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Synthesis, characterization, aggregation and thermal properties of a novel polymeric metal-free phthalocyanine and its metal complexes

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ABSTRACT

A novel polymeric metal-free phthalocyanine (M = 2H) and its metal complexes (M = Zn, Cu, Co and Ni) were prepared by the tetramerization reaction of 3,6,9-Tris(p-toluenesulfonyl)-1,11-bis(3,4-dicyanophenoxy)-5,6,9-triazadodecane 5 with the appropriate materials. The electrical conductivities of the metal-free phthalocyanine and the metal complexes, measured in air, were found to be \( \sim 10^{-6} \text{ to } 10^{-8} \text{ S m}^{-1} \). The aggregation property of the zinc complex 7 was investigated with Ni, Cu, Co, Pb, Cd and Ag cations. Thermal analysis of the polymers was done by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) at a heating rate of 10°C min\(^{-1}\) under a nitrogen atmosphere. All the novel compounds were characterized by using elemental analysis, UV–Vis, FT–IR, NMR and MS spectral data and DSC, DTA/TG techniques.

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1. Introduction

Phthalocyanines (Pcs) consisting of a planar macrocycle with an 18 π-electron system have been extensively studied due to their unique optical, electronic, catalytic and structural properties [1]. There has been growing interest in the use of phthalocyanines in a variety of new technological fields such as semiconductor devices [2], electrochromic display devices [3], liquid crystals [4], Langmuir–Blodgett films [5], catalysts [6], gas sensors [7–9] and as photosensitizers in photodynamic therapy of cancer [10].

Polymeric phthalocyanines are also very interesting since they belong to a class of π-conjugated semiconductor polymers, which offer a unique combination of properties. Being discovered in the 1950s, polymeric phthalocyanine remains an enigmatic material and many of its intrinsic properties are known rather insufficiently [11–13]. Polymeric phthalocyanines were prepared via polycyclotetramerization reactions of bifunctional monomers such as aromatic tetracarboxanilides, various oxy-, arylenedioxy- and alkylenedioxy-bridged diphthalonitriles, and other nitriles or tetracarboxylic acid derivatives in the presence of metal salts or metals [11,12,14–16]. 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 [14–16]. Their structural similarity to chlorophyll has also made them useful for applications in artificial solar cells [17]. The ion-binding ability of phthalocyanines containing homo- and hetero-donor atoms in peripheral substituent groups is receiving considerable attention in view of their effect on the aggregation of the molecules. After polymerization reactions, polymeric phthalocyanines will have many donor atoms and thus high metal binding ability.

Recently, several types of monomeric and polymeric phthalocyanines with various functional groups have been synthesized by our group. These phthalocyanines have peripheral substituents with several macrocyclic or podand units [15,16,18–22].

In the present work, we describe the synthesis and characterization of a novel polymeric metal-free phthalocyanine and metal complexes containing peripherally long triazadioxo derivatives which may allow the new functionalized materials to be of importance in the preparation of analytical chemicals such as new kinds of heavy metal extraction agents. We have examined the electrical conductivities of the polymers in air atmosphere. The aggregation properties of the polymer 7 and the thermal properties of all the polymers were investigated.

2. Experimental

2.1. Materials

Phosphorus pentoxide (\( \text{P}_2\text{O}_5 \)), p-toluenesulfonyl chloride, diethylenetriamine, ethylene carbonate, potassium hydroxide, methanol, activated carbon, celite, 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), ethanol, 1-pentanol, dimethylformamide (DMF), tetrahydrofuran (THF), chloroform, dichloromethane, petroleum ether,
quinoiline, sulfuric acid, hydrochloric acid, pyridine, acetone, sodium thiosulfate, acetonitrile, sodium carbonate, dioxane, n-hexane, lithium, glacial acetic acid, silica gel, ammonia, MgSO₄, CoCl₂·6H₂O, NiCl₂·6H₂O, Cu(AC₂)₂·H₂O and Zn(AC₂)₂·2H₂O were received from Merck and used as supplied. Potassium carbonate was received from Merck and used after drying in 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 [23].

N,N,N’-Tris(p-tolylsulfonyl)diethylene-triamine was synthesized according to the literature [24].

