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The synthesis and characterization of a new metal-free phthalocyanine substituted with four diloop macrocyclic moieties

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Abstract—Symmetrically tetrasubstituted metal-free phthalocyanine **6** with four 14-membered dioxadithia macrocycles each of which is attached to a 15-membered crown ether has been prepared in a multi-step reaction sequence. The new compounds were characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR, UV–vis and MS spectral data. © 2003 Published by Elsevier Science Ltd.

The self-assembly of supramolecular compounds bearing multiple binding sites is of great interest in a wide range of applications such as molecular electronics, bio and chemical sensors, and energy storage devices as well as the biomimicking of natural systems.[1] Since 1970, when polynuclear complexes of macrocycles were first synthesized,[2] this area of coordination and host–guest chemistry has seen intensive growth.[3] Especially, polynucleating systems containing several substrate- or metal-binding sites which do not reside within the same macrocyclic framework is a very active current research activity.[4] One concept for the preparation of multi-site receptors, by which any number and type of macrocyclic binding compartment can be generally linked together utilises a spiro skeleton. However, multiloop systems including more than three individual and defined crown ether, polyaza or mixed donor macrocycles have not been described so far.

Phthalocyanines and metallophthalocyanines have attracted considerable attention as a consequence of their diverse, optical, electronic, structural and coordination properties. These compounds have found wide applications in diverse areas such as biomedical agents for diagnosis and therapy, liquid crystals, Langmuir–Blodgett films, electronic devices, molecular metals, gas and chemical sensors, nonlinear optics, electrochromic devices, photosensitisers and ladder polymers.[5] There is also a great interest in exploring novel structural modifications to the phthalocyanine system, including the study of polynuclear derivatives and derivatives with specially-designed peripheral substituents which coordinate alkaline or transition metals.[6]

We recently outlined a concept for the synthesis of a new type of phthalocyanine with various functional groups. Most of these have N-, O- and S-containing functionalities such as tetraazatetraoxa,[7] diazatetrathia,[8] diazatetraoxadithiamacrobicycle, cylindrical macrotricycle, and spherical macrotricycle.[9]

In this paper, we describe the synthesis of a new phthalocyanine attached multifunctional substituent (Scheme 1). This compound contains a central *Pc* core, four 14-membered dioxodithia macrocycles, and four 15-crown-5 moieties linked via benzene units to the mixed donor macrocycles.

Reaction of two equivalents of 2-mercaptoethanol **2** and potassium with 2,3-bis-(bromomethyl)-6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxabenzocyclopentadecene **1**[10] in DMF at reflux temperature under argon for 52 h afforded 15,16-bis{[(2-hydroxyethyl)thio]methyl}-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopetadecene **3**[11] in ca. 95% yield after crystallization from chloroform–ethyl acetate. The EI mass spectrum of **3** exhibited a molecular ion peak at m/z 448, which supports the structure. The ^{1}H NMR spectrum of **3** showed characteristic signals for aromatic, ethereal, SCH_2 and $HOCH_2$ protons at $\delta = 2.69$ and 3.67 ppm, respectively. The proton-decoupled ^{13}C NMR spectrum of **3** also clearly indicated the

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Keywords: metal-free phthalocyanine; diloop compound; isoiminoindoline; mixed-donor macrocycle.

