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The microwave-assisted synthesis and characterization of novel polymeric phthalocyanines containing resorcinarene

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Abstract

Novel metal phthalocyanine (Cu, Zn, Co, Ni) polymers containing resorcinarene moieties were prepared; the resorcinarene was obtained by the acid-catalysed cyclocondensation of resorcinol and acetaldehyde under microwave irradiation. The resorcinarene phthalonitrile compounds were then synthesized by treating resorcinarene with 4,5-dichloro-1,2-dicyanobenzene and 4-nitro-1,2-dicyanobenzene under microwave irradiation, respectively. Cu(II), Co(II) and Ni(II) chlorides were employed in order to synthesize the corresponding metal phthalocyanine polymers and $Zn(CH_3CO_2)$ was used to prepare zinc phthalocyanine polymers. Structures were characterized by elemental analyses, ^1H NMR, ^{13}C NMR, UV–vis and FTIR spectroscopy.

Keywords: Microwave-assisted; Polymeric phthalocyanines; Resorcinarene

1. Introduction

Since their first synthesis in early last century, phthalocyanines have established themselves as blue and green dyestuffs par excellence. Phthalocyanines are an important industrial commodity used primarily in inks, coloring for plastics and metal surfaces, and dyestuffs for jeans and other clothings [1]. The importance of phthalocyanines in many fields, including electrochromic display devices [2,3], photodynamic reagents for cancer therapy [4] and other medical applications [1], optical computer read/write discs [5], laser dyes, new red-sensitive photocopying applications [1,2] and liquid crystal color display applications, is increasing rapidly as a result of the synthesis of new compounds [6]. Phthalocyanines can be obtained by the classical template reactions of diverse precursors such as phthalonitrile, cyano-benzamide, phthalamide and phthalic acid with metal salts in high-boiling nonaqueous solvents at elevated temperatures [7,8].

Metal phthalocyanine polymers have been described for use as dyes [9], industrial high-tech materials [10,11], and are also of additional interest because of their high thermostability [12,13]. We have previously synthesized novel polymeric phthalocyanines which are capable of binding to transition metal cations [14–16]. Microwave processing has attracted potential interest as an alternative to classical thermal processing because of the inherent advantages of microwave heating, which is selective, direct, rapid, internal and controllable [17–19]. The synthesis of phthalocyanines under microwave irradiation reduces reaction times and enhances yields in comparison with classical method [20]. We have previously reported about microwave-assisted synthesis of phthalocyanines containing substituents (e.g. phenoxyl [20], triazole [21], and oxa-aza [22]). The acid-catalysed condensation of resorcinol and aldehydes produces resorcinarenes [23]. Resorcinarenes are known to possess hydrophilic (upper rim) and hydrophobic (lower rim) regions and a cavity, which can accommodate small organic molecules [23]. As a result of these structural motifs, resorcinarenes and cavitands have enjoyed use as surfactants and liquid crystals, in the complexation of metals,

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ammonium compounds, alcohols, diols, sugars, amino acids and carboxylic acids [24,25].

In this study, we report microwave-assisted synthesis and characterization of the new metal phthalocyanine (Cu, Zn, Co, Ni) polymers containing resorcinarene moieties. These are firstly synthesized polymers containing both phthalocyanine and recorcinarene groups. Therefore, they have interesting properties and applications on polymer chemistry.

