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Novel phthalocyanine polymers with very flexible pentathiatetraethylene units

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Abstract

A series of polymeric metal-free and metallophthalocyanine (M = 2H, Ni, Co, Fe, Pb, Cu and Zn) polymers were prepared by polymeric tetramerization reaction of bisphthalonitrile monomer with proper materials. The Co–phthalocyanine polymer was prepared by two different methods. The metal-free (**3**) and the Co-containing phthalocyanine polymer (**5**) were chemically doped with iodine (I_2) and nitrosyl tetrafluoroborate ($NOBF_4$), respectively. The electrical conductivities of the polymeric phthalocyanines measured as gold sandwiches were found to be 10^{-8}–10^{-4} S cm^{-1} in vacuum and in argon. The electrical conductivities of I_2-doped metal-free phthalocyanine (**3a**) and $NOBF_4$-doped Co–phthalocyanine (**5a**) polymers were found to be approximately 110 and 89 times higher than those of undoped versions, respectively. The extraction ability of **3** was also evaluated in tetrahydrofuran using several transition metal picrates such as Ag^+, Hg^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+}. The extraction affinity of **3** for Ag^+ was found to be highest in the heterogeneous phase extraction experiments. The aggregation and disaggregation properties of **3** were investigated with silver(I), mercury(II) and methanol as solvent. All the novel compounds were characterized by using elemental analysis, UV–vis, FT-IR, NMR and MS spectral data and DTA/TG.

Keywords: Bisphthalonitrile; Electrical conductivity; Polymeric phthalocyanines

1. Introduction

Phthalocyanines are attractive materials because of their rigidity, high stability and strong, well-defined coupling of the electronic π-systems. For a long time phthalocyanines have been used mostly as industrial dyes, but they reveal also a wide range of useful structural, electrical and optical characteristics which make phthalocyanines and their derivatives promising compounds for various applications such as catalysis, photodynamic therapy, for using in various sensors, solar cells. 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 1950s, polymeric phthalocyanine remains an enigmatic material and many of its intrinsic properties are known rather insufficiently [1,2]. Polymeric phthalocyanines were mainly prepared *via* cyclotetramerization reactions of bifunctional monomers such as tetracarbonitriles [3–6], various oxy-, arylenedioxy- and alkylenedioxy-bridged diphthalonitriles [7–11], and other nitriles [12,13] or tetracarboxylic acid derivatives [14–17] in the presence of metal salts or metals. Recently, we have reported some papers about phthalocyanines containing spherical or cylindrical macrotricyclic, macrobicyclic, diloop macrocyclic and *p*-xylylenebis-(oxathia-propan) bridged polymeric phthalocyanines [18]. A very flexible 1,3,6,9,11-pentathiaundecane bridged bisphthalonitrile monomer compound can be more advantageous than a rigid tetranitrile monomer in the polycyclotetramerization reaction for the synthesis of polymeric phthalocyanines. Besides, the presence of such flexible units increases the electrical conductivity of polymeric phthalocyanines due to a cofacially stacked arrangement of phthalocyanine units.

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We report here, the synthesis and characterization of metal-free and metallophthalocyanine polymers which contain very flexible 1,3,6,9,11-pentathiaundecane moieties. We examined the electrical conductivities of the polymers as Au/MPc/Au sandwiches in vacuum and in argon atmosphere. The viscosity properties of all the polymers and heavy metal extraction ability and aggregation or disaggregation properties of the polymer (**3**) were also investigated. Heavy metals in wastewater have long been a concern due to environmental and health problems. So, it can be very useful to prepare such highly flexible phthalocyanine polymers containing sulphur atoms for removing heavy metals from wastewater.

2. Experimental section

2.1. Materials

Phosphorus pentoxide (P_2O_5), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), ethyl alcohol, *n*-pentanol, dimethyl sulfoxide (DMSO) and dimethylformamide (DMF), tetrahydrofuran (THF), chloroform, dichloromethane, methanol, acetone, methanesulfonyl chloride, 1,2-ethanedithiol, petroleum ether, quinoline, sulphuric acid, hydrochloric acid, sodium hydroxide, pyridine were received from Merck and used as supplied. Potassium carbonate (K_2CO_3) was received from Merck and used after drying in oven at 250 °C for 36 h. 3-Thiapentan-1,5-diol was received from Fluka and used as supplied. All organic solvents were dried and purified by usual methods. 4-Nitrophthalonitrile was synthesized as described in the literature [19]. 3-Thiapentan-1,5-dimesylate was synthesized according to the literature [20].

2.2. Equipment

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 with $CDCl_3$ and DMSO-d_6 as solvents and tetramethylsilane as the internal standard. ^{13}C NMR spectra were recorded on a Varian Mercury Plus 75 MHz spectrometer with DMSO-d_6 as the solvent and tetramethylsilane as the internal standard. Transmission IR spectra of samples were recorded on a FT-IR 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 a 1 cm pathlength cuvettes at room temperature. 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. 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. Differential thermal analysis (DTA/TG) was performed on a Linseis L81 instrument under nitrogen atmosphere with a heating rate of 10 °C/min in a temperature range of 50–700 °C. Intrinsic viscosities of freshly prepared dilute solutions of phthalocyanine polymers were measured in conc. H_2SO_4 at 25 °C by use of an Ubbelohde viscometer.

2.3. Preparation of 3,6,9-trithiaundecane-1,11-dithiol (*1*)

A mixture of 1,2-ethanedithiol (9.45 g, 100 mmol), powdered NaOH (4.2 g, 100 mmol) and dry THF (150 mL) was charged into a 500-mL three-necked flask and stirred at room temperature under nitrogen inert atmosphere and degassed several times. The reaction mixture was refluxed under nitrogen atmosphere for 45 min. A THF solution (25 mL) of crude 3-thiapentan-1,5-dimesylate (5.56 g, 20 mmol) was added dropwise to the reaction mixture for 3 h. The reaction mixture was refluxed for 20 h under nitrogen atmosphere. The reaction mixture was cooled to about 0 °C and then poured into ice-cooled hydrochloric acid (8 vol.%, v/v) until pH of the solution was about 2. The crude product was extracted with dichloromethane (4 × 50 mL). The organic extract was dried over $MgSO_4$ and filtered. The filtrate was concentrated *in vacuo* to yield pale yellow solid product. The pale yellow product was filtered and recrystallized with the minimum volume of dichloromethane. The final product was dried under vacuum over P_2O_5 at room temperature. Yield was 3.29 g (60%), m.p. 63–65 °C. The final pale yellow solid (**1**) was soluble in common organic solvents such as chloroform, dichloromethane, DMF, pyridine, 1,2-dichloroethane and DMSO.

^{1}H NMR ($CDCl_3$): $\delta = 2.85-2.72$ (m, 16H, $S-CH_2$), 1.64–1.61 (t, 2H, SH).

^{13}C NMR ($CDCl_3$): $\delta = 35.96$ ($S-\mathit{C}H_2-CH_2-SH$), 32.79 ($S-\mathit{C}H_2-CH_2-S$), 32.54 ($S-CH_2-\mathit{C}H_2-S$), 24.72 ($\mathit{C}H_2-SH$).

FT-IR (KBr): 2980–2840 ($-CH_2-$), 2550 (S–H), 1435, 1265, 1218, 740, 680 ($-CH_2-S-$) and 640 cm^{-1}.

Elemental analyses $C_8H_{18}S_5$ (274.55) calcd: C 35.00, H 6.61, S 58.39; found: C 35.24, H 6.35, S 58.52.

MS (electron impact) (EI), *m/z*: 276 $[M+1]^+$.