2.2. Measurements

Melting points of the compounds were determined with an electrothermal melting point apparatus and were uncorrected. 1H NMR spectra were measured on a Bruker AMX-400 MHz NMR spectrometer in DMSO-d₆ with Me₄Si as an internal reference. 13C NMR spectra were recorded on a Bruker AMX 100 MHz NMR spectrometer with DMSO-d₆ as the solvent and with Me₄Si as an internal reference. Transmission IR spectra of the samples were obtained on a FT–IR spectrophotometer (Shimadzu FT–IR-8201 PC) with the samples in KBr pellets. Optical spectra in the UV–Vis region were recorded with a model Shimadzu 1600 UV–Vis spectrophotometer using 10 mm pathlength cuvettes at room temperature. For the electrical measurements, the surfaces of the samples were covered with silver paste to form electrodes. The dielectric permittivity and AC conductivity of the samples were performed between 100 Hz and 1 MHz frequency range at room temperature by using a LCR meter (Agilent 4284A). Mass spectra were measured on a Micromass LCT Mass spectrometer. Elemental analyses were performed on a CHNS-932 LECO elemental analyzer. The metal contents of the metallophthalocyanine polymers were determined with a Unicam 929 AA spectrophotometer. Differential thermal analysis was performed on a TGA Q600 TA instrument under nitrogen (100 mL/min) at a heating rate of 10 °C/min over the temperature range 30–700 °C. The reaction mixture was then allowed to cool to 90 °C and 10 mL of ethanol was added through the condenser as rapidly as possible. 0.15 g of activated carbon was added to the solution and refluxed for 30 min. The temperature was then increased to 120 °C and the suspension was stirred for 30 min longer, and filtered through Celite. Water (10 mL) was added dropwise to the stirred solution, but no precipitate was observed. The reaction mixture was extracted with chloroform (5 × 35 mL). After drying on MgSO₄, the solvent was evaporated. The product 3 was a viscous brown liquid. After dissolving in toluene, the solution was stirred for 6 days. The reaction was monitored by a thin layer chromatography (CHCl₃/MeOH, 7:3). At the end of this period, the mixture was cooled and poured into ice (100 g), and mixed for 4 more hours. The precipitate that formed was filtered and washed with water and EtOH. After recrystallization from MeOH, the obtained product 5 was dried over P₂O₅ in a vacuum oven at 50 °C to yield a light yellow powder.

Yield: 5.38 g (88%). M.p.: 138–139 °C. Anal. Calc. C₄₅H₄₃N₇O₈S₃ (906.06): C, 59.65; H, 4.78; N, 10.62. Found: C, 59.42; H, 5.02; N, 10.60; S, 10.75. FT–IR (KBr, cm⁻¹): 3086–3043 (Aromatic C≡C), 2980–2880 (aliphatic CH₂), 2223 (C=O–N), 1599 (aromatic C=C), 1564, 1493, 1458, 1339–1308 (SO₂), 1256 (Ar=O–CH₃), 1157 (SO₃), 1089, 979, 814, 719, 698, 646, 549. 1H NMR (DMSO-d₆, δ ppm): 8.21 (d, 2H, ArH), 8.01 (d, 2H, ArH), 7.96 (s, 2H, ArH), 7.69–7.54 (m, 6H, ArH), 7.38–7.26 (m, 6H, ArH), 4.21 (br. s, 4H, ArOC=O), 3.53 (br. s, 4H, NHC₆H₄CH₂OAr), 3.33–3.18 (m, 8H, NCH₂CH₂NHCH₂CH₂N), 2.38 (s, 3H, ArCH₃), 2.35 (s, 3H, ArCH₃). 13C NMR (DMSO-d₆, δ ppm): 161.9, 145.1, 143.2, 135.3, 134.9, 131.2, 130.4, 128.7, 127.5, 119.8, 118.6, 117.2, 115.4 (CN), 114.9 (CN), 107.8, 69.6 (CH₂OAr), 52.6, 49.7, 49.3, 21.4, 20.9. MS (ES⁺), m/z: 907.2 [M+H⁺], 751.1 [M+Ts⁻].

