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The synthesis and characterization of novel metal-free and metallophthalocyanines bearing four 27-membered dioxadiazapentathia macrocycles

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Abstract

Novel metal-free phthalocyanines **9**, **10** and metallophthalocyanines **11**, **12** bearing four 27-membered dioxadiazapentathia macrocycles moieties on peripheral positions were synthesized in a multi-step reaction sequence. The new compounds were characterized by a combination of elemental analysis and ^{1}H NMR, ^{13}C NMR, IR, UV–vis and MS spectral data.

Keywords: 2-Aminothiophenol; Mixed-donor macrocycle; Phthalocyanines; Template effect; Transition metal

1. Introduction

Phthalocyanines (Pcs) have aroused extensive interest in the past decades since their unique properties led to their use in a wide number of applications in the area of materials science, such as chemical sensors, liquid crystals, catalysis, anisotropic conductors and nonlinear optics [1–6]. In addition, their properties have been considered to have potential applications in cancer photodynamic therapy (PDT) [7–9].

For most of these applications, metal-free or metallophthalocyanines with long alkyl or alkoxy chains or macrocyclic polyether moieties [10–15] had to be synthesized in order to facilitate the above-mentioned purposes and to enhance solubility.

Since crown ethers were first recognized by Pedersen as having selective metal-ion binding properties [16,17], various crown ethers have been prepared and their complexation behaviour have been studied extensively. The coordination chemistry of mixed nitrogen and sulfur donor macrocycles has also been an area of increasing interest over the past 15 years. These ligands are of interest as they offer coordination of both hard σ-donor N-ligands and soft σ-donor and potential π-acceptor S-ligands [18,19].

We have previously described the synthesis of metal-free and metallophthalocyanines which contain four 20-membered diazatetraoxa macrocycles each attached to a 15-crown-5 unit [20] and macrobicyclic moieties [21]. In the present paper, we describe the synthesis and characterization of new metal-free phthalocyanines and metallophthalocyanines containing a central Pc core, four 27-membered dioxadiazapentathia macrocycles (Scheme 1). The new compounds may allow very important novel functionalized materials to be prepared for analytical chemistry as new kinds of alkali, alkaline earth and transition metal extraction agents.

2. Experimental

1,2-Bis(2′-aminophenylsulfonylethoxy)-4,5-dibromobenzene **1** was prepared according to literature [22]. All reagents and solvent were of reagent grade quality and were obtained

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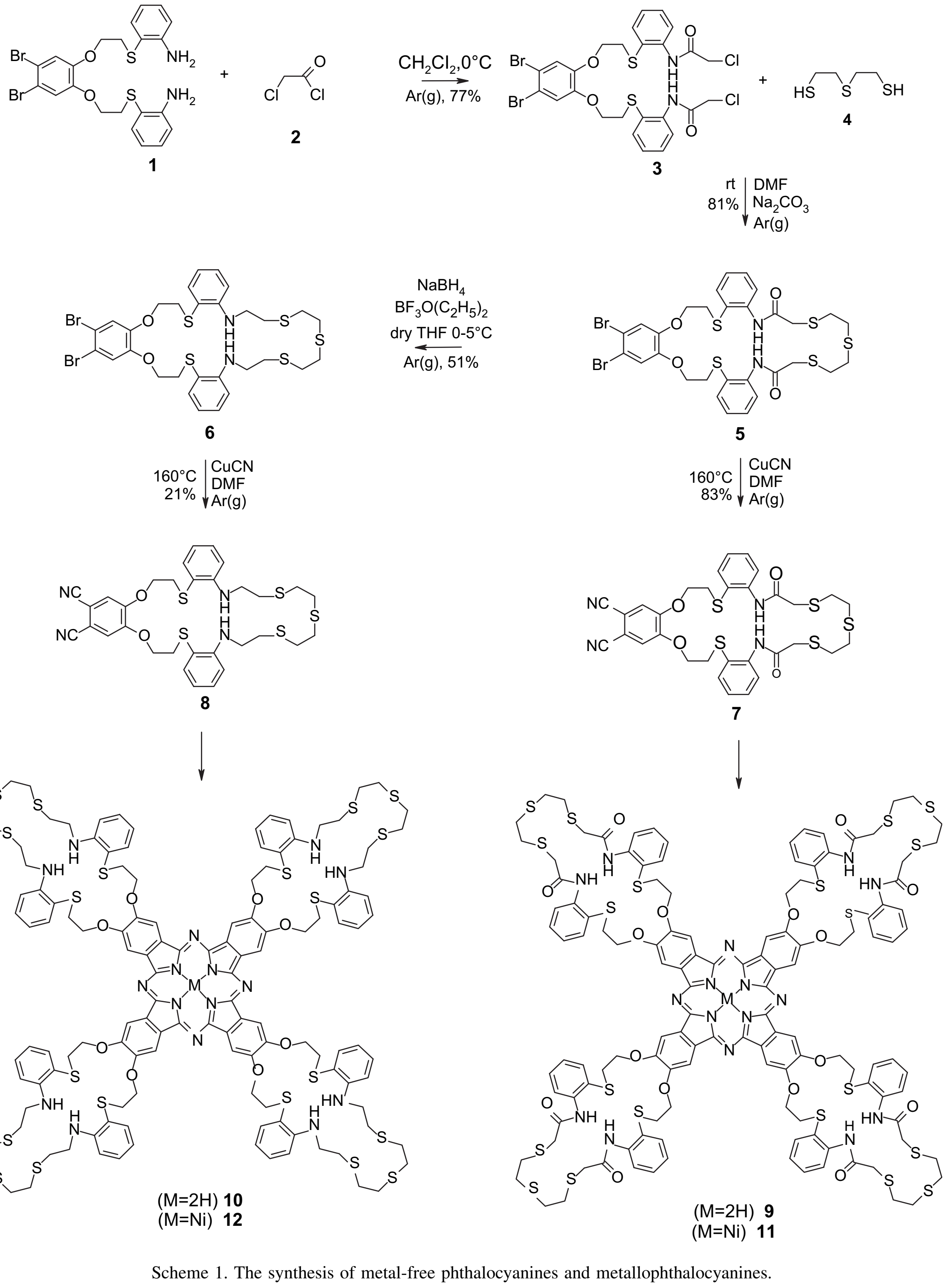

