spectra were recorded on a Varian Mercury Plus 75 MHz spectrometer with CDCl₃ as the solvent and tetramethylsilane as the internal standard. Transmission IR spectra of samples were recorded on a FTIR spectrophotometer (Shimadzu FTIR-8201 PC) with the samples in KBr pellets. Optical spectra in the UV–Vis region were recorded with a model Shimadzu 1601 UV–Vis spectrometer using standard cuvettes with a fixed 1 cm pathlength at room temperature. The d.c. conductivity was measured by a Autolab 30 Voltammetry-FRA 2 frequency analyser. The frequency range was of 100–1 MHz and applied amplitude (rms) was 10 mV. Mass spectra were measured on a Varian MAT 711 and on Micromass Quatro LC/ULTIMA LC-MS MS spectrometers. The elemental analysis of the compounds was determined on a CHNS-932 LECO instrument. The metal contents of the metallophthalocyanine polymers were determined with a Unicam 929 AA spectrophotometer in solutions prepared by decomposition of the metallophthalocyanines in conc. sulfuric acid and conc. nitric acid solution followed by digestion in conc. hydrochloric acid solution and deionize water. Differential thermal analysis (DTA/TG) was performed on a Linseis L81 instrument in air atmosphere with a heating rate of 10 °C/min in a temperature range of 50–750 °C. Intrinsic viscosities of freshly prepared dilute solutions of phthalocyanine polymers were measured in conc. H₂SO₄ at 25 °C by use of an Ubbelohde viscometer.

2.3. Synthesis

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

A mixture of 1,10-diaza-18-crown-6 (3 g, 11.44 mmol) and methanol (20 mL) was charged into a 250-mL three-necked flask on ice-bath. Ethylene oxide (2.7 mL) was cooled to −20 °C and then added dropwise into the reaction flask over a period of 10 min. After adding, ice-bath was changed with oil-bath. The reaction mixture was refluxed first for 4 h with a condenser which was cooled to −20 °C and then 3 more hours with an ordinary condenser under nitrogen atmosphere at 65–70 °C. The reaction was ended and the solvent, methanol, was evaporated. The residue was distilled under vacuum at 200–210 °C (0.10-mm Hg) to yield pale yellow product. Refractive index of the product was 1.4937 at 20 °C. After the product was cooled to −10 °C, some part of the product was precipitated as white crystals. They were mechanically separated from the mother liquor; m.p., 49–51 °C.

Compound 3: yield, 2.88 g (72%). Anal. Calc. for C₁₁₆H₁₄₅N₂O₆: C, 54.84; H, 9.78; N, 7.99. Found: C, 55.01; H, 9.64; N, 8.12%. IR (KBr): v_max (cm⁻¹): 3327 (s, OH), 2955–2810 (–CH₂–), 1483, 1477, 1442, 1361, 1353, 1255, 1126–1045 (s, CH₂O–), 954, 875. H NMR (CDCl₃): δ = 4.43 (s, broad, 2H, D₂O exchangeable, OH), 3.69 (q, J = 6.44 Hz, 8H, NCH₂C₂H₃OH), 5.69 (NCH₂H₂O), 60.14 (NCH₂H₂O), 56.43 (NCH₂CH₂-OH), 54.15 (NCH₂CH₂OH), MS (Electron impact, EI), m/z (%): 369.08 (3.12) [M + H₂O⁺]⁺, 352.22 (1.23) [M + 2]⁺, 351.25 (1.90) [M + 1]⁺, 350.25 (1.8) [M⁺], 349.11 (1.02) [M – 1]⁺, 333.31 (1.24) [M – OH]⁺, 319.36 (100.00) [M – CH₂O⁺], 289.17 (23.36) [M + 1 – 2CH₂OH]⁺, 275.42 (20.13) [M + 1 – C₅H₅O₂]⁺, 188.32 (10.29), 176.20 (10.81), 162.45 (25.52), 146.43 (20.73), 132.09 (18.32), 114.28 (35.67), 100.39 (40.56).
organic phase was dried over MgSO₄. Chloroform was evaporated and oily brown crude product was obtained. The yield was recrystallized from a mixture of ethanol:diethyl ether (3:1; v/v) and dried again under vacuum over P₂O₅. The final brown solid 5 was soluble in chloroform, DMF, DMSO, pyridine, THF and dichloromethane.

