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Synthesis and properties of 1,4-bis[*N*-(2-tolylsulphonylaminoethyl)]-1,4-diazacyclohexane bridged network polymeric phthalocyanines

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Abstract

1,4-Bis[*N*-(2-tolylsulphonylaminoethyl)]-1,4-diazacyclohexane bridged metal-free and metal phthalocyanine polymers were prepared. The metal-free phthalocyanine polymer was obtained by the reaction of 4,4′-[2,2′-(piperidine-1,4-diyldiethylene)di(tosylimino)]diphthalonitrile with hydroquinone. The chloride derivatives of Cu(I), Ni(II) and Co(II) were employed in order to synthesize the corresponding metal–phthalocyanine polymers. $Zn(CH_3CO_2)_2$ was used for the preparation of the zincphthalocyanine polymer. For the preparation of the Co-containing polymer, ammonium molybdate had to be added as catalyst. The new polymers have been characterized by elemental analysis, IR, NMR, UV–VIS and DTA.

Keywords: 4,4′-[2,2′-(Piperidine-1,4-diyldiethylene)di(tosylimino)]diphthalonitrile; Network polymers; Phthalocyanine

1. Introduction

The chemistry of phthalocyanine (pc) compounds were discovered over 60 years ago [1]. Phthalocyanines comprise a remarkably robust and versatile class of chemical compounds. They are of enormous technological importance for the manufacture of green and blue pigments. Other areas of current interest include applications in colours, catalysis, thermal stability batteries, chemical sensors, electrochromizm, liquid crystals, photodynamic therapy and modified supports for gas–solid chromatography as a result of newly synthesized compounds [1]. The growing use of phthalocyanines as advanced materials during the last decade has encouraged the research on the synthesis of new derivatized materials which differ from one another in the central metal ion and in the peripheral substituents [2]. Low-molecular-weight metal phthalocyanines are generally prepared in high yield by cyclotetramerization of phthalic acid derivatives, such as 1,2-benzene dicarbonitrile or benzene-1,2-dicarboxylic anhydrides, with urea and metal salts. Starting with bifunctional reactants, such as 1,2,4,5-benzenetetracarboxylic dianhydrides or 1,2,4,5-benzenetetracarbonitrile, metal polymeric phthalocyanines can be prepared via polytetracyclomerization [3–5]. In addition to the synthetic advantage in using a linked diphthalonitrile as opposed to a rigid monomer, such as benzenetetracarbonitrile, in the synthesis of polymeric phthalocyanines is the higher flexibility of the linkage resulting in a higher group mobility [3–5].

We have previously synthesized novel phthalocyanines carrying macrocyclic substituents (e.g. aza [6–8], oxathia [9,10], oxadithiadiaza macrocycles [11]) which

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are capable of binding to transition metal cations. While phthalocyanines with N–, O– and S– donor substituents have frequently been described, those with N–O, O–S or N–S donor moieties together have not been extensively described [12–14]. An additional advantage of using an aza macrocycle substituent was the solubility in water obtained by quaternization of the aza function [6,7]. Phthalocyanines substituted with 12-membered tetraazamacrocycles provided donor sites for binding transition metal ions, leading to nonanuclear complexes [6].

In this present paper, we report the preparation and characterization of metal and metal-free phthalocyanine polymers containing 1,4-bis[*N*-(2-tolylsulphonylaminoethyl)]-1,4-diazacyclohexane moiety.

