

Synthesis and electrical properties of novel supramolecular octa-phthalocyaninato-dicobalt(II)-hexazinc(II) and dicobalt(II)-dimeric-phthalocyanine with six ferrocenylimin pendant groups

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Abstract

In this study supramolecular octakis phthalocyaninato-diCo(II)hexakis-Zn(II) has been synthesized in two steps. Starting with tetracyanodibenzo(1,4,7,10-tetrathia-(12-crown)) (1) and 4-nitro-1,2-dicyanobenzene (2), nitro-substituted dimeric phthalocyanine (3) was synthesized. Compound 3 reacted with unsymmetric Zn(II) phthalocyanine (4) to furnish a supramolecular assemble of a Co(II) dimer with six Zn(II) phthalocyanines through azo bridges (5). Co(II) dimeric phthalocyanine with six ferrocenyl groups (7) was obtained by the condensation of 6 with ferrocenylaldehyde. Compounds 3, 5, 6 and 7 were characterized by elemental analysis, ICP-MS, IR, UV-Vis and ¹H NMR spectroscopy. The electronic properties of a thin film of the compounds were investigated by impedance spectroscopy and d.c. conductivity measurements as a function of temperature. The a.c. conductivity is found to vary with frequency, ω , as ω^s with index $s \leq 1$, suggesting a hopping conduction mechanism for 3 and 6. Whereas a frequency independent conductivity was observed for 5. It was found that reducing the nitro group to amines and azo coupling by the asymmetric nitro groups increases the electrical conductivity. The higher conductivity of 5 can be attributed to the increase in the mobility of charge carriers due to overlap of the π electron systems along the stacking direction of the molecules.

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1. Introduction

The design of novel substituted phthalocyanines closely follows the requirements of their intended applications. Phthalocyanines, in particular their readily soluble peripherally substituted derivatives, possess a wide range of chemical and physical properties that make them interesting building blocks for a number of applications and new materials [1]. Among these properties are the presence of highly conjugated π -electron systems, high absorptivity in the near-IR region, the ability to exhibit varying conductivity upon doping and photocatalytic effects [2]. The impor-

tance of phthalocyanines in many fields including chemical sensors, solar cells, electrochromism, batteries, photodynamic therapy, semiconductive materials and liquid crystals is increasing rapidly as a result of newly synthesized compounds [3–6]. Starting from simple monofunctional substituents, more complex structures such as crown ethers [7], tetraaza [8], diazatrioxa [9], diazadithia [10], tetraaza-crown ether double layer [11] and tetrathia macrocycles [12], which are capable of binding transition metal ions leading to homo- and heteropentamuclear complexes, have been introduced into the periphery of the phthalocyanines nucleus. Various strategies have been promulgated in efforts to achieve products with different substituents on each of the benzo units. Although at a first glance it appears possible to obtain asymmetrically substituted phthalocyanines by cyclotetramerization of a mixture

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of two or more phthalonitrile derivatives with different substituents, isolation of each isomer is hardly possible, and the yield of the desired product could be very low [1,13,14]. Some unsymmetrical structures have been acquired by making use of boron subphthalocyanines [15].

Many binuclear phthalocyanines have been synthesized and various properties have been reported in last decade [16]. In our previous study, starting from a tetracyano compound with 12-membered dioxo-dithia macrocycles, in which oxygen and sulfur atoms are diagonally positioned, it has been possible to prepare either polymeric or dimeric phthalocyanines over iminoisoindoline compounds with subphthalocyanine [17] using the statistically mixed method [18]. In applications phthalocyanines are usually prepared by depositing the phthalocyanine molecules as thin films onto an appropriate substrate, using different methods (LB technique, high vacuum evaporation, spin coating, etc.). While the phthalocyanine thin films are used for the fabrication of practical devices, their electrical (d.c. and a.c.) properties must be taken into account. For example, to produce any device whose active layer is made of phthalocyanine films, we need to know the effect of the temperature on both a.c. and d.c. electrical properties of the film, so as to carry out an accurate design. The aim of this study is to synthesize binuclear octaphthalocyanine and dimeric phthalocyanine with six ferrocenyl groups. For this purpose, nitro-substituted dimeric phthalocyanine **3** was reacted with unsymmetric **4**, NaOH solution and activated zinc powder in THF to obtain **5**. In the second step, using hydrazine hydrate as a reductant, amine-substituted dimeric phthalocyanine **6** was synthesized from nitro-substituted dimeric phthalocyanine **3**. Finally, using ferrocenylaldehyde, **7** was prepared. The electrical properties of **3**, **5** and **6** were examined.