2. Results and discussion

4-Nitro-1,2-dicyanobenzene and 4,5-dichloro-1,2-dicyanobenzene are used to prepare mono and disubstituted phthalonitrile derivatives through base-catalysed nucleophilic aromatic displacement [26,27]. In order to obtain polymeric phthalocyanines containing resorcinarene moieties, firstly, resorcinarene (**1**) was obtained by acid-catalysed cyclocondensation of resorcinol and acetaldehyde under 360 W microwave irradiation for 10 min. All spectroscopic data of resorcinarene (**1**) show good agreement with the values reported in the literature [24]. The synthesis of phthalonitrile compounds was the most important step in these reaction sequences. For this purpose, compound **2** containing tetra phthalonitrile groups and compound **3** containing octa pthalonitrile groups were synthesized by treating resorcinarene (**1**) with 4,5-dichloro-1,2-dicyanobenzene and 4-nitro-1,2-dicyanobenzene, respectively, in DMF using K_2CO_3 as the base for nucleophilic substitution under 360 W microwave irradiation for 10 min [20–22]. The chemical structures of compounds **2** and **3** were determined according to previously reported paper by Cram et al. [28]. At the last step, metal phthalocyanine (Cu, Zn, Co, Ni) polymers were synthesized using microwave irradiation from the corresponding resorcinarene phthalonitrile derivatives and metal salts in DMAE for 10 min [20–22]. Solubility of metal phthalocyanine polymers containing resorcinarene moieties was slightly in common organic solvent such as DMF and DMSO. The purification of metal phthalocyanine polymers was carried out by washing with various solvents. All attempts for the preparation of metal-free phthalocyanine polymer containing resorcinarene moieties under microwave irradiation were not successful. Phthalocyanines can be obtained by the metal-template effect [29], however, metal-free phthalocyanine polymer containing resorcinarene moieties could not be obtained due to absence of metal-template effect. Characterization of the products involved a combination of methods including elemental analyses, FTIR, UV–vis, ^1H NMR and ^{13}C NMR spectroscopies. ^1H NMR and ^{13}C NMR data could not be obtained for metal phthalocyanine polymers due to its poor solubility in polar solvents such as $CHCl_3$, DMF and DMSO. Elemental analyses of the phthalonitrile derivatives and the phthalocyanines show good agreement with the calculated values. Phthalonitrile compounds **2** and **3** are repeated units in the structures of the newly synthesized metal phthalocyanine (Cu, Zn, Co, Ni) polymers containing resorcinarene. Microwave-assisted synthetic route of resorcinarene and the new metal phthalocyanine (Cu, Zn, Co, Ni) polymers containing resorcinarene can be seen in Schemes 1 and 2.

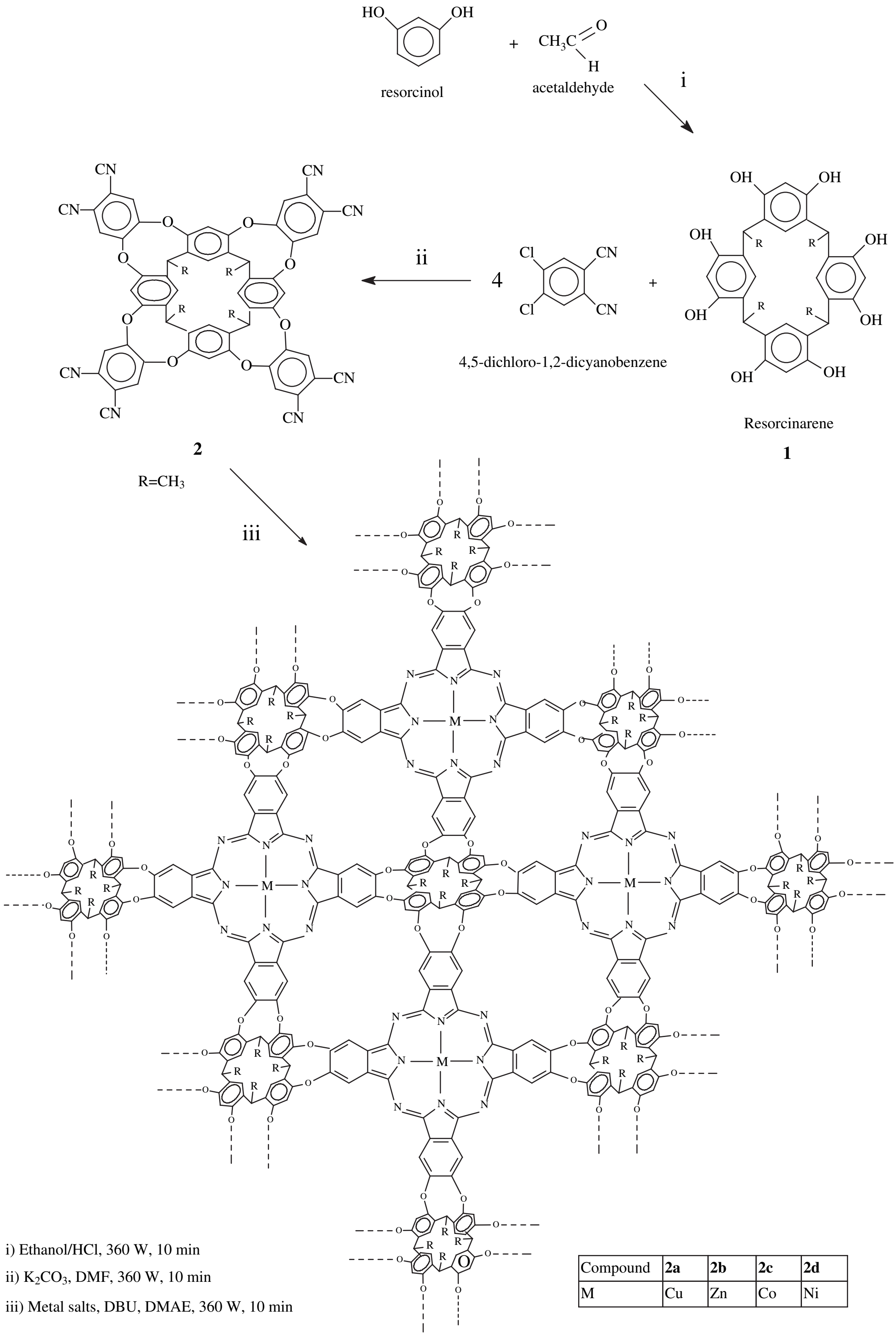
FTIR spectrum of resorcinarene **1** shows good agreement with the values reported in the literature [24]. The formation of compound **2** was clearly indicated by the disappearance of the OH band at 3418 cm^{-1} and appearance of the C≡N band at 2236 cm^{-1} in its FTIR spectrum. The FTIR spectra of the polymeric phthalocyanines (**2a–d**) clearly indicate the cyclotetramerization of the phthalonitrile derivatives with the disappearance of the C≡N peak at 2236 cm^{-1}. But, the polymeric phthalocyanines (**2a–d**) have cyano end groups together with imide functions [24,25], as indicated by the weak absorptions C≡N at 2234, 2233, 2232, 2233 cm^{-1}, imide at 1774, 1774, 1775, 1774 cm^{-1} and 1722, 1721, 1724, 1724 cm^{-1}, respectively. The formation of compound **3** was clearly indicated by the disappearance of the OH band at 3418 cm^{-1} and appearance of the C≡N band at 2232 cm^{-1} in its FTIR spectrum. The polymeric phthalocyanines (**3a–d**) have cyano end groups together with imide functions [14–16], as indicated by the weak absorptions C≡N at 2231, 2232, 2230, 2232 cm^{-1}, imide at 1770, 1771, 1770, 1771 cm^{-1} and 1716, 1720, 1718, 1718 cm^{-1}, respectively.

