

Synthesis, characterization, and electrical, electrochemical and gas sensing properties of a novel ball-type four *t*-butylcalix[4]arene bridged binuclear zinc(II) phthalocyanine†

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Received (in Cambridge, UK) 20th July 2005, Accepted 28th October 2005

First published as an Advance Article on the web 21st November 2005

DOI: 10.1039/b510225a

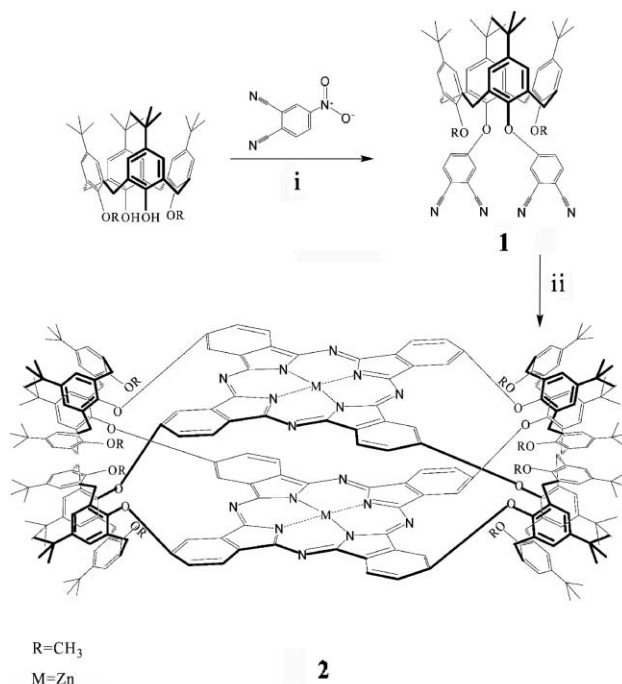
1,3 dimethoxy-4-*t*-butylcalix[4]arene has been used to synthesize a novel ball-type dimeric zinc(II) phthalocyanine, [Zn₂Pc₂(tbca)₄] that exhibits mixed-valence behaviour and non-Arrhenius type dependence of conductivity.

The synthesis and study of binuclear or oligonuclear and sandwich type phthalocyanines (Pcs) containing two metal centers are among the priorities of modern phthalocyanine chemistry.^{1–7} These complexes show a wide range of interaction between the Pc rings, mainly depending on the metal center, bridging links and the presence or absence of axial ligands. The species having flexible bridging units usually do not exhibit any measurable interaction while rigid systems such as the anthracene and naphthalene bridged species do, however, exhibit strong interactions. The synthesis and properties of binuclear Pcs with great numbers of cross-links have been involved rarely in the literature. Recently, a binuclear ball-type ZnPc, containing *o*-phenylidene bridges has been reported in the literature.^{1,2}

In the present work, we have carried out the synthesis of a bisphthalodinitrile derivative containing calix[4]arene substitution **1** (Scheme 1†). Tetramerization of **1** with Zn(OAc)₂·2H₂O in dry DMF gives rise to a novel ball-type binuclear Zn(II)Pc **2**. We also present the results of a.c. and d.c. electrical, gas sensing, and cyclic voltammetry measurements.

The electronic absorption spectroscopic data of **2** is given in the reaction procedure. The energies and relative intensities, and broadening of the bands observed are consistent with the pattern that would be anticipated on the basis of excitation coupling theory for the phthalocyanine dimers. Also an additional weak band centered at ca. 68 nm to the blue of the normal Q band as a result of exciton coupling between the Pc units.⁸

All the MALDI-TOF results showed that complex **2** was successfully synthesized. The spectrum of **2** (Fig. 1) was obtained only in a 3,5-dinitrobenzoic acid matrix with high protonated molecular ion peak intensity. A protonated molecular ion peak was observed at 3849.6 Da that exactly overlapped with the mass



Scheme 1 Reagents and conditions: (i) K₂CO₃, DMSO, 85 °C. (ii) DMF, Zn(OAc)₂·2 H₂O, 24 h, 190 °C.

of **2**, calculated theoretically from the elemental composition of the complex. Beside the protonated molecular ion peak, the other two peaks were observed at 3704.6 and 3559.6 in the high mass range. These two peak masses indicated that a fragmentation occurred from the protonated molecular ion of **2** with 145 Da mass from both sides of the complex. This fragment pointed out that the

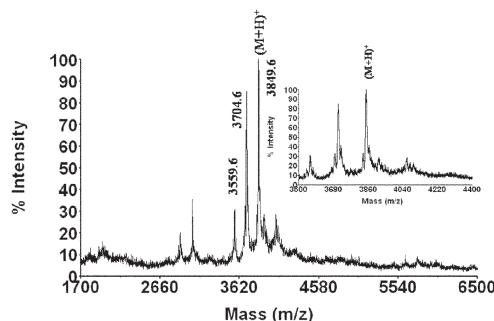


Fig. 1 The MALDI-TOF mass spectrum of **2**.