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

A mixture of 5 (0.906 g, 1.0 mmol), n-pentanol (5.0 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.15 mL, 0.16 g, 1.0 mmol) was placed in a standard Schlenk tube under nitrogen atmosphere and degassed two times. Then temperature was increased to 160 °C. The reaction mixture was stirred at 160 °C for 18 h. After the reaction mixture was cooled to room temperature, ethyl alcohol (10 mL) was added dropwise and mixed for half an hour. The dark green precipitate was filtered and washed with MeOH and diethyl ether. The dark green product 6 was dried at 50 °C under vacuum over P₂O₅.

Yield: 0.78 g (86%). M.p.: >300 °C. Anal. Calc. (C₁₈₀H₁₇₄N₅₂O₅₀S₂₁)ₙ (3626.25) (for nitric acid end groups); C, 59.62; H, 4.84; N, 10.82; S, 10.61. Found: C, 59.43; H, 6.27; N, 6.17; S, 14.94%. FT–IR (KBr, cm⁻¹): 3390 (O–H), 3068–3030 (Aromatic C≡C), 2944–2882 (–CH₂–), 1599 (C=O), 1494, 1456, 1332 (SO₂), 1261, 1160 (SO₂), 1089–1001 (CH₂O–), 909, 812, 717, 645, 552. 1H NMR (DMSO-d₆, δ ppm): 7.74–7.67 (d, 6H, ArH), 7.45–7.36 (d, 6H, ArH), 4.87 (br. s, 2H, OH), 3.60–3.18 (m, 16H, NCH₂OCH₂), 2.42 (s, 3H, ArCH₃), 2.40 (s, 6H, ArCH₃). 13C NMR (DMSO-d₆, δ ppm): 143.9, 143.6, 135.7, 135.4, 129.8, 127.4, 126.9 (ArC), 59.9 (CH₂OAr), 49.3, 49.1 (CH₂N), 21.5 (CH₃), 21.3 (CH₃). MS (ES⁺), m/z: 676.2 [M+Na⁺].

2.4. Preparation of 3,6,9-Tris(p-tolylsulfonyl)-1,11-bis(3,4-dicyanophenoxy)-3,6,9-triazaundecane (5)

A mixture of compound 5 (0.906 g, 1.0 mmol), zinc acetate dihydrate (0.114 g, 0.5 mmol) or cupric acetate monohydrate (0.100 g, 0.50 mmol) and amyl alcohol (5 mL) was put in a standard
Schlenk tube and the temperature was increased to 90 °C. DBU (0.15 mL, 1.0 mmol) was added dropwise to the suspension at the same temperature. Then the temperature was increased to 160 °C and the reaction was stirred at 160 °C for 18 h under a nitrogen atmosphere. After the reaction mixture was cooled to room temperature, ethanol (10 mL) was added and mixed for 30 min. The crude products were collected by filtration and washed with methanol, DMF, water and acetone. The final green 7 and dark green 8 products were dried under vacuum over P2O5 at 50 °C.

2.6.1. Compound 7

Yield: 0.98 g (96.1%). M.p.: >300 °C. Anal. Calc. C180H176N24O40S12Ni (3765.61): C, 57.41; H, 4.71; N, 8.93; S, 10.22; Zn, 1.74. Found: C, 57.72; H, 4.46; N, 8.65; S, 10.47; Zn, 1.95%. FT-IR (KBr, cm−1): 3402 (imide N–H), 3275 (N–H), 3056 (Aromatic =CH), 2928–2864 (CH2), 1770 (sym. C=O), 1718 (asym. C=O), 1645 (C=N–), 1601 (Aromatic –C=C–), 1487, 1456, 1395, 1334 (SO2), 1222 (ArOCH2), 1155 (SO2), 1085–1043, 940, 810, 715, 650, 543.

