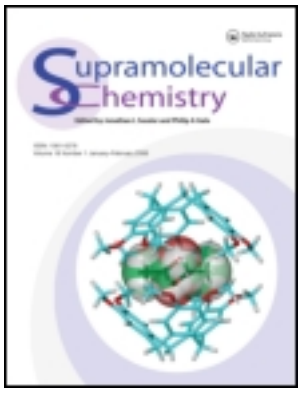


Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsch20

Synthesis and characterisation of new porphyrazinato magnesium containing macrobicyclic moieties

Nilgün Kabay [a] & Yaşar Gök [a]

[a] Department of Chemistry, Pamukkale University, Kinikli-Denizli, Turkey

Available online: 01 Jun 2011

To cite this article: Nilgün Kabay & Yaşar Gök (2011): Synthesis and characterisation of new porphyrazinato magnesium containing macrobicyclic moieties, Supramolecular Chemistry, 23:8, 587-592

To link to this article: http://dx.doi.org/10.1080/10610278.2011.575468

Supramolecular Chemistry
Vol. 23, No. 8, August 2011, 587–592

Synthesis and characterisation of new porphyrazinato magnesium containing macrobicyclic moieties

Nilgün Kabay and Yaşar Gök*

Department of Chemistry, Pamukkale University, Kinikli-Denizli, Turkey

(*Received 17 January 2011; final version received 21 March 2011*)

Novel porphyrazinato magnesium (MgPz) containing symmetrically four diaza-tetrathia-macrobicycles on peripheral positions was synthesized by the cyclotetramerisation reaction of 5,8,16,23-tetrathia-1,12-diazabicyclo[9.7.7]pentacosane-6-en-6,7-dicarbodinitril (**9**), which was prepared by sequence reaction of *N*-tosyl-bis[3-bis(tosyloxypropyl)] amine (**1**) and disodium *cis*-1,2-dicyano-1,2-ethylenedithiolate (**8**). Elemental analysis, IR, NMR, MS and UV–vis data confirmed the ability of bulky cryptand moieties to induce steric isolation of Pz core in the solid state.

Keywords: cryptand; macrocyclisation; porphyrazine; magnesium complex; template effect

Introduction

Porphyrinic macrocycles are the subject of great interest in many directions such as industrial dyes and pigments, growth of micro-organisms (*1*), electrocatalysts (*2*), electrochromic displays (*3*), photodynamic therapy (*4*), chemical sensors, Langmuir–Blodgett films, liquid crystals and non-linear optics, including their applications in material science (*5*). Porphyrazines are similar to phthalocyanines so they can also be used in similar applications as phthalocyanines. In contrast, the similarities, prophyrazines and their derivatives such as amino-porphyrazines, porphyrazinols and porphyrazinethiolates have been less studied since their first synthesis, which took place almost 60 years ago (*6*). Recently, a variety of porphyrazines have been obtained, which show interesting and novel physico-chemical properties, including fluorescence and inter-system crossing properties (*7*). Porphyrazine derivatives, which contain soft S donör atoms, play an important role in affecting the solid–state interactions. The first synthesis of crown-fused porphyrazines has been reported by group Hoffman and Nolte (*8*). The coordination chemistry, agregation and electrical properties of these compounds have been investigated (*9*). Dithiacrowned porphyrazine offers an advantage over its phthalocyanine counterparts in which two S atoms in each crown moiety are in direct conjugation with 18 π-electron core of the porphyrazine (*10*).

A significant disadvantage of porphyrazines is their low solubility in common organic solvents. This disadvantage can be abolished by connecting bulky or long chain groups such as alkyl, alkoxy, sulfo and macrocyclic units with the peripheral sides of porphyrazines (*11*). In addition, the attachment of oxacrown, azacrown or polyaza–polythia macrocycles to porphyrazine has received considerable attention as they are suitable for enhancing cation selectivity, cation binding capability and complex stability through changing the numbers and types of macrocycle donors (*12*).

Cryptands are formed by linking two units together through two bridges and consist of three cavities containing two lateral circular cavities as in central cavity. A very active current research activity in this area led to the development of numerous procedures for effecting macrobicylisation such as template effects and high dilution techniques (*13*). These kinds of compounds show extraordinary solubility in common organic solvents and selectivity towards alkali and alkaline earth metal cations leading to complexation in aqueous and organic solutions (*14*).

Our studies on porphyrazine systems carrying peripherally mixed donor such as sulphur or nitrogen macrocycles have been extensively directed towards the synthesis and characterisation of novel porphyrazine macrocycles (*15*). Herein, we report the first synthesis of porphyrazinato magnesium (MgPz) bearing macrobicyclic substituents in peripheral positions.

