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Synthesis and characterization of novel metal-free phthalocyanines substituted with four diazadithiatetraoxa or diazahexaoxamacrobicyclic moieties

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Abstract—The new metal-free phthalocyanines 9,10-fused symmetrically in the peripheral positions with four diazadithiatetraoxa and diazahexaoxamacrobicycles, respectively, have been synthesized by bicyclotetramerization of isoindolinediimine derivatives of cryptands **7** and **8** and characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR, UV–vis and MS spectroscopic data. © 2002 Published by Elsevier Science Ltd.

Phthalocyanine derivatives have attracted considerable attention as a consequence of their diverse optical, electronic and coordination properties which have led to wide-ranging research for over 60 years.[1] These compounds have been prepared for various applications in the areas of non-linear optics, liquid crystals, electrochromic processes involving thin films, gas or chemical sensors, photosensitizers, catalysts, and for mercaptan oxidations and as therapeutic agents in pharmacology.[2] A disadvantage of metal-free and metallophthalocyanines is their limited solubility in common organic solvents. For most of these applications, metal-free or metallophthalocyanines with long alkyl or alkoxy chains or macrocyclic polyether moieties[3] had to be synthesized in order to facilitate the above mentioned purposes and to enhance solubility.

Lehn and co-workers in 1969 succeeded in combining the chemical features of two closely related classes, macrocyclic diamines and macrocyclic polyethers, in forming the azapolyoxamacrocycles, which are known as cryptands.[4] These compounds show extraordinary solubility and selectivity towards specific alkali and alkaline earth metal cations leading to complexation in aqueous and organic solutions, indeed more so than macrocyclic polyethers.[5] The attachment of benzo rings into the bridging polyether strands of cryptand 2.2.2 results in cryptand $2.2.2_B$. The benzo-substituted cryptands are hydrated less extensively than the unsubstituted ones due to the combined effects of decreased cavity size and their increased hydrophobicity.[6]

In this study, we describe the synthesis and characterization of a new class of metal-free phthalocyanines, the diazadithiatetraoxa or diazahexaoxamacrobicycles and phthalocyanines which may allow novel functionalized materials to be prepared of importance for analytical chemistry as new kinds of alkali or alkaline earth metal extraction agents.

We report here the synthesis and structural properties of macrobicyclic compounds **4** and **5** prepared in high yield by the 1:1 reaction of 4,13-diaza-18-crown-6 **1**[7] and a 25% excess of 1,2-bis(2-iodoethylmercapto)-4,5-dicyanobenzene **2**[8] or 1,2-dibromo-4,5-bis(2-iodoethoxy)benzene **3**,[9] a three-fold excess of Cs_2CO_3, and 0.25 equiv. of NaI in acetonitrile (Scheme 1). Final purification by recrystallization or chromatography afforded products **4** and **5** in 74% (mp 204°C) and 72% (oily) yields, respectively. These compounds **4** and **5** displayed the expected molecular ion peaks at $m/z=506$ $[M]^+$ and 582.1 $[M]^+$. The transformation of the substituted phthalonitrile **4**[10] into the isoiminoindoline derivative **7**[11] was performed according to Linstead.[12] The isolation of this product required column chromatographic separation on silica gel using methanol–chloroform (8:2) as eluent and gave an 84% yield [mp 215°C (decomp.)]. ^{1}H and ^{13}C NMR spectra of this product indicated the formation of **7**. This was also supported by the presence of the characteristic molecular ion peak at $m/z=523$ $[M]^+$ in the mass spectrum obtained using the FAB technique.

Keywords: metal-free phthalocyanine; mixed-donor macrobicycles; isoiminoindolines; template effect.