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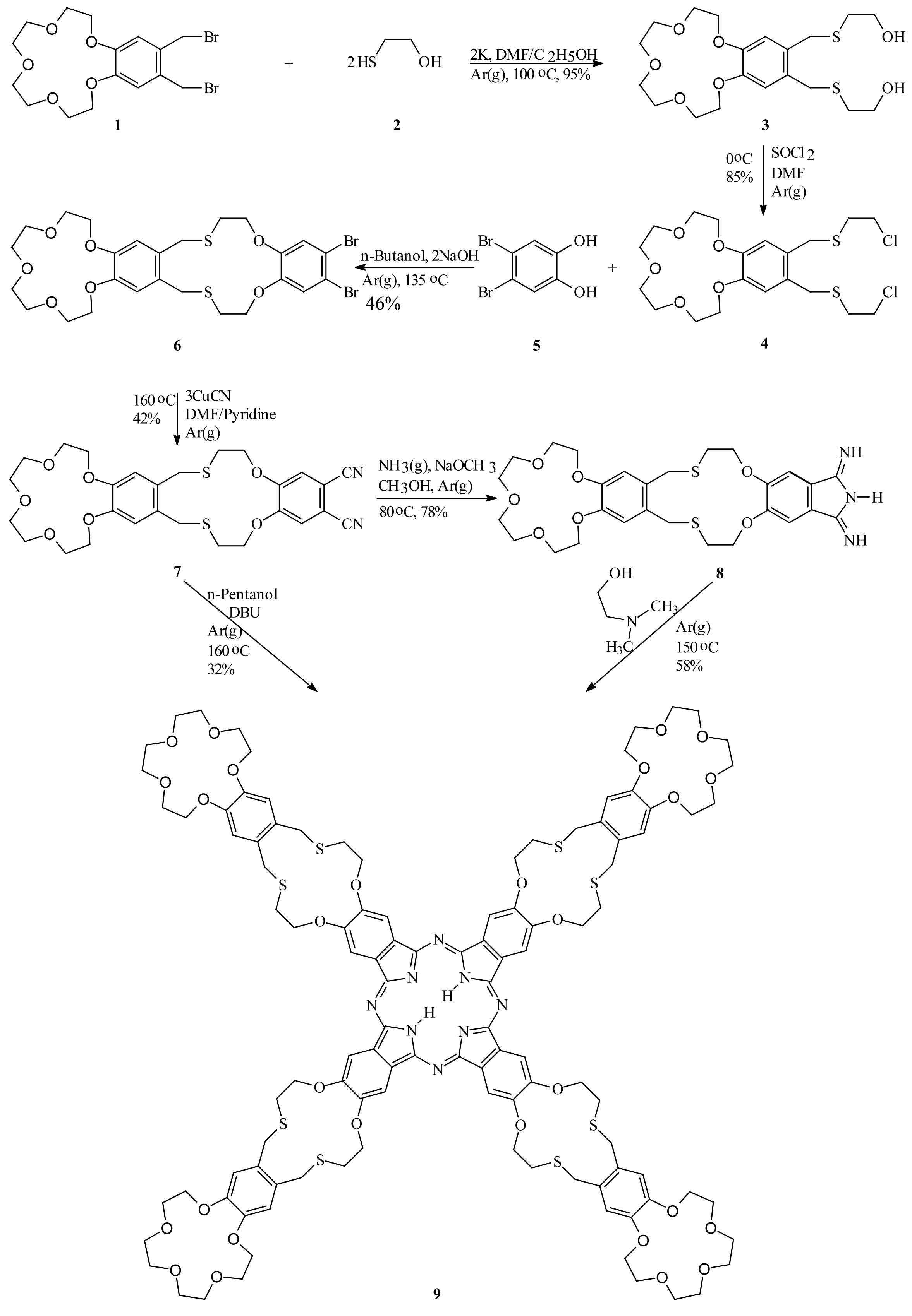

Scheme 1. Synthesis of the metal-free phthalocyanine.

presence of expected signals. The absence of S–H and the presence of O–H stretching vibrations in the IR spectrum confirmed the formation of **3**.

The conversion of **3** into the chloro derivative **4**[12] was achieved in 86% yield when **3** was reacted with freshly distilled $SOCl_2$ in DMF at room temperature after removal of the solvent and final purification by recrystallization from ethyl alcohol to afford **4**. The EI mass spectrum and elemental analysis confirmed the formation of **4** (m/z 485 $[M]^+$). The aromatic and aliphatic protons and carbons in the proton and ^{13}C NMR spectra of **4** were very similar to those of precursor **3** except for the signals of the methylene bonded to chloride ($-CH_2Cl$).