Experimental

General

All reactions were performed using oven-dried glassware under argon atmosphere. ^{1}H and ^{13}C NMR spectra were determined on a Varian Mercury 200-NMR spectrometer. Chemical shifts for ^{1}H NMR are reported in parts per million and calibrated to TMS. Infrared spectra were recorded in

*Corresponding author. Email: gyasar@pau.edu.tr

ISSN 1061-0278 print/ISSN 1029-0478 online

DOI: 10.1080/10610278.2011.575468
http://www.informaworld.com

Perkin–Elmer Spectrum One spectrometer. Mass spectra were measured on micrOTOF (Bruker, Massachusetts, USA) and Micromass Quattro Ultima LC-MS/MS spectrometers. The elemental analyses were performed on a Costech ECS 4010 instrument. UV–vis spectra were measured using Shimadzu UV-1601 spectrophotometer. Melting points were determined on an electrothermal apparatus and are uncorrected. *N*-Tosylbis[3-(tosyloxy)propyl)]amine (*16*) and 1,10-diiodo-5,6-dicyano-4,7-dithia-6-decene (*17*) were prepared according to the methods described in the literature. Other reagents were commercially available and were used without further purification unless otherwise noted. All solvents were dried and purified according to the standard procedure before use (*18*).

Synthesis

*Synthesis of N-tosylbis(3-iodopropyl)amine (**2**)*

A solution of **1** (3.93 g, 6.6 mmol) in dry acetone (25 ml) was added to a solution of dry NaI (6 g, 40 mmol) in dry acetone (60 ml) in a round-bottom two-necked flask under argon atmosphere. The reaction mixture was refluxed and stirred for 3 h. The reaction was monitored by a thin layer chromatography (TLC) [silica gel (chloroform)]. At the end of this period, the reaction mixture was filtered off, washed with dry acetone and then evaporated to dryness under reduced pressure. The pale yellow crude product was crystallised from methanol. Yield 81%, 2.74 g; mp 84–85°C. FT-IR (KBr disc, cm^{-1}): 3033, 2932–2863, 1595, 1455, 1336, 1162, 913, 715, 653, 575.^{1}H NMR (200 MHz, $CDCl_3$): δ 7.71 (d, 2H, ArCH), 7.38 (m, 2H, Ar–CH), 3.18 (m, 8H, I–CH_2, N–CH_2), 2.40 (s, 3H, CH_3), 2.10 (m, 4H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ 141.32 (ArCH), 133.49 (ArCH), 127.54 (ArCH), 124.90 (ArCH), 47.49 (I–CH_2), 30.29 (NCH_2), 29.27 (CH_2), 19.24 (CH_3). Elemental anal. calcd: C, 30.77; H, 3.75, N, 2.76. Found: C, 30.88; H, 3.60; N, 2.84.MS (ES): *m/z*:508 $[M + 1]^+$, 530 $[M + Na]^+$.

*Synthesis of N-tosylbis(3-bromopropyl)amine (**3**)*

Dry NaBr (8.47 g, 82 mmol) was added to a solution of **1** (9.57 g, 16 mmol) in dry DMF(60 ml) under argon atmosphere. The reaction mixture was stirred in an oil bath at 120°C for 5.5 h. The viscous product was poured into a rapidly stirred ice–water mixture (350 ml, 1:1). The white solid product was filtered off, washed with cold water and dried *in vacuo* over P_2O_5. The white crude product was crystallised from methanol. Yield 77%, 5.09 g; mp 79–80°C. FT-IR (KBr disc, cm^{-1}): 3032, 2940–2870, 1596, 1491, 1457, 1337, 1158, 909, 720, 653, 571. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.75 (d, 2H, ArCH), 7.36 (m, 2H, ArCH), 3.42 (q, 4H, Br–CH_2), 3.22 (q, 4H, N–CH_2), 2.42 (s, 3H, CH_3), 2.14 (m, 4H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ 143.89 (ArCH), 135.98 (ArCH), 130.09 (ArCH), 127.49 (ArCH), 48.16 (Br–CH_2), 32.23 (NCH_2), 30.54 (CH_2), 21.78 (CH_3). Elemental anal. calcd: C, 37.77; H, 4.60; N, 3.39. Found: C, 37.87; H, 4.73; N, 3.21.MS (ES): *m/z* 414.$[M + 1]^+$, 436 $[M + Na]^+$.