Scheme 1. The synthesis of metal-free phthalocyanines and metallophthalocyanines.

from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [23]. Melting points were determined with an electrothermal apparatus and were uncorrected. FTIR spectra were measured on a Mattson 1001 Fourier-transform spectrometer using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer using $CDCl_3$ and DMSO-d_6 (99.9%). Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC–MS/MS spectrometer. Optical spectra in the UV–vis region were recorded with a Varian Cary 50 Conc spectrophotometer using 1 cm pathlength cuvettes at room temperature. Elemental analyses were obtained from LECO Elemental Analyser (CHNS 0932) and Unicam 929 AA spectrophotometer. The homogeneity of the products was tested in each step using TLC.

*2.1. 2-Chloro-N-{2-[2-(4,5-dibromo-2-{2-[2-(2-chloro-acetylamino)-phenylsulfonyl]-ethoxy}-phenoxy)-ethylsulfonyl]-phenyl}-acetamide (**3**)*

Chloroacetic anhydride **2** (11.58 g, 0.102 mol) in CH_2Cl_2 (250 ml) was added dropwise through a dropping funnel to a stirred solution of 1,2-bis(2′-aminophenylsulfonylethoxy)-4,5-dibromobenzene **1** (23.38 g, 0.041 mol) in CH_2Cl_2 (750 ml) at 0–5 °C over a 1.5 h period. The mixture was stirred for an additional overnight period under argon atmosphere at room temperature. At the end of this period, the mixture was filtered off and the white precipitate was washed with saturated aqueous $NaHCO_3$, water, acetone and diethyl ether and then dried in vacuum. This white solid was used to prepare the appropriate macrocyclic without further purification. Yield: 22.82 g (77%), mp 185–186 °C. Anal. calcd. for $C_{26}H_{24}Br_2Cl_2N_2O_4S_2$: C, 43.17; H, 3.34; N, 3.87%. Found: C, 42.64; H, 3.63; N, 3.58. IR (KBr disc) ν_{max}/cm^{-1}: 3278 (–NH), 3169, 3111, 3060 (CH_{Ar}), 2996, 2965, 2922, 2876 (CH_3), 1678 (C=O), 1582, 1528, 1498, 1459, 1438, 1424, 1351, 1326, 1303, 1285, 1248, 1200, 1011, 841, 722, 760, 650 (C–Br), 582. ^1H NMR (DMSO-d_6) δ: 9.63 (s, 2H, NH), 7.68 (d, 2H, ArH), 7.57 (d, 2H, ArH), 7.30 (t, 2H, ArH), 7.26 (s, 2H, ArH), 7.20 (t, 2H, ArH), 4.43 (s, 4H, O=CCH_2Cl), 4.12 (t, 4H, OCH_2), 3.21 (t, 4H, SCH_2). ^{13}C NMR (DMSO-d_6) δ: 164.88 (C=O), 148.10, 141.18, 137.06, 131.84, 127.73, 126.09, 124.17, 118.91, 114.72 (ArC), 68.00 (OCH_2), 43.09 (O=CCH_2Cl), 32.87 (SCH_2). MS (LC-MS/MS) *m/z*: 724 $[M+1]^+$.