2.4. Preparation of 1,11-bis(3,4-dicyanophenylthio)-3,6,9-trithiaundecane (*2*)

A mixture of 4-nitrophthalonitrile (3.46 g, 20 mmol) and dry DMF (10 mL) was charged into a 200-mL three-necked flask and stirred at room temperature under nitrogen inert atmosphere. Compound **1** of 2.74 g (10 mmol) was added to the solution and the temperature was increased up to 50 °C. Powdered K_2CO_3 of 4.15 g (30 mmol) was added to the system in eight equal portions at 2 h intervals with efficient stirring and the reaction system was stirred at the same temperature (50 °C) for 5 days. Aliquots were taken periodically to check for completeness of the reactions and observed by thin layer chromatography (TLC) [7:2:1 chloroform:petroleum ether:methanol]. The reaction mixture was cooled and poured into ice–HCl (5 vol.%, v/v) solution and then mixed for a day. Precipitate was filtered and washed with distilled water until the washings were neutral. The crude product was washed with diethyl ether and dried under vacuum over P_2O_5. The yield was recrystallized from a mixture of methanol:chloroform (3:1; v/v) and dried under vacuum over P_2O_5 again. Yield was 4.6 g (86%), m.p. 196 °C. The final light green solid (**2**) was soluble in chloroform, DMF, DMSO, pyridine, THF and dichloromethane.

^{1}H NMR ($CDCl_3$): $\delta = 8.09-8.06$ (d, 2H, ArH), 7.95–7.92 (d, 2H, ArH), 7.79–7.76 (dd, 2H, ArH), 3.16–3.05 (t, 4H, ArS–C*H*$_2$), 2.86–2.78 (m, 4H, S–C*H*$_2$–CH_2S–Ar), 2.58–2.53 (m, 8H, S–C*H*$_2$–C*H*$_2$S–).

^{13}C NMR ($CDCl_3$): $\delta = 146.52$ (C_4), 133.97 (C_6), 131.08 (C_5), 130.96 (C_3), 116.16 (C_2), 115.84 (C_7–C_8), 110.88 (C_1), 32.35 (C_{11}–C_{12}), 32.07 (C_9), 30.89 (C_{10}).

FT-IR (KBr): 3090 (aromatic =CH), 2930–2780 (CH_2), 2240 (C≡N), 1580 (aromatic –C=C–), 1550, 1470, 1420, 1194, 1070, 830, 720 (Ar–S–C), 680 (–CH_2–S–CH_2–) and 520 cm^{-1}.

Elemental analyses $C_{24}H_{22}N_4S_5$ (526.79) calcd: C 54.72, H 4.21, N 10.64, S 30.43; found: C 54.59, H 4.48, N 10.86, S 30.65.

MS (electron impact) (EI), *m/z* (%): 606.13 (11.25) $[M+2K+1]^+$, 527.36 (12.80) $[M]^+$, 366.24 (8.25) $[M-(C_8H_3SN_2+2)]^+$, 286.16 (14.41) $[M-(C_8H_5SN_2+2K+2)]^+$, 207.06 (11.88) $[M-(C_{12}H_{11}S_3N_2+K+2)]^+$, 195.01 (25.38) $[M-(C_{13}H_{13}S_3N_2+K)]^+$, 158.96 (39.38) $[M-(C_{16}H_{19}S_4N_2)]^+$ 157.95 (79.35) $[M-(C_{16}H_{19}S_4N_2+1)]^+$, 129.94 (100) $[M-(C_{16}H_{19}S_5N_2+2)]^+$, 127.93 (66.25) $[M-(C_{16}H_{19}S_5N_2+1)]^+$.

2.5. Preparation of metal-free polymeric phthalocyanine (3)

A mixture of **2** (1.052 g, 2 mmol), *n*-pentanol (5 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.310 g, 2 mmol) was placed in a standard Schlenk tube under nitrogen atmosphere and degassed several times. The temperature was gradually increased up to 90 °C and degassed again with nitrogen. Then the reaction mixture was stirred at 145 °C for 12 h. After the reaction mixture was cooled and decanted, the remaining part was stirred with 10 mL of methanol:petroleum ether mixture (1:1; v/v). The product (**3**) was filtered off, washed with DMF, methanol, acetone and diethyl ether and dried in air. Yield was 70% (1.17 g). The final dark green solid (**3**) was soluble in H_2SO_4, hot pyridine and poorly soluble in chloroform, dichloromethane and THF.

FT-IR (KBr): 3280 (N–H), 3040 (aromatic =CH), 2926–2854 (CH_2), 2224 (C≡N), 1640 (–C=N–), 1590 (aromatic –C=C–), 1506, 1488, 1469, 1320, 1288, 1242, 1094, 999, 940–833, 702 (Ar–S–C), 685 (–CH_2–S–CH_2–) and 527 cm^{-1}.

Elemental analyses (for CN end groups) $(C_{96}H_{90}N_{16}S_{20})_n$ $(2109.17)_n$ calcd: C 54.67, H 4.30, N 10.63, S 30.40; found: C 54.78, H 4.21, N 10.44, S 30.72.

2.6. Preparation of Ni-containing polymer (4)

A mixture of bisphthalonitrile compound (**2**) (1.052 g, 2 mmol), dry quinoline (2 mL) and $NiCl_2\cdot 6H_2O$ (0.243 g, 1.0 mmol) was charged into a standard Schlenk tube and degassed three times with nitrogen. The temperature was increased up to 210 °C and treated for 12 h under reflux and nitrogen inert atmosphere. The system was cooled to room temperature and 20 mL of methanol:water (1:1; v/v) mixture was added to the system and stirred at room temperature for 45 min. The product was washed with DMF, methanol, distilled water, petroleum ether and filtered off. The final green product (**4**) was dried under vacuum over P_2O_5 at 50 °C. Yield was 72% (1.46 g). The product (**4**) was soluble in H_2SO_4 and poorly soluble in pyridine.

FT-IR (KBr): 3404 (imide N–H), 3042 (aromatic =CH), 2944–2828 (CH_2), 1768 (sym. C=O), 1706 (asym. C=O), 1598 (aromatic –C=C–), 1580, 1487, 1422, 1318, 1250, 1160, 970, 810 and 705–680 cm^{-1}.

Elemental analyses (for imide end groups) $(C_{96}H_{92}N_{12}S_{20}O_8Ni)_n$ $(2241.87)_n$ calcd: C 51.43, H 4.14, N 7.50, S 28.60, Ni 2.62; found: C 51.36, H 4.33, N 7.69, S 29.01, Ni 2.49.

2.7. Preparation of Co-containing polymer (route 1) (5)

A mixture of bisphthalonitrile compound (**2**) (1.052 g, 2 mmol), dry quinoline (2 mL) and $CoCl_2\cdot 6H_2O$ (0.240 g, 1.0 mmol) was kept in a flask and degassed three times with nitrogen. The reaction mixture was treated at 210–220 °C for 12 h under reflux and nitrogen inert atmosphere. After 12 h of stirring, the reaction mixture was cooled and then 25 mL of ethyl alcohol was added. The reaction was filtered after 30 min of stirring. The solid part was washed with DMF, hot ethanol, acetone and filtered off. The final product (**5**) was dried under vacuum over P_2O_5 at 100 °C. Yield was 64% (1.29 g). The final green product (**5**) was soluble in H_2SO_4 and poorly soluble in pyridine.

FT-IR (KBr): 3415 (imide N–H), 3035 (aromatic =CH), 2918–2736 (CH_2), 1765 (sym. C=O), 1720 (asym. C=O), 1596 (Aromatic –C=C–), 1584, 1482, 1420, 1316, 1240, 1163, 972, 800 and 730–669 cm^{-1}.

Elemental analyses (for imide end groups) $(C_{96}H_{92}N_{12}S_{20}O_8Co)_n$ $(2242.09)_n$ calcd: C 51.43, H 4.14, N 7.50, S 28.60, Co 2.63; found: C 51.59, H 4.42, N 7.36, S 28.92, Co 2.74.

