

## Synthesis, characterization, and electrical and electrochemical properties of sandwich dilutetium tetraphthalocyanine

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$\text{Lu}_2\text{Pc}_2$  and lithium hexylthio-phthalocyanine have been used to synthesize  $[\text{Lu}_2(\text{Pc})_4]$  which exhibits variable range hopping conductivity as inorganic semiconductors and also observed electrochromic effect from cyclic voltammetric (CV) measurement.

Rare-earth-, especially lutetium-, phthalocyanines (Pcs) are very important compounds for their intrinsic optical, electrical and redox properties which find a wide range of applications in various fields.<sup>1,2</sup> As accounted for in many unsubstituted metal free or metallo Pcs, Lu(Pcs) are insoluble in most organic solvents. This

hinders their applications in solutions. The introduction of different substituents on the benzene ring of Pc enhanced solubility.<sup>3</sup> Lu(Pc)<sub>2</sub> with various substitutions have been described recently.<sup>4-7</sup>

In order to obtain a novel sandwich dilutetium tetraphthalocyanine **4**, dimeric dilutetium phthalocyanine **3** has been synthesized according to Scheme 1. 4',5',4'',5''-Tetraimino-isoindoline-[1,4,7,10-tetrathia-(12-crown-4)] **1** and 4,5-bis(hexylthio)-1,2-diimino-isoindoline **2** were prepared by published methods,<sup>8,9</sup> respectively.

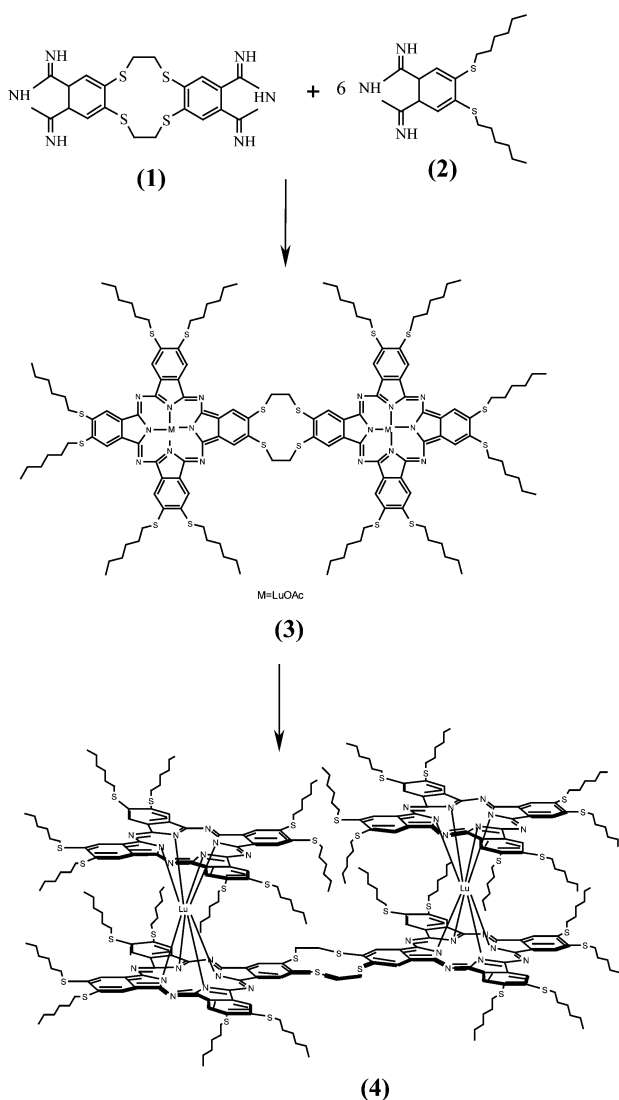
$[\text{Lu}_2(\text{Pc})_4]$  (**4**) has been synthesized *in situ* by the reaction of dimeric dilutetium phthalocyanine **3** and two equivalents of dilithium octakis-hexylsulfanylphthalocyanine in amyl alcohol.‡

In the electronic absorptions spectra (Fig. 1), Q-bands of **3** and **4** occur at 715 nm and 703 nm respectively. Fig. 2 shows the ESR spectrum of **4** which corresponds to a radical system.