2.6.2. Compound 8

Yield: 0.92 g (91.5%). M.p.: >300 °C. Anal. Calc. C180H176N24O40S12Cu (3763.78): C, 57.44; H, 4.71; N, 8.93; S, 10.22; Cu, 1.69. Found: C, 57.72; H, 4.53; N, 9.27; S, 10.49; Cu, 1.46%. FT-IR (KBr, cm−1): 3386 (imide N–H), 3064 (Aromatic =CH), 2951–2824 (CH2), 1772 (sym. C=O), 1714 (asym. C=O), 1645 (C=N–), 1607 (Aromatic –C=C–), 1510, 1454, 1450, 1340 (SO2), 1229 (ArOCH2), 1157 (SO2), 1089–1018, 954, 814, 718, 646, 548.

2.7. Preparation of polymeric cobalt and nickel complexes (9, 10)

A mixture of compound 5 (0.906 g, 1 mmol), dry quinoline (3 mL) and CoCl2·6H2O (0.120 g, 0.5 mmol) or NiCl2·6H2O (0.122 g, 0.5 mmol) was charged in a standard Schlenk tube and degassed several times with nitrogen. The reaction mixture was treated at 210−220 °C for 18 h under a nitrogen inert atmosphere. After 18 h of refluxing, the reaction mixture was cooled to room temperature and then 10 mL of ethanol was added to the mixture slowly and stirred for 30 min. The obtained green 9 and dark green 10 products were filtered off. The crude products were washed with water, MeOH and diethyl ether. The final products (9 and 10) were dried under vacuum over P2O5 at 50 °C.

2.7.1. Compound 9

Yield: 1.0 g (97.4%). M.p.: >300 °C. Anal. Calc. C180H176N24O40S12Co (3759.17): C, 57.51; H, 4.72; N, 8.94; S, 10.23; Co, 1.57. Found: C, 57.29; H, 4.93; N, 8.65; S, 10.42; Co, 1.74%. FT-IR (KBr, cm−1): 3368 (imide N–H), 3048 (Aromatic =CH), 2953–2729 (CH2), 1770 (sym. C=O), 1719 (asym. C=O), 1640 (C=N–), 1598 (Aromatic –C=C–), 1474, 1325 (SO2), 1224 (ArOCH2), 1126 (SO2), 1084–1024, 984, 785, 735, 546.

2.7.2. Compound 10

Yield: 1.01 g (98.2%). M.p.: >300 °C. Anal. Calc. C180H176N24O40S12Ni (3758.92): C, 57.52; H, 4.72; N, 8.94; S, 10.23; Ni, 1.56. Found: C, 57.81; H, 4.97; N, 9.19; S, 9.87; Ni, 1.83%. FT-IR (KBr, cm−1): 3437 (imide N–H), 3053 (Aromatic =CH), 2926–2731 (CH2), 1768 (sym. C=O), 1721 (asym. C=O), 1640 (C=N–), 1533, 1489, 1460, 1341 (SO2), 1234 (ArOCH2), 1155 (SO2), 1089–1020, 991, 810, 723, 651, 546.

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

A sample of compound 6 (150 mg) was dissolved in a minimum volume of H2SO4 (96 wt-%) at room temperature. After 3–4 h of stirring, the reaction mixture was filtered. The filtered part was poured into excess amount of ice-water mixture. The dark green crude product was washed with distilled water until the residue washing water was neutral. Then the final product 6a was washed with ethanol, diethyl ether and dried under vacuum over P2O5 at 50 °C.


2.9. Metal analysis of the polymeric metal complexes

A sample of the polymeric metal complexes (7–10) (10 mg) was added into concentrated sulfuric acid (2.5 mL) and concentrated nitric acid (3.5 mL). The mixture was heated for 2 h at 160 °C in an oil-bath. The solution was finally digested in conc. HCl acid solution and then diluted with deionized water (500 mL). The determination of metal ions was conducted by atomic absorption measurements.