**Compound 5**: yield, 3.96 g (92%); m.p., 156 ºC. *Anal. Calc. for C₁₂₂H₉₅N₆O₆: C, 63.77; H, 6.36; N, 13.94. Found: C, 63.94; H, 6.22; N, 13.65%. IR (KBr): vₘₐₓ (cm⁻¹): 3040 (aromatic =CH), 2920–2865 (aliphatic CH₂), 1610 (aromatic =C–C=), 1420, 1389, 1260 (Ar–O–C), 1126–1049 (CH₂–O–CH₂), 943 and 881. **¹H NMR (CDCl₃)**: δ = 7.99 (d, J = 8.00 Hz, 2H, ArH), 7.53 (d, J = 8.53 Hz, 2H, ArH), 7.44 (dd, J = 9.30 Hz, 2H, ArH), 4.18 (t, J = 7.23 Hz, 4H, N-CH₂–CH₂–O–Ar), 3.65 (s, 8H, –OC₂H₅–CH₂O), 3.11 (t, J = 6.82 Hz, 8H, NCH₂CH₂O), 2.80 (t, J = 7.23 Hz, 4H, NCH₂CH₂O–), 2.55 (t, J = 6.82 Hz, 8H, NCH₂CH₂O). **¹³C NMR (CDCl₃)**: δ = 162.92 (C₄), 135.42 (C₉), 121.95 (C₃), 119.81 (C₄), 117.32 (C₂), 116.48 (C₇), 115.96 (C₈), 110.00 (C₁), 71.39 (C₉), 69.58 (C₁₃), 67.37 (C₁₂), 55.49 (C₁₁), 55.08 (C₁₀). MS, m/z (%): 736.73 (7.17) [M + Cs + 1]⁺, 603.74 (10.26) [M + 1]⁺, 602.58 (11.42) [M]+, 527.38 (35.06), 459.25 (12.76) [M – C₆H₅N₃O⁺], 445.36 (48.17) [M – C₇H₄N₂O⁺], 316.43 (60.21) [M – C₈H₆N₂O₂⁺], 288.12 (100.00) [M – C₉H₇N₃O₃⁺], 188.16 (21.03), 176.78 (16.54), 143.47 (70.73), 127.82 (38.34), 114.48 (42.23), 100.02 (31.26).

2.3.3. Preparation of metal-free polymeric phthalocyanine (6)

A mixture of compound 5 (0.602 g, 1 mmol), n-penta- nol (5 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.155 g, 1 mmol) was placed in a standard Schlenk tube under nitrogen atmosphere and degassed several times. The temperature was gradually increased up to 90 ºC and degassed again with nitrogen. Then the reaction mixture was stirred at 145 ºC for 12 h. After the reaction mixture was cooled and decanted, the residue was stirred with methanol:petroleum ether mixture (10 mL, 1/1; v/v). The product 6 was filtered off, washed with DMF, methanol, acetone and diethyl ether and dried in air. The final dark green solid 6 was soluble in H₂SO₄, hot pyridine and poorly soluble in chloroform, dichloromethane and THF.

**Compound 6**: yield, 0.43 g; m.p., >300 ºC. *Anal. Calc. for (C₁₂₈H₁₅₄N₂₈O₆Zn)ₙ (2549.05): C, 60.24; H, 6.16; N, 10.98; Zn, 2.56. Found: C, 60.45; H, 6.37; N, 10.69; Zn, 2.67%. IR (KBr): vₘₐₓ (cm⁻¹): 3390 (imide N–H), 3054 (aromatic =CH), 2900–2789 (CH₂), 1770 (sym. C=O), 1720 (asym. C=O), 1640 (–C≡N–), 1598 (aromatic –C=C–), 1485, 1421, 1326, 1254 (Ar–O–C), 1160–1040 (C–O–C), 957, 842 and 590 cm⁻¹.