*2.2. 27,28-Dibromo-9,10,12,13,23,24,31,32-octahydro-5H,15H-tribenzo[b,h,w][1,4,7,13,16,19,25,10,22]dioxapentathiadiazacycloheptacosine-6,16(7H,17H)-dione (**5**)*

A solution of 2,2′-dithioethanthiol **4** (2.69 g, 17.45 mmol) in dry dimethyl formamide (315 ml) in a dropping funnel and a hot solution of compound **3** (12.61 g, 17.45 mmol) in dry dimethyl formamide (315 ml) in a dropping funnel were added simultaneously under stirring and dry inert gas to dry DMF (315 ml) containing anhydrous sodium carbonate (7.4 g, 69.8 mmol) over 2.5 h at room temperature and during the addition, the dropping funnel containing a solution of compound **3** was heated to prevent precipitation. After addition was completed, reaction mixture was stirred at room temperature for another 2 h. The reaction was monitored by thin layer chromatography [pentane:ethyl acetate (6:4)]. At the end of this period, the mixture was filtered off and the filtrate was evaporated under reduced pressure to dryness. Water (500 ml) was added to the crude product and stirred at room temperature for 1 h and then filtered off. The white precipitate was washed with ethanol and diethyl ether and then dried in vacuum. Yield: 11.4 g (81%), mp 183–184 °C. Anal. calcd. for $C_{30}H_{32}Br_2N_2O_4S_5$: C, 44.78; H, 4.01; N, 3.48%. Found: C, 44.31; H 4.22; N, 3.25. IR (KBr disc) ν_{max}/cm^{-1}: 3266 (–NH), 3057 (CH_{Ar}), 2924 (CH_3), 1664 (C=O), 1578, 1515, 1491, 1415, 1351, 1298, 1246, 1190, 1009, 850, 762, 748, 652 (C–Br), 530. ^1H NMR (DMSO-d_6) δ: 9.66 (s, 2H, NH), 7.78 (d, 2H, ArH), 7.55 (d, 2H, ArH), 7.28 (t, 2H, ArH), 7.23 (s, 2H, ArH), 7.18 (t, 2H, ArH), 4.14 (t, 4H, OCH_2), 3.43 (s, 4H, O=CCH_2), 3.18 (t, 4H, SCH_2), 2.80 (m, 8H, SCH_2). ^{13}C NMR (DMSO-d_6) δ: 167.84 (C=O), 148.23, 132.73, 137.97, 128.07, 127.17, 125.40, 123.35, 119.32, 114.83 (ArC), 68.30 (OCH_2), 35.45 (O=CCH_2S), 33.41, 32.31, 30.85 (SCH_2). MS (LC-MS/MS) *m/z*: 805 $[M+1]^+$.

*2.3. 27,28-Dibromo-6,7,9,10,12,13,16,17,23,24,31,32-dodecahydro-5H,15H-tribenzo[b,h,w] [1,4,7,13,16,19,25,10,22]dioxapentathiadiazacycloheptacosine (**6**)*

A solution of compound **5** (6.12 g, 7.62 mmol) in dry THF (300 ml) was heated and stirred under argon until compound **5** was dissolved, and the mixture was allowed to cool to room temperature and then placed in an ice salt bath. $NaBH_4$ (2.62 g, 18.56 mmol) was added to stirring mixture at 0–5 °C under argon. Boron trifluoride ethyl etherate (11.89 g, 83.79 mmol) was added dropwise through a dropping funnel to stirring mixture over a period during which the temperature of the solution was kept at 0–5 °C, and then stirring was continued at room temperature overnight. The reaction was monitored by thin layer chromatography [Pentane:ethyl acetate (6:4)]. At the end of this period, the mixture was filtered and filtrate was neutralized with aqueous sodium hydroxide (15%) at 0–5 °C until the pH value of the mixture was to 8–9. Tetrahydrofuran was evaporated under reduced pressure and the residue was filtered off, washed with water, ethanol and diethyl ether and then dried in vacuum. The crude product was purified by chromatography on silica gel. The elution was carried out with dichloromethane:pentane (9:1). The product was obtained as white solid. Yield: 3.1 g (51%), mp 102–103 °C. Anal. calcd. for $C_{30}H_{36}Br_2N_2O_2S_5$: C, 46.39; H, 4.67; N, 3.61%. Found: C, 46.12; H, 4.33; N, 3.43. IR (KBr disc) ν_{max}/cm^{-1}: 3346 (–NH), 3058, 3023 (CH_{Ar}), 2959, 2919, 2875 (CH_3), 1593, 1494, 1463, 1425, 1353, 1248, 1210, 1195, 1006, 879, 848, 746, 738, 654 (C–Br), 540. ^1H NMR ($CDCl_3$) δ: 7.46 (d, 2H, ArH), 7.24 (t, 2H, ArH), 6.96 (s, 2H, ArH), 6.65 (t, 2H, ArH), 6.61 (d, 2H, ArH), 5.53 (s, 2H, NH), 4.06 (t, 4H, OCH_2), 3.35 (t, 4H, NCH_2), 3.07 (t, 4H, SCH_2), 2.81 (t, 4H, SCH_2), 2.68 (m, 8H, SCH_2). ^{13}C NMR ($CDCl_3$) δ: 148.83, 148.17, 137.10, 130.78, 118.70, 117.12, 116.20, 115.37, 110.21 (ArC), 68.03 (OCH_2), 42.39 (NCH_2), 33.58, 32.29, 32.12, 31.69 (SCH_2). MS (LC-MS/MS) *m/z*: 777 $[M+1]^+$.