2.8. Synthesis of Co-containing polymer (route 2) (5)

A mixture of bisphthalonitrile compound (**2**) (1.052 g, 2 mmol), ethylene glycol (2.5 mL), ammonium molybdate (40 mg) and $CoCl_2\cdot 6H_2O$ (0.240 g, 1 mmol) was kept in a flask and degassed several times with nitrogen. The reaction was treated at 200–210 °C for 10 h under reflux and nitrogen inert atmosphere. The reaction mixture was cooled and then 50 mL of ethyl alcohol was added. The reaction was filtered after 1 h of stirring. The solid part was washed with hot methanol, hot ethanol, DMF, distilled water and acetone. The final product (**5**) was dried under vacuum over P_2O_5 at 100 °C. Yield was 78% (1.57 g).

The spectral analyses of **5** were the same as that of Co-containing polymer which was synthesized by route 1.

2.9. Preparation of Fe-containing polymer (6)

Bisphthalonitrile compound (**2**) (1.052 g, 2 mmol) and ethylene glycol (10 mL) were kept in a flask. The temperature was increased up to 160 °C and refluxed under nitrogen atmosphere. $Fe(CO)_5$ of 0.137 mL (1.0 mmol, 0.196 g) was slowly added with a syringe and left stirring at 160 °C. After 12 h of stirring, the reaction mixture was cooled to room temperature and precipitated with 100 mL of ethyl alcohol. The product was filtered and washed with 100 mL (10 vol.%, v/v) of HCl to remove excess of iron. The reaction mixture was filtered again and washed with distilled water until the washings were neutral. The final green product (**6**) was washed with ethyl alcohol and acetone and dried under vacuum over P_2O_5 at 50 °C. Yield was 84% (1.05 g).

FT-IR (KBr): 3420 (imide N–H), 3052 (aromatic =CH), 2965–2820 (CH_2), 1756 (sym. C=O), 1706 (asym. C=O), 1598 (aromatic –C=C–), 1582, 1485, 1422, 1320, 1238, 1161, 970, 802 and 731–673 cm^{-1}.

Elemental analyses (for imide end groups) $(C_{96}H_{92}N_{12}S_{20}O_8Fe)_n$ $(2242.09)_n$ calcd: C 51.50, H 4.14, N 7.51, S 28.64, Fe 2.49; found: C 51.87, H 4.46, N 7.29, S 29.05, Fe 2.70.

2.10. Preparation of Pb-containing polymer (7)

A mixture of bisphthalonitrile compound (**2**) (1.052 g, 2 mmol), yellow lead(II) oxide (PbO) (0.224 g, 1.0 mmol) and ethylene glycol (10 mL) was charged into a flask and degassed three times under nitrogen atmosphere. The reaction was treated at 200 °C for 12 h under reflux and nitrogen inert atmosphere. After cooling, 5 mL of HCl (10 vol.%, v/v) was added to the system and stirred for 45 min. The crude product was filtered and washed with ethanol and HCl (5 vol.%, v/v) to remove excess of PbO. The product was washed with distilled water until the washings were neutral. The product was washed with acetone and put into a desiccator. The final product (**7**) was dried under vacuum over P_2O_5 at 50 °C. Yield was 61% (1.19 g).

FT-IR (KBr): 3390 (imide N–H), 3045 (aromatic =CH), 2935–2860 (CH_2), 1760 (sym. C=O), 1717 (asym. C=O), 1596 (aromatic –C=C–), 1580, 1486, 1420, 1322, 1241, 1157, 967, 798 and 730–678 cm^{-1}.

Elemental analyses (for imide end groups) $(C_{96}H_{92}N_{12}S_{20}O_8Pb)_n$ $(2390.35)_n$ calcd: C 48.24, H 3.88, N 7.03, S 26.83, Pb 8.67; found: C 48.57, H 3.65, N 6.89, S 27.26, Pb 9.08.

2.11. Preparation of Cu-containing polymer (8)

A mixture of bisphthalonitrile compound (**2**) (1.052 g, 2 mmol), $Cu(CH_3COO)_2 \cdot H_2O$ (0.200 g, 1.0 mmol) and amyl alcohol (5 mL) was put into a flask. The temperature was increased up to 190 °C and degassed three times under nitrogen atmosphere. Then, 0.15 mL (0.155 g, 1.0 mmol) of DBU was added drop by drop with a syringe into the system. The reaction was treated at 190 °C for 12 h under reflux and nitrogen atmosphere. The reaction mixture was cooled, 5 mL of *n*-pentanol 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 P_2O_5 at 50 °C. Yield was 84% (1.57 g).

FT-IR (KBr): 3380 (imide N–H), 3068 (aromatic =CH), 2940–2870 (CH_2), 1758 (sym. C=O), 1715 (asym. C=O), 1598 (aromatic –C=C–), 1582, 1490, 1415, 1321, 1237, 1154, 960, 801 and 731–665 cm^{-1}.

Elemental analyses (for imide end groups) $(C_{96}H_{92}N_{12}S_{20}O_8Cu)_n$ $(2246.71)_n$ calcd: C 51.32, H 4.13, N 7.48, S 28.54, Cu 2.83; found: C 48.57, H 3.65, N 6.89, S 27.26, Cu 9.08.

2.12. Preparation of Zn-containing polymer (9)

A mixture of bisphthalonitrile compound (**2**) (1.052 g, 2 mmol), zinc acetate dihydrate $[Zn(CH_3COO)_2 \cdot 2H_2O]$ (0.223 g, 1.0 mmol) and amyl alcohol (10 mL) was put into a flask and the temperature was increased up to 160 °C. DBU of 0.153 mL (0.155 g, 1.0 mmol) was added dropwise with a syringe to the system at the same temperature. The reaction was treated at 160 °C for 12 h under reflux and nitrogen atmosphere. After cooling, 20 mL of methanol–water mixture (1:1, v/v) was added to the system and stirred for 1 h. The crude product was filtered and washed with methanol, DMF, distilled water, petroleum ether and acetone. The final green product (**9**) was dried under vacuum over P_2O_5 at 50 °C. Yield was 76% (1.49 g).

FT-IR (KBr): 3395 (imide N–H), 3055 (aromatic =CH), 2980–2820 (CH_2), 1772 (sym. C=O), 1714 (asym. C=O), 1640 (–C=N–), 1600 (aromatic –C=C–), 1578, 1489, 1421, 1326, 1241, 1150, 964, 803 and 730–660 cm^{-1}.

Elemental analyses (for imide end groups) $(C_{96}H_{92}N_{12}S_{20}O_8Zn)_n$ $(2248.53)_n$ calcd: C 51.28, H 4.12, N 7.48, S 28.52, Zn 2.91; found: C 51.57, H 4.49, N 7.11, S 28.83, Zn 3.24.

2.13. Iodine doping. Reaction of the polymeric metal-free phthalocyanine with iodine (3a)

A mixture of the metal-free polymeric phthalocyanine (**3**) (100 mg), iodine (I_2) (100 mg) and *n*-heptane (25 mL) was charged into a flask and stirred at 45 °C for 48 h under nitrogen atmosphere. The colour of the mixture became dark green at the end of the reaction time. After cooling, the mixture was filtered and washed with diethyl ether. The final dark green solid product (**3a**) was dried in a desiccator under vacuum over P_2O_5 for 10 h (10^{-3} Torr). Yield was 90 mg (45%).

FT-IR (KBr): 3288 (N–H), 3065 (aromatic =CH), 2916–2856 (CH_2), 2223 (C≡N), 1645 (–C=N–), 1599 (aromatic –C=C–), 1509, 1482, 1464, 1327, 1283, 1240, 1070, 1010, 941–838, 712, 688 and 521 cm^{-1}.

2.14. Nitrosyl tetrafluoroborate doping. Reaction of the Co-containing polymeric phthalocyanine with nitrosyl (**5a**)

The neutral Co-containing polymeric phthalocyanine (**5**) (100 mg) was reacted with nitrosyl tetrafluoroborate ($NOBF_4$) (100 mg) in 5 mL of dry CH_2Cl_2 at room temperature for 24 h to yield a pale green suspension of the oxidized complex. The mixture was filtered and washed with diethyl ether. The final pale green solid product (**5a**) was dried in a desiccator under vacuum over P_2O_5 for 8 h (10^{-3} Torr). Yield was 0.12 g (62%).