2.3.5. Preparation of Cu-containing polymer (8)

A mixture of biphthalonitrile compound 5 (0.602 g, 1 mmol), Cu(CH₃COO)₂·H₂O (0.100 g, 0.5 mmol) and amyl alcohol (3 mL) was put in a flask. The temperature was increased up to 160 ºC and degassed three times under nitrogen atmosphere. Then, DBU (0.08 mL, 0.08 g, 0.5 mmol) was added drop by drop with a syringe into the system. The reaction was treated at 160 ºC for 12 h under reflux and nitrogen atmosphere. The reaction mixture was cooled, diethyl ether–methanol mixture (5 mL, 1:1) was added and stirred for 1 h. The mixture was filtered and the solid part was washed with distilled water, DMF, ethanol and diethyl ether. The final product 8 was dried under vacuum over P₂O₅ at 100 ºC.

**Compound 8**: yield, 0.38 g; m.p., >300 ºC. *Anal. Calc. for (C₁₂₈H₁₅₆N₂₀O₃₂Cu)ₙ (2548.05): C, 60.28; H, 6.17; N, 10.98; Cu, 2.49. Found: C, 60.51; H, 6.43; N, 11.17; Cu, 2.26%. IR (KBr): vₘₐₓ (cm⁻¹): 3360 (imide N–H), 3054 (aromatic =CH), 2900–2853 (CH₂), 1774 (sym. C=O), 1713 (asym. C=O), 1636 (–C≡N–), 1601 (aromatic –C=C–), 1493, 1428, 1330, 1262 (Ar–O–C), 1155–1020 (C–O–C), 964, 856 and 590 cm⁻¹.

2.3.6. Preparation of Co-containing polymer (9)

A mixture of biphthalonitrile compound 5 (0.602 g, 1 mmol), dry quinoline (2 mL) and CoCl₂·6H₂O (0.120 g, 0.5 mmol) was kept in a flask and degassed three times with nitrogen. The reaction mixture was treated at 220 ºC under reflux and nitrogen inert atmosphere. After 24 h of stirring, the reaction mixture was cooled and then diethyl ether (25 mL) was added and then filtered off. The solid part was washed with methanol:diethyl ether mixture (20 mL, 1:1), DMF, hot ethanol, acetone and filtered off. The final product 9 was dried under vacuum over P₂O₅ at 100 ºC. The final green product 9 was soluble in H₂SO₄ and poorly soluble in pyridine.
2.3.7. Preparation of Ni-containing polymer (10)

A mixture of bisphthalonitrile compound 5 (0.602 g, 1 mmol), dry quinoline (1.5 mL) and NiCl$_2$·6H$_2$O (0.122 g, 0.5 mmol) was charged in a standard Schlenk tube and degassed three times with nitrogen. The temperature was increased up to 220 °C and treated for 24 h under reflux and nitrogen inert atmosphere. The system was cooled to room temperature and methanol:water (10 mL, 1:1; v/v) mixture was added to the system and stirred at room temperature for 1 h. The product was filtered off and washed with DMF, methanol, distilled water, petroleum ether. The final green product was soluble in H$_2$SO$_4$ and poorly soluble in pyridine.

**Compound 10**: yield, 0.37 g; m.p. >300 °C. *Anal. Calc.* for (C$_{128}$H$_{158}$N$_2$O$_{32}$Ni)$_n$ (2543.05): C, 60.40; H, 6.18; N, 11.01; Ni, 2.31. Found: C, 60.64; H, 6.06; N, 11.35; Ni, 2.52%. IR (KBr): $\nu_{\text{max}}$ (cm$^{-1}$): 3143 (imide N–H), 3048 (aromatic $\equiv$CH), 2925–2875 (CH$_2$), 1772 (sym. C=O), 1718 (asym. C=O), 1641 ($\nu$=C=N–), 1612 (aromatic $\equiv$C=C–), 1500, 1435, 1323, 1265 (Ar–O–C), 1148–1032 (C–O–C), 972, 870 and 623 cm$^{-1}$.