*Synthesis of N-tosylbis(3-thioacetoxypropyl)amine (**4**)*

To a solution of **3** (3.10 g, 8 mmol) in a mixture of dichloromethane:acetonitrile (100 ml, 1:1) solid potassium thioacetate (3.66 g, 32 mmol) was added and stirred at 40°C for 72 h. The reaction mixture was monitored by TLC [alumina (chloroform:hexane) (95:5)]. At the end of this period, the oily product was filtered off, washed with dichloromethane and then evaporated to dryness under reduced pressure. Pale brown oily product chromatographed on alumina column [(chloroform:hexane) (95:5)] gave **4** as a viscous pale brown oil. Yield 68%, 2.2 g. FT-IR (NaCl disc, cm^{-1}): 3038, 2927–2870, 1694, 1598, 1451, 1340, 1158, 959, 816, 727, 922.^{1}H NMR (200 MHz, $CDCl_3$): δ 7.65 (d, 2H, ArCH), 7.35 (d, 2H, ArCH), 3.18 (m, 4H, N–CH_2), 2.90 (m, 4H, S–CH_2), 2.42 (s, 3H, CH_3), 2.18 (s, 6H, CH_3), 1.82 (m, 4H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ 195.55 (C═O), 143.47 (ArCH), 135.09 (ArCH), 47.45 (N–CH_2), 30.44 (S–CH_2), 28.74 (CH_2), 26.49 (C–CH_3), 21.49 (CH_3). Elemental anal. calcd: C, 50.62; H, 6.20; N, 3.47. Found: C, 50.47; H, 6.35; N, 3.67.MS (ES): *m/z* 404 $[M + 1]^+$, 421 $[M + H_2O]^+$.

*Synthesis of N-tosylbis(3-mercaptopropyl)amine (**5**)*

Concentrated HCl (7 ml) was added to a solution of **4** (1.6 g, 3.97 mmol) in dry ethanol (70 ml) while refluxed and stirred under argon atmosphere for 24 h and then evaporated to dryness under reduced pressure. The yellow crude product was dissolved in chloroform, washed with water and dried over $MgSO_4$ and then evaporated to dryness. The product **5** was obtained as a white crystalline waxy solid. Yield 90%, 1.1 g. FT-IR (NaCl disc, cm^{-1}): 3030, 2929–2866, 2571, 1598, 1457, 1337, 1157, 1090, 960, 815; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.57 (d, 2H, ArCH), 7.24 (d, 2H, ArCH), 3.10 (m, 4H, N–CH_2), 2.45 (m, 4H, S–CH_2), 2.32 (s, 3H, CH_3), 1.74 (m, 4H, CH_2), 1.42 (s, 2H, SH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 142.95 (ArCH), 135.61 (ArCH), 46.88 (N–CH_2), 32.42 (S–CH_2), 28.85 (CH_2), 21.80 (CH_3). Elemental anal. calcd: C, 48.90; H, 6.58; N, 4.39. Found: C, 49.17; H, 6.42; N, 4.60.MS (ES): *m/z* 320 $[M + 1]^+$.

*Synthesis of N,N′-bistosyl-4,11-diaza,1,9-dithiacyclohexadecane (**6**)*

A solution of **2** (1.27 g, 2.5 mmol) in dry DMF (50 ml) and **5** (0.8 g, 2.5 mmol) in dry DMF (50 ml) was added under

argon atmosphere over a period of 20 h to a stirred suspension of pre-dried Cs_2CO_3 (2.96 g, 9.1 mmol) in dry DMF (250 ml) at 30°C. The reaction mixture was stirred at this temperature for 10 h. The DMF was removed under reduced pressure and the residue dissolved with chloroform. The organic phase was washed with water (30 ml × 3) and dried over $MgSO_4$ and then evaporated under reduced pressure to give a white solid product. The white crude product was crystallised from methanol. Yield 77%, 1.1 g; mp 183–184°C. FT-IR (KBr disc, cm^{-1}): 3031, 2948–2871, 1598, 1460, 1332, 1155, 1091, 929, 814, 728. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.70 (d, 4H, ArCH), 7.32 (d, 4H, Ar–CH), 3.18 (m, 8H, N–CH_2), 2.58–2.45 (m, 8H, S–CH_2), 2.41 (s, 6H, CH_3), 1.95 (m, 8H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ 143.91 (ArCH), 135.72 (ArCH), 130.01 (ArCH), 127.15 (ArCH), 49.45 (N–CH_2), 30.18 (S–CH_2), 29.10 (CH_2), 21.65 (CH_3). Elemental anal. calcd: C, 54.74; H, 6.67; N, 4.91. Found: C, 54.50; H, 6.52; N, 5.10.MS (ES): *m/z*: 571 $[M + 1]^+$.

*Synthesis of 5,13-diaza-1,9-dithiacyclohexadecane (**7**)*

Compound **6** (2.12 g, 3.68 mmol) was added slowly to a stirred suspension of $LiAlH_4$ (1.64 g, 43.2 mmol) in dry of THF (175 ml) under argon atmosphere. After the addition all the reactants, the mixture was stirred under reflux for 72 h. At the end of this period, the reaction mixture was cooled to room temperature, the excess $LiAlH_4$ was destroyed by dropwise addition of 75 ml of THF–H_2O mixture (2:1). The reaction mixture was filtered over Celite and the precipitate was carefully washed with a little CH_2Cl_2. The filtrate was evaporated to dryness under reduced pressure to give a white crystalline waxy solid. Yield 71%, 0.69 g. FT-IR (NaCl disc, cm^{-1}): 3268, 2925–2825, 1474, 1448, 1361, 1262, 1094, 1103, 1053, 936, 839, 805. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.80–2.55 (m, 16H, S–CH_2 and N–CH_2), 1.82 (q, 8H, —CH_2—), 1.51 (s, 2H, NH). ^{13}C NMR (50 MHz, $CDCl_3$): δ 46.58 (N–CH_2), 29.02 (S–CH_2), 28.31 (CH_2). Elemental anal. calcd: C, 54.96; H, 9.92; N, 10.69. Found: C, 55.25; H, 9.74; N, 10.96.MS (ES): *m/z* 263.16 $[M + 1]^+$.