*2.4. 27,28-Dicyano-9,10,12,13,23,24,31,32-octahydro-5H,15H-tribenzo[b,h,w][1,4,7,13,16,19, 25,10,22]dioxapentathiadiazacycloheptacosine-6,16(7H,17H)-dione (**7**)*

A Schlenk tube was charged with the precursor dibromo compound **5** (5 g, 6.28 mmol), CuCN (1.7 g, 18.65 mmol) and dry dimethyl formamide (75 ml) under argon atmosphere at room temperature. The reaction mixture was held and stirred at 160 °C for 21 h in oil bath. During that time, the reaction mixture became dark brown. Heating was stopped and the reaction mixture was allowed to cool to room temperature, opened to air and diluted with aqueous NH_4OH (200 ml) and air was passed through the solution for 24 h. During the period, the solution became dark blue and a brown precipitate was formed. The reaction mixture was filtered and washed with dilute aqueous NH_4OH (10%) and with water until the filtrate was neutral and then dried. The obtained crude product was purified by silica gel column chromatography. Elution was carried out successively with ethyl acetate. Yield: 3.6 g (83%), mp 180–182 °C. Anal. calcd. for $C_{32}H_{32}N_4O_4S_5$: C, 55.15; H, 4.63; N, 8.04%. Found: C, 54.72; H, 4.77; N, 7.61. IR (KBr disc) ν_{max}/cm^{-1}: 3263 (–NH), 3058 (CH_{Ar}), 2968, 2925 (CH_3), 2228 (C≡N), 1659 (C=O), 1578, 1508, 1434, 1357, 1285, 1212, 1093, 761, 748, 661, 530. ^1H NMR (DMSO-d_6) δ: 9.71 (s, 2H, NH), 7.76 (d, 2H, ArH), 7.65 (s, 2H, ArH), 7.57 (d, 2H, ArH), 7.27 (t, 2H, ArH), 7.15 (t, 2H, ArH), 4.26 (t, 4H, OCH_2), 3.43 (s, 4H, $O{=}CCH_2$), 3.24 (t, 4H, SCH_2), 2.80 (m, 8H, SCH_2). ^{13}C NMR (DMSO-d_6) δ: 167.82 (C=O), 151.10, 137.81, 132.67, 126.96, 128.03, 125.30, 123.38, 117.38 (ArC), 116.03 (C≡N), 107.64 (ArC), 68.14 (OCH_2), 35.22 ($O{=}CCH_2S$), 32.71, 32.09, 30.59 (SCH_2). MS (LC-MS/MS) *m/z*: 697 $[M+1]^+$.

2.5. 6,7,9,10,12,13,16,17,23,24,31,32-Dodecahydro-5H,15H-tribenzo[b,h,w]1,4,7,13,16,19, 25,10,22] dioxapentathidiazacycloheptacosine-27,28-dicarbonitrile (8)

A Schlenk tube was charged with the precursor dibromo compound **6** (2.5 g, 3.22 mmol), CuCN (0.88 g, 9.66 mmol) and dry dimethyl formamide (40 ml) under argon atmosphere at room temperature. The reaction mixture was held and stirred at 155 °C for 24 h in oil bath. During that time, the reaction mixture became dark brown. Heating was stopped and the reaction mixture was allowed to cool to room temperature, opened to air and diluted with aqueous NH_4OH (300 ml) and air was passed through the solution for 24 h. During the period, the solution became dark blue and a brown precipitate was formed. The reaction mixture was filtered and washed with dilute aqueous NH_4OH (10%) and with water until the filtrate was neutral and then dried. The obtained crude product was purified by silica gel column chromatography. The elution was carried out successively with dichloromethane:ethyl acetate (9.7:0.3). The product obtained as white solid. Yield: 0.455 g (21%), mp 137–138 °C. Anal. calcd. for $C_{32}H_{36}N_4O_2S_5$: C, 57.45; H, 5.42; N, 8.37%. Found: C, 56.97; H, 5.48; N, 8.03. IR (KBr disc) ν_{max}/cm^{-1}: 3308 (–NH), 3057, 3023 (CH_{Ar}), 2938, 2900 (CH_3), 2230 (C≡N), 1593, 1494, 1423, 1357, 1284, 1222, 1213, 1093, 977, 890, 742, 629, 532. ^1H NMR ($CDCl_3$) δ: 7.46 (d, 2H, ArH), 7.26 (t, 2H, ArH), 6.92 (s, 2H, ArH), 6.68 (t, 2H, ArH), 6.65 (d, 2H, ArH), 5.48 (s, 2H, NH), 4.15 (t, 4H, OCH_2), 3.37 (t, 4H, NCH_2), 3.10 (t, 4H, SCH_2), 2.83 (t, 4H, SCH_2), 2.68 (m, 8H, SCH_2). ^{13}C NMR ($CDCl_3$) δ: 151.51, 148.71, 137.20, 131.20, 117.23, 116.20, 115.51 (ArC), 115.44 (C≡N), 110.41, 108.77 (ArC), 67.97 (OCH_2), 42.13 (NCH_2), 32.40, 32.26, 32.02, 31.76 (SCH_2). MS (LC–MS/MS) *m/z*: 669 $[M+1]^+$.