The diloop macrocycle 21,22-dibromo-2,3,5,6,8,9,11,12,15,17,18,25,26,28-tetradecahydro [1,4,7,12]benzodioxadithiacyclotetradeceno[6,7 - *b*][1,4,7,10,13]benzopentaoxacyclopentadecene **6**[13] was obtained from **4** by reaction with 4,5-dibromocatechol **5**[14] in the presence of NaOH as a template agent, and in DMF at reflux in a Schlenk tube under argon. Purification by column chromatography [silica gel, chloroform:ethyl acetate (7:2) (v/v)] gave **6** in 46% yield. Analytical and spectroscopic data of **6** clearly confirmed the success of the macrocyclization reaction. In the ^1H NMR spectrum of **6**, the signals belonging to OH protons in the precursor compound **5** were absent after the macrocyclization reaction. A singlet at $\delta = 4.32$ ppm corresponded to the new aromatic group connected to OCH_2. The carbon resonances at $\delta = 148.42$, 117.46 and 114.73 ppm are also in good agreement with the proposed structure. The molecular ion peak at $m/z = 681$ $[M+1]^+$ together with some reasonable ion fragments were obtained by the FAB technique.

The 21,22-dicyano substituted diloop macrocycle **7**[15] was obtained from the dibromo derivative in 42% yield by refluxing in dry DMF with three equivalents of CuCN according to the Rosenmund von Braun reaction.[16] In the IR spectrum of **7**, an intense IR absorption band at 2229 cm^{-1} corresponded to the $C{\equiv}N$ groups. The proton-decoupled ^{13}C NMR spectrum of **7** also indicated the presence of nitrile carbon atoms at $\delta = 115.06$ ppm. The rest of the spectra of this compound was closely similar to that of the precursor dibromide. Compound **7** displayed the expected molecular ion peak in its FAB spectrum at $m/z = 572.2$ $[M]^+$.

The diloop macrocycle **7**[15] was reacted with anhydrous ammonia in the presence of sodium methoxide in refluxing dry methanol to give the corresponding isoiminoindoline **8**.[17] The isolation of this compound required column chromatographic separation on silica gel using chloroform:petroleum ether:methanol (7:2:1) as eluent and gave an oily product in 78% yield. A broad signal at $\delta = 8.22$ ppm in the ^1H NMR spectrum of **8** due to the imino groups provided evidence for the formation of an isoiminoindoline. The disappearance of the $C{\equiv}N$ signals, along with the appearance of new resonances at $\delta = 163.48$ ppm corresponding to $C{=}NH$ groups was in agreement with the proposed structure. The disappearance of the $C{\equiv}N$ stretching vibrations in the IR spectrum of **8** also suggested the formation of compound **8**. The mass spectrum (FAB positive, matrix *m*-nitrobenzyl alcohol) of **8**, which showed a molecular ion peak at $m/z = 590.3$ $[M+1]^+$, confirmed the structure of **8**.

Condensation of four isoiminoindoline derivatives to give the metal-free phthalocyanine **9**[18] was carried out in 2-(dimethylamino)ethanol at reflux temperature for 48 h in a Schlenk tube under argon to afford **9** in 58% yield as a dark green product after purification by column chromatography on silica gel [chloroform:methanol (9:1)]. This compound can be prepared directly from dicyano compound **7**. The isoiminoindoline procedure is more convenient than the phthalonitrile route since the reaction conditions employing isoiminoindoline are mild in comparison with that employing phthalonitrile. The ^1H NMR spectrum of **9** displayed broad signals, and the inner core protons of the H_2Pc could not be observed due to strong aggregation of the molecules.[14] The aromatic and aliphatic protons belonging to the diloop moieties and phthalocyanine skeleton gave relevant signals. An IR spectrum of **9** showed absorbances for the N–H groups. The mass spectrum (FAB positive) of **9** contained a strong peak at $m/z = 2291.3$ $[M+1]^+$ for the parent ion (Fig. 1).