FT-IR (KBr): 3391 (imide N–H), 3063 (aromatic =CH), 2922–2865 (CH_2), 1895 (NO), 1771 (sym. C=O), 1721 (asym. C=O), 1605 (aromatic –C=C–), 1580, 1520, 1423, 1348, 1261, 1084–1038 (BF_4), 932, 833, 742, 685–644 and 556 cm^{-1}.

2.15. The conversion of cyano end groups of the metal-free polymeric phthalocyanine into imido groups (**3b**)

A sample of the metal-free polymeric phthalocyanine (**3**) (150 mg) was dissolved in a minimum volume of H_2SO_4 (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 washing water was neutral. Then the final product (**3b**) was washed with ethanol and diethyl ether and dried under vacuum over P_2O_5 at 100 °C. Yield was 0.13 g (87%).

FT-IR (KBr): 3395 (imide N–H), 3270 (N–H), 3058 (aromatic =CH), 2975–2860 (CH_2), 1769 (sym. C=O), 1717 (asym. C=O), 1633 (–C=N–), 1598 (aromatic –C=C–), 1508, 1491, 1448, 1324, 1238, 1102, 988, 940–840, 704 (Ar–S–C), 691 (–CH_2–S–CH_2–) and 534 cm^{-1}.

Elemental analyses (for imide end groups) $(C_{96}H_{94}S_{20}N_{12}O_8)_n$ $(2185.18)_n$ calcd: C 52.77, H 4.34, N 7.69, S 29.35; found: C 53.12, H 4.63, N 7.34, S 29.64.

2.16. Measurement of the heavy metal-binding properties of the polymeric metal-free phthalocyanine

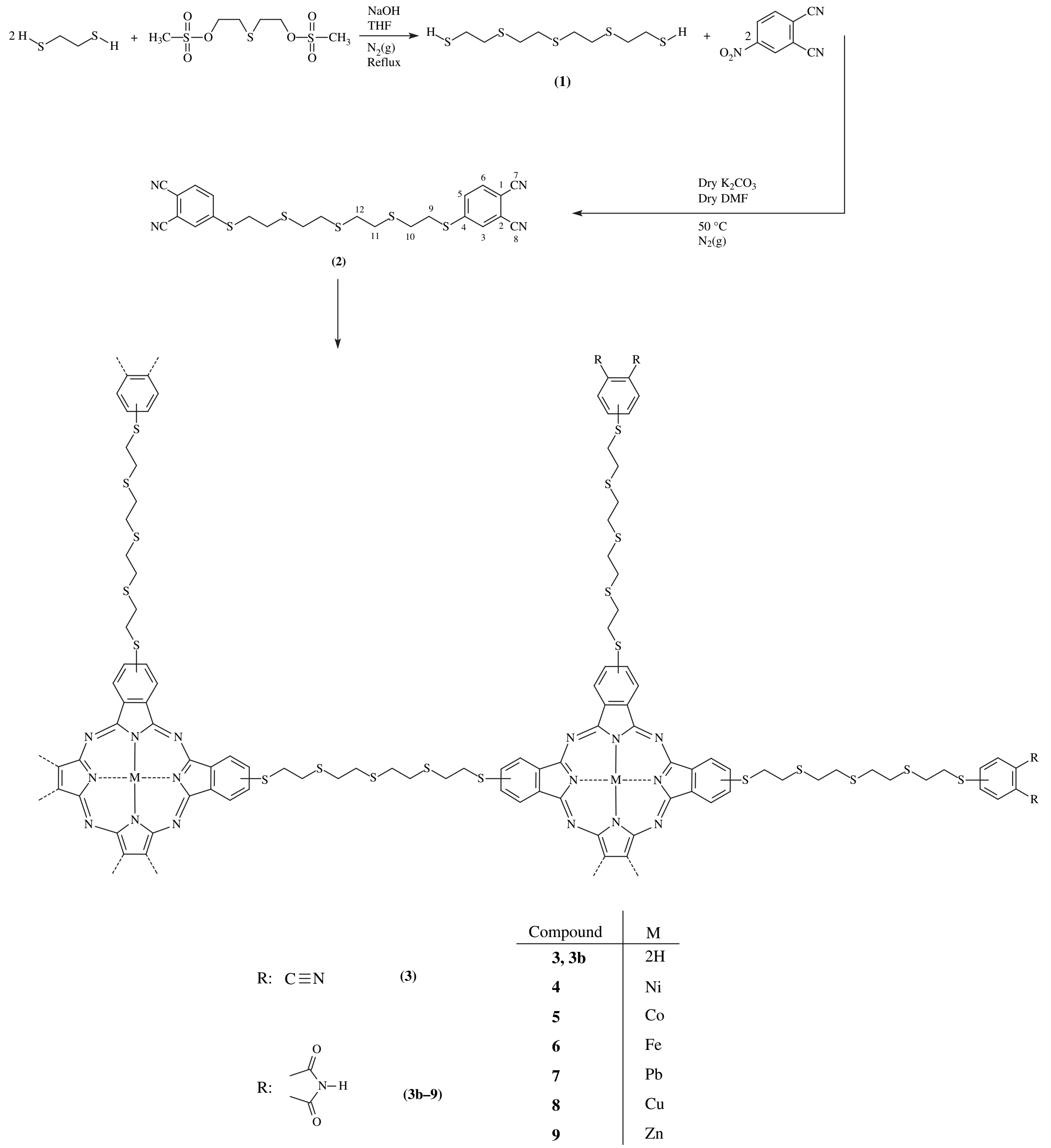
The extraction properties of the metal-free polymeric phthalocyanine (**3**) were investigated under solid–liquid phase and neutral conditions by using heavy metal picrates (Ag^+, Cd^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+} and Zn^{2+}) as substrates and the UV–vis measurement was carried out for measuring the amounts of picrate in THF phase before and after treatment with polymers in suspension. Heavy metal picrates were prepared by the mixture of metal nitrates (4.5×10^{-3} M) and picric acid (1.5×10^{-3} M) in THF. Suspensions were prepared by mixing THF (10 mL) and 25 mg of the polymeric metal-free phthalocyanine (**3**), which was ground in a ballmill for 4 h to assure the same particle size. Then equal volumes of both metal picrate solutions and compound suspensions were added into plastic bottles and kept closed, then shaken vigorously for 24 h using shaker at room temperature. After shaking, the THF phases were separated and the percent of picrate salt extracted (*E*%) was determined by UV–vis spectrophotometry. For each combination of host and metal picrate, the picrate extraction was conducted on three different samples, and the average value of percent picrate extracted, with standard deviation, was calculated. Results and experimental conditions are reported in Table 4. In the absence of host (**3**), blank experiment, no metal ion picrate extraction was detected. The extractability was determined based on the absorbance of picrate ion in the THF suspensions. The extractability was calculated by using below equation:

$$E(\%) = \left[\left(A_{\text{before}} - A_{\text{after}}\right)/A_{\text{before}}\right] \times 100$$