^1H NMR and ^{13}C NMR spectra of resorcinarene **1** show good agreement with the values reported in the literature [24]. In the ^1H NMR spectrum of compound **2**, the aromatic protons appear as three singlets at 8.63, 7.95 and 7.44 ppm and aliphatic protons appear as a multiplet at 4.44–4.41 ppm and a doublet at 1.59–1.57 ppm. The ^{13}C NMR spectrum of compound **2** indicated the presence of nitrile carbon atoms at 114.8 ppm and methyl carbon atoms at 21.1 ppm. In the ^1H NMR spectrum of compound **3**, the aromatic protons appear as three singlets at 7.72, 7.55, and 6.90 ppm and as two doublets at 7.98–7.97 ppm and 7.46–744 ppm and aliphatic protons appear as a multiplet at 4.44–4.40 ppm and a doublet at 1.63–1.60 ppm. The ^{13}C NMR spectrum of compound **3** indicated the presence of nitrile carbon atoms at 117.1 and methyl carbon atoms at 20.1 ppm. ^1H NMR and ^{13}C NMR measurements of the metal phthalocyanine (Cu, Co, Ni) polymers were precluded due to its paramagnetic nature. ^1H NMR and ^{13}C NMR spectra could not be obtained for polymeric phthalocyanines **2b** and **3b** due to its poor solubility in polar solvents such as $CHCl_3$, DMF and DMSO.

The best indication for the phthalocyanine systems is their UV–vis spectra in solutions. The newly synthesized metal phthalocyanine (**2a–d**) polymers showed typical electronic spectra with two strong absorption regions, one of them in UV region at about 294 nm (B band) and the other in the visible region at 710, 699 and 693 nm, respectively (Q band) in DMF. The other newly synthesized metal phthalocyanine (**3–3d**) polymers showed two absorption regions at 342 nm (B band) and in the visible region at 750, 750, 755, and 755 nm, respectively (Q band) in H_2SO_4. Q bands shifted to above values due to polymerization of phthalonitrile derivatives [30].