3. Results and discussion

The synthesis of the 3,6,9-Tris(p-tolylsulfonyl)-3,6,9-triaza-undecane-1,11-diol (3) was performed by starting with N,N,N′,N′-Tris(p-tolylsulfonyl)diethylenetriamine 1 (Scheme 1). Compound 1 was synthesized as described in the literature [24]. Elemental analysis and mass spectral data of 3 were satisfactory: 676.2 [M+Na]+. Compound 3 was characterized by NMR and IR spectroscopy techniques. In the 1H NMR (DMSO-d6) spectrum of 3, the NH group of 1 had disappeared, as expected, and a new signal at δ = 4.87 (br. s, 2H, OH) appeared. The proton-decoupled 13C NMR spectrum of 3 indicates the presence of the corresponding carbon atoms at δ = 59.9 (CH2OH) and 49.8 (CH2N). The IR spectrum of 3 was easily verified with the disappearance of N–H and the presence of O–H stretching vibrations at 3390 cm−1. The difference between the IR spectra of 3 and 1 is clear from the absence of characteristic vibrations such as N–H.

3.6,9-Tris(p-tolylsulfonyl)-1,11-bis(3,4-dicyanophenoxy)-3,6,9-triazaundecane (8) was prepared by the reaction of 4-nitrophthalonitrile and 3 in the presence of K2CO3, in dry DMF. Final purification of the bisphthalonitrile derivative by recrystallization afforded 8, for which elemental analysis and ES mass spectral data were satisfactory m/z: 907.2 [M+H]+, 751.1 [M-Ts]−. In the 1H and 13C NMR spectra of 8, the OH groups of compound 3 disappeared and nitrile carbon atoms appeared as expected. The disappearance of O–H stretching vibrations at 3390 cm−1. The difference between the IR spectra of 3 and 1 is clear from the absence of characteristic vibrations such as N–H.

Table 1
Wavelength and absorption coefficients of the UV-Vis spectra of the polymers.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M</th>
<th>Solvent</th>
<th>( \lambda ) (nm)/(log ( \varepsilon )) Ratioa UV-Vis</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6)</td>
<td>2H</td>
<td>Pyridine</td>
<td>704(4.29) 674(4.28) 648(4.12) 616(4.02) 396(4.03) 334(4.39)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H(_2)SO(_4)</td>
<td>888(3.92) 828(3.98) 733(3.19) 499(3.37) 307(4.05) 242(4.60)</td>
</tr>
<tr>
<td>(7)</td>
<td>Zn</td>
<td>Pyridine</td>
<td>684(4.24) 618(3.71) 358(4.07) 310(3.69)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H(_2)SO(_4)</td>
<td>828(3.86) 733(2.26) 523(2.73) 311(3.57) 219(4.26)</td>
</tr>
<tr>
<td>(8)</td>
<td>Cu</td>
<td>Pyridine</td>
<td>682(4.13) 618(3.83) 346(3.98) 305(3.79)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H(_2)SO(_4)</td>
<td>814(4.06) 738(2.91) 515(1.52) 307(3.56) 240(4.21)</td>
</tr>
<tr>
<td>(9)</td>
<td>Co</td>
<td>Pyridine</td>
<td>676(4.22) 615(3.89) 333(3.45) 314(4.36)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H(_2)SO(_4)</td>
<td>812(4.13) 723(3.71) 503(2.75) 301(4.51) 242(4.60)</td>
</tr>
<tr>
<td>(10)</td>
<td>Ni</td>
<td>Pyridine</td>
<td>676(4.26) 624(4.12) 330(4.26) 314(4.37)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H(_2)SO(_4)</td>
<td>812(4.21) 722(3.35) 503(2.66) 414(3.23) 308(4.17) 240(4.12)</td>
</tr>
</tbody>
</table>

*a* Intensity ratio of absorption B bands at \( \lambda = 219–334 \) nm and Q bands at \( \lambda = 676–888 \) nm (\( C = 1.0 \times 10^{-4} \) g/L in H\(_2\)SO\(_4\) and 1.0 \times 10^{-4} \) g/L in pyridine).
analysis was satisfactory. In the IR spectra for 6a, the disappearance of the peak at 2225 cm\(^{-1}\) due to the cyano groups of 6 and the appearance of new peaks at \(~1774–1720\) cm\(^{-1}\) due to imido groups supports the conversion of the cyano groups into imido groups.