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

3. Results and discussion

Metal-free and metallophthalocyanine polymers were synthesized by polymeric tetramerization reaction of bisphthalonitrile monomer with proper materials (Scheme 1). At the beginning, 3,6,9-trithiaundecane-1,11-dithiol (**1**) was synthesized according to the literature [20] by modifying the regarding procedure. After that, the base-catalyzed nucleophilic aromatic nitro displacement [21] of 4-nitrophthalonitrile with **1** afforded the bisphthalonitrile monomer (**2**). In the last step, metal-free and metallophthalocyanine polymers were synthesized. The yields of all synthesized polymers were between 61 and 87% conversion. It can be due to the purification methods. The metal-free phthalocyanine polymer (**3**) was synthesized by the polycyclotetramerization reaction of **2** with a basic catalyst, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in *n*-pentanol. Ni-containing polymeric phthalocyanine (**4**) was synthesized by the reaction of **2** with $NiCl_2 \cdot 6H_2O$ in quinoline. Co-containing polymeric phthalocyanine (**5**) was synthesized by two different methods. In the first route **5** was synthesized by the reaction of **2** with $CoCl_2 \cdot 6H_2O$ in quinoline and in the second route **5** was synthesized by the reaction of **2** with $CoCl_2 \cdot 6H_2O$ and ammonium molybdate as a catalyst in ethylene glycol. We could not synthesize the Co-containing polymeric phthalocyanine in the second route without using ammonium molybdate. In the second route the yield (78%) was relatively higher than that of the first route (yield 64%) probably due to catalyst. Fe-containing polymeric phthalocyanine (**6**) was prepared by the reaction of **2** with $Fe(CO)_5$ in ethylene glycol. Pb-containing polymeric phthalocyanine (**7**) was prepared by the reaction of **2** with yellow lead(II) oxide (PbO) in ethylene glycol. Cu-containing polymeric phthalocyanine (**8**) was synthesized by the reaction of **2** with $Cu(CH_3COO)_2 \cdot H_2O$ in amyl alcohol. Zn-containing polymeric phthalocyanine (**9**) was prepared by the reaction of **2** with $Zn(CH_3COO)_2 \cdot 2H_2O$ in amyl alcohol. Iodine doped metal-free phthalocyanine polymer (**3a**) was prepared by the reaction of the metal-free polymeric phthalocyanine (**3**) and iodine in *n*-heptane. Nitrosyl tetrafluoroborate doped Co–phthalocyanine polymer (**5a**) was prepared by the reaction of



Compound	M
3, 3b	2H
4	Ni
5	Co
6	Fe
7	Pb
8	Cu
9	Zn

Scheme 1. Synthesis of new network polymeric phthalocyanine polymers with flexible pentathiatetraethylene peripheral units.

Co-containing polymer (**5**) and nitrosyl tetrafluoroborate ($NOBF_4$) in dry dichloromethane.

In order to compare the polymerization degrees of all the polymers, cyano end groups of the metal-free phthalocyanine polymer were converted into imido end groups (**3b**).

The molecular weights of the polymers could not be determined either by conventional methods because of their poor solubility in organic solvents, or by comparison of the IR absorption bands of the end groups with those of the bridging groups [7,22].

The disappearance of $-SO_2-$ (asym. 1360 and sym. 1145 cm^{-1}) and the presence of S–H stretching vibration which occur absorption at 2550 cm^{-1} in IR spectrum of **1** confirm the formation of **1**. Elemental analysis and EI mass spectral data were satisfactory: 276 [M + 1]. ^1H NMR spectrum of **1** showed new signals at $\delta = 2.85-2.72$ (m, 16H, S–CH_2), 1.64–1.61 (t, 2H, SH). The proton-decoupled ^{13}C NMR spectrum of **1** indicates the presence of primary thiol carbon atom at $\delta = 24.72$ ($\mathit{C}H_2$–SH) and other carbon atoms at $\delta = 35.96$ (S–$\mathit{C}H_2$–CH_2–SH), 32.79 (S–$\mathit{C}H_2$–CH_2–S), 32.54 (S–CH_2–$\mathit{C}H_2$–S).

In the IR spectrum of **2**, the disappearance of NO_2 and S–H stretches, along with the appearance of new bands at 2240 and 720 cm^{-1} arising from C≡N and Ar–S–C groups, respectively, are in agreement with the proposed structure. Elemental analysis and EI mass spectral data were satisfactory: 527.36 $[M]^+$.

^1H NMR ($CDCl_3$) spectrum of **2** showed new signals at $\delta = 8.09$–8.06 (d, 2H, ArH), 7.95–7.92 (d, 2H, ArH), 7.79–7.76 (dd, 2H, ArH), 3.16–3.05 (t, 4H, ArS–$C\mathit{H}_2$), 2.86–2.78 (m, 4H, S–$C\mathit{H}_2$–CH_2S–Ar), 2.58–2.53 (m, 8H, S–$C\mathit{H}_2$–$C\mathit{H}_2$S–). The resonances absorbed at $\delta = 146.52$ (C_4), 133.97 (C_6), 131.08 (C_5), 130.96 (C_3), 116.16 (C_2), 115.84 (C_7–C_8), 110.88 (C_1), 32.35 (C_{11}–C_{12}), 32.07 (C_9), 30.89 (C_{10}) in the ^{13}C NMR (DMSO-d_6) spectrum of **2** should be related to the corresponding carbon atoms.

As reported in Fig. 1, IR spectrum of the metal-free phthalocyanine polymer (**3**) is slightly broadened and reduced in intensity. It can be attributed to a difficulty in grinding the sample. The peaks at 3280 and 1093 cm^{-1} are the characteristic metal-free phthalocyanine N–H stretching and pyrrole ring vibration bands. Besides, deuterium exchange with D_2O causes the N–H absorption in the infrared to shift from 3280 to 2490 cm^{-1}, confirming the IR assignment. A weak –C=N– absorption at 1640 cm^{-1} was detected. Also, the 702 (Ar–S–C) and 685 cm^{-1} bands are present in the spectrum. Elemental analysis was satisfactory.

The IR spectra of the metallophthalocyanine polymers (**4**–**9**) were very similar, except from the metal-free phthalocyanine polymer (**3**) which showed an N–H stretching band at 3280 and 1093 cm^{-1} due to the inner core [8]. These bands disappear in 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 are not overlapped by strong bisphthalonitrile monomer absorptions [4].

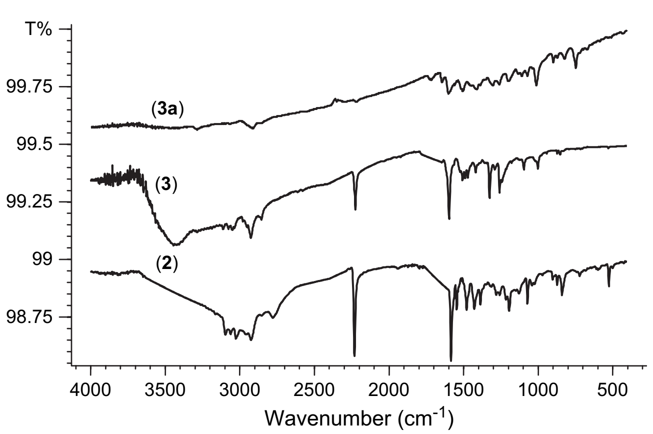


Fig. 1. FT-IR spectra of **2**, **3** and **3a**.

The end groups of the metal-free phthalocyanine polymer were cyano groups (2224 cm^{-1}) while the end groups of the metallophthalocyanine polymers were imido groups (~1770–1705 cm^{-1}). The existence of imido groups in the case of metallophthalocyanine polymers was attributed to the presence of moisture during 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 [4,23]. As expected, the spectra are quite complex and show 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 [24].

Iodine doped metal-free phthalocyanine polymer (**3a**) showed characteristic phthalocyanine absorptions [25,26] in its IR spectrum. As iodine doping increased, the IR peaks broadened were finally obscured due to the superposition of electronic excitation absorption [27,28]. As can be seen in Fig. 1, the IR spectrum of iodine doped polymer was broadened.

In the IR spectra for **3b**, the disappearances of peak at 2224 cm^{-1} due to cyano groups of **3** and the appearance of new peaks at ~1755–1716 cm^{-1} due to imido groups support the conversion of cyano groups into imido groups.

The $NOBF_4$-doped product (**5a**) exhibited the IR vibration of BF_4 at 1084 and 1038 cm^{-1}. Also, IR vibration of NO was detected at 1895 cm^{-1}.

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 only few cases [29]. We determined the degree of molecular weight after converting cyano end groups of the metal-free phthalocyanine polymer into imido end groups due to a relatively good intensity of C=O imide groups to nitrile groups. After this, the ratios of the absorption intensities of –C=C– (aromatic) groups of the polymers (~1595 cm^{-1}) to asym. C=O groups of the imides (~1718 cm^{-1}) were calculated [compound/$\log_{10} I_{1595}/I_{1718}$: (**3b**)/0.35, (**4**)/0.72, (**5**)/5.23, (**6**)/1.01, (**7**)/0.86, (**8**)/0.62, (**9**)/0.98]. The polymerization degrees follow the order: (**5**) > (**6**) > (**9**) > (**7**) > (**8**) > (**4**) > (**3b**). On the other hand, the IR spectrum of **3** shows low degree of molecular weight due to the high intensity of the nitrile groups (Fig. 1).