*Synthesis of 5,8,16,24-tetrathia-1,12-diazabicyclo[10.7.7]oktakos-6-en-6,7-dicarbodinitrile (**9**)*

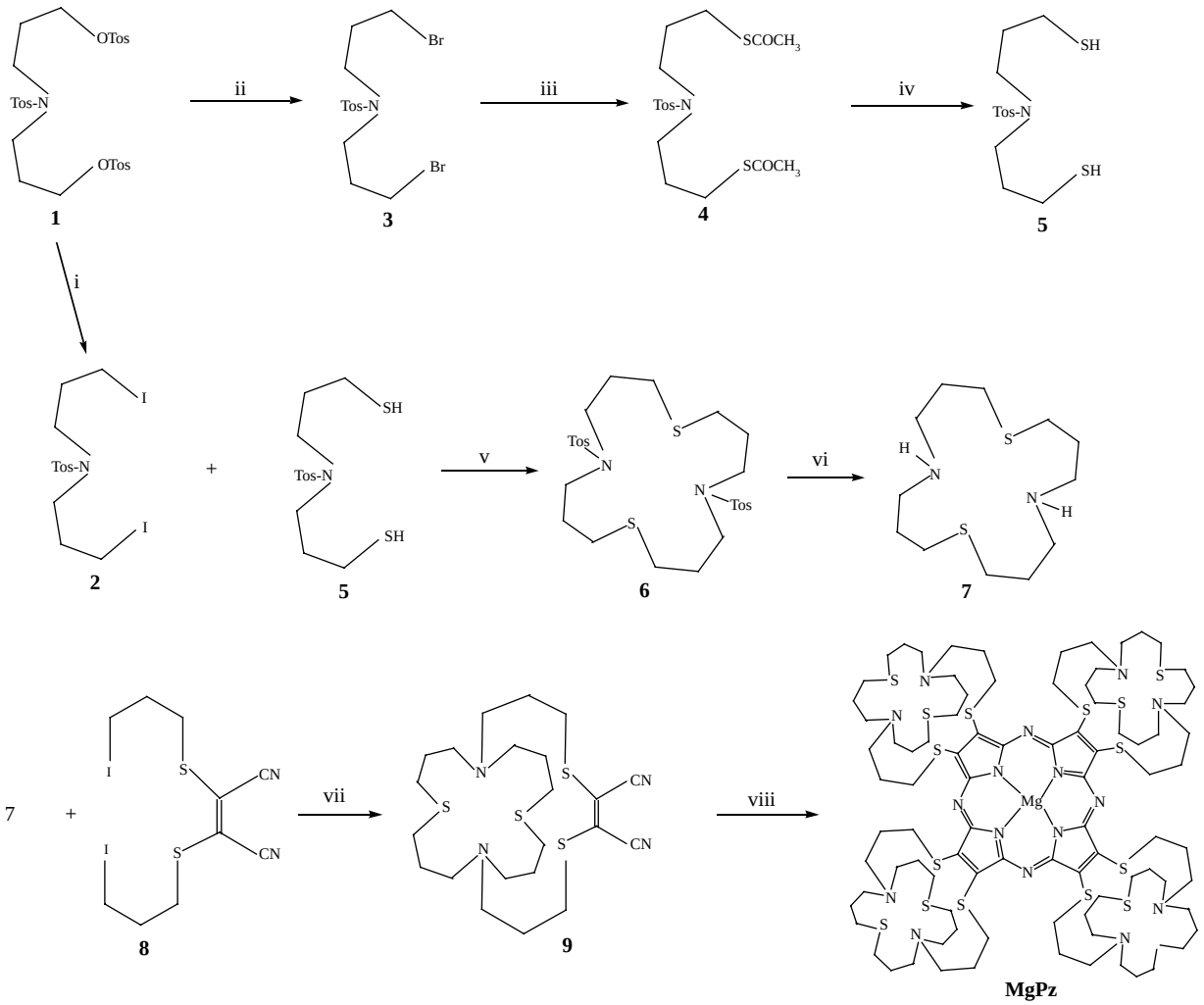
A round-bottom two-necked flask (500 ml) containing pre-dried Cs_2CO_3 (4.90 g, 15.0 mmol) in dry acetonitrile (100 ml) and fitted with a condenser was evacuated, refilled three times with argon and connected to a vacuum line. Under inert conditions, the flask was charged with compound **7** (1.31 g, 5.0 mmol) at room temperature. A solution of **8** (2.38 g, 5.0 mmol) in dry acetonitrile (100 ml) was added to this mixture and the reaction mixture was stirred at 35°C for 72 h. The reaction was monitored by TLC [hexzane:chloroform (2:3)]. At the end of this period, the reaction mixture was filtered off, washed with dry acetonitrile and evaporated to dryness under reduced pressure. The oily crude product was dissolved in chloroform and filtered over Celite and then evaporated to dryness, yielding a dark brown oil that was purified by column chromatography [silica gel (hexane:chloroform) (2:3)]. Yield 62%, 1.51 g. FT-IR (NaCl disc, cm^{-1}): 2951–2810, 2206, 1565, 1461, 1439, 1376, 1278, 1235, 1172, 1113, 1044, 813. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.41 (m, 4H, NCH_2), 2.80 (m, 4H, NCH_2), 2.42 (m, 12H, SCH_2), 2.35 (m, 4H, CH_2), 1.80 (m, 8H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ 121.70 (C═C), 112.79 (C≡N), 56.06 (N–CH_2), 55.17 (N–CH_2), 38.71 (S—C═), 30.06 (SCH_2), 28.51 (CH_2), 27.26 (CH_2). Elemental anal. calcd: C, 54.54; H, 7.44; N, 11.57. Found: C, 54.85; H, 7.09; N, 11.21.MS (ES): *m/z* 485 $[M + 1]^+$.