3. Conclusion

The preparation of metal (Cu, Zn, Co, Ni) phthalocyanine polymers containing resorcinarene moieties has been achieved using microwave irradiation. The microwave-assisted synthetic route reduces reaction times and enhances the yield of the reactions.



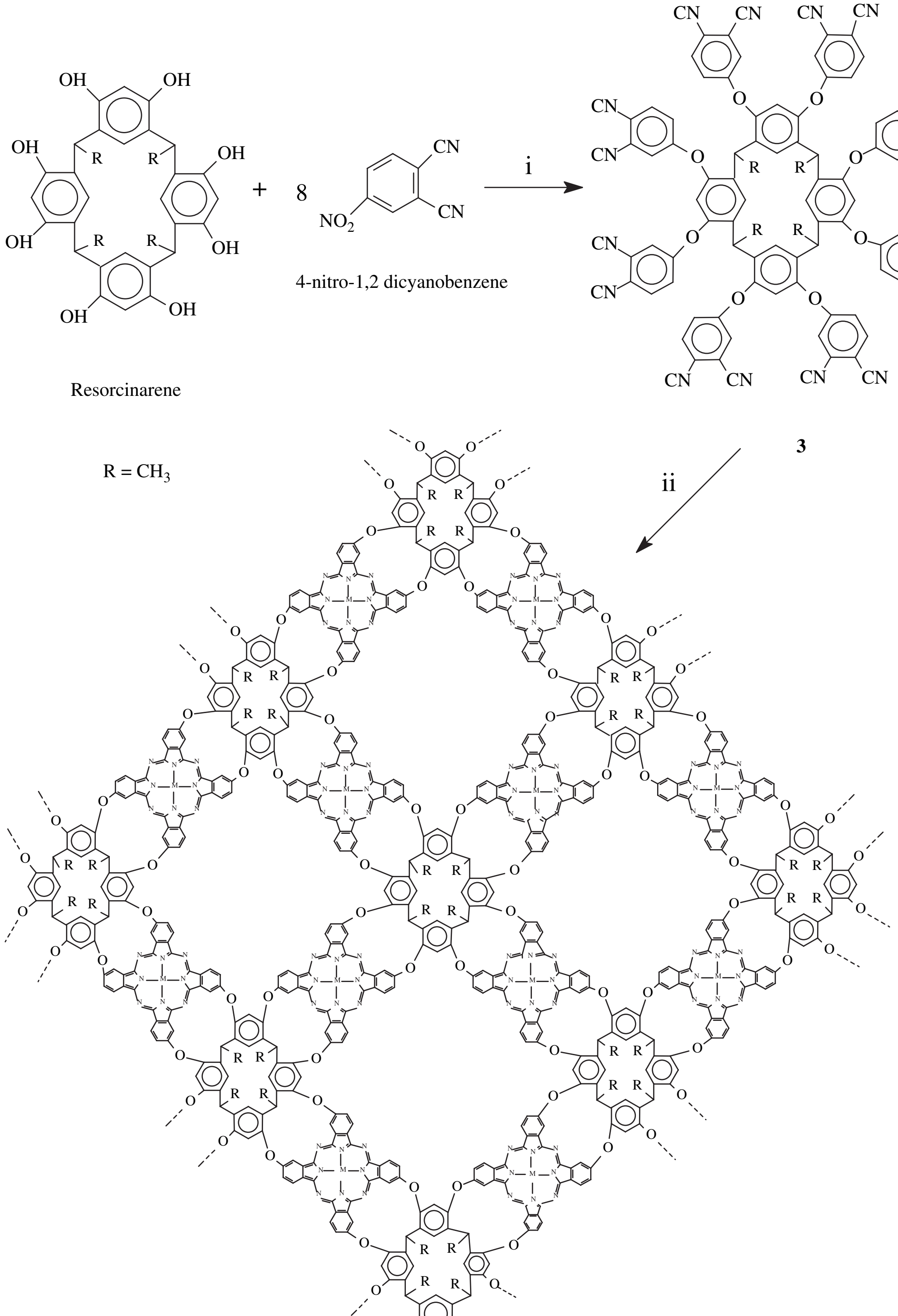
i) Ethanol/HCl, 360 W, 10 min

ii) K_2CO_3, DMF, 360 W, 10 min

iii) Metal salts, DBU, DMAE, 360 W, 10 min

Compound	**2a**	**2b**	**2c**	**2d**
M	Cu	Zn	Co	Ni

Scheme 1. Microwave-assisted synthesis of resorcinarene **1**, compound **2** and metal phthalocyanine polymers (**2a**–**2d**).