The transition metal complexes (7–10) were prepared from the bisphthalonitrile compound 5 and the corresponding metal salt in the appropriate solvent (Scheme 1). The IR spectra of the metal complex polymers (7–10) are very similar, except for the metal-free phthalocyanine polymer 6. The metal-free phthalocyanine polymer showed an N–H stretching band at 3294 and 1035 cm\(^{-1}\) due to the inner core [25]. These bands disappear in the spectra of the metal complex polymers. These bands are especially beneficial for characterization of metal-free phthalocyanine polymers, as there is little frequency dependence on the ring substitution and they are not overlapped by strong bisphthalonitrile monomer absorptions [14–16]. The end groups of the metal-free phthalocyanine polymer were cyano groups (2225 cm\(^{-1}\)), while the end groups of the metal complex polymers were imido groups (\(~1772–1714\) cm\(^{-1}\)). The existence of imido groups in the case of the metal complex polymers was attributed to the presence of moisture during the work-up and the hydrated metal salts. There was little shift to longer wavelength numbers in most of the IR bands of the metal complexes with respect to the metal-free analogues [14–16,26]. The spectra of the complexes are quite complex and reveal many metal-independent ligand absorptions, and metal-N vibrations were expected to appear at 400–100 cm\(^{-1}\), but they were not detected using KBr pellets [27]. The elemental analyses of the metal free (6, 6a) and metal complex polymers (7–10) were satisfactory.

![Figure 1](image-url)
It is very difficult to determine the molecular weight of polymeric phthalocyanines because of their poor solubility in common organic solvents. One possible procedure to determine the degree of polymerization is IR spectroscopy, by comparison of the intensity of the end cyano groups to other ring vibrations. This method has been applied to a few cases [28,29]. We determined the degree of polymerization after converting the cyano end groups of the metal-free phthalocyanine polymer into imido end groups, due to the relatively good intensity of C=O imide groups to nitrile groups. After this, the ratios of the absorption intensities of (Ar–O–C) (etheric groups) of the polymers (~1230 cm\(^{-1}\)) to asy. C=O groups of the imides (~1714 cm\(^{-1}\)) were calculated [compound/ log\(10\)\(\sqrt{I_{1230}/I_{1714}}\): 6a:0.52, 7:1.84, 8:1.23, 9:1.57, 10:1.14]. The polymerization degrees follow the order: 7 > 9 > 8 > 10 > 6a. On the other hand, the IR spectrum of 6 shows a low degree of polymerization due to the high intensity of the nitrile groups.

The metal-free phthalocyanine 6 and the metal complexes (7–10) gave the typical UV–Vis absorption spectra of phthalocyanines (Table 1). As can be seen in Table 1, there is a shoulder at the slightly higher energy side for polymeric metal-free phthalocyanine and the metal complexes. The presence of shoulders in the UV–Vis spectra of the polymers corresponds to aggregated or non-aggregated species in conc. sulfuric acid and pyridine. The metal-free phthalocyanine polymer (6) decomposes slowly by hydrolysis in conc. H\(_2\)SO\(_4\), which is demonstrated by a decrease of the absorption coefficient at longer wavelengths and also the color of the solution turns from green to brown with time. However the metal complex polymers (7–10) were more stable in conc. sulfuric acid than the metal-free polymer and there was no color change in the case of the metal complexes even after a day. When going from organic solvents to concentrated H\(_2\)SO\(_4\), the long-wave absorption band underwent a significant bathochromic shift, which was due to weak protonation of the phthalocyanine ring at the nitrogen atoms. The intensity of these absorptions also decreased. The UV–Vis spectrum of 6 was obtained in pyridine and conc. H\(_2\)SO\(_4\). The electronic absorption spectra of (6–10) in pyridine and H\(_2\)SO\(_4\) at room temperature are shown in Fig. 1. There was a single Q band for 7–10 while there was a split Q-band, as expected, and two strong bands in the visible region for 6 [30]. The split Q-band, which is characteristic for metal-free phthalocyanines, was observed at \(\lambda_{\text{max}}\) 705 and 674 nm, with shoulders at 647 and 617 nm, for (6) indicating the monomeric species; monomeric species with D\(_{2h}\) symmetry show two intense absorptions at around 703 and 640 nm [31]. On the other hand, such split-Q band absorptions are due to a \(\pi\pi^*\) transition of this fully conjugated 18\(\pi\) electron system [32]. In the case of a H\(_2\)SO\(_4\) solution of 6, the primary band in the visible region was broadened and shifted to longer wavelength (182 nm). In all cases the intensities in the UV (Soret band transition) and vis (Q-band transition) spectra were \(k_{\text{UV}}/k_{\text{Vis}} \leq 1\) (Table 1). This result can be attributed to the absence of poly(isoindoline) co-units in all of the polymeric metal complexes (7–10).