2.6. Metal-free phthalocyanine (9)

Compound **7** (0.4 g, 0.574 mmol) and dry 2-(dimethylamino)ethanol (4.5 ml) were placed under argon atmosphere in a standard Schlenk tube. The reaction mixture was refluxed and stirred under argon for 24 h. After cooling to room temperature, the green mixture was diluted with ethanol (10 ml) until the crude product was precipitated and the product was filtered off, washed with diethyl ether and dried in vacuum. The solid product was purified by column chromatography [silica gel (tetrahydrofuran:methanol) (9:1)]. Yield: 0.046 g (11.47%), mp 133–135 °C. Anal. calcd. for $C_{128}H_{130}N_{16}O_{16}S_{20}$: C, 55.11; H, 4.70; N, 8.03%. Found: C, 54.78; H, 5.07; N, 7.68. IR (KBr disc) ν_{max}/cm^{-1}: 3294 (–NH), 3057 (CH_{Ar}), 2916, 2865, 2821, 2777 (CH_3), 1664 (C=O), 1606, 1577, 1510, 1478, 1433, 1414, 1378, 1272, 1197, 1099, 1063, 1034, 1013, 857, 746. ^1H NMR ($CDCl_3$) δ: 9.70 (s, 8H, NH), 7.71–6.49 (m, 40H, ArH), 4.13 (t, 16H, OCH_2), 3.41(s, 16H, $O{=}CCH_2$), 3.13 (t, 16H, SCH_2), 2.77 (m, 32H, SCH_2). UV–vis [chloroform:pyridine (1:1)] λ_{max} (nm) ($\log \varepsilon$) 304 (4.99), 623 (3.40), 686 (3.84). MS (LC–MS/MS) *m/z*: 2790 $[M+1]^+$.

2.7. Metal-free phthalocyanine (10)

Compound **8** (0.2 g, 0.299 mmol) and dry 2-(dimethylamino)ethanol (2.25 ml) were placed under argon atmosphere in a standard Schlenk tube. The reaction mixture was refluxed and stirred under argon for 24 h. After cooling to room temperature, the green mixture was diluted with ethanol (10 ml) until the crude product was precipitated and the product was filtered off, washed with diethyl ether and dried in vacuum. The solid product was purified by column chromatography [silica gel (dichloromethane:methanol) (9.9:0.1)]. Yield: 0.045 g (22.8%), mp 120–121 °C. Anal. calcd. for $C_{128}H_{146}N_{16}O_8S_{20}$: C, 57.41; H, 5.50; N, 8.37%. Found: C, 56.99; H, 5.88; N, 7.81. IR (KBr disc) ν_{max}/cm^{-1}: 3369 (–NH), 3064 (CH_{Ar}), 2918, 2866 (CH_3), 1709, 1587, 1500, 1449, 1425, 1378, 1277, 1203, 1012, 744. ^1H NMR ($CDCl_3$) δ: 7.42 (d, 8H, ArH), 7.14 (t, 8H, ArH), 7.10 (s, 8H, ArH), 6.57 (m, 16, ArH), 5.46 (s, 8H, NH), 4.11 (t, 16H, OCH_2), 3.27 (t, 16H, NCH_2), 3.05 (t, 16H, SCH_2), 2.74 (t, 16H, SCH_2), 2.61 (m, 32H, SCH_2). UV–vis (chloroform) λ_{max} (nm) ($\log \varepsilon$) 250 (5.05), 314 (4.77), 362 (4.45), 446 (4.28), 671 (4.12), 707 (4.16), 767 (4.14). MS (LC–MS/MS) *m/z*: 2678 $[M+1]^+$.