i) K_2CO_3, DMSO, 360 W, 10 min
ii) Metal salts, DBU, DMAE, 360 W, 10 min

Compound	**3a**	**3b**	**3c**	**3d**
M	Cu	Zn	Co	Ni

Scheme 2. Microwave-assisted synthesis of compound **3** and metal phthalocyanine polymers (**3a–d**).

4. Experimental

4.1. General

4,5-Dichloro-1,2-dicyanobenzene and 4-nitro-1,2-dicyanobenzene were prepared by a reported procedure [26,27]. FTIR spectra were recorded on a Jasco FTIR/430 Fourier Transform Infrared Spectrometer as KBr pellets. UV–vis spectra were recorded on a Mattson UNICAM UV–vis spectrometer. ^{1}H NMR and ^{13}C NMR studies were done on a Bruker AC-200 or FT-200 FT-NMR spectrometer. Elemental analyses were performed by the Instrumental Analyses

Laboratory of the TÜBİTAK Gebze Research Center. Microwave-assisted syntheses were carried out using a modified BEKO MD domestic microwave oven.

*4.1.1. Microwave-assisted synthesis of resorcinarene (**1**)*

Acetaldehyde (1.2 g, 27 mmol) and concentrated HCl (6.8 ml) were added to a solution of resorcinol (3 g, 27 mmol) in absolute ethyl alcohol (20 ml). This mixture was heated by microwaves for 10 min with a fixed power of 360 W. The reaction mixture was poured in an ice bath and the formed solid material was filtered off and washed by water to eliminate acid trace. The filtrate was dried at 70 °C. All spectroscopic data of product show good agreement with the values reported in the literature [24]. Yield 2.96 g, 80%; mp > 280 °C; FTIR ν_{max}/cm^{-1}: 3418 (OH), 2967 (CH), 1621, 1506, 1426, 1271, 1200, 1115, 837 cm^{-1}; ^{1}H NMR (($CD_3)_2SO$): δ 8.98 (8H, s, OH), 6.92 (4H, s, ArCH), 6.37 (4H, s, ArCH), 4.45–4.41 (4H, m, CH), 1.63–1.59 (12H, d, CH_3) ppm; ^{13}C NMR (($CD_3)_2SO$): δ 152.7, 127.4, 125.2, 102.6, 29.1, 20.1 ppm. Anal. Calcd for $C_{32}H_{32}O_8$: C, 70.57; H, 5.92. Found: C, 70.79; H, 5.85.

*4.1.2. Microwave-assisted synthesis of phthalonitrile compound (**2**)*

Resorcinarene (**1**) (4.44 g, 8.16 mmol), 4,5-dichloro phthalonitrile (6.44 g, 32.69 mmol), and K_2CO_3 (9.2 g, 66 mmol) were added to *N*,*N*-dimethyl formamide (DMF) (20 ml). This mixture was heated by microwaves for 10 min with a fixed power of 360 W [20,22]. The reaction mixture was poured in an ice bath and the formed solid material was filtered off and HCl solution was added to eliminate base trace and washed with water until the filtrate became neutral. The crude product was purified by two successive column chromatographic separations (silica gel, DMF/methanol = 40:1). This compound was soluble in DMF and DMSO. Yield 7.2 g, 84%; mp > 300 °C; FTIR ν_{max}/cm^{-1}: 3101 (C=C), 2972 (CH), 2236 (C≡N), 1584, 1556, 1381, 1194, 1101, 897 cm^{-1}; ^{1}H NMR (($CD_3)_2SO$): δ 8.63 (8H, s, ArCH), 7.95 (4H, s, ArCH), 7.44 (4H, s, ArCH), 4.44–4.41 (4H, t, CH), 1.59–1.57 (12H, d, CH_3) ppm; ^{13}C NMR (($CD_3)_2SO$): δ 156.7, 136.5, 129.4, 127.2, 114.8 (C≡N), 104.6, 30.1, 21.1 (CH_3) ppm. Anal. Calcd for $C_{64}H_{32}N_8O_8$: C, 73.84; H, 3.10; N, 10.76. Found: C, 73.79; H, 3.35; N, 10.53.