The UV–vis spectra of the polymers were taken in conc. H_2SO_4 and pyridine (Table 1). There is a shoulder at the slightly higher energy sides for all the products. The metal-free phthalocyanine polymer (**3**) decomposes slowly by hydrolysis in conc. H_2SO_4, which is demonstrated by a decrease of the absorption coefficient at longer wavelengths. The metal-containing polymers (**4**–**9**), however, were stable. When going from organic solvents to conc. H_2SO_4, the long-wave absorption band underwent a significant bathochromic shift, which is due to protonation of the phthalocyanine ring at the *meso* nitrogen atoms. The intensity of these absorptions also decreased. The UV–vis spectrum of the metal-free phthalocyanine polymer was obtained in pyridine and conc. H_2SO_4.

Table 1
Wavelength and absorption coefficients of the UV–vis spectra of polymeric phthalocyanines

Compound	M	Solvent	λ/nm (log ε)	Ratio[a] UV/vis
3	2H	Pyridine	715 (2.72), 687 (2.71), 655 (2.34), 624 (2.14), 420 (2.41), 372 (2.69), 318 (2.73), 306 (2.35), 290 (2.83)	0.96
		H_2SO_4	812 (3.27), 719 (3.23), 674 (2.90), 607 (2.78), 393 (3.01), 344 (3.34), 319 (3.38), 271 (3.47)	1.06
4	Ni	H_2SO_4	856 (3.53), 741 (3.04), 612 (2.72), 456 (3.36), 360 (3.48), 310 (3.68), 268 (3.72)	1.05
5	Co	H_2SO_4	842 (3.64), 720 (3.34), 647 (3.10), 617 (2.95), 430 (3.51), 307 (3.81), 285 (3.89)	1.07
6	Fe	H_2SO_4	791 (3.51), 729 (3.40), 656 (3.26), 612 (2.04), 378 (3.71), 315 (3.91), 265 (3.88)	1.11
7	Pb	H_2SO_4	874 (2.93), 817 (2.75), 726 (3.14), 640 (3.75), 606 (2.13), 473 (3.46), 325 (3.87), 287 (3.94), 263 (4.10)	1.40
8	Cu	H_2SO_4	875 (3.73), 796 (3.56), 645 (3.41), 603 (3.06), 440 (3.67), 314 (3.86), 259 (3.96)	1.18
9	Zn	H_2SO_4	883 (3.84), 788 (3.56), 652 (3.23), 620 (2.97), 495 (3.32), 415 (3.65), 305 (3.94), 264 (3.76)	0.98

[a] Intensity ratio of absorption B bands at $\lambda = 259–290$ nm and Q bands at $\lambda = 715–883$ nm ($C = 1.5 \times 10^{-4}$ g/L in H_2SO_4, 1.0×10^{-3} g/L in pyridine).

The electronic absorption spectrum of the metal-free phthalocyanine (**3**) in pyridine at room temperature is shown in Fig. 2. It displayed the split Q-band as expected and there are two strong bands in the visible region [30]. The split Q-band, characteristic of metal-free phthalocyanines, is observed at λ_{max} 715 and 687 nm with a shoulder at 655 nm, indicating the monomeric species; the monomeric species with D_{2h} symmetry show two intense absorptions at around 700 nm [31]. On the other hand, such split Q-band absorptions in pyridine are due to $\pi \Rightarrow \pi^*$ transition of this fully conjugated 18π electron systems [18a]. The longer wavelength encountered for the intense band of **3** is especially noteworthy. The shift of this band to the near-IR region is a result of S-substitution [32]. In the case of a H_2SO_4 solution of **3**, the primary band in the visible region was broadened and shifted to longer wavelength ($\sim$100 nm). In all cases the intensities in the UV (Soret band transition) and vis (Q band transition) were $I_{UV}/I_{vis} \leq 1$ (Table 1). This result indicates that all of the polymeric phthalocyanines (**3**–**9**) were structurally uniform and the absence of poly(isoindolinine) co-units.

Aggregation and disaggregation of the metal-free polymeric phthalocyanine (**3**), followed by the changes in the visible spectra after the addition of a metal cation, constitute an effective route for characterizing the complexation behavior of the pentathiatetraethylene peripheral substituents. Firstly we clarified whether methanol has any effect or not on the visible spectrum of **3**. For this purpose, different amounts of methanol were added to the solution of metal-free polymeric phthalocyanine in pyridine. As can be seen in Fig. 2 a slight aggregation and decreases in the intensities of Q bands were observed in the visible absorption spectrum of **3** with increasing amounts of methanol due to the increasing polarity. However, the decreasing tendency in the intensities of Q bands was not in the same ratio. The decrease in the intensity of the band at 715 nm was more pronounced than that of the band at 687 nm. This behavior was attributed to the presence of dimeric or oligomeric species [33]. Then the different amounts of $AgNO_3$ and $Hg(NO_3)_2$ solutions in methanol (10^{-3} M) were added to the metal-free polymeric phthalocyanine (**3**) solution in pyridine (10^{-3} g/L). When we added $Hg(NO_3)_2$ solution to the metal-free polymeric phthalocyanine solution, it caused a dramatic change due to aggregation in the visible spectrum of **3** (Fig. 3). As explained above a little part of the aggregation effect comes from the methanol as solvent. While addition of small increments of Hg^{2+} leads to gradual disappearance of monomeric species which show absorption bands at 687 and 715 nm and a new absorption band appears at 706 nm with increasing $Hg(NO_3)_2$ salt concentration (Fig. 3). Dimerization of the Pc units by intermolecular complexation through pentathiatetraethylene peripheral units with Hg^{2+} ions forms sandwich type complexes and causes the new absorption band. The new band can be ascribed to

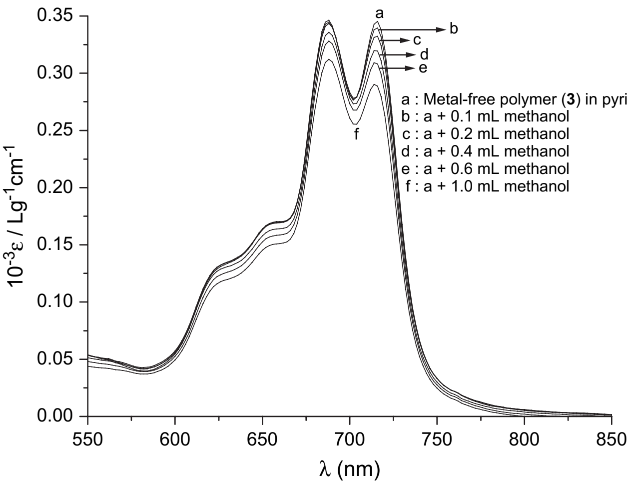


Fig. 2. Changes in the visible spectra of **3** in pyridine (10^{-3} g/L) after the addition of different amounts of methanol.