Synthesis of MgPz

Magnesium turnings (0.02 g, 0.83 mmol) and a small crystal of I_2 were added to dry *n*-butanol (10 ml) under argon atmosphere in a Schlenk tube. The mixture was refluxed and stirred until the magnesium had completely reacted to form a suspension of magnesium butoxide within 24°C. A solution of **9** (0.63 g, 1.3 mmol) in dry *n*-butanol (5 ml) was added to the refluxing suspension. After 24 h, the reaction mixture was filtered while hot. The dark green product was purified by column chromatography technique [silica gel (chloroform:methanol) (95:5)]. Yield 17%, 0.42 g; mp > 300°C. FT-IR (KBr disc, cm^{-1}): 2963–2910, 1632, 1251, 1096, 1022, 864, 801. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.55 (m, 48H, NCH_2), 3.12 (m, 48H, SCH_2), 2.55 (m, 24H, CH_2), 2.07 (m, 24H, CH_2) UV–vis. λ (nm) [10^{-5} ε (mol^{-1} cm^{-1})]: 675 (4.39), 616 (4.00), 506 (3.82), 365 (4.49), 344 (4.50), 245 (4.88). Elemental anal. calcd: C, 53.88; H, 7.35; N, 11.43.Found: C, 53.39; H, 6.99; N, 11.05.MS (ES): *m/z* 2038.4 $[M + 2K]^+$.

Results and discussion

The synthetic routes related to compounds **1**–**9** and MgPz are summarised in Scheme 1. In this work, we reported the synthesis and structural properties of novel MgPz(II). According to Scheme 1, *N*-tosylbis(3-iodopropyl)amine **2** and N-tosyl-bis(3-bromo-propyl) amine **3** were synthesized in yields of 81.1 and 77.2%, respectively. Starting from **3**, *N*-tosylbis(3-thioacetoxypropyl)amine **4** was prepared in 68.1% yield by the reaction of **3** and potassiumthioacetate, and then hydrolysed with concentrated HCl that afforded compound **5** in 90.12% yield. These compounds were characterised by their spectroscopic and analytical data. In the ^{1}H NMR spectrum of **2**–**5**, characteristic signals concerning I–CH_2, Br–CH_2,



Scheme 1. (i) NaI/aceton; (ii) NaBr/DMF; (iii) $KSCOCH_3/CH_2Cl_2$:CH_3CN; (iv) %37 HCl/ethanol; (v) Cs_2CO_3/DMF; (vi) $LiAlH_4$/THF; (vii) Cs_2CO_3/DMF and (viii) Mg/n−butanol/I_2.