2. Results and discussion

The synthesis of 4,4′-[2,2′-(piperidine-1,4-diyldiethylene)di(tosylimino)]-diphthalonitrile was the most important step in these reaction sequences. For this purpose, treatment of 2-aminoethanol with tosylchloride yielded compound *N*-[2-[(*p*-tolylsulphonyl)oxy]ethyl]-*p*-tolylsulphonamide which was converted to tosylaziridine in the presence of KOH in toluene [15]. In the second step, 1,4-bis[*N*-(2-tolylsulphonylaminoethyl)]-1,4-diazacyclohexane (**1**) was synthesized by treating *N*-(*p*-tolylsulphonyl)aziridine with piperazinehexahydrate in acetonitrile [16]. The general route for the synthesis of the new phthalocyanine polymers is shown in Scheme 1, 4-nitrophthalonitrile has been used to prepare 4-substituted phthalonitrile derivatives through base catalysed nucleophilic displacement [17]. The same route was applied to prepare 4,4′-[2,2′-(piperidine-1,4-diyldiethylene)di(tosylimino)]diphthalonitrile (**2**) from 1,4-bis[*N*-(2-tolylsulphonylaminoethyl)]-1,4-diazacyclohexane and 4-nitrophthalonitrile. The reaction was carried out in dimethylsulphoxide at room temperature and gave moderate yield (40.5%). Single crystals of compound **2** was obtained via slow evaporation in DMF [18]. The metal-free phthalocyanine polymer **3** was synthesized by heating a mixture of the dicyano compound **2** with freshly sublimed hydroquinone in the absence of solvent [19]. The metallo phthalocyanine polymers were prepared from the dicyano derivative and the corresponding metal salt in high-boiling anhydrous solvents (e.g. quinoline or ethylene glycol). The yields were satisfactory, and depended upon the transition metal ion.

All attempts of detosylation of copper and cobalt phthalocyanine polymer complexes in conc. sulphuric acid at 100 °C and 125 °C for 5 h failed owing to the decomposition of the phthalocyanine polymers. The most evident feature of metal-free phthalocyanine polymers and metallophthalocyanine polymers is not soluble in common organic solvents such as chloroform, dichloromethane, ethanol, methanol and benzene but they are rather soluble in dimethylsulphoxide, dimethylformamide and sulphuric acid. The solubilities in dimethylsulphoxide or dimethylformamide are lower than those of phthalocyanine polymers containing O and S, or S, O and N-substituent polymers [10,20–22].

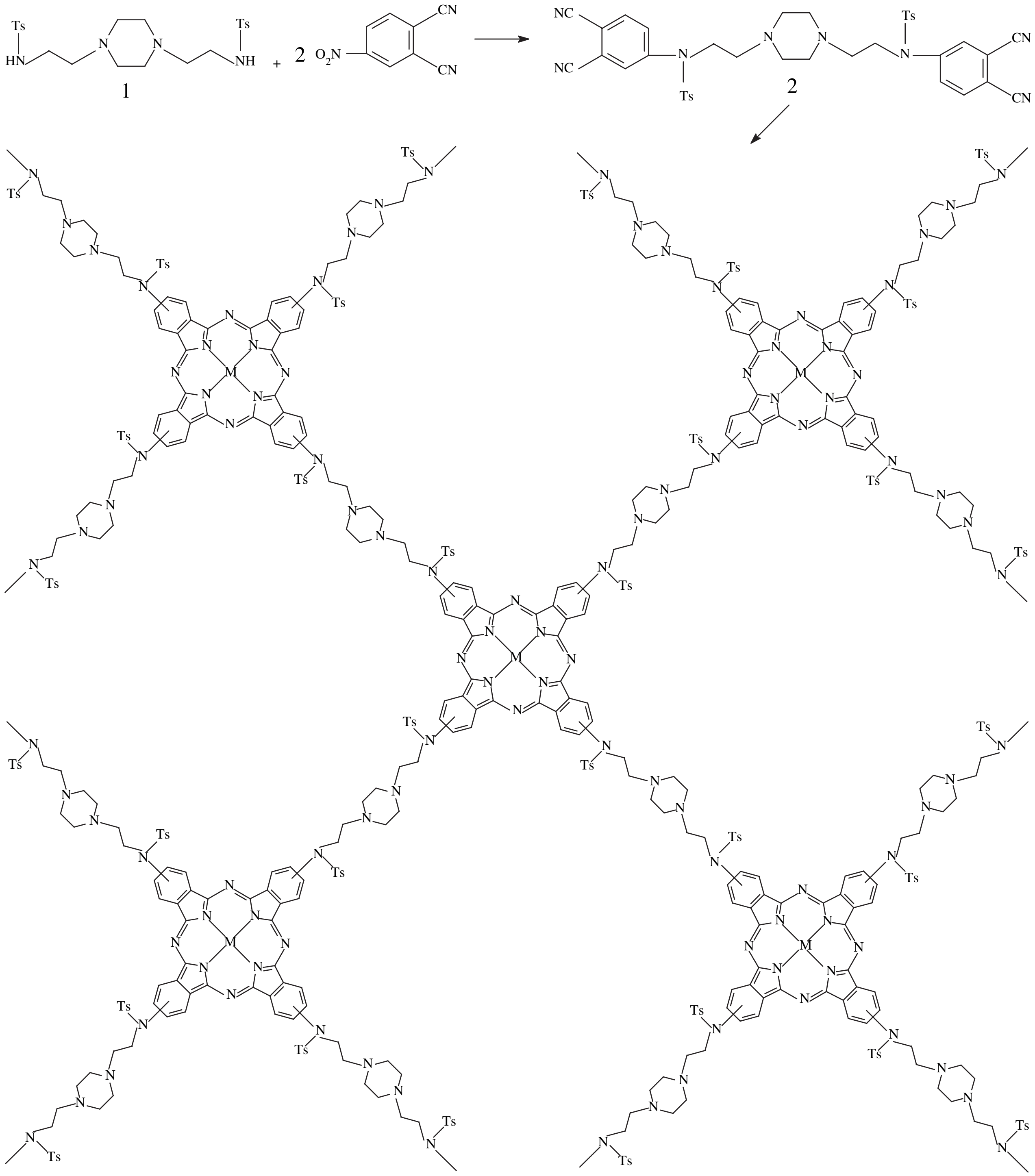
The elemental analysis results of the starting materials and the phthalocyanine polymers show good agreement with the calculated values. Characterization of the products involved a combination of methods including IR, elemental analysis, UV–VIS spectroscopy and ^{1}H and ^{13}C NMR spectroscopy (Table 1).