UV–Vis titrations were performed with several heavy metal cations (Ni\(^{2+}\), Cu\(^{2+}\), Co\(^{2+}\), Pb\(^{2+}\), Cd\(^{2+}\), Zn\(^{2+}\) and Ag\(^{+}\)) to investigate the metal-binding capabilities of complex 7 with triaza-dioxa long peripheral substituents. Firstly, we clarified whether methanol has any effect or not on the visible spectrum of 7. For this purpose, different amounts of methanol were added to a solution of 7 in pyridine. There was only a little change in the intensities of the Q-bands in the visible absorption spectra of 7 with increasing the amounts of methanol, due to the increasing polarity. Then different concentrations of metal salt (e.g. AgNO\(_3\), NiCl\(_2\), H\(_2\)O, Co(N-O\(_3\))\(_2\), H\(_2\)O, Pb(NO\(_3\))\(_2\), Zn(CH\(_2\)COO\(_2\)), H\(_2\)O, Cd(NO\(_3\))\(_2\), H\(_2\)O and CuCl\(_2\)), H\(_2\)O) solutions in methanol (1.0 \(\times\) \(10^{-4}\) M) were added to the solution of the zinc complex 7 in pyridine (1.0 \(\times\) \(10^{-4}\) g/L). When we added Ni\(^{2+}\), Cu\(^{2+}\) and Co\(^{2+}\) solutions to the zinc complex solution, the Q band of 7 broadened and shifted to the low-wave-length region. The addition of Ni\(^{2+}\), Cu\(^{2+}\) and Co\(^{2+}\) solutions caused a dramatic change due to aggregation. The increasing interactions between the polymer chains due to the intermolecular complexation through triaza-dioxa peripheral units with Ni\(^{2+}\), Cu\(^{2+}\), Cd\(^{2+}\) ions forms sandwich type complexes and causes the new absorption bands. The new bands can be attributed to the presence of dimeric and oligomeric phthalocyanine species. Further addition of Ni\(^{2+}\), Cu\(^{2+}\) and Cd\(^{2+}\) solutions caused no observable effect. On the other hand, when solutions of Pb\(^{2+}\), Cd\(^{2+}\), Zn\(^{2+}\) and Ag\(^{+}\) were added, the intensity of the bands at 684 and 618 nm gradually decreased without any shift and no optical change was observed (Fig. 3). The decrease in the intensity
of the bands can be attributed to the dilution effect and the very weak or non-coordination of the N and O atoms to Pb\(^{2+}\), \(\text{Cd}^{2+}\), \(\text{Zn}^{2+}\) and \(\text{Ag}^{+}\) ions, thus leaving the \(\text{Pb(NO}_3\text{)}_2\), \(\text{Cd(NO}_3\text{)}_2\text{4H}_2\text{O}\), \(\text{Zn(CH}_3\text{COO)}_2\text{2H}_2\text{O}\) and \(\text{AgNO}_3\) units only loosely coordinated via oxygen and nitrogen donors.

The powder samples of the polymeric metal-free phthalocyanine and metal complexes were pressed in the form of pellets of 10 mm diameter and thickness ranging from 1 to 3 mm for AC conductivity measurements. The surfaces of the polymers were covered with silver paste to form electrodes. Then, the capacitance and the dielectric loss factor of each sample were measured between 10 kHz and 1 MHz frequency range at room temperature.