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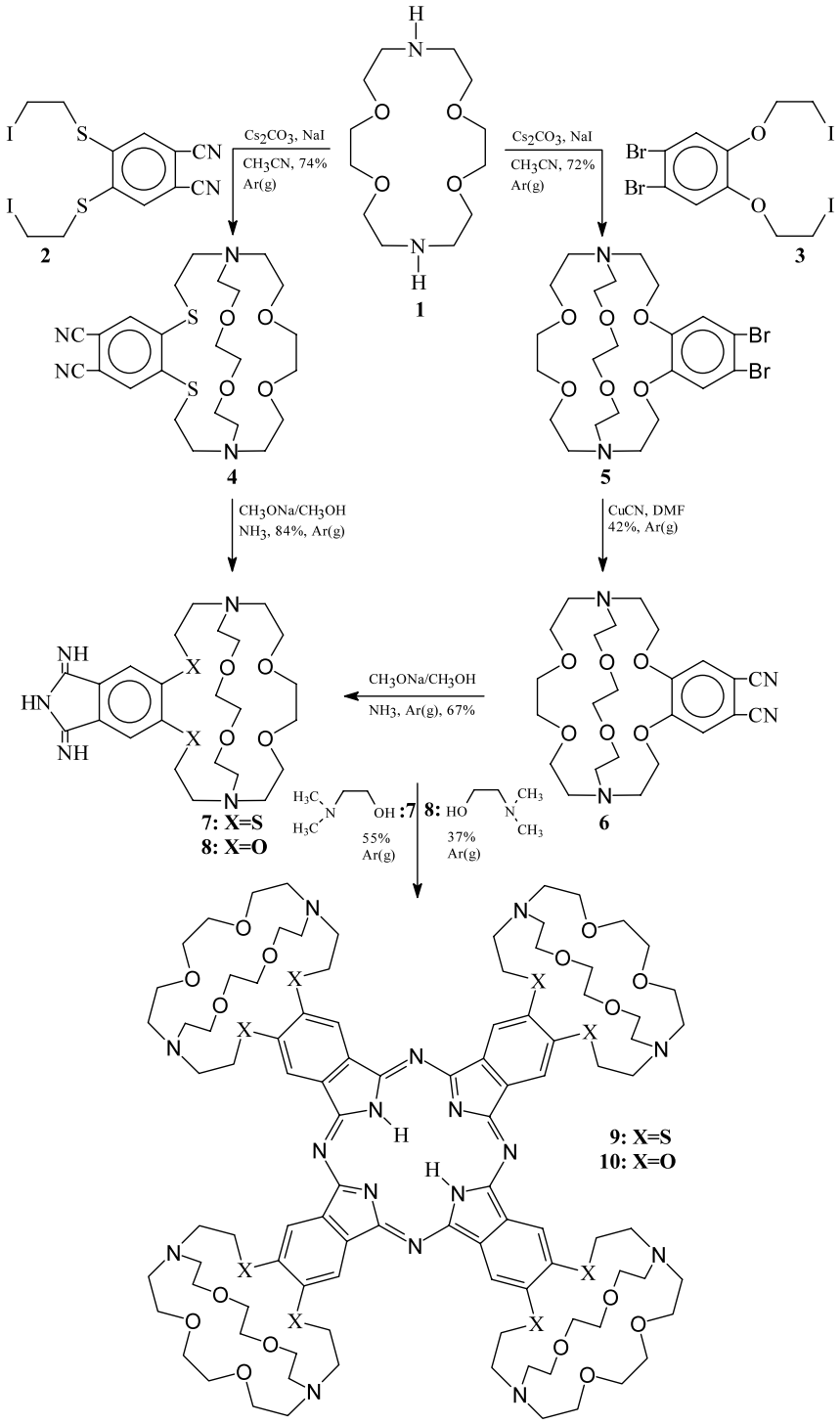

Scheme 1. The synthesis of the metal-free phthalocyanines.