S−CH_2, CH_2, SH, CH_3 and tosyl groups were observed at $\delta = 3.18$, 3.42, 2.90–2.45, 2.14–1.74, 1.42 and 2.32 ppm, respectively, as expected. Proton-decouplet ^{13}C NMR spectral data of the same compounds indicated the presence of related carbon atoms. The presence of new signals at $\delta = 195.55$ ppm (**4**) due to C═O groups also supported the formation of proposed compound. In the MS spectra of these compounds, the presence of characteristic molecular ion peaks confirmed the formation of **2**–**5**. Treatment of **2** with *N*-tosylbis(3-thiopropyl)amine (**5**) in dry DMF in the presence of Cs_2CO_3 resulted in the formation of desired diazadithiamacrocycle **6** in 77% yield, which was confirmed by IR, NMR, MS spectra and elemental analysis data. It was found that ^1H NMR spectrum of **6** clearly showed the characteristic emerged signals for the 16-membered macrocycle at $\delta = 3.18$, 2.58, 1.95 and 2.41 ppm concerning N, S connected methylene, bridging methylene groups and methyl protons, respectively. Compound **6** contained two tosyl moieties and was substantiated by two characteristic doublets at $\delta = 7.70$ and 7.32 ppm as expected. Characteristic signals of the ^{13}C NMR spectrum of the same compound were similar to those of the precursor compounds **2** and **4**. In the MS spectrum of this compound, a peak corresponding to $[M + 1]^+$ at $m/z = 571$ was in good accord with the suggested structure. Detosylation of **6** performed a reductive detosylation by using $LiAlH_4$ to minimise the cleavage of the thioether functional groups (*19*). The preparation of **7** was first carried out by Kaden and then by Lindoy et al. (*20*). Alternatively, the unsubstituted macrocycle **7** was synthesized in 71% yield by detosylation reaction of **6** with excess $LiAlH_4$. After the removal of the tosyl groups from **6**, two terminal NH groups were observed in the ^1H NMR spectrum at $\delta = 1.51$ ppm as expected (*20*). The other proton-NMR signals of **7** closely resemble those of the precursor compound (**6**). The proton-decoupled ^{13}C NMR spectrum of **7** also clearly indicated the presence of expected signals. The disappearance of the

characteristic signals concerning tosyl groups, along with the appearance of resonances at $\delta = 46.58$, 29.02 and 28.31 ppm corresponding to $N-CH_2$, $S-CH_2$ and CH_2 carbons, respectively, was in agreement with the proposed structure. This was also supported by the presence of the characteristic peak at $m/z = 263.16$ $[M + 1]^+$ in the mass spectrum using the ES technique.

Treatment of **7** with *cis*-1,2-dicyano-1,12-ethylene dithiolate (**8**) in dry MeCN in the presence of excess amount of Cs_2CO_3 resulted in the formation of the desired macrobicycle **9** in 62.2% yield, which was confirmed by IR, NMR and MS spectra. Compound **8** contained a conformation of bicycle skeleton and dicyano subunit was substantiated by characteristic signals at $\delta = 1.80$ and 2.42 ppm for the new bridging methylene and SCH_2 protons, respectively, in the ^1H NMR spectrum. The bicycle formation was in the proposed structure as confirmed by its ^{13}C NMR spectrum, in which the characteristic signals at $\delta = 112.79$ and 121.70 ppm for the C≡N and C=C carbons of the macrobicycle moiety were present, and the other characteristic signals at $\delta = 27.26$ ppm for the bridging methylene carbons were also present. A diagnostic feature of macrobicycle formation from compounds **7** and **8** is the appearance of the sharp intense C≡N vibrational bands at 2206 cm^{-1} in the IR spectrum. Structure of macrobicycle formation **9** was also confirmed by its MS spectrum at 485, in which the peak corresponding to $[M + 1]^+$ was observed.

MgPz was obtained as dark green solids from Linstead macrocyclisation (*21*) of compound **9** using magnesium butoxide in *n*-butanol in 17.2% yield after purification by column chromatography on silica gel [chloroform:methanol (95:5)]. In the IR spectrum of this compound, a diagnostic feature of the formation of MgPz from **9** is the disappearance of the sharp C≡N resonances and the presence of C=N stretching vibrations at 1632 cm^{-1} confirms the formation of MgPz. In the ^1H NMR spectrum of MgPz, the signals relating to $N-CH_2$, $S-CH_2$ and CH_2 groups in the macrobicycle moieties gave significant resonance characteristics of the proposed structure. The structure of this compound was also confirmed by its MS spectrum, in which the peak at $m/z = 2038.4$ corresponding to $[M + 2K]^+$ was observed.

Electronic spectrum of magnesium porphyrazine (Figure 1) exhibits a Q band at 675 nm, a less broad band at 506 nm and a Soret region at 365–344 nm. The two bands in the UV–vis spectrum of MgPz display maxima at around 675 and 616 nm caused by a $\pi \rightarrow \pi^*$ transition of the Pz ring, which is characteristic of tetrapyrrolic macrocycle with D_{4h} symmetry (*9*, *22*). In agreement with other peripherally heterosubstituted porphyrazines, they tentatively assigned the less intense broad peak at 506 nm to the $n \rightarrow \pi^*$ transition from the lone pairs electron on the peripheral sulphur atoms into a π^* ring orbital concerning inner core. The second intense and broad $\pi \rightarrow \pi^*$ transition in the range of B-band corresponds to deep $\pi \rightarrow \pi^*$ transition from the a_{1u}, a_{2u} HOMOs to the double degenerate LUMOs (*10*).