Comparison of the IR spectral data clearly indicated the formation of compound **1** by the disappearance of the NH band of 1,4-bis[*N*-(2-tolylsulphonylaminoethyl)]-1,4-diazacyclohexane at 3460 cm^{-1}, and the appearance of a new absorption at 2240 cm^{-1} (CN). In the IR spectrum of **2**, the strong absorption vibration at 2240 cm^{-1} corresponding to the CN groups disappear after their conversion to the metallophthalocyanine polymers **4–7** and metal-free phthalocyanine polymer **3**. The rest of the IR spectra are very similar to those of **1** including the characteristic vibration of functional group. The IR spectrum of **2** exhibits characteristic frequencies at 3080–2880 (Ar–H and C–H), 2240 (CN) and 1360, 1165 (SO_2) cm^{-1}. In the ^{1}H NMR spectrum of **2**, the singlet at δ: 2.44 (Ar–CH_3), the triplet at δ: 2.18–2.24 (Ts–N–CH_2–CH_2–N–), the singlet at δ: 3.43 (N–CH_2–CH_2–N) and the multiplets at δ: 7.28–7.77 ppm correspond to aromatic protons. The ^{13}C NMR of **2** in $CDCl_3$ gave signals at 144.85, 144.67, 140.22, 134.22, 134.13, 132.65, 132.51, 130.10, 127.30 (Ar), 116.48 (CN), 114.92, 114.70, 113.78, 56.12, 52.61, 47.20 (–CH_2–) and 21.65 ppm (Ar–CH_3).

The IR spectrum of **2** is very similar to that of **1**. This spectrum indicates new NH bands at 3360 and 1020 cm^{-1}. A diagnostic feature of the phthalocyanine polymer formation from the dicyano derivative (**2**) is the appearance of the precursor compound.