Condensation of four molecules of the isoiminoindoline derivative into the metal-free phthalocyanine **9**[13] was carried out in 2-(dimethylamino)ethanol at reflux for 48 h under argon and afforded the target compound **9** in 55% yield (mp >300°C) as a green amorphous solid after purification by using column chromatography on silica gel [chloroform:petroleum ether (6:4)]. In the preparation of **9**, the isoiminoindoline route is more convenient than the phthalonitrile route since the reaction conditions employing isoiminoindolines are mild in comparison to those employing phthalonitriles.[14] The ^{1}H NMR spectrum of the tetrameric metal-free phthalocyanine **9** showed the typical shielding of inner core protons as a broad resonance at $\delta = -3.85$ ppm which was attributed to the NH protons and identified easily with deuterium exchange. The mass spectrum of **9** contained a strong peak at $m/z = 2027.2$ $[M]^+$ for the parent ion, which can be attributed the formation of phthalocyanine.

The conversion of the dibromo compound **5**[15] into the dicyano analogue **6**[16] was the most problematical step in the synthesis of target compound **7**: reaction with CuCN in dry DMF at 140°C produced dicyano derivative **6** in an optimized yield of 42% (mp 224–226°C) after chromatographic separation from undesired side products. The structure proposed for this new compound is consistent with the data obtained from its elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopic data. The FAB mass spectrum of **6** exhibits an intense peak at $m/z=474$ due to $[M]^+$, which is in accordance with the proposed structure.

The usual synthetic route involving the reaction of substituted dinitrile **6** in the presence of the strong, but not nucleophilic base, 1,8-diazabicyclo[5.4.0]undec-7-ene under reflux in dry pentanol[17] or hydroquinone in a sealed tube was applied to synthesize the metal-free phthalocyanine **10**. However, all efforts to accomplish this reaction failed and no phthalocyanine was observed. The best way of synthesizing **10** was found to involve conversion of **6** into the diiminoisoindoline derivative **8**[18] with ammonia at reflux temperature for 8 h under argon in 67% yield (mp 246–248°C) and then to react this product with 2-(dimethylamino)ethanol at reflux to give up to a 37% yield of product **10** (mp >300°C). Spectroscopic data, elemental analysis and FAB mass spectra were entirely consistent with the structures of compound **8** and the target phthalocyanine structure **10**.[19] The ^{1}H and ^{13}C NMR spectra of **10** in $CDCl_3$ gave the characteristic signals expected for macrobicycles and the phthalocyanine moiety. In addition, the inner core protons of **10** could not be observed in the ^{1}H NMR spectrum as observed for other metal-free phthalocyanines.[20] The mass spectrum of **10** obtained by the FAB technique using a *m*-nitrobenzyl alcohol matrix, showed a molecular ion at $m/z=1899$ $[M+1]^+$ and a fragmentation pattern closely following that of **8** indicating the high stability of the phthalocyanine moiety.

The UV–vis spectra of compounds **9** and **10** in chloroform at room temperature are displayed in Fig. 1. These spectra show the two characteristic intense bands of metal-free phthalocyanines, the Q and B bands (325–349 nm). The split Q band for compounds **9** and **10**, which is characteristic of metal-free phthalocyanines, is observed at $\lambda=736$, 706, 671 and 685, 662, 618 nm suggesting monomeric species, respectively. While the monomeric species with D_{2h} symmetry show two intense absorptions of comparable intensity around 700 nm, those having D_{4h} symmetry give only a single absorption in this region. These two absorptions around 700 nm[21] are due to the $\pi\rightarrow\pi^*$ transition of the fully conjugated 18π electron system.