*4.1.3. Microwave-assisted synthesis of phthalonitrile compound (**3**)*

Resorcinarene (**1**) (2 g, 3.67 mmol), 4-nitro phthalonitrile (5.08 g, 29.36 mmol) and K_2CO_3 (4.04 g, 29.27 mmol) were added to *N*,*N*-dimethyl formamide (DMF) (20 ml). This mixture was heated by microwaves for 10 min with a fixed power of 360 W [20,22]. The reaction mixture was poured in an ice bath and the formed solid material was filtered off and HCl solution was added to eliminate base trace and washed with water until the filtrate became neutral. The crude product was purified by two successive column chromatographic separations (silica gel, DMF/methanol = 40:1). This compound was soluble in DMF and DMSO. Yield 4.56 g, 80%; mp 194 °C; FTIR ν_{max}/cm^{-1}: 3076 (C=C), 2971 (CH), 2232 (C≡N), 1590, 1484, 1283, 1246, 1107, 843 cm^{-1}; ^{1}H NMR (($CD_3)_2SO$): δ 7.98–7.97 (8H, d, ArCH), 7.72 (8H, s, ArCH), 7.55 (4H, s, ArCH), 7.46–7.44 (8H, d, ArCH), 6.90 (4H, s, ArCH), 4.44–4.40 (4H, t, CH), 1.63–1.60 (12, d, CH_3) ppm; ^{13}C NMR (($CD_3)_2SO$): δ 161.8, 150.1, 138.7, 118.1, 117.1 (C≡N), 116.4, 115.4, 108.7, 29.9, 20.1 (CH_3) ppm. Anal. Calcd for $C_{96}H_{48}N_{16}O_8$: C, 74.22; H, 3.11; N, 14.43. Found: C, 73.93; H, 3.25; N, 14.55.

*4.1.4. Microwave-assisted synthesis of phthalocyanines containing resorcinarene (**2a–d**)*

The general procedure employed for the synthesis of various metal phthalocyanine (Cu, Zn, Co, Ni) polymers was described as follows. Compound **2** (0.5 g, 0.12 mmol), metal salts ($CuCl_2$, $Zn(CH_3COO)_2$, $CoCl_2$, $NiCl_2$ (0.03 mmol)), DMAE (*N*,*N*-dimethylaminoethanol) (5 ml) and 2–3 drops DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) were charged together into round bottomed flask. The reaction flask was irradiated by a microwave oven at 360 W for 10 min [20,22]. After cooling to room temperature, the reaction mixture was treated with water to precipitate the product which was filtered off. The green product was washed with hot DMF, hot ethanol and hot chloroform (4 × 50 ml). All of synthesized polymeric phthalocyanines were slightly soluble in DMF and DMSO. Yield, melting point, elemental analysis, FTIR and UV–vis spectra of the products were as follows.

Cu-containing polymer (**2a**): Yield 0.39 g, 78%; mp > 300 °C; FTIR ν_{max}/cm^{-1}: 3101 (C=C), 2961 (CH), 2234 (C≡N), 1774, 1722, 1662, 1594, 1488, 1397, 1285, 1179, 1097, 895 cm^{-1}; UV–vis λ_{max} (DMF)/nm: 293, 710 nm. Anal. Calcd for $C_{256}H_{128}N_{32}O_{32}Cu$: C, 72.73; H, 3.05; N, 10.60. Found: C, 72.53; H, 3.15; N, 10.53.

Zn-containing polymer (**2b**): Yield 0.36 g, 72%; mp > 300 °C; FTIR ν_{max}/cm^{-1}: 3101 (C=C), 2962 (CH), 2233 (C≡N), 1774, 1721, 1662, 1594, 1483, 1397, 1284, 1179, 1099, 894 cm−1; UV–vis λ_{max} (DMF)/nm: 294, 699 nm. Anal. Calcd for $C_{256}H_{128}N_{32}O_{32}Zn$: C, 72.70; H, 3.05; N, 10.60. Found: C, 72.57; H, 3.20; N, 10.50.