2.8. Nickel (II) phthalocyanine (11)

A mixture of compound **7** (0.3 g, 0.431 mmol), anhydrous $NiCl_2$ (0.014 g, 0.107 mmol) and quinoline (1.3 ml) was heated and stirred at 190 °C for 8 h in a Schlenk tube under argon. After cooling to room temperature, the dark green mixture was diluted with ethanol (10 ml). The product was filtered off, washed with the hot ethanol and diethyl ether, the green solid was then treated with CH_2Cl_2 and then dried in vacuum. Yield: 0.05 g (16.6%), mp > 300 °C. Anal. calcd. for $C_{128}H_{128}N_{16}NiO_{16}S_{20}$: C, 53.97; H, 4.60; N, 7.87%. Found: C, 53.62; H, 4.81; N, 7.49. IR (KBr disc) ν_{max}/cm^{-1}: 3288 (−NH), 3057 (CH_{Ar}), 2918 (CH_3), 1677 (C=O), 1605, 1577, 1511, 1477, 1432, 1273, 1203, 1101, 1062, 1011, 751. ^{1}H NMR (DMSO-d_6) δ: 9.65 (s, 8H, NH), 7.70−6.50 (m, 40H, Ar−H), 4.26 (t, 16H, OCH_2), 3.41 (s, 16H, $O{=}CCH_2$), 3.15 (t, 16H, SCH_2), 2.77 (m, 32H, SCH_2). UV−vis (pyridine) λ_{max} (nm) (log ε) 306 (4.80), 402 (4.44), 607 (4.09), 643 (4.08), 671 (4.34). MS (LC−MS/MS) *m/z*: 2847 $[M+1]^+$.

2.9. Nickel (II) phthalocyanine (**12**)

A mixture of compound **8** (0.225 g, 0.338 mmol), anhydrous $NiCl_2$ (0.011 g, 0.084 mmol) and quinoline (1.12 ml) was placed in a well-stopped Schlenk tube under argon atmosphere. The mixture was heated and stirred gently to 195 °C and then refluxed at this temperature for 7.5 h. The crude product was cooled to room temperature and ethanol (10 ml) was added to this mixture. The resulting dark green precipitate was filtered off and then refluxed four times with ethanol and dichloromethane and then filtered off. Finally dark green metallophthlocyanine was obtained by washing with ethanol and diethyl ether. Then it was dried in vacuum. Yield: 0.014 g (6.2%), mp 141−143 °C. Anal. calcd. for $C_{128}H_{144}N_{16}NiO_8S_{20}$: C, 56.18; H, 5.38; N, 8.19%. Found: C, 56.20; H, 5.25; N, 7.85. IR (KBr disc) ν_{max}/cm^{-1}: 3364 (−NH), 3062 (CH_{Ar}), 2915 (CH_3), 1586, 1494, 1446, 1422, 1372, 1278, 1201, 1099, 749. ^{1}H NMR ($CDCl_3$) δ: 7.41−7.16 (m, 24H, ArH), 6.64 (m, 16H, ArH), 5.61 (br, 8H, NH), 4.11 (t, 16H, OCH_2), 3.32 (t, 16H, NCH_2), 2.98 (t, 16H, SCH_2), 2.67 (m, 48H, SCH_2). UV−vis (chloroform) λ_{max} (nm) (log ε) 248 (5.03), 290 (4.86), 311 (4.83), 401 (4.38), 617 (4.15), 677 (4.46). MS (LC−MS/MS): *m/z* 2733 $[M-1]^+$.

3. Result and discussion

The preparation of the target metal-free phthalocyanines **9**, **10** and metallophthalocyanines **11**, **12** is shown in Scheme 1. The structures of novel compounds were characterized by a combination of elemental analysis and ^{1}H NMR, ^{13}C NMR, IR, UV−vis and MS spectral data. 1,2-Bis(2′-aminophenylsulfonylethoxy)-4,5-dibromobenzene **1** was synthesized as described according to reported procedure [22]. Reaction of 1,2-bis (2′-aminophenylsulfonylethoxy)-4,5-dibromobenzene **1** with 2.5 equivalents of chloroacetic anhydride **2** in dichloromethane at 0−5 °C under argon atmosphere afforded 2-chloro-*N*-{2-[2-(4,5-dibromo-2-{2-[2-(2-chloro-acetylamino)-phenylsulfonyl]-ethoxy}-phenoxy)-ethylsulfonyl]-phenyl}-acetamide **3** in 77% yield. In the IR spectrum of compound **3**, the disappearance of $-NH_2$ vibrations after introduction of amide function, and presence of C=O vibrations and free −NH stretching vibrations at 1678 and 3317, 3278 cm^{-1} confirmed the proposed structure. In the ^{1}H NMR spectrum of compound **3**, the singlet at $\delta = 4.43$ ppm corresponded to methylene protons being in between C=O and Cl groups. The protons of −NH group were observed at $\delta = 9.66$ ppm as a singlet. The C=O group of compound **3** gave a carbon resonance at $\delta = 164.86$ ppm in the ^{13}C NMR spectrum of compound **3**. The formation of compound **3** was also supported by the presence of the characteristic molecular ion peak at $m/z = 724$ $[M+1]^+$ in the mass spectrum obtained using the LS−MS/MS technique.