In order to obtain the phthalocyanine polymers containing metals **3–7**, the dinitrile derivative **2** was directly treated with the anhydrous transition metal salts [CuCI, $NiCI_2$, $CoCI_2$, $Zn(CH_3COO_2)$]. The deep green products were soluble in dimethylsulphoxide, dimethylformamide and sulphuric acid.

Elemental analyses, IR, UV–VIS, ^{1}H and ^{13}C NMR spectra confirmed the proposed structures of the metallophthalocyanine polymers. The intensity of the absorption bands of the end group is a clear indication of the degree of polymerization in network polymers [23]. The IR spectra of the phthalocyanines **2–7** do not show the presence of cyano groups, so it is not possible to make any evaluation on the degree of polymerization by comparing their intensities with the intensity of other groups (e.g. alkene groups) not affected during this reaction [4,20,24]. Also, no appreciable amount of imide



Complex	M
3	2H
4	Cu
5	Ni
6	Co
7	Zn

Scheme 1. Structure of polymeric phthalocyanines (Ts = *p*-Toluenesulphonyl).

Table 1
Analytical and physical data for the starting material and the phthalocyanine polymers

	Formula	Analysis (%)			T_1 (°C)	T_2 (°C)	Yield (g)	λ (nm) [10^{-3} ε (l mol^{-1} cm^{-1})]	IR (υ_{max} (cm^{-1}))
		C	H	N					
2	$C_{38}H_{36}N_8S_2O_4$	62.65 (62.28)	4.93 (4.95)	15.44 (15.29)	[b]	–	8.13	–	3080–2880 (CH), 2240 (CN), 1602, 1490, 1450, 1360 (SO_2), 1165 (SO_2), 1110, 1020, 982, 820, 780, 710, 700, 690, 660, 560
3	$C_{152}H_{146}N_{32}S_8O_{16}$	61.00 (62.17)	4.33 (4.97)	14.79 (15.28)	260	465	0.80	262 (65.1), 332 (53.2),[a] 645 (20.3),[a] 675 (25.1), 747 (23.5)	3360 (NH), 3060–2850 (CH), 1715, 1640, 1610, 1585, 1530, 1370–1320 (SO_2), 1150 (SO_2), 1085, 1020, 952, 815, 755, 670, 550
4	$C_{152}H_{144}N_{32}S_8O_{16}Cu$	59.05 (60.96)	4.85 (4.85)	14.31 (14.97)	265	468	0.57	264 (15.4), 334 (9.3),[a] 583 (1.8),[a] 613 (3.8),[a] 646 (6.0), 675 (12.1)	3080–2800 (CH), 1715, 1650, 1590, 1450, 1390, 1340 (SO_2), 1150 (SO_2), 1090, 950, 810, 750, 710, 665, 570, 545
5	$C_{152}H_{144}N_{32}S_8O_{16}Ni$	59.90 (60.09)	4.34 (4.82)	14.70 (14.98)	240	485	0.40	276 (88.3), 340 (53.9),[a] 463 (21.0),[a] 615 (28.7),[a] 647 (36.5),[a] 679 (60.1)	3080–2850 (CH), 1760, 1710, 1620–1590, 1550, 1520, 1440, 1400, 1370–1320 (SO_2), 1150 (SO_2), 1080, 945, 895, 810, 745, 710, 655, 605, 550
6	$C_{152}H_{144}N_{32}S_8O_{16}Co$	59.60 (61.05)	4.48 (4.85)	14.06 (14.99)	238	475	0.32	296 (54.1), 381 (16.5),[a] 652 (20.9),[a] 739 (119)	3080–2850 (CH), 1775–1723, 1620, 1540, 1490, 1390, 1340 (SO_2), 1180 (SO_2), 1100, 925, 840, 765, 713, 660, 560
7	$C_{152}H_{144}N_{32}S_8O_{16}Zn$	59.47 (60.99)	4.61 (4.82)	14.57 (14.59)	270	430	0.20	261 (57.8), 355 (51.6), 616 (23.9), 651 (27.3),[a] 682 (123.9)	3080–2850 (CH), 1790, 1735, 1630–1600, 1490, 1450, 1390, 1350 (SO_2), 1160 (SO_2), 1095, 1050, 940, 820, 750, 700, 690, 670, 570

Required values are given parantheses. **2–6** Phthalocyanines polymers were calculated for monomeric phthalocyanines (for CN end groups). T_1, Temperature of initial decomposition; T_2, temperature of major decomposition.

