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Synthesis and characterization of new metal-free phthalocyanine substituted with four diazatetrathiamacrobicyclic moieties

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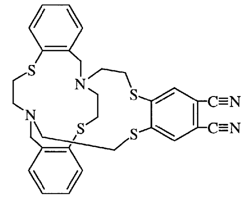
A novel metal-free phthalocyanine 3 fused in peripheral position with four diazatetrathiabicyclomacrocycles has been prepared by bicyclotetramerization of cryptand 1 and its isoindolinediimine derevative 2; the new compounds were characterized by elemental analyses, IR, ^{1}H and ^{13}C NMR, UV–VIS and MS spectroscopy.

The first synthesis of a soluble copper phthalocyanine with crown ether moieties was reported in 1986[1] and its high tendency towards aggregation by solvents, cations and complexation properties was investigated.[2] Such compounds contain a metal center that is complexed by a phthalocyanine ring and four macrocyclic binding sites.[3] The attachment of polyaza or polyaza-polythia macrocycles to phthalocyanine has received considerable attention because of the transition metal-binding properties of the macrocyclic cavities.[4] Phthalocyanines containing polyaza or mixed-donor macrocycles[5] can form homo- and hetero-pentanuclear transition metal complexes which may allow new functionalized materials to be obtained which are of importance for both biochemistry and materials science.[6]

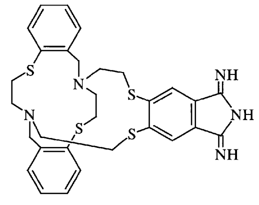
A range of three-dimensional polycyclic ligand systems (cryptands) have recently been investigated most intensively with respect to their strong selectivity towards individual alkali and alkaline-earth metal ions.[7] The majority of such ligands contain donor sets in which polyether donor functions predominate. However, ligands of general type, incorporating mixed donors such as diaza and/or dithia groups, have also been synthesized.[8] Such ligands show increased affinity for transition metals and many other heavy metals.[9]

This study, describing the synthesis of compound **3**, displaying a suitable combination of diazatetrathiamacrobicycles and phthalocyanine may allow new functionalized materials to be prepared, which are of importance for analytical chemistry as a new type of heavy metal extraction agent. On the other hand, the importance of this new type of phthalocyanine may be regarded as an important step in that it may be a viable sensor material.

The synthesis of macrobicyclic compound **1**, was performed starting from a 14-membered diazadithia macrocycle[10] and 1,2-bis(2-iodoethylmercapto)-4,5-dicyanobenzene[11] in dilute conditions using Cs$^+$ cation as promotor[12] in acetonitrile. Final purification by recrystallization afforded **1** in 73.2% yield (mp 136 °C).† Compound **1** displays the expected molecular ion peak at m/z = 574 [M]$^+$. Conversion of the dicyano compound **1** into the isoiminoindoline derivative **2** was accomplished by bubbling ammonia gas through a solution of **1** in dry methanol in the presence of sodium methoxide for 6 h. Compound **2** was purified by column chromatography on silica gel, using ethanol–chloroform (1 : 1) as eluent and obtained in 63.4% yield (mp 284 °C (decomp.)].† The C, H and N elemental analyses for **2** were satisfactory and a reproductible mass spectrum was obtained using the FAB technique (M$^+$ at m/z 591 corresponding to the molecular ion).



1



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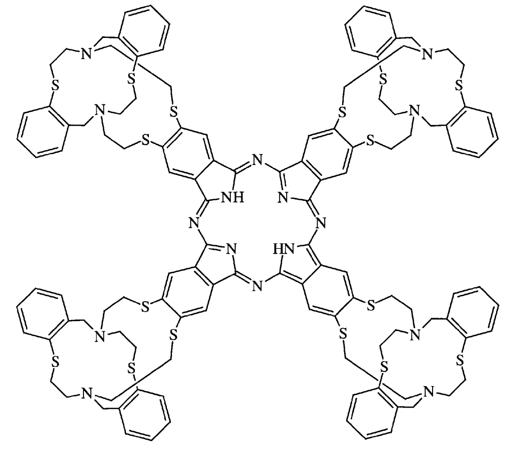

3

The usual synthetic routes could be applied to synthesize the metal-free phthalocyanine **3**.† Thus, either **1** was cyclotetramerized to **3** in a high boiling solvent such as pentanol at reflux temperature in the presence of a strong organic base such as 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU) or alternatively condensation of four isoiminoindoline units **2** into the metal-free