The synthesis of macrocyclic compound **5** was performed by adding a solution of 2,2′-dithioethanthiol **4** and a solution of compound **3** simultaneously into a DMF solution containing Na_2CO_3 as a template agent at room temperature, affording the macrocycle 27,28-dibromo-9,10,12,13,23, 24,31,32-octahydro-5*H*,15*H*-tribenzo[*b*,*h*,*w*][1,4,7,13,16,19,25,10,22]dioxapentathiadiazacyclo-heptacosine-6,16(7H,17H)-dione **5** in 81% yield. The yield of macrocyclization reaction was rather high. This can be attributed to the probable hydrogen bonding between the amide oxygen atoms of the bis(α-chloroamide) and the amine hydrogen atoms of the bis-secondary amines and the template effect of sodium cations [24]. The IR spectrum of compound **5** is almost identical to that of compound **3** with small changes in wavenumbers. The formation of macrocycle was confirmed by the appearance of a new resonance for SCH_2 protons at $\delta = 2.80$ ppm as multiplet in the ^{1}H NMR spectrum of compound **5** in DMSO-d_6. The ^{13}C NMR spectrum of compound **5** indicated two new resonance for SCH_2 carbons between $\delta = 35.45$ and 30.85 ppm when compared with the ^{13}C NMR spectrum of compound **3**. The mass spectrum of compound **5** displayed the expected molecular ion peak at $m/z = 805$ $[M+1]^+$.

The reduced macrocycle 27,28-dibromo-6,7,9,10,12,13,16, 17,23,24,31,32-dodecahydro-5*H*,15*H*-tribenzo[*b*,*h*,*w*][1,4,7, 13,16,19,25,10,22]dioxapentathiadiazacycloheptacosine **6** was obtained from the precursor bisamide macrocyclic compound **5** by using sodium borohydride−boron trifluoride ethyl etherate in dry THF at 0−5 °C under argon atmosphere. Purification by column chromatography [silica gel, dichloromethane:pentane (9:1)] gave compound **6** in 51% yield. Analytical and spectroscopic data of compound **6** clearly confirmed the success of the reduction reaction. In the IR spectrum of compound **6**, the stretching vibrations belonging to C=O group in the precursor compound **5** were absent after the reduction reaction. The disappearance of the singlets at $\delta = 9.66$ and 3.43 ppm in the bisamide macrocyclic compound **5** and appearance of a singlet at $\delta = 5.53$ for −NH protons and a triplet at $\delta = 3.35$ ppm for $-NCH_2$ protons confirmed the proposed structure. The disappearance of the C=O signals, along with the appearance of a new peak at $\delta = 42.39$ ppm concerning NCH_2 group in the ^{13}C NMR spectrum of compound **6** can be taken as a clear evidence for the formation of reduced macrocycle. The expected molecular ion peak for compound **6** was observed at $m/z = 777$ $[M+1]^+$.

The dibromo derivatives **5** and **6** were converted into dicyano derivatives **7** and **8** by refluxing in dry DMF with three equivalents of CuCN according to the Rosenmund von Braun reactions [25,26]. Final purification by column chromatography [silica gel, ethyl acetate or dichloromethane:ethyl acetate(9.7:0.3)] afforded compounds **7** and **8** in 83% and 21% yield, respectively. However, the cyanation of compound **6** employing the Rosenmund von Braun reactions did not give very high yield, probably because of the localized electron pair of the secondary amine in the crown subunit. The delocalisation of the electron pair of the nitrogen atom by the amide function enables the cyanation process to proceed easily in the case of compound **5** [27]. In the IR spectra of compounds **7** and **8**, an intense IR absorption bands at 2228 and 2230 cm^{-1}, respectively, corresponded to the C≡N groups. In the ^1H NMR spectra of compounds **7** and **8**, the aromatic protons at cyano-substituted benzene were observed at $\delta = 7.65$ and 6.92 ppm, respectively. The ^{13}C NMR spectra of compounds **7** and **8** also indicated the presence of nitrile carbons at $\delta = 116.03$ and 115.44 ppm, respectively. The rest of the spectra of these compounds were closely similar to those of the precursors. In the LC–MS mass spectrum of compounds **7** and **8**, the presence of characteristic molecular ion peaks at $m/z = 697$ $[M+1]^+$ and 669 $[M+1]^+$, respectively, confirmed the proposed structures.