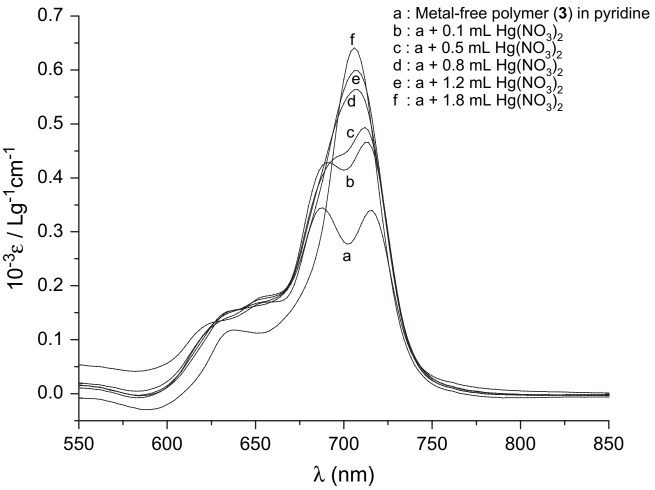


Fig. 3. Changes in the visible spectra of **3** in pyridine (10^{-3} g/L) after the addition of $Hg(NO_3)_2$ solutions in methanol (10^{-3} M).

the presence of dimeric and oligomeric phthalocyanine species. Further addition of $Hg(NO_3)_2$ salt caused no observable effect. On the other hand, when a solution of $AgNO_3$ was added the intensity of the bands at ∼687 and 715 nm increased and the bands became sharp without any shift in spite of aggregation effect of methanol (Fig. 4). The enhancement of the bands can be attributed to the disaggregation (monomerization) of **3** by trapped Ag^+ ions in the pentathiatetraethylene peripheral units and there is no intermolecular complexation between the phthalocyanine units [34]. The trapped bulky Ag^+ ions in the pentathiatetraethylene peripheral units prevent the phthalocyanine macrocycle aggregation by simple steric hindrance.

The intrinsic viscosities of dilute solutions of polymers were measured by means of Ubbelohde No. 2 viscometer. The intrinsic viscosity of the metal-free polymer was higher than that of the metallophthalocyanine polymers (Table 2). The intrinsic viscosities of metallophthalocyanine polymers were very similar. The higher intrinsic viscosity of the metal-free polymeric phthalocyanine can be probably due to easier protonation and higher polymerization degree. Fig. 5 shows the viscosities of polymers as a function of polymer concentration. Fig. 5 indicates that viscosities decreased depending on 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 at the periphery of each phthalocyanine polymer.

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 as Au/MPc/Au sandwiches in vacuum and in argon atmosphere. Table 2 also shows the d.c. electrical conductivities of polymers (**3a**, **5a**, **3**–**9**). These values correspond to semiconductive materials as encountered in number-substituted phthalocyanine derivatives [35]. The conductivity values obtained under an argon atmosphere for most of the phthalocyanine polymers showed an increase of about 10-fold. The enhancement of the conductivity in argon for the phthalocyanine polymers may be due to absorbed oxygen in argon [36]. A first approximation to achieve higher electrical conductivities in phthalocyanines is to reach partially oxidized states. For this purpose, polymeric metal-free phthalocyanine (**3**) and Co-containing polymer (**5**) were doped with I_2 and $NOBF_4$, respectively. The conductivities of doped products (**3a**) and (**5a**) were approximately 110 and 89 times higher than those of the parent compounds, (**3**) and (**5**).

Table 2
Electrical conductivity and intrinsic viscosities of the polymeric phthalocyanines at room temperature

Compound	M	Conductivity ($S\,cm^{-1}$)		Pellet thickness (mm)	Intrinsic viscosity $[\eta]$ (H_2SO_4)
		In argon	In vacuum		
3	2H	8.76×10^{-6}	7.12×10^{-7}	0.65	2.76
3a	**3**$(I_2)_n$	9.65×10^{-4}	3.24×10^{-4}	0.40	–
4	Ni	4.13×10^{-5}	2.63×10^{-6}	0.45	2.50
5	Co	5.48×10^{-6}	9.16×10^{-7}	0.55	2.47
5a	**5**$(NOBF_4)_n$	4.87×10^{-4}	5.72×10^{-5}	0.45	–
6	Fe	4.57×10^{-5}	2.56×10^{-6}	0.40	2.43
7	Pb	3.27×10^{-5}	2.52×10^{-5}	0.45	2.22
8	Cu	7.08×10^{-5}	6.51×10^{-6}	0.50	2.27
9	Zn	2.71×10^{-5}	2.48×10^{-5}	0.55	2.08

Thermal properties of the metal-free and metallophthalocyanine polymers were investigated by DTA/TG. Phthalocyanine polymers are resistant to thermal oxidation [37]. DTA thermograms of the polymers can be seen in Figs. 6 and 7. DTA curves exhibited exothermic changes for all polymeric phthalocyanines (**3**–**9**) in the region investigated [38]; melting point was observed only in the case of **3**, that is there was no melting point in the case of metallophthalocyanine polymers (**4**–**9**). The glass transition of **3** was found at 45 °C. The initial decomposition temperature decreased in the order: (**9**) > (**4**) > (**5**) > (**5a**) > (**7**) > (**6**) > (**8**) > (**3**) > (**3a**) (Table 3). Cu-containing polymer (**8**) was the most rapidly degraded metallophthalocyanine while Zn-, Ni- and Co-containing metallophthalocyanine polymers showed good

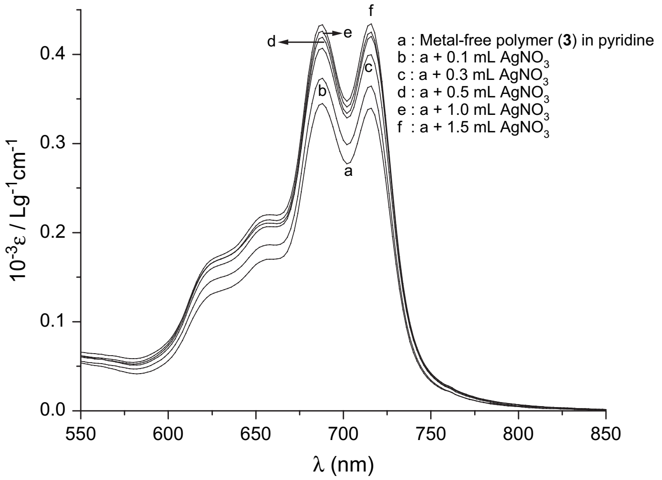


Fig. 4. Changes in the visible spectra of **3** in pyridine (10^{-3} g/L) after the addition of $AgNO_3$ solutions in methanol (10^{-3} M).

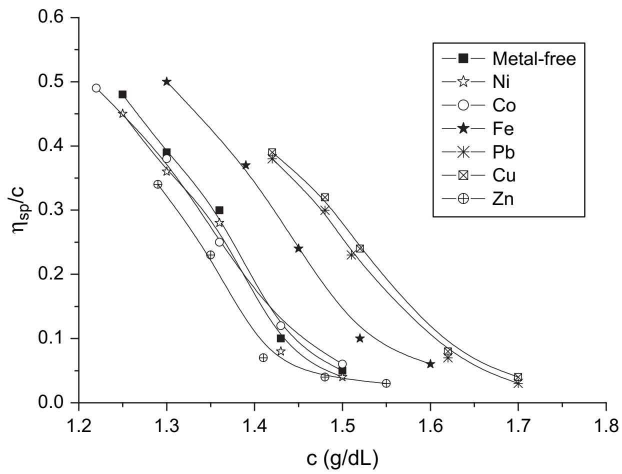


Fig. 5. Viscosity curves of the metal-free and metallophthalocyanine polymers.