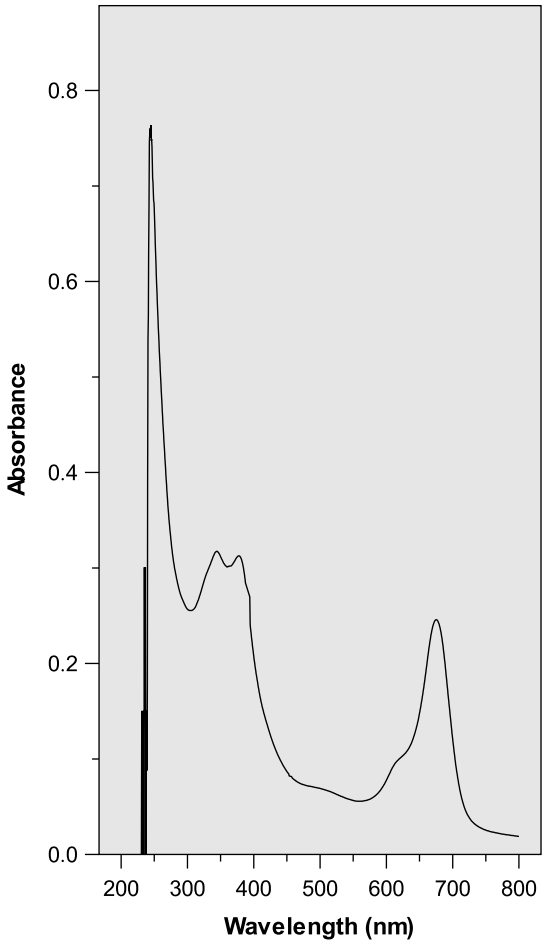


Figure 1. Electronic absorption spectrum of MgPz (1.0×10^{-5} M) in $CHCl_3$.

Conclusions

In this study, the new MgPz fused with diazatetrathiamacrobicycles in peripheral positions have been prepared by bicyclotetramerisation of the newly synthesized dithiomaleonitrile derivatives of cryptand in the presence of magnesium butanolate as template agent. MgPz complex contains symmetrically four large macrobicyclic cavities, hence it has the potential to be related to supramolecular areas.

Acknowledgements

This study was supported by the Research Fund of Pamukkale University, Project number 2008 FBE 002 (Denizli/Turkey). One of the authors (N.K.) also thanks TÜBİTAK (The Scientific and Technological Research Council of Turkey-ANKARA) for financial support.

References

(1) *Phthalocyanines: Properties and Applications*; Leznoff, C.C., Lever, A.B.P., Eds.; VCH: New York, **1989–1996**; Vols 1–4.

(2) Tanaka, A.A.; Fierro, C.; Sherson, D.A.; Yaenger, E. *Mater. Chem.* **1989**, *22*, 431–456.

(3) Yamana, M.; Kashiwazaki, N.; Yamamoto, M.; Nakano, T. *Jpn J. Appl. Phys. Part 2* **1987**, *26*, L1113.

(4) Bonnet, R. *Chem. Soc. Rev.* **1995**, *24*, 19–33.

(5) Hanack, M.; Lang, M. *Adv. Mater.* **1994**, *6*, 819–833; Collins, G.E.; Armstrong, R.N.; Pankow, J.W.; Oden, C.; Brina, R.; Arbour, C.; Dodelet, J.-P. *J. Vac. Sci. Technol.* **1993**, *A.11*, 1383–1391.

(6) Velazquez, C.S.; Baumann, T.F.; Olmstead, M.M.; Barrett, A.G.M.; Hoffman, B.M. *J. Am. Chem. Soc.* **1993**, *115*, 9997–10003; Mani, N.S.; Beall, L.S.; Miller, T.; Anderson, O.P.; Hope, H.; Parkin, S.R.; Williams, D.J.; Barrett, A.G.M.; Hoffman, B.M. *J. Chem. Soc. Chem. Commun*. **1994**, 2095–2096; Cook, A.S.; Williams, D.B.G.; White, A.J.P.; Williams, D.J.; Lange, S.J.; Barrett, A.G.M.; Hoffman, B.M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 760–761; Fuchter, M.J.; Zhong, C.; Zong, H.; Hoffman, B.M.; Barrett, A.G.M. *Aust. J. Chem.* **2008**, *61*, 235–255.

(7) Lange, S.J.; Nie, H.; Stern, C.L.; Barrett, A.G.M.; Hoffman, B.M. *Inorg. Chem.* **1998**, *37*, 6435–6443; Sakellariou, E.G.; Montalban, A.G.; Meunier, H.G.; Ostler, R.B.; Rumbles, G.; Barrett, A.G.M.; Hoffman, B.M. *J. Photochem. Photobiol. A Chem.* **2000**, *136*, 185–187.