**Table 2**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>M</th>
<th>(T_g)</th>
<th>Initial decomposition temperature in °C</th>
<th>Main decomposition temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2H</td>
<td>42</td>
<td>360</td>
<td>417</td>
</tr>
<tr>
<td>7</td>
<td>Zn</td>
<td>51</td>
<td>336</td>
<td>395</td>
</tr>
<tr>
<td>8</td>
<td>Cu</td>
<td>50</td>
<td>358</td>
<td>378</td>
</tr>
<tr>
<td>9</td>
<td>Co</td>
<td>56</td>
<td>310</td>
<td>371</td>
</tr>
<tr>
<td>10</td>
<td>Ni</td>
<td>45</td>
<td>341</td>
<td>367</td>
</tr>
</tbody>
</table>

**Fig. 3.** Changes in the visible spectra of \(7\) in pyridine (\(C = 1.0 \times 10^{-4}\) g/L) after the addition of \(\text{AgNO}_3\), \(\text{Pb(NO}_3\text{)}_2\), \(\text{Cd(NO}_3\text{)}_2\text{4H}_2\text{O}\) and \(\text{Zn(CH}_3\text{COO)}_2\text{2H}_2\text{O}\) and \(\text{AgNO}_3\) solutions in methanol (\(C = 1.0 \times 10^{-4}\) M).

**Fig. 4.** The frequency versus AC conductivity of polymers (6-10) at room temperature.

**Fig. 5.** DTA/TG thermograms of \(\text{H}_2\text{Pc}\) (6), \(\text{ZnPc}\) (7) and \(\text{CoPc}\) (9).
by using a LCR meter (Agilent 4284A). From the measured values of the dielectric permittivity and the dielectric loss factor, the AC conductivity was calculated. The conductivity values correspond to those of semi-conductive materials encountered in most of the substituted phthalocyanine derivatives [33]. The dielectric permittivity of the samples was calculated using the relation:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d}$$

where $C$ is the capacitance of the sample, $\varepsilon_0$ is the permittivity of air, $A$ is the surface area of the sample, $d$ is the thickness of the sample and $\varepsilon_r$ is the dielectric permittivity of the sample. The frequency versus AC conductivity graph was plotted at room temperature and is depicted in Fig. 4. From the figure, it can be seen that the value of the AC conductivity does not show a clear variation at lower frequencies at room temperature. That is, there is no appreciable change in AC conductivity of the polymers at low frequencies (<10$^5$ Hz), above 10$^5$ Hz, there is a rapid increase with frequency.

We have presented the synthesis and characterization of the new bisphthalonitrile 5 and polymeric metal-free (6) phthalocyanine and metal complexes (7–10) with diazatrioxa peripheral units. The polynuclear (6–10) complexes were prepared using a bisphthalonitrile monomer and the appropriate precursors. No obvious correlation between the transition metal ion in the phthalocyanine ring and the corresponding main decomposition temperatures could be established. The electrical conductivities of the polymeric materials measured in air at room temperature and were found to be 10$^{-6}$ to 10$^{-5}$ S m$^{-1}$ in air. The polymeric zinc complex 7 had a clear aggregation tendency with the addition of Ni$^{2+}$, Cu$^{2+}$ and Co$^{2+}$ solutions. On the other hand, there was no shift or optical change with the addition of Pb$^{2+}$, Cd$^{2+}$, Zn$^{2+}$ and Ag$^{+}$ solutions.

4. Conclusion

We have presented the synthesis and characterization of the new bisphthalonitrile 5 and polymeric metal-free (6) phthalocyanine and metal complexes (7–10) with diazatrioxa peripheral units. The polynuclear (6–10) complexes were prepared using a bisphthalonitrile monomer and the appropriate precursors. No obvious correlation between the transition metal ion in the phthalocyanine ring and the corresponding main decomposition temperatures could be established. The electrical conductivities of the polymeric materials measured in air at room temperature and were found to be 10$^{-6}$ to 10$^{-5}$ S m$^{-1}$ in air. The polymeric zinc complex 7 had a clear aggregation tendency with the addition of Ni$^{2+}$, Cu$^{2+}$ and Co$^{2+}$ solutions. On the other hand, there was no shift or optical change with the addition of Pb$^{2+}$, Cd$^{2+}$, Zn$^{2+}$ and Ag$^{+}$ solutions.

Acknowledgements

This study was supported by the Scientific and Technical Research Council of Turkey (TUBITAK), Project No. TBAG-2453(104T065) (Ankara, Turkey).

References