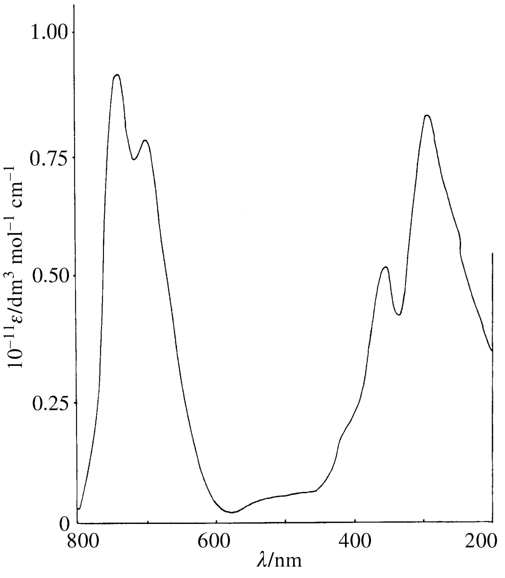

Fig. 1 UV–VIS spectra of **3** in pyridine.

phthalocyanine **3** was carried out in 2-(*N*,*N*-dimethylamino)-ethanol at reflux temperature. In the preparation of the metal-free phthalocyanine, the isoiminoindoline route is more convenient than the phthalonitrile route since the reaction conditions employing isoiminoindolines are mild in comparison to those employing phthalonitriles.[13] The yields (11.3–12.7%) of these reactions were rather low, as encountered for metal-free phthalocyanine with other bulky groups.[5] Elemental analytical results and ^{1}H NMR, IR, MS and UV-VIS spectral data of the new phthalocyanine are consistent with the assigned formulation. A mass spectrometry study by FAB on this compound gave a molecular ion peak the value of which showed good agreement with the calculated value for **3** (*m/z* 2298.3 [M]$^+$).

Fig. 1 shows the electronic absorption spectrum of **3** in pyridine. This spectrum of the phthalocyanine indicates features of both the metal-free phthalocyanine and macro-bicyclic moieties. The cryptand containing phthalocyanine **3** shows intense Q bands at 734 and 704 nm suggesting monomeric species since such species (of D_{2h} symmetry) show two intense absorptions around 700 nm.[13,14] Such split Q band absorptions in pyridine is due to the $\pi \Rightarrow \pi^*$ transition of this fully conjugated 18π electron system.

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Notes and references

† Compounds **1** and **2** were characterized by elemental analysis and spectral methods. Compound **1**: anal. Calc. for $C_{30}H_{30}N_4S_4$: C, 62.71; H, 5.22; N, 9.75. Found: C, 62.96; 5.04; N, 9.94%. IR (KBr disc): ν/cm^{-1} 3054, 2916, 2818, 2229, 1588, 1585, 1463, 1429, 1260, 1109, 970, 753. $\delta_{\mathrm{H}}(\mathrm{CDCl_3})$ 7.58(s), 7.55(s), 7.46–7.07(m), 5.89–5.79(m), 3.86(s),3.36(s), 3.28–3.21(m), 2.76–2.70(m). $\delta_{\mathrm{C}}(\mathrm{CDCl_3})$ 142.58, 138.47, 132.36, 131.31, 129.32, 128.31, 127.70, 125.98, 115.14, 112.58, 110.74, 51.52, 45.06, 33.07, 28.01. Compound **2**: anal. Calc. for $C_{30}H_{33}N_5S_4$: C, 60.91; H, 5.58; N, 11.84. Found: C, 61.16; H, 5.40, N, 11.67%. IR (KBr disc): ν/cm^{-1} 3385, 3177, 3048, 2921, 2816, 1636, 1609, 1585, 1541, 1459, 1420, 1376, 1287, 1107, 872, 750. $\delta_{\mathrm{H}}(\mathrm{CDCl_3})$ 7.75 (br), 7.58(s), 7.53(s), 7.33–6.71(m), 5.67–5.58(m), 4.24(m), 3.85(s), 3.34–3.22(m), 2.73–2.67(m). $\delta_{\mathrm{C}}(\mathrm{CDCl_3})$ 138.49, 135.52, 133.49, 132.28, 130.90, 128.82, 128.08, 127.85, 125.46, 121.82, 51.93, 45.25, 33.29, 28.93. Compound **3**: anal. Calc. for $C_{120}H_{122}N_{16}S_{16}$: C, 62.66; H, 5.30; N, 9.74. Found: C, 62.44; H, 5.51; N, 9.59%. Selected spectroscopic data: IR (KBr disc): ν/cm^{-1} 3406, 3055, 2932, 2841,1636, 1617, 1589, 1560, 1508, 1474, 1458, 1423, 1381, 1344, 1296, 1121, 1079, 897, 754; λ_{max}/nm (log ε) (pyridine): 734 (11.44), 704 (10.15), 348 (6.70), 285 (10.74). $\delta_{\mathrm{H}}(\mathrm{DMSO\text{-}d_6})$ -4.38(s),7.84(m), 7.62–7.50(m), 7.38–6.66(m), 4.28(m), 3.82(s), 3.42–3.29(m), 2.81–2.70(m).

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