(8) Sibert, J.W.; Lange, S.J.; Stern, C.L.; Hoffman, B.M.; Barrett, A.G.M. *Abstract of Papers, 206th National Meeting of American Chemical Society, Chicago, IL*, **1993**, INOR 60; Nostrum, C.F.; Benneker, F.B.G.; Nolte, R.J.M.; Veldman, N.; Spek, A.L.; Schouten, A.J. *Recl. Trav. Chim. Pays-Bas.* **1994**, *113*, 109–110.

(9) Nostrum, C.F.; Benneker, F.B.G.; Brussaard, H.; Kooijman, H.; Veldman, N.; Spek, A.L.; Schoonman, J.; Feiters, M.C., Nolte, R.J.M. *Inorg. Chem.* **1996**, *35*, 959–969; Siber, J.W.; Lange, S.J.; Stern, C.L.; Barrett, A.G.M.; Hoffman, B.M. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2020–2022.

(10) Hou, R.; Jin, L.; Yin, B. *Inorg. Chem. Commun.* **2009**, *12*, 739–743.

(11) Kandaz, M.; Özkaya, A.R.; Koca, A.; Salih, B. *Dyes Pigments* **2007**, *74*, 483–489; Ehrlich, L.A.; Skrdla, P.J.; Jarrell, W.K.; Sibert, J.W.; Armstrong, N.R.; Saavedra, S.S.; Barrett, A.G.M.; Hoffman, B.M. *Inorg. Chem.* **2000**, *39*, 3963–3969; Nie, H.; Barrett, A.G.M.; Hoffman, B.M. *J. Org. Chem.* **1999**, *64*, 6791–6796.

(12) Sibert, J.W.; Lange, S.J.; Stern, C.L.; Hoffman, B.M.; Barrett, A.G.M. *J. Chem. Soc. Chem. Commun.* **1994**, 1751–1752; Nostrum, C.F.; Nolte, R.J.M. *J. Chem. Soc. Chem. Commun*. **1996**, 2385–2392; Pullen, A.E.; Faulmann, C.; Cassoux, P. *Eur. J. Inorg. Chem.* **1999**, 269–276; Sibert, J.W.; Lange, S.J.; Barrett, A.G.M.; Hoffman, B.M. *Tetrahedron* **2000**, *56*, 7371–7377.

(13) Popov, A.I.; Lehn, J.-M.; Melson, G.A. (Ed.) *Coordination Chemistry of Macrocyclic Compounds*, Plenum Press: New York, 1979, p. 537; Lindoy, L.F. *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press: Cambridge, **1990**, p. 125; Jerald, H.A.; Bradshaw, J.S.; Izatt, R.M. *Chem. Rev.* **1992**, *92*, 543–572; Bilgin, A.; Ertem, B.; Gök, Y. *Tetrahedron Lett*. **2003**, *44*, 6937–6941.

(14) Lehn, J.-M. *Appl. Chem.* **1977**, *49*, 857–870; Lehn, J.-M. *Supramolecular Chemistry*, VCH: Weinheim, **1995**, p. 111; Zolotov, Y.A. (Ed.), *Macrocyclic Compounds in Analitical Chemistry*, Wiley-Interscience: New York, **1997**, p. 5.

(15) Karadeniz, H.; Gök, Y. *Dyes Pigments* **2008**, *77*, 351–356; Bilgin, A.; Ertem, B.; Gök, Y. *Dyes Pigments* **2009**, *80*, 187–193; Kabay, N.; Söyleyici, S.; Gök, Y. *Inorg. Chem. Commun.* **2009**, *12*, 304–307.

(16) Chak, B.; McAuley, A.; Whitcombe, T.W. *Inorg. Chim. Acta* **1996**, *246*, 349–360.

(17) Karadeniz, H.; Gök, Y.; Kantekin, H. *Dyes Pigments* **2007**, *75*, 498–504.

(18) Perin, D.D.; Armarego, W.L.F. *Purification of Laboratory Chemicals*; 2nd ed.; Pergamon Press: Oxford, **1980**.

(19) Chak, B.M.C.; McAuley, A. *Can J. Chem.* **2006**, *84*, 187–195.

(20) Siegfried, L.; Kaden, T.A. *Helv. Chim. Acta* **1984**, *67*, 29–38; Groth, A.M.; Lindoy, L.F.; Meehan, G.V. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1553–1558.

(21) Ficken, G.E.; Linstead, R.P. *J. Chem. Soc*. **1952**, 4846–4854.

(22) Sağlam, Ö.; Gül, A. *Polyhedron* **2001**, *20*, 269–275; Hachiya, S.C.; Cook, A.S.; Williams, D.B.G.; Montalban, A.G.; Barrett, A.G.M.; Hoffman, B.M. *Tetrahedron* **2000**, *56*, 6565–6569.