2.3.8. The conversion of cyano end groups of the metal-free polymeric phthalocyanine into imido groups (6a)

A sample of the metal-free polymeric phthalocyanine (6) (150 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 filtrate was poured into excess amount of ice-water mixture. The dark green crude product was washed with distilled water until the notes the absorbance in THF suspension phase after

2.3.10. Measurement of the alkali metal-binding properties of the polymeric metal-free phthalocyanine

The extraction properties of 6 were investigated under solid–liquid phase condition by using alkali metal picrates (Li$^+$, Na$^+$, K$^+$ and Cs$^+$) as substrates and measuring by UV–Vis the amounts of picate in THF phase before and after treatment with polymers in suspension. Suspensions were prepared by mixing 25 mg of the polymeric metal-free phthalocyanine (6) and the alkali metal picrate solutions as described in previous article [26g]. The prepared suspensions were put in plastic bottles and shaken vigorously for 24 h at room temperature. Results and experimental conditions are reported in Table 1. In the absence of host 6, blank experiment, no metal ion picate extraction was detected. The extractability was determined based on the absorbance of picate ion in the THF suspensions. The extractability was calculated by using the following equation:

$$E(\%) = \frac{(A_0 - A)}{A_0} \times 100$$

where $A_0$ is the absorbance in the absence of ligand. $A$ denotes the absorbance in THF suspension phase after extraction.

3. Results and discussion

The synthesis of the $N,N'\text{-bis}(2\text{-hydroxyethyl})$-4,13-diaza-18-crown-6 (3) was performed by starting with 4,13-diaza-18-crown-6 (1) and ethylene oxide (2) in methanol (Scheme 1). The yield (72%) was higher than the known procedure (51%) [29] and the product was partly solid (m.p., 49–51 °C) while it was said to be oily in the literature reference. Elemental analysis and mass spectral data of 3 were satisfactory: 350.25(1.8) [M]$^+$. In $^1$H NMR (CDCl$_3$) spectrum of 3, NH group of compound 1 disappeared as expected. $^1$H NMR spectrum of 3 showed new signal at $\delta = 4.43$ (s, broad, 2H, OH) and also the proton-decoupled $^{13}$C NMR spectrum of 3 indicates the presence of primary alcohol carbon atoms at $\delta = 60.14$ (NCH$_2$CH$_2$OH) and 56.43 (NCH$_3$CH$_3$OH), respectively. The IR spectrum of 3 was easily verified with the disappearance of N–H and
presence of O–H stretching vibrations at 3327 cm\(^{-1}\). The difference between the IR spectra of 1 and 3 is clear from the absence of characteristic vibrations such as N–H. 4-Nitrophthalonitrile (4) was treated with 3 in the presence of Cs\(_2\)CO\(_3\)in DMF to afford tetranitrile monomer 5 with high yield (92%). Final purification of tetranitrile derivative 5 by recrystallization afforded 5 for which elemental analysis and EI mass spectral data were satisfactory: 602.58 [M]+. In \(^1\)H NMR spectrum of 5, OH group of compound 3 disappeared as expected. The disappearance of OH and the presence of Ar–O–C at 1260 cm\(^{-1}\) and the presence of C\(\equiv\)N functional group at 2230 cm\(^{-1}\) in the IR spectrum.
of compound 5 confirm the formation of desired compound 5.

The metal-free phthalocyanine polymer was synthesized by heating mixture of 5, DBU and amyl alcohol in a Schlenk tube [30]. The transition metal complexes were prepared from the tetracyano compound 5 and the corresponding metal salt in proper solvent (Scheme 1).

The molecular weights of the polymers could not be determined using traditional methods because of their poor solubility in organic solvents, but by comparison of the IR absorption bands of the end groups with those of the bridging groups [15,31]. On the other hand, according to the FAB mass spectra analysis of 6 using the soluble part (~80%) of 6 in pyridine, we can say that 6 is a tetramer molecule. The 1H NMR spectrum of the soluble part of the 6 in pyridine-d5 displayed broad signals, and the protons of the phthalocyanine core were invisible, even at elevated temperatures. This effect was attributed to strong aggregation of the molecules.