[a] Shoulder (C: 1.67×10^{-5} M) **3–5**, **7** in DMSO and **6** in H_2SO_4.

[b] M.p. = 188–190 °C.

formation has been observed by IR spectra while concentrated acid procedure has been employed in the work-up processes. The fact that the intensity of the end groups can not be seen, so can be taken as conformation of a higher degree of polymerization when compared with the results reported for tetracyanobenzene, tetracyanodibenzo-18-crown-6 or alkylthio derivatives [4,20,24,25]. The M–N vibrations were expected to appear at 400–100 cm^{-1} but they were not observed in KBr pellets [26].

The lower solubility of the polymers meant that their spectra could be obtained in dimethylsulphoxide and sulphuric acid. The UV–VIS absorption spectra of these polymers exhibit Q and B bands, which are the characteristic bands for phthalocyanine polymers (Table 1).

There is a shoulder at the slightly higher energy side for all products. The longer wavelength was encountered for the intense band compounds of **2–7**. The UV–VIS spectra of the phthalocyanine polymers are very similar to those of crown ether [20], thia [21], oxa-thia [10], aza [22] substituted phthalocyanine polymers. The experimental UV–VIS bands of the phthalocyanine polymers were slightly different from theoretical values [27], and the results of mononuclear [7,8], binuclear [28], pentanuclear [29] and nono-nuclear [6] phthalocyanine. The spectral line shapes are similar and absorption maxima occur at the near-IR region with respect to the corresponding phthalocyanine model compounds. The phthalocyanine ring is a relatively large and symmetrical structure which has a strong tendency to associate in solution [19]. Solvent effects on the UV–VIS characteristics of polymeric phthalocyanines were regular, and red shifts of the spectra bands showed systematic changes. For a more precise understanding of solvent effects, more detailed solvent influences must also be taken into consideration [30].

The thermal stability of polymeric phthalocyanines (**2–7**) has been investigated by thermal gravimetric analysis (Table 1). The initial decomposition of the polymers determined by thermogravimetry occurs at ca. 238–270 °C and then extensive decompositions occurs at temperatures between 430 and 485 °C. The initial decomposition temperatures of the compounds are in the order Zn > Cu > 2H > Ni > Co. No obvious correlation between the transition metal ions in the phthalocyanine rings is observed. The main decomposition temperatures of these phthalocyanine polymers are lower than crown ether [20], azamacrocycle [22] and alkylthio [21,25] substituted phthalocyanine polymers.

The main purpose of the substitutions is to enhance the very limited solubility, and to enable the convenient preparation of a series of new phthalocyanine polymers.

3. Experimental

IR spectra were recorded on a Mattson 1000 FTIR spectrometer (KBr), Electronic spectra were recorded on a Unicam UV–VIS spectrometer ^{1}H NMR and ^{13}C NMR studies were made on a Bruker AC-200 FT–NMR spectrometer. Thermogravimetric analyses were obtained on a RİKAGU TG 8110 simultaneous thermal analyzer combined with a TAS 100 at 10 °C $\min^{-1}$ in a nitrogen flow. Elemental analysis was performed by the Instrumental Analysis Laboratory of Tübitak Gebze Resarch Center.

4-Nitrophthalonitrile [17] was synthesized according to the reported procedures. All other reagents and solvents were of reagent-grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [31]. The solvents were stored over molecular sieves (4 Å). The homogeneity of the products was tested by TLC (SiO_2 or Al_2O_3).