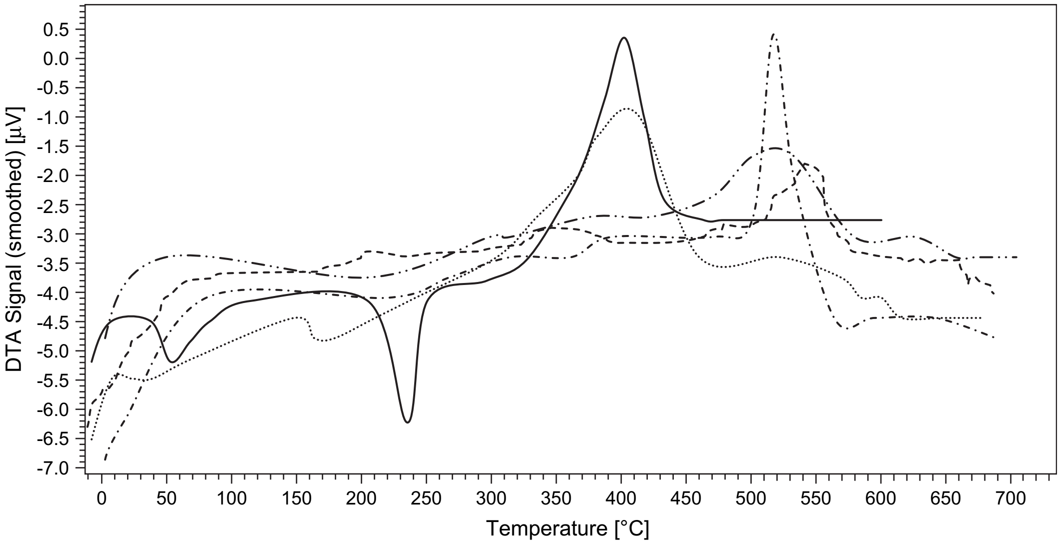


Fig. 6. DTA thermograms of **3** (—), **3a** (……), **4** (----), **5** (-·-·-·) and **5a** (—··—··).

thermal stability under working conditions. These results are in good agreement with the literature [39]. DTA thermogram of **3a** showed an endothermic peak at 156 °C due to the dissociation of iodine. The sharpness of the melting point (233 °C) gives an indication on the purity of **3**. The thermal stabilities of **3a** and **5a** were lower than those of undoped analogues, (**3**) and (**5**). The thermal stability of **3a** indicates that the dopant is rather weakly bonded in the polymer.

The heavy metal-binding ability of polythiamacrocyclic units is a well known property. Due to their insolubility, heterogeneous phase extraction of heavy metal picrates from THF suspensions to the solid metal-free polymer was investigated. As can be seen in Table 4, the highest extraction affinity of **3** was determined as 88.81% for Ag^+. The extraction affinity of **3** for Hg^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} were determined as 56.74, 34.46, 62.54, 49.66 and 40.60%, respectively. Silver and lead ions' adsorption onto chemical oxidative polymers was studied in detail by Li and co-workers [40] and the metal-free polymeric phthalocyanine exhibits lower silver- and lead-ion extractability compared to the reference work. The lower extractabilities can be attributed to (1) the lower polymerization degree of **3** and thus the decrease in the number of the donor atoms, (2) the difficulty in grinding the sample (**3**) to a small particle size and thus the smaller specific surface area and (3) the different polymer structure and concentration. The extraction ability values of **3** are higher than those of previous polymeric phthalocyanine which has *p*-xylene-bis-(oxa-thia-propan) moiety [18d]. The higher extraction ability values are attributed to (1) the higher amount of soft sulphur atoms and (2) the higher flexibility in the present polymer. Higher values for Hg^{2+}, Ag^+ and Cd^{2+} were the expected results. This is because, sulphur containing ligands are especially appropriate for complexation with heavy metal ions such as Hg^{2+}, Ag^+ and Cd^{2+} due to the softness of

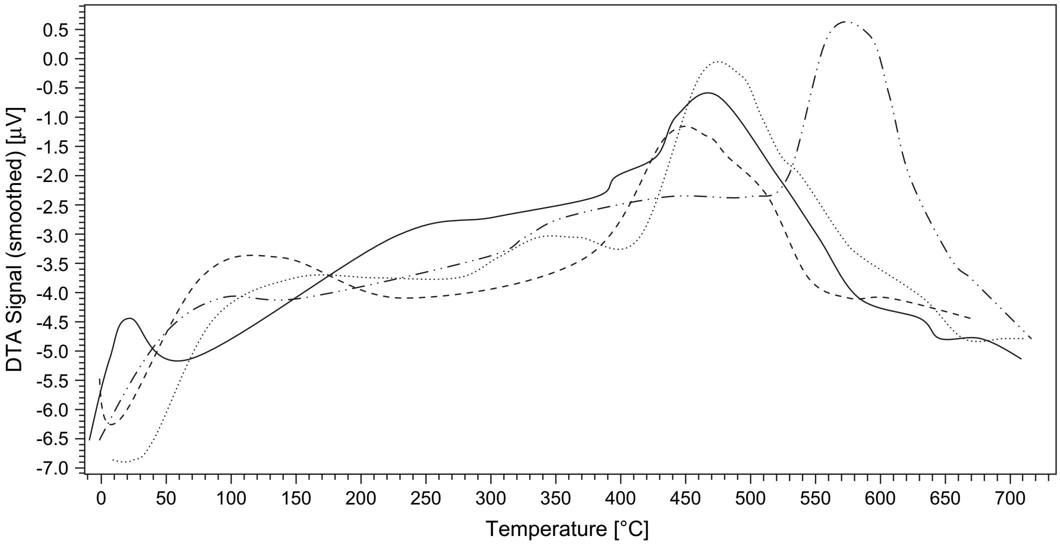


Fig. 7. DTA thermograms of **6** (—), **7** (……), **8** (----) and **9** (—··—··).

Table 3
Thermal properties of the polymeric phthalocyanines

Compound	M	Melting point (°C)	Dissociation of I_2 and $NOBF_4$ (T_{max}, °C)	Initial decomposition temp. (°C)	Main decomposition temp. (°C)
3	2H	233	–	335	400
3a	**3**$(I_2)_n$	–	156	320	410
4	Ni	–	–	526	547
5	Co	–	–	510	542
5a	**5**$(NOBF_4)_n$	–	–	495	529
6	Fe	–	–	430	456
7	Pb	–	–	437	465
8	Cu	–	–	423	449
9	Zn	–	–	546	553

Table 4
Heavy metal picrate extractions for compound (**3**)[a] under solid–liquid two-phase conditions

Metal ion	Extractability of the metal-free polymeric phthalocyanine (**3**)[b] (%)	λ_{max} (nm) of metal picrate
Ag^+	88.81 ± 0.01	354
Hg^{2+}	56.74 ± 0.01	356
Pb^{2+}	34.46 ± 0.01	358
Cd^{2+}	62.54 ± 0.01	360
Cu^{2+}	49.66 ± 0.01	351
Zn^{2+}	40.60 ± 0.01	348

[a] Temperature 25 ± 1 °C; THF phase (10 mL), [picrate] $= 4.5 \times 10^{-3}$ M; host molecule = 25 mg.

[b] Average and standard deviation for three independent measurements.

sulphur [41]. On the other hand, the metal-free phthalocyanine core has to be taken into consideration for the extraction process. There are many articles on the metal extraction properties of metal-free phthalocyanines [42] and the highest extraction affinity was determined for Ag^+. In addition, as can be seen in Figs. 3 and 4, Hg^{2+} forms sandwich type complex with the metal-free phthalocyanine units while Ag^+ is trapped by the metal-free phthalocyanine units. That is, there are more phthalocyanine units which can coordinate with more Ag^+ cations. Consequently, Ag^+ has higher extraction affinity than Hg^{2+} under present conditions.

4. Conclusion

We have presented the synthesis and characterization of new polymeric metal-free and metallophthalocyanine (M = 2H, Ni, Co, Fe, Pb, Cu and Zn) phthalocyanines. Zn-, Ni- and Co-containing polymers showed good thermal stability while Cu-containing polymer was the most rapidly degraded one. The electrical conductivities of the polymeric phthalocyanines were found to be 10^{-8}–10^{-4} S cm^{-1} *in vacuo* and in argon. The electrical conductivities of iodine doped metal-free phthalocyanine (**3a**) and nitrosyl tetrafluoroborate doped Co–phthalocyanine (**5a**) were found to be approximately 110 and 89 times higher than those of undoped analogues, respectively. The extraction ability of **3** was evaluated in THF and the highest extraction affinity was observed for Ag^+. The intrinsic viscosity of the metal-free polymer was higher than those of metallophthalocyanine polymers. The higher intrinsic viscosity is probably due to easier protonation and higher degree of polymerization. The metal-free polymeric phthalocyanine (**3**) had aggregation tendency with the addition of methanol and $Hg(NO_3)_2$ whereas disaggregation tendency with the addition of $AgNO_3$.

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