Acknowledgements

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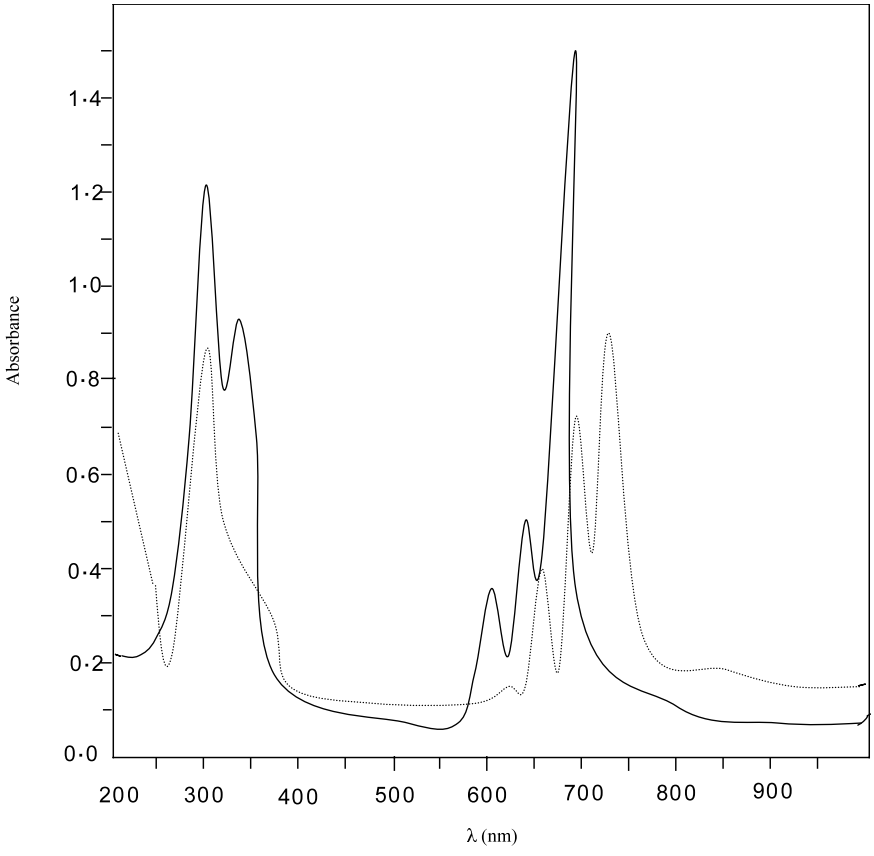

Figure 1. UV–vis spectra of **9** (dotted line) in chloroform and **10** (solid line) in pyridine.