Co-containing polymer (**2c**): Yield 0.45 g, 94%; mp > 300 °C; FTIR ν_{max}/cm^{-1}: 3102 (C=C), 2963 (CH), 2232 (C≡N), 1775, 1724, 1662, 1594, 1484, 1397, 1285, 1179, 1101, 895 cm^{-1}; UV–vis λ_{max} (DMF)/nm: 294, 693 nm. Anal. Calcd for $C_{256}H_{128}N_{32}O_{32}Co$: C, 72.81; H, 3.06; N, 10.61. Found: C, 72.65; H, 3.20; N, 10.54.

Ni-containing polymer (**2d**): Yield 0.44 g, 94%; mp > 300 °C. FTIR ν_{max}/cm^{-1}: 3101 (C=C), 2964 (CH), 2233 (C≡N), 1774, 1724, 1661, 1592, 1482, 1395, 1283, 1176, 1100, 897 cm−1; UV–vis λ_{max} (DMF)/nm: 294, 693 nm. Anal. Calcd for $C_{256}H_{128}N_{32}O_{32}Ni$: C, 72.82; H, 3.06; N, 10.61. Found: C, 72.66; H, 3.15; N, 10.55.

*4.1.5. Microwave-assisted synthesis of phthalocyanines containing resorcinarene (**3a–d**)*

The general procedure, employed for synthesis of various metal phthalocyanine (Cu, Zn, Co Ni) polymers was described as follows. Compound **3** (0.5 g, 0.32 mmol), metal salts ($CuCl_2$, $Zn(CH_3COO)_2$, $CoCl_2$, $NiCl_2$ (0.08 mmol)), DMAE

(*N*,*N*-dimethylaminoethanol) (5 ml) and 2–3 drops of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) were charged together into round bottomed flask. The reaction flask was irradiated by a microwave oven at 360 W for 10 min [20,22]. After cooling to room temperature, the reaction mixture was treated with water to precipitate the product which was filtered off. The green product was washed with hot DMF, hot ethanol and hot chloroform (4 × 50 ml). Yield, melting point, elemental analysis, FTIR and UV–vis spectra of the products were as follows.

Cu-containing polymer (**3a**): Yield 0.40 g, 80%; mp > 300 °C; FTIR ν_{max}/cm^{-1}: 3060 (C═C), 2961 (CH), 2231 (C≡N), 1770, 1716, 1593, 1476, 1278, 1093, 836 cm−1; UV–vis λ_{max} (H_2SO_4)/nm: 342, 750 nm. Anal. Calcd for $C_{192}H_{96}N_{32}O_{16}Cu$: C, 72.73; H, 3.05; N, 14.14. Found: C, 72.93; H, 3.17; N, 14.65.

Zn-containing polymer (**3b**): Yield 0.40 g, 80%; mp > 300 °C; FTIR ν_{max}/cm^{-1}: 3060 (C═C), 2964 (CH), 2232 (C≡N), 1771, 1720, 1592, 1476, 1277, 1091, 836 cm^{-1}; UV–vis λ_{max} (H_2SO_4)/nm: 342, 750 nm. Anal. Calcd for $C_{192}H_{96}N_{32}O_{16}Zn$: C, 72.69; H, 3.05; N, 14.13. Found: C, 72.97; H, 3.20; N, 14.85.

Co-containing polymer (**3c**): Yield 0.44 g, 88%; mp > 300 °C; FTIR ν_{max}/cm^{-1}: 3060 (C═C), 2956 (CH), 2230 (C≡N), 1770, 1718, 1593, 1473, 1275, 1091, 834 cm^{-1}; UV–vis λ_{max} (H_2SO_4)/nm: 342, 755 nm. Anal. Calcd for $C_{192}H_{96}N_{32}O_{16}Co$: C, 72.84; H, 3.06; N, 14.16. Found: C, 72.98; H, 3.15; N, 14.86.

Ni-containing polymer (**3d**): Yield 0.45 g, 88%; mp > 300 °C; FTIR ν_{max}/cm^{-1}: 3061 (C═C), 2957 (CH), 2232 (C≡N), 1771, 1718, 1592, 1471, 1273, 1099, 835 cm^{-1}; UV–vis λ_{max} (H_2SO_4)/nm: 342, 755 nm. Anal. Calcd for $C_{192}H_{96}N_{32}O_{16}Ni$: C, 72.85; H, 3.04; N, 14.16. Found: C, 72.99; H, 3.14; N, 14.54.

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