The dc conductivity of spin coated **3** and **4** thin films were measured as a function of temperature from 50 to 290 K in the dark and under a vacuum of  $10^{-3}$  mbar. Fig. 3 displays the dependence of  $\ln$  dc conductivity,  $\ln \sigma_{\text{dc}}$ , on the inverse of the temperature,  $1000/T$ , for **3** and **4** thin films. It is clear from Fig. 3 that the temperature dependence of the conductivity of **3** thin film can be explained by the conventional band conduction mechanism. The linear relationship of **3** suggests that there is one type of conduction channel contributing to the conductivity and the linearity over the whole temperature range for **3**, which indicates that  $\sigma$  exhibits activated behavior in the relationship:

$$\sigma = \sigma_0 \exp(-E_A/kT) \quad (1)$$

But the non-linear relationship between these two parameters for **4** film cannot be explained by the band conduction model. The variation of the conductivity with the inverse temperature is characteristic of variable range hopping (VRH) of barriers in 3-dimensions. It is clear from the  $\ln \sigma$  versus  $1/T$  graph that the conductivity does not follow eqn. (1) for **4**. In this case, the



Scheme 1

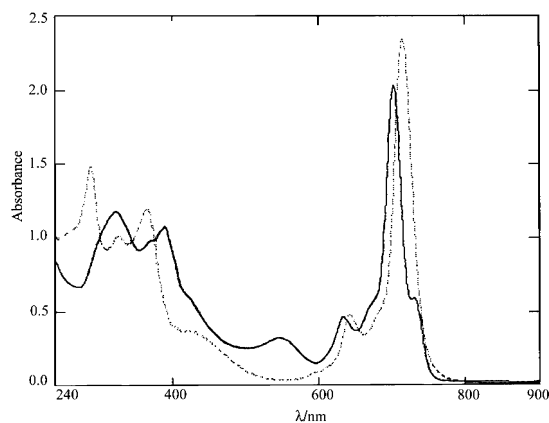


Fig. 1 Absorption spectrum of **3** (.....) and **4** (—) in  $\text{CHCl}_3$ .

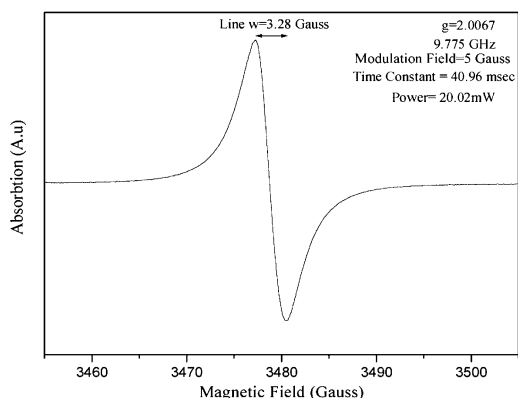


Fig. 2 ESR spectrum of **4**.

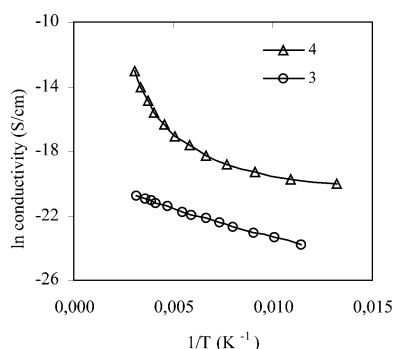


Fig. 3 Arrhenius plot for **3** and **4**.

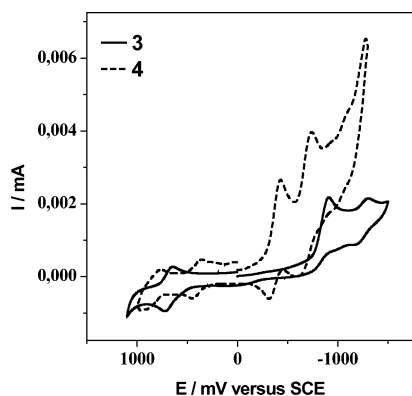


Fig. 4 Cyclic voltammograms of **3** ( $1.00 \times 10^{-4}$  M) and **4** ( $2.50 \times 10^{-4}$  M) at  $0.050 \text{ V s}^{-1}$  on Pt in THF/TBAP.

dominant conduction mechanism is due to the hopping of carriers between localized states around the Fermi level.