2. Experimental

2.1. Synthesis

All chemicals used were of reagent grade. All solvents were dried and purified as described by Perrin and Armarego [19]. The solvents were stored over molecular sieves. Soluble derivatives with eight alkylthio substituents have been synthesized through cyclotetramerization of 4,5-bis(hexylthio)phthalonitrile which has been prepared directly from the 4,5-dichloro compound with hexanethiol [20]. 4-Nitrophthalonitrile **2** was synthesized by the method described previously in the literature [21]. The progress of the reactions was monitored by thin layer chromatography (TLC). Column chromatography was used for purification of the complexes.

Elemental analyses were performed on a LECO CHNS 932 instrument. ^1H NMR spectra were determined with a Varian UNITY INOVA 500 MHz NMR spectrometer. IR spectra were recorded as KBr disks in the range of 400–4000 cm^{-1} on a SHIMADZU FTIR-8300 spectrometer. The electronic absorption spectra were measured in

CHCl_3 for compounds **4**, **5** and DMSO for **3**, **6** with a UNICAM UV2-100 UV/VISIBLE spectrometer. Zinc, cobalt and iron contents in the digested mixture were determined on a Thermo X-Series/X7 ICP-MS. Before the ICP-MS measurements, compound **5** and **7** were digested with HNO_3 .

2.2. [5'-6'-Bis(17',25',32'-trinitro-phthalocyaninyl)-(1,4,7,10-tetrathia-12-crown)dicobalt(II)] (**3**)

A mixture of **1** (0.062 g, 0.142 mmol), 4-nitrophthalonitrile **2** (0.150 g, 0.853 mmol) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.067 g, 0.284 mmol) was refluxed in amyl alcohol under argon for 6 h. The reaction mixture was cooled down to room temperature and precipitated by adding methanol. After filtration, the product was washed with methanol, chloroform and acetone. This compound was soluble in tetrahydrofuran (THF), dimethylformamide (DMF) and dimethylsulfoxide (DMSO). Yield: 75 mg (33%). UV-Vis (DMSO, $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$)): 337 (5.090), 430(sh) (4.080), 642(sh) (4.610) and 682 (4.77). IR (KBr pellet) ν/cm^{-1} : 3060, 2983, 2923, 2858, 1620, 1523, 1344, 1260, 1090, 902, 742. Anal. Calc. for $\text{C}_{68}\text{H}_{30}\text{N}_{22}\text{S}_4\text{O}_{12}\text{Co}_2$: C, 51.56; H, 1.84; N, 19.55; S, 8.04. Found: C, 51.72; H, 1.70; N, 19.49; S, 7.95%.

2.3. [3-Nitro-9,10,16,17,23,24-hexakis(hexylthio)-phthalocyaninato Zn(II)] (**4**)

A well-powdered mixture of **2** (0.173 g, 1 mmol) and 4,5-bis(hexylthio) phthalonitrile (1.442 g, 4 mmol) were dissolved in dry DMF (3 mL) in a tube. Zinc(II) acetate (0.878 g, 4 mmol) was added to this solution and the mixture was sealed and heated at 170–180 °C for 6 h. to give an unsymmetrical substituted Pc. The reaction mixture was cooled down to room temperature and precipitated by adding methanol. After filtration, the dark green product was washed with methanol and purified by column chromatography (silica gel) with CHCl_3 . Yield: 514 mg (39%). UV-Vis (CHCl_3 , $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$)): 337 (4.780), 363 (4.860), 440 (4.263), 638 (4.613) and 710 (5.269). IR (KBr pellet) ν/cm^{-1} : 3058, 2983, 2923, 2858, 1618, 1265, 902, 742; ^1H NMR (500 MHz, CDCl_3) δ : 0.88 (s, 18H, $-\text{CH}_3$), 1.92–2.16 (m, 36H, $-\text{CCH}_2$), 2.22 (br, 12H, SCH_2), 2.62 (br s, 12H, $-\text{SCCH}_2$), 6.70–8.20 (m, 9H, Ar-H). Anal. Calc. for $\text{C}_{68}\text{H}_{87}\text{N}_9\text{S}_6\text{O}_2\text{Zn}$: C, 61.86; H, 6.64; N, 9.55. Found: C, 61.58; H, 6.77; N, 9.39%.

2.4. {17,25,32,17',25',32'-Hexakisazo-69,69'-hexakis[74',75',81',82',88',89'(hexylthio)-phthalocyaninyl-hexazinc(II)]-[bis-phthalocyaninatodicobalt(II)]} (**5**)

Compound **3** (0.064 g, 0.040 mmol) and compound **4** (0.320 g, 0.243 mmol) were dissolved in THF. A solution of NaOH (1 mL, 0.268 M) and activated zinc powder were added to the reaction mixture and refluxed for 24 h, after which time the solvent was evaporated under

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