The IR spectra of metal-free 6, 6a and metallophthalocyanine polymers (7–10) are very similar. The significant difference is the presence of ν(N–H) vibrations of the inner phthalocyanine core which are assigned to a weak band at 3275 cm⁻¹ in the metal-free molecule. These bands disappear in the spectra of the metallophthalocyanine polymers. These bands are especially beneficial for characterization of metal-free phthalocyanine polymers, as there is little frequency dependence on ring substitution and they are not overlapped by strong tetratetrinile monomer absorptions [10]. The end groups of the metal-free phthalocyanine polymer were cyano groups (2223 cm⁻¹) while the end groups of the metallophthalocyanine polymers were imido groups (~1776–1710 cm⁻¹). The existence of imido groups in the case of metallophthalocyanine polymers was attributed to the presence of the moisture during work-up and the case of metallophthalocyanine polymers was imido groups (1776–1710 cm⁻¹). The significant differences in the intensities of Q bands were observed in the visible region is broadened and shifted to longer wavelength (104 nm). In all cases the intensities in the UV (Soret band transition) and Vis (Q-band transition) were IUV/Ivis ≤ 1 (Table 2). This result indicates the absence of poly(isoindolino) co-units in all of the polymeric phthalocyanines (6–10).

Disaggregation of the metal-free polymeric phthalocyanine (6), followed by changes in the visible spectra after the addition of methanol, several alkali and NH₄⁺ cation, constitute an effective route for characterizing the complexation behavior of the ethyleneoxy diaza-18-crown-6 peripheral substituents. Firstly, we clarified whether methanol has any effect or not on the visible spectrum of 6. For this purpose, different amounts of methanol were added to the solution of 6 in pyridine. As can be seen in Fig. 1 decreases in the intensities of Q bands were observed in the visible absorption spectrum of 6 with increasing the amounts of methanol. This can be due to the dilution. Then the different concentration of metal salts (e.g. NaNO₃, KNO₃, NH₄NO₃) solutions in methanol (1.0 × 10⁻³ M)

Table 2 Wavelength and relative absorbance intensities of the UV–Vis spectra of the polymeric phthalocyanines

<table>
<thead>
<tr>
<th>Compound</th>
<th>M Solvent</th>
<th>λ/ nm (Arel × 10⁻²)</th>
<th>Ratio² UV–Vis</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2H pyridine</td>
<td>H₂SO₄</td>
<td>706 (2.19) 672 (2.24) 640b (1.48) 606 (1.48) 389 (2.14) 360 (2.19) 320 (2.40) 301 (2.51) 285 (2.00)</td>
</tr>
<tr>
<td>7</td>
<td>Zn H₂SO₄</td>
<td>850 (2.88) 819b (2.40) 736 (1.12) 619 (0.26) 458 (2.24) 365 (1.95) 327 (1.51) 297 (1.38)</td>
<td>0.48</td>
</tr>
<tr>
<td>8</td>
<td>Cu H₂SO₄</td>
<td>832 (1.20) 773b (0.78) 732 (0.52) 617 (0.19) 430 (0.85) 412 (0.53) 338 (0.69) 304 (1.10)</td>
<td>0.92</td>
</tr>
<tr>
<td>9</td>
<td>Co H₂SO₄</td>
<td>816 (1.74) 755b (0.89) 720 (0.55) 663 (0.08) 391 (2.40) 377 (1.45) 326 (2.14) 292 (2.45)</td>
<td>1.41</td>
</tr>
<tr>
<td>10</td>
<td>Ni H₂SO₄</td>
<td>816 (2.51) 755b (0.79) 719 (0.52) 639 (0.33) 460 (2.57) 414 (2.24) 378 (2.00) 297 (2.88)</td>
<td>1.14</td>
</tr>
</tbody>
</table>

a Intensity ratio of absorption B bands at λ = 274–304 nm and Q bands at λ = 719–850 nm (C = 1.0 × 10⁻⁴ g/L in H₂SO₄, 1.0 × 10⁻³ g/L in pyridine).

b Shoulder.
were added to the solution of the metal-free polymeric phthalocyanine (6) in pyridine (1.0 × 10⁻³ g/L). When we added NaNO₃, KNO₃ and NH₄NO₃ solutions to the metal-free polymeric phthalocyanine (6) solution caused a dramatic change due to disaggregation in the visible spectrum of 6 even in spite of dilution effect of methanol. This observation can be attributed to the disaggregation of 6 by trapped Na⁺, K⁺ and NH₄⁺ ions in the diaza-18-crown-6 units, the radius cavity of which is harmonious with these ions and there is no intermolecular complexation between the phthalocyanine units [36] (Figs. 2–4).