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† Electronic supplementary information (ESI) available: UV spectrum of phthalocyanine. See DOI: 10.1039/b510225a

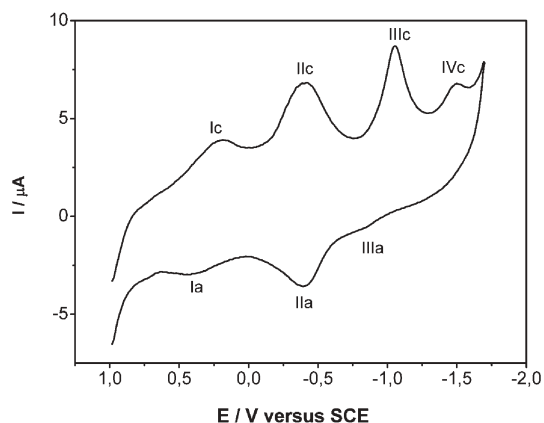


Fig. 2 Cyclic voltammogram of **2** (1.50×10^{-4} M) at 0.100 V s^{-1} on Pt in DMSO/TBAP.

leaving group could be $\text{C}_{10}\text{H}_9\text{O}$ which exists as an end group of the **2** structure.

Cyclic voltammetry of **2** on a platinum electrode in solution (DMSO/TBAP) showed two one-electron oxidation and two one-electron reduction couples. A typical cyclic voltammogram of **2** is shown in Fig. 2. The voltammetric data is compatible with the rigid structure of **2**. The high splitting of the $\text{Pc}(-1)/\text{Pc}(-2)$ and $\text{Pc}(-2)/\text{Pc}(-3)$ redox processes was detected with the mixed-valence splitting, ΔE_s , values of 0.69 V and 0.44 V, respectively. This gives evidence of the delocalization of charge among the cofacial Pc rings in the dimer, and thus the formation of electrochemically stable oxidized and reduced mixed-valence species. However, it appears that the species produced by the reduction processes (III and IV) are chemically unstable since these processes have very weak (III) or no (IV) anodic signal. The $\text{Pc}(-1)/\text{Pc}(-2)$ redox process of each Pc ring in **2** (couples I and II in Fig. 2) was observed at a remarkably less positive potential, as compared with the corresponding first oxidation potential in monophthalocyanines, which lies in the range 0.80–1.00 V vs. SCE.⁹ This negative potential shift results from the HOMO–HOMO interactions between the cofacial Pc rings. The separation between the first ring oxidation (couple II) and the first ring reduction (couple III), $\Delta E_{1/2}$, value for **2** was found to be 0.57 V. This low value, as compared with monophthalocyanines should

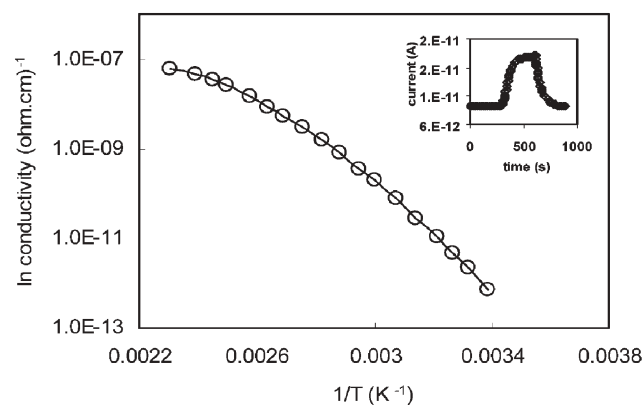


Fig. 3 Arrhenius plot of d.c. conductivity for the **2** film and its response characteristic to 50 ppm toluene vapor at room temperature (inset).

also be a consequence of the splitting of molecular orbitals due to the strong electronic interactions between the π -electron systems.