*3.1. 4,4′-[2,2′-(Piperidine-1,4-diyldiethylene)-di(tosylimino)]diphthalonitrile (**2**)*

1,4-Bis[*N*-(2-tolylsulphonylaminoethyl)]-1,4-diazacyclohexane (13.16 g, 27.42 mmol) was dissolved in DMSO (150 ml) under nitrogen and 4-nitrophthalonitrile (10.11 g, 58.43 mmol) was added. After stirring for 10 min, finely ground anhydrous K_2CO_3 (19.73 g, 142.97 mmol) was added portion-wise in 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at room temperature for 24 h. Water was then added and the product was filtered and washed with water until the filtrate was neutral. The residue was washed with hot methanol and diethyl ether, and dried. The compound was soluble in chloroform, ethyl acetate, dichloromethane, pyridine, DMF and DMSO. ^{1}H NMR ($CDCl_3$): δ 7.77–7.28 (16H, m, Ar–H), 3.43 (8H, s, N–CH_2–CH_2–N), 2.24–2.18 (8H, t, Ts–N–CH_2–CH_2–), 2.44 (6H, s, Ar–CH_3). ^{13}C NMR: δ 144.85, 144.67, 140.22, 134.22, 134.13, 132.65, 132.51, 130.10, 127.30 (Ar), 116.48, 114.92, 114.70, 113.78 (CN), 56.12, 52.61, 47.20 (N–CH_2–CH_2–N), 21.65 (Ar–CH_3).

*3.2. Metal-free phthalocyanine polymer (**3**)*

A mixture of **2** (2 g, 2.72 mmol) and hydroquinone (0.55 g, 5 mmol) (purified by sublimation) was gently heated under N_2 and then cooled. This mixture was heated to 200 °C under a nitrogen atmosphere and held at this temperature for 2 h. After cooling to room temperature, it was diluted with hot ethanol and the product was filtered and then refluxed with ethanol. The resulting dark green precipitate was washed with ethanol, ethyl acetate and diethyl ether. This polymer was soluble in DMF and DMSO.

*3.3. Cu-containing polymer (**4**)*

A mixture of **2** (1.13 g, 1.54 mmol), CuCl (0.16 g, 1.61 mmol) and urea (0.1 g, 1.67 mmol) was heated at 180–190 °C for 3 h under nitrogen. After cooling, the reaction mixture was diluted with ethanol and refluxed, and the residue filtered off. The product was washed with NH_4OH (30 ml %24) and then with water until the filtrate became neutral. It was then refluxed with ethanol and ethyl acetate, the filtered dark green product was washed with ethanol, ethyl acetate and diethyl ether. This polymer was soluble in DMF and DMSO.

*3.4. Ni-containing polymer (**5**)*

A mixture of **2** (1 g, 1.36 mmol), $NiCl_2$ (0.20 g, 1.54 mmol) and dry quinoline (25 ml) was heated and stirred at 220 °C for 16 h under nitrogen. After cooling, the reaction mixture was diluted with ethanol and the precipitate was filtered off. It was treated with boiling ethanol twice to dissolve any unreacted metal salts. The green product washed with hot ethanol, ethyl acetate, diethyl ether and water and dried. This polymer was soluble in DMF and DMSO.

*3.5. Co-containing polymer (**6**)*

A mixture of **2** (1 g, 1.36 mmol), $CoCl_2$ (0.20 g, 1.54 mmol), ammonium molybdate (0.05 g) and ethylene glycol (30 ml) was refluxed and stirred at 220–230 °C for 7 h under nitrogen. After cooling, liquor was filtered and the residue digested with hot ethanol and ethyl acetate, washed with acetone, diethyl ether and water and dried. This polymer was soluble in DMF and DMSO.

*3.6. Zn-containing polymer (**7**)*

A mixture of **2** (1 g, 1.36 mmol), anhydrous zinc acetate (0.30 g, 1.64 mmol) and dry quinoline (30 ml) was heated and stirred at 210–220 °C for 6 h under nitrogen. After cooling, the reaction mixture was diluted with ethanol and precipitate was filtered off. The green product was washed with hot ethanol, ethyl acetate, diethyl ether and water and dried. This polymer was soluble in DMF and DMSO.

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