The metal-free phthalocyanine **9** displayed a typical electronic spectrum with two significant absorption bands, one of them in the visible region at about 640–710 nm (λ_{max} 708 and 641 nm) corresponding to the Q band, and the other in the UV, at 300 nm. The Q band absorptions in chloroform:pyridine mixture (1:1) at 708, and 641 nm and the other absorptions at 292 nm are consistent with the results obtained previously for similar phthalocyanines.[19] The split Q band absorption is present in **9** with a small distortion. This result indicates that the symmetry of the metal-free phthalocyanine is D_{2h}. The D_{2h} symmetry of **9** is verified by the two absorptions in visible region.[20]

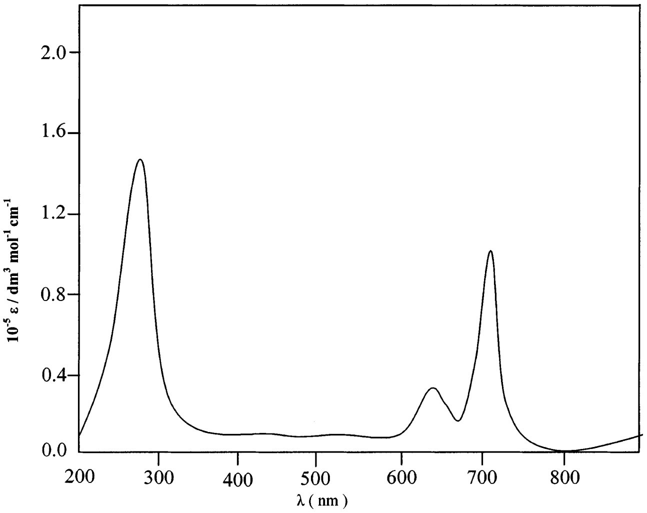

Figure 1. UV–vis spectra of **9** in chloroform/pyridine (1:1 v/v).