Voltammetric measurements on platinum electrode in THF/TBAP showed that **3** undergoes two reductions and a single oxidation, while two reductions and two oxidations are observed for **4** (Fig. 4). All redox signals are Pc-ring based, and have a quasi-reversible behaviour. The separations between the first ring

reduction and the first ring oxidation,  $\Delta E_{1/2}$  values for **3** and **4** were found to be 1.51 V and 0.78 V, respectively. These values are consistent with the difference in molecular geometries of the complexes. The low value of  $\Delta E_{1/2}$  for **4** should be a consequence of the splitting of molecular orbitals due to the strong electronic interactions between the  $\pi$ -electron systems of the Pc rings.<sup>10–12</sup> The voltammetric behaviours of **3** and **4** in a film on a bare ITO coated glass in contact with an aqueous or non-aqueous (DMSO) solution of  $\text{KClO}_4$  were also examined with respect to characteristic colour changes. Fast and stable transitions between the green, blue and purple coloured redox states associated with two well-defined reduction couples were observed clearly for each complex.

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## Notes and references

† Reaction procedure for **3**: A mixture of 0.040 g (0.085 mmol) **1**, 0.220 g (0.580 mmol) **2** and 0.0075 g (0.0426 mmol) lutetium acetate were refluxed in amyl alcohol under argon for 6 h and finally evaporated under reduced pressure. The green precipitate chromatographed on a column of silica gel.  $\text{CHCl}_3$  was first used as eluent. After collection of the dark green product, a 2%  $\text{CH}_3\text{OH}$  98%  $\text{CHCl}_3$  solution was used as eluent and green solution was obtained in this way. Yield: 50 mg (19.23%). UV-VIS ( $\text{CHCl}_3$ ,  $\lambda_{\text{max}}$ /nm) 289, 365, 642 and 715;  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.89 (t, 36H,  $\text{CH}_3$ ), 1.19–1.58 (m, 96,  $\text{CH}_2$ ), 1.91 (t, 24H,  $\text{SCH}_2$ ), 3.03 (br s,  $\text{COCH}_3$ ), 3.36 (s, 8H,  $\text{SCH}_2$ ), 7.15–7.25 (m, 16H, ArH). Found (%): C, 56.92; H, 6.30; N, 7.49; S, 16.18. Calc. for  $\text{C}_{144}\text{H}_{186}\text{N}_{16}\text{S}_{16}\text{O}_4\text{Lu}_2$  (%): C, 56.4; H, 6.07; N, 7.31; S, 16.70.

‡ Reaction procedure for **4**: 0.115 g (0.32 mmol) **2** and Li metal and 20 mL dry amyl alcohol was stirred at  $50^\circ\text{C}$  under an argon atmosphere until complete dissolution of Li. It was then refluxed for 6 h more and to this reaction mixture 0.050 g (0.016 mmol) **3** was added and refluxed for a further 15 h. After evaporation to dryness, the very dark green product was washed with methanol and purified by column chromatography (silica gel) with  $\text{CHCl}_3$ . Yield: 32 mg (34.40%). UV-VIS ( $\text{CHCl}_3$ ,  $\lambda_{\text{max}}$ /nm) 322, 390, 547, 634 and 703;  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.83–0.94 (m, 84H,  $\text{CH}_3$ ), 1.18–1.52 (m, 224H,  $\text{CH}_2$ ), 1.19–2.1 (m, 56H,  $\text{SCH}_2$ ), 3.38 (s, 8H,  $\text{SCH}_2$ ), 7.14–7.26 (m, 32H, ArH). Found (%): C, 62.05; H, 7.13; N, 7.18; S, 17.19. Calc. for  $\text{C}_{300}\text{H}_{404}\text{N}_{32}\text{S}_{32}\text{Lu}_2$  (%): C, 61.79; H, 6.93; N, 7.69; S, 17.58.

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