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10. Compound **4**: mp 204°C; IR (KBr disc, cm^{-1}): 3078, 2942–2830, 2228, 1596, 1564, 1262, 1223, 1120; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.51 (s, 2H, ArH), 3.76 (m, 16H, CH_2O), 3.42 (m, 12H, CH_2N), 2.89 (s, 4H, CH_2S); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 138.34 (ArCS), 132.37 (ArCH), 114.89 (CN), 112.73 (ArC), 68.67–66.76 (OCH_2), 54.13 (NCH_2), 28.02 (SCH_2). Anal. calcd for $C_{24}H_{34}N_4O_4S_2$: C, 56.91; H, 6.71; N, 11.06. Found: C, 56.73; H, 6.55; N, 11.28%.
11. Compound **7**: mp 215°C; IR (KBr disc, cm^{-1}): 3434, 3248, 3072, 2942–2845, 1624, 1587, 1543, 1278, 1143; ^1H NMR ($CDCl_3$, 200 MHz): δ 8.46 (br, 3H, NH), 7.63 (s, 2H, ArH), 3.83 (m, 16H, OCH_2), 3.64 (m, 12H, NCH_2), 2.75 (s, 4H, SCH_2); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 169.18 (C=NH), 141.24 (ArCS), 131.43, (ArCH), 133.34 (ArC), 68.95–67.06 (OCH_2), 55.03 (NCH_2), 28.47 (SCH_2). Anal. calcd for $C_{24}H_{37}N_5O_4S_2$: C, 55.06; H, 7.07; N, 13.38. Found: C, 55.29; H, 7.22; N, 13.19%.
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13. Compound **9**: mp >300°C; IR (KBr disc, cm^{-1}): 3394, 3066, 2917–2849, 1627, 1595, 1569, 1268, 1123; ^1H NMR ($CDCl_3$, 200 MHz): δ −3.85 (br, 2H, NH), 7.89 (m, 8H, ArH), 3.85 (m, 64H, OCH_2), 3.60 (m, 48H, NCH_2), 2.81 (m, 16H, SCH_2); ^{13}C NMR ($CDCl_3$/pyridine-d_5, 50 MHz): δ 152.66 (C=N), 139.46 (ArCS), 133.93 (ArCH), 120.12 (ArC), 69.32–67.58 (OCH_2), 55.41 (NCH_2), 28.64 (SCH_2). Anal. calcd for $C_{96}H_{138}N_{16}O_{16}S_8$: C, 56.86; H, 6.81; N, 11.05. 11.05. Found: C, 56.71; H, 6.92; N, 11.31%.
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15. Compound **5**: oil; IR (KBr disc, cm^{-1}): 3051, 2877, 1592, 1581, 1493, 1248, 1199, 651. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.33 (s, 2H, ArH), 4.27 (s, 4H, $ArOCH_2$), 3.88 (m, 16H, OCH_2), 3.29 (m, 12H, NCH_2). ^{13}C NMR ($CDCl_3$, 200 MHz): δ 148.12 (ArCO), 118.49 (ArCH), 116.25 (ArCBr), 72.19 ($ArOCH_2$), 69.37–66.74 (OCH_2), 55.86 (NCH_2). Anal. calcd for $C_{22}H_{34}Br_2N_2O_6$: C, 45.36; H, 5.84; N, 4.81. Found: C, 45.51; H, 5.69; N, 5.04%.
16. Compound **6**: mp 226°C; IR (KBr disc, cm^{-1}): 3049, 2920–2849, 2230, 1596, 1506, 1255, 1132; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.24 (s, 2H, ArH), 4.35 (s, 4H, $ArOCH_2$), 3.85 (m, 16H, OCH_2), 3.33 (m, 12H, NCH_2); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 148.51 (ArCO), 120.23 (ArH), 115.67 (ArC), 113.30 (CN), 71.96 ($ArOCH_2$), 68.22–67.19 (OCH_2), 55.53 (NCH_2). Anal. calcd for $C_{24}H_{34}N_4O_6$: C, 60.75; H, 7.17; N, 11.81. Found: C, 60.91; H, 6.88; N, 11.68%.
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18. Compound **8**: mp 248°C; IR (KBr disc, cm^{-1}): 3348, 3055, 2928–2853, 1632, 1599, 1457, 1289, 1125; ^1H NMR ($CDCl_3$, 200 MHz): δ 8.87 (br, 3H, NH), 7.35 (s, 2H, ArH), 4.27 (s, 4H, $ArOCH_2$), 3.82 (m, 16H, OCH_2), 3.25 (m, 12H, NCH_2); ^{13}C NMR ($CDCl_3$, 50

MHz): δ 168.76 (C=NH), 148.31 (ArCO), 111.80 (ArCH), 126.47 (ArC), 71.66 ($ArOCH_2$), 68.08–66.88 (OCH_2), 55.15 (NCH_2). Anal. calcd for $C_{24}H_{37}N_5O_6$: C, 58.65; H, 7.53; N, 14.25. Found: C, 58.47; H, 7.37; N, 14.43%.

19. Compound **10**: mp >300°C; IR (KBr disc, cm^{-1}): 3415, 3041, 2915–2840, 1603, 1592, 1493, 1412, 1291, 1137, 1072; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.47 (m, 8H, ArH), 4.35 (m, 16H, $ArOCH_2$), 3.85 (m, 64H, OCH_2), 3.35 (m, 48H, NCH_2); ^{13}C NMR ($CDCl_3$/pyridine-d_5, 50 MHz): δ 152.17 (C=N), 148.16 (ArCO), 115.67 (ArCH), 127.20 (ArC), 71.60 ($ArOCH_2$), 68.24–66.94 (OCH_2), 55.26 (NCH_2). Anal. calcd for $C_{96}H_{138}N_{16}O_{24}$: C, 60.69; H, 7.27; N, 11.80. Found: C, 60.86; H, 7.51; N, 11.98%.
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