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11. For **3**: mp 105°C. Anal. calcd for $C_{20}H_{32}O_7S_2$: C, 53.57; H, 7.14. Found: C, 53.42; H, 7.32%. IR (KBr disc, cm^{-1}): 3330, 3051, 2925–2871, 1594, 1517, 1455, 1349, 1277, 1216, 1120, 1046; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.81 (s, 2H, ArH), 4.85 (s, 2H, OH), 4.14 (t, $J=4.48$ Hz, 4H, $ArOCH_2$), 3.90 (m, 8H, OCH_2), 3.82 (t, $J=5.32$ Hz, 4H, OCH_2), 3.67 (t, $J=4.33$ Hz, 4H, $HOCH_2$), 2.92 (m, 4H, $ArCH_2$), 2.69 (t, $J=4.35$ Hz, 4H, SCH_2); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 148.13 (ArC), 130.91 (ArC), 116.24 (ArCH), 70.95–68.13 (OCH_2), 60.71 ($HOCH_2$), 34.87 (SCH_2), 33.18 ($ArCH_2$).
12. For **4**: mp 100°C. Anal. calcd for $C_{20}H_{30}O_5S_2Cl_2$: C, 49.48; H, 6.18. Found: C, 49.67; H, 6.13%. IR (KBr disc, cm^{-1}): 3037, 2919–2870, 1597, 1515, 1454, 1349, 1277, 1211, 1127, 1048. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.80 (s, 2H, ArH), 4.12 (t, $J=4.54$ Hz, 4H, $ArOCH_2$), 3.93 (m, 8H, OCH_2), 3.76 (m, 4H, OCH_2), 3.57 (t, $J=7.72$, 4H, $ClCH_2$), 2.90 (m, 4H, $ArCH_2$), 2.78 (t, $J=7.72$ Hz, 4H, SCH_2); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 148.10 (ArC), 128.56 (ArC), 116.34 (ArCH), 71.04–69.42 (OCH_2), 43.11 ($ClCH_2$), 35.56 (SCH_2), 33.88 ($ArCH_2$).
13. For **6**: mp 218°C; Anal. calcd for $C_{26}H_{32}O_7S_2Br_2$: C, 45.89; H, 4.70. Found: C, 45.78; H, 4.94%. IR (KBr disc, cm^{-1}): 3044, 2910–2881, 1598, 1590, 1510, 1496, 1450, 1355, 1280, 1215, 1121, 1091; ^{1}H NMR ($CDCl_3$, 200 MHz): 7.13 (s, 2H, ArH), 6.73 (s, 2H, ArH), 4.32 (t, $J=4.42$ Hz, 4H, $ArOCH_2$), 4.08 (t, $J=5,18$ Hz, 4H, $ArOCH_2$), 3.89 (m, 8H, OCH_2), 3.79 (m, 4H, OCH_2), 3.51 (m, 4H, $ArCH_2$), 3.18 (t, $J=5.2$ Hz, 4H, SCH_2); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 148.42 (ArC), 148.06 (ArC), 129.92 ($ArCH_2$), 117.46 (ArBr), 116.11 (ArCH), 114.73 (ArCH), 71.42–68.88 (OCH_2), 67.12 ($ArOCH_2$), 35.12 ($ArCH_2$), 30.37 (SCH_2).
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15. For **7**: mp 136–138°C. Anal. calcd for $C_{28}H_{32}N_2O_7S_2$: C, 58.74; H, 5.59; N, 4.89. Found: C, 58.90; H, 5.80; N, 4.71%. IR (KBr disc, cm^{-1}): 3044, 2924–2854, 2224, 1598, 1513, 1457, 1358, 1269, 1215, 1127, 1106, 1057, 947; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.30 (s, 2H, ArH), 6.87 (s, 2H, ArH), 4.37 (t, $J=4.67$ Hz, 4H, $ArOCH_2$), 4.22 (t, $J=5.7$ Hz, 4H, OCH_2), 3.92 (m, 8H, OCH_2), 3.84 (m, 4H, OCH_2), 3.51 (m, 4H, $ArCH_2$), 3.34 (t, $J=5.35$ Hz, 4H, SCH_2); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 151.88 (ArC), 148.42 (ArC), 129.93 ($ArCH_2$), 121.17 (ArCH), 115.06 ($C\equiv N$), 114.92 (ArC), 114.04 (ArCH), 72.16–68.79 (OCH_2), 35.14 ($ArCH_2$), 31.94 (SCH_2).
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17. For **8**: oil. Anal. calcd for $C_{28}H_{35}N_3O_7S_2$: C, 57.04; H, 5.94; N, 7.13: Found: C, 56.88; H, 6.17; N, 7.34%. IR (KBr disc, cm^{-1}): 3353, 3052, 2952–2882, 1667, 1613, 1591, 1451, 1411, 1349, 1304, 1275, 1177, 1124, 1056, 936. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.22 (br, 3H, NH), 7.41 (s, 2H, Ar-H), 6.82 (s, 2H, ArH), 4.35 (s, 4H, $ArOCH_2$), 4.13 (t, $J=4.55$ Hz, 4H, $ArOCH_2$), 4.03 (m, 8H, OCH_2), 3.90 (m, 4H, OCH_2), 3.49 (m, 4H, $ArCH_2$), 3.30 (t, $J=4.58$ Hz, 4H, SCH_2). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 163.48 (C=NH), 151.74 (ArC), 150.85 (ArC), 131.96 ($ArCH_2$), 126.86 (ArC), 118.45 (ArCH), 114.21 (ArCH),

71.67-69.11 (OCH_2), 66.94 ($ArOCH_2$), 36.45 ($ArCH_2$), 31.87 (SCH_2).

18. For **9**: mp >300°C. Anal. calcd for $C_{112}H_{130}N_8O_{28}S_8$: C, 58.68; H, 5.67; N, 4.89. Found: C, 58.84; H, 5.45; N, 5.16%. IR (KBr disc, cm^{-1}): 3413 (N–H), 3057 (ArH), 2919–2846 (C–H), 1621 (C=N), 1603 (N–H), 1594, 1487, 1448, 1398, 1322, 1157, 1119, 1086. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.45 (m, 8H, ArH), 6.71 (m, 8H, ArH), 4.28 (m, 16H, $ArOCH_2$), 4.09 (m, 16H, $ArOCH_2$), 3.98 (m, 32H, OCH_2), 3.83 (m, 16H, OCH_2), 3.41 (m, 16H, $ArCH_2$), 3.17 (m, 16H, SCH_2). UV–vis [chloroform:pyridine (1:1), λ_{max}/nm (log ε)]: 708 (4.90), 641 (4.41), 330 (5.08).
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