The intrinsic viscosities of dilute solutions of polymers were measured by means of Ubbelohde viscometer. The intrinsic viscosities of all polymers were similar (Table 3). Fig. 5 shows the viscosities of polymers as a function of polymer concentration, and indicates that viscosities decreased depending on polymer concentration. This behavior can be explained by two effects: (1) degradation of the polymers and (2) weakly protonation of the four bridging nitrogen atoms at the periphery of each phthalocyanine polymer and the nitrogen atoms of the diaza-18-crown-6 units. On the other hand, there were linear decreasing in the case of 7 and 9 while polynomial decreasing in the case of 6, 8 and 10 (Fig. 5). It can be probably due to lower stability of 6, 8 and 10 than those of others, 7 and 9.

The structure of the polymers was an Au/MPc/Au sandwich in the configuration commonly used for the electrical conductivity measurements [37]. To prepare the samples, powdered materials were pressed at a load of 2 tons for 3 min into disk-shaped compacts with a thickness of 0.45–0.60 mm. The d.c. conductivity was measured by a Autolab 30 Voltammetry-FRA 2 frequency analyser. The frequency range was of 100 Hz–1 MHz and applied amplitude (rms) was 10 mV. The electrical conductivities of the polymers were measured in a vacuum and in argon atmosphere (rms) was 10 mV. The electrical conductivities of the polymers and (2) weakly protonation of the four bridging nitrogen atoms at the periphery of each phthalocyanine. On the other hand, there were linear decreasing in the case of 7 and 9 while polynomial decreasing in the case of 6, 8 and 10. These values correspond to semi-conductive materials as encountered in number-substituted phthalocyanine derivatives [26g]. The conductivity values obtained under an argon atmosphere were higher than those of under vacuum for all polymers probably due to absorbed oxygen in argon [38].

The thermal stability of the phthalocyanine polymers (6–10) was determined by thermal analysis. Due to high thermal stability of the phthalocyanine core, cleavage of the substituent macrocycles takes place first and then the main decomposition occurs above 400 °C [39]. But, the crown ether units are not stable at temperatures above 300 °C even under inert conditions [40]. The initial decomposition temperature decreased in the order 7 > 9 > 10 > 8 > 6 (Table 4).
Cu-containing polymer 8 was the most rapidly degraded metallophthalocyanine while Zn-, Ni- and Co-containing metallophthalocyanine polymers showed good thermal stability under working conditions.

The alkali metal-binding ability of diaza-18-crown-6 units containing polymers were evaluated. Due to their insolubility, heterogeneous phase extraction of alkali metal picrates from THF solutions to the solid metal-free polymer was investigated. Picrate was used as counter anion for all compounds. The results can be seen in Table 1. Examinations of the data reveal the following results: (a) the tendency of binding alkali picrates goes parallel with the increase in the ionic diameter except for Cs+ and (b) the highest extraction affinity of 6 was determined as 94.25% for K+. The extraction affinity of 6 for Li+, Na+, K+, Cs+ were determined as 6.01%, 77.17%, 94.25% and 22.16%, respectively. The highest extraction affinity in the case of K+ is probably due to the more compatibility of K+ with macrocyclic unit than the other ions.

4. Conclusions

We have presented the synthesis and characterization of polymeric phthalocyanines with diaza-18-crown-6 ethyleneoxy bridges. The metal-free phthalocyanine polymer (6) and metallophthalocyanine polymers were prepared using a tetranitrile monomer and proper materials. Zn-, Ni- and Co-containing polymers showed good thermal stability while Cu-containing and the metal-free polymers were the most rapidly degraded. The electrical conductivities of the polymeric phthalocyanines measured as gold sandwiches were found to be $10^{-3}$–$10^{-4}$ Sc m$^{-1}$ in vacuo and argon. The extraction ability of 6 was evaluated in THF by using several alkali metal picrates and the highest extraction affinity was observed for K+. The intrinsic viscosity of the metal-free polymer and metallophthalocyanine polymers were similar. The metal-free polymeric phthalocyanine (6) had a clear disaggregation tendency with the addition of KNO$_3$, NaNO$_3$ and NH$_4$NO$_3$.

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