The cyclotetramerization of the phthalonitrile derivatives **7** and **8** to the metal-free phthalocyanines **9** and **10** was accomplished in dry 2-(dimethylamino)ethanol at reflux temperature for 24 h under argon in a Schlenk tube to afford compounds **9** and **10** in 11% and 22% yield, respectively, as dark green amorphous solids, after purification by column chromatography using silica gel [tetrahydrofuran:methanol (9:1) for **9** and dichloromethane:methanol (9.9:0.1) for **10**]. The ^1H NMR spectra of compounds **9** and **10** displayed broad signals, and the inner core protons of the H_2Pcs could not be observed due to strong aggregation of molecules [28]. The disappearance of the C≡N stretching vibrations on the IR spectra of compounds **7** and **8** also suggested the formation of compounds **9** and **10**. In addition to the results of elemental analysis, the mass spectra were also determined. The molecular ion peaks at $m/z = 2790$ $[M+1]^+$ for compound **9** and 2678 $[M+1]^+$ for compound **10** were found by LC–MS/MS technique for metal-free phthalocyanines.

The preparation of metallophthalocyanines **11**, **12** from dicyano compound were carried out in a Schlenk system in quinoline at reflux temperature for 8 h and 7 h, respectively. A common feature of the ^1H NMR spectra of the Ni(II) phthalocyanines **11** and **12** is the broad absorption when compared with that of the precursor dicyano compounds. In the IR spectra of compounds **11** and **12**, the disappearance of the strong C≡N stretching vibrations of precursors **7** and **8** can be taken as clear evidence for metallophthalocyanine formation. This is also supported by the presence of the characteristic molecular ion peaks in the mass spectra of compound **11** at $m/z = 2847$ $[M+1]^+$ and of compound **12** at 2733 $[M-1]^+$.

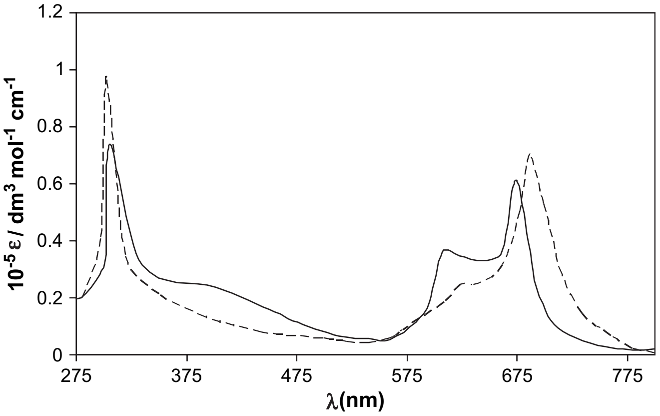

Fig. 1. UV–vis spectra of compounds **9** (dotted line) and **11** (solid line).

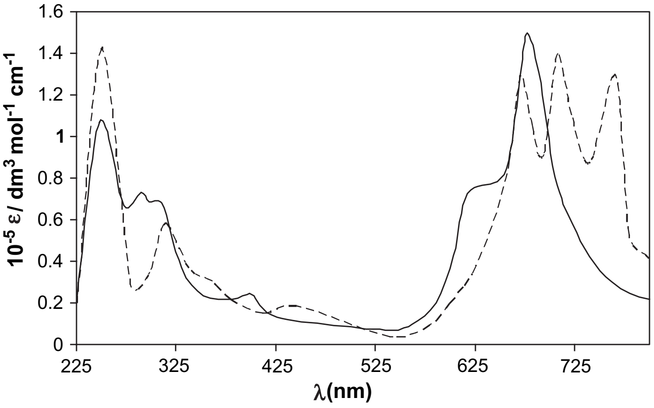

Fig. 2. UV–vis spectra of compounds **10** (dotted line) and **12** (solid line).

The UV–vis spectra of compounds **9** and **10** at room temperature are displayed in Figs. 1 and 2. The metal-free phthalocyanines **9** and **10** displayed a typical electronic spectrum with two significant absorption bands, one of which in the visible region, corresponding to the Q bands, at λ_{max} 686, 623 and 767, 707, 671 and the other B bands in the UV region at λ_{max} 302 and 314, 250 nm, respectively. The monomeric species with D_{2h} symmetry show two intense absorptions at around 700 nm [29–31]. On the other hand such split Q band absorptions are due to the π–π* transitions of this fully conjugated 18π electron systems [32,33].

The UV–vis absorption spectra of the metallophthalocyanines **11** and **12** show intense Q band absorptions at λ_{max} 671 and 667 nm (Figs. 1 and 2), with weaker absorptions at λ_{max} 643, 607 and 617 nm, respectively. The single Q bands in metallo derivatives and the split form in their metal-free derivatives are characteristic [34]. The result is typical of metal complexes of substituted and unsubstituted phthalocyanine with D_{4h} symmetry [35]. When Ni(II) metal-ions are included in the phthalocyanine core of compounds **9** and **10**, the average position of the Q bands of the resulting metallophthalocyanines **11** and **12** is slightly shifted to blue with respect to the parent metal-free phthalocyanines. B band absorptions of the nickel(II) phthalocyanines **11** and **12** were observed at λ_{max} 402, 306 and 401, 314, 290 nm, respectively, as expected.

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