D.c and detailed impedance spectroscopy techniques have been used to investigate the charge transport mechanism and gas sensing properties of spin coated films of **2** as a function of temperature (295–433 K) and gas concentration. In general, Pcs are characterized by the Arrhenius type dependence of their electrical conductivity. As shown in Fig. 3, a strong deviation from Arrhenius law was observed for this film as it does in fast ion conducting glasses which are the basis of electrochemical energy-based devices. The a.c. conductivity $\sigma_{a.c.}(\omega)$ varied as ω^s , where the exponent s is found to be a temperature dependent variable and always less than unity. The measured a.c. conductivity data can be explained by the correlated barrier hopping model. The response characteristics of the film for the toluene vapor were also investigated. As shown inset in Fig. 3 very high sensitivity was obtained for the 50 ppm toluene vapour at room temperature.

Notes and references

‡ Reaction procedure for **1**: 1,3-dimethoxy-4-*t*-butylcalix[4]arene (1.9 g, 2.8 mmol) and 4-nitrophthalonitrile (0.972 g, 5.6 mmol) were added successively with stirring to dry DMSO (60 ml). After they were dissolved, anhydrous K_2CO_3 (1.16 g, 8.4 mmol) was added and the reaction mixture was stirred at 85°C for 76 h. The reaction was monitored by TLC. Then, the reaction mixture was poured into 200 ml of cold water, acetic acid (2 ml) was added, and then stirred for 15 min. The precipitate was filtered off, flushed several times with cold water until the filtrate was neutral and dried in air, then at 70°C . This compound was readily soluble in the majority of organic solvents such as ethanol, methanol, chloroform, THF, acetone, diethyl ether, DMF and DMSO. Yield: 2.26 g (87%). m.p. $165\text{--}168^\circ\text{C}$; $^1\text{H-NMR}$ (CDCl_3): δ , ppm 7.78–6.31 (m, 14H, arom.), 3.73–3.23 (m, 6H, OCH_3), 2.66 (s, 8H, Ar- CH_2), 1.63–1.12 (m, 36H, *t*Bu CH_3). IR (KBr): ν , cm^{-1} 3046, 2959–2869 (CH aliph.), 2822, 2357, 2323, 2229 (C=N), 1734, 1596 (Ar C=C), 1476, 1359, 1290, 1245 (Ar-O-Ar), 1193, 1117, 1017, 949, 873, 834, 523. Anal. calcd. for $\text{C}_{62}\text{H}_{64}\text{N}_4\text{O}_4$ (928): C 80.17, H 6.89, N 6.03; found: C 79.83, H 6.68, N 5.94.

§ Reaction procedure for **2**: The mixture of compound **1** (0.40g, 0.437 mmol) and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.047 g, 0.218 mmol) was refluxed for 23 h under N_2 stirring in dry DMF (2.7 ml). After cooling to room temperature, 5 ml of distilled water was added to the blue-green mixture to precipitate the product. The precipitate was suction filtered, multiply washed at first with hot water and then with hot ethanol in order to eliminate the unreacted starting materials and dried *in vacuo*. Then, the crude product was repeatedly flushed with CHCl_3 . After the filtrate had been evaporated to dryness, it was washed with ethanol until the filtrate was colorless and dried *in vacuo*. This compound is soluble in ethyl acetate, acetic acid, CH_2Cl_2 , CHCl_3 and warm DMSO. Yield: 0.0275 g, 6.5%. m.p. $> 300^\circ\text{C}$. UV-VIS λ_{max} (CHCl_3 , 78.08 μM) ($\log \epsilon/\text{l mol}^{-1} \text{cm}^{-1}$): 342 (3.455), 620 (3.996), 688 (4.538) nm. $^1\text{H-NMR}$ (CDCl_3): δ , ppm 8.57–7.11 (m, 56H, arom.), 3.23–3.3.18 (t, 24H, OCH_3), 2.85 (d, 32H, Ar- CH_2), 1.68–1.57 (t, 144H, *t*Bu CH_3). IR (KBr): ν , cm^{-1} 3057, 2956–2866 (CH aliph.), 2330, 1730, 1658, 1605, (Ar C=C), 1472, 1359, 1285 (Ar-O-Ar), 1193, 1118, 1021, 942, 871, 757, 675, 621. Anal. calcd. for $\text{C}_{248}\text{H}_{256}\text{N}_{16}\text{O}_{16}\text{Zn}_2$ (3847.6): C 77.41, H 6.70, N 5.82; found: C 77.14, H 6.74, N 6.18.

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