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# Synthesis and characterization, novel across adjacent ring formed phthalocyanine

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Novel mononuclear Zn(II) 4, Co(II) 5 and Cu(II) 6 metallophthalocyanines have been synthesized from 4,4'(ethane-1,1-p-phenol-2,2-p-phenoxy)phthalonitrile 3, which can be obtained by the reaction of 4-nitrophthalonitrile 1 with 1,1,2,2-tetrakis(p-hydroxy-phenyl)-ethane 2. The target water-soluble derivatives of 7–9 were acquired from a boiling suspension of the compounds in aqueous 20% KOH solution. The synthesized complexes have been characterized by UV-vis, IR, <sup>1</sup>H NMR and MALDI-TOF-mass spectroscopies. In addition, the geometric and electronic structures of 2-6 were investigated by ab initio/DFT quantum mechanical calculations using the Gaussian 03 program with HF theory at the B3LYP/3-21G level. The redox properties of the complexes 4-6 were examined by cyclic voltammetry on platinum in DMSO/TBAP. These complexes displayed one-electron metallophthalocyanine-based and multi-electron hydroxyphenyl-based redox processes. The effect of temperature on the d.c. conductivity and impedance spectra of spin coated films of compounds were investigated at the temperatures between 300-452 K and in the frequency range of 40-105 Hz. Thermally activated conductivity dependence on temperature was observed for all compounds. A.c. results indicated that conduction mechanism can be explained by classical hopping barriers mechanism

Phthalocyanines (Pcs) and their metal complexes forms are the most studied class of functional organic materials. The functions of these compounds arise mainly from their conjugated  $18\pi$ electron system having rich electron transfer ability, which depends on the kind and number of metal centres and substituents. A great deal of attention has been paid to the properties and applications of phthalocyanine (Pc) compounds, including electrodichroism, optical disks, laser dyes, liquid crystals, catalysis and electrocatalysis, non-linear optics, photoelectrochemistry, gas sensors, jet printing inks, display devices, data storage, chemical sensors, solar cells and photonic devices.1 In addition to traditional applications, in the field of cancer treatment, using phthalocyanines for photodynamic therapy (PDT) in is a new technique.<sup>2</sup>

We have published a number of papers on ball-type Pcs and in recent years a new class of Pcs has appeared in the literature.<sup>3,5</sup> These compounds, with various bridging units, two co-facial Pc rings and

for all films. Introduction

homo or hetero metals showed intrinsic electrochemical, electrical, gas sensing, non-linear optical and catalytic properties.<sup>3,4</sup> In one of our previous studies, pentaerythritol was employed to obtain ball-type Pcs. Firstly, two of four hydroxyl groups were protected by forming two monoacetyls before replacement reaction with 5nitrophthalonitril. After separation of the ball-type Pc with four pentaerythritol bridging units, acetyl groups were removed by a known procedure, in order to obtain ball-type Pc with eight free hydroxyl groups. Further reactions of functional hydroxyl groups allowed us to prepare various novel ball-type Pcs, which showed interesting physical properties.<sup>3,4,6</sup> Therefore, it would be worthwhile to design and synthesize ball-type Pcs using distinct bridged molecules carrying four or more hydroxyl groups. In this regard, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane 2 was the choice as an interesting bridged compound in this study. The reaction of 4,4'(ethane-1,1-p-phenol-2,2-p-phenoxy)phthalo-nitrile 3 with zinc, cobalt and copper in pentanol gave the relevant mononuclear metal Pcs. In our continuing efforts, we changed the experimental conditions to the "heating of the solid phase" method with the aim of the synthesizing novel ball-type Pcs. However, the products were the same mononuclear Pcs synthesized in pentanol, due to remarkable guest selectivity of ligand 2 with strong affinity towards one guest.7 Thus, we report here in detail the synthesis and characterization of mononuclear Pcs and their water-soluble derivatives. Density functional theory (DFT) is one of the most successful and widely used powerful theoretical tools in the computational quantum chemistry, as an approximation method for ab initio

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Scheme 1 (i) 24 h,  $K_2CO_3$ , DMF, (ii) 1-pentanol, reflux, 24 h, a:  $Zn(CH_3COO)_2 \cdot 2H_2O$ , b:  $Co(CH_3COO)_2 \cdot 4H_2O$ , c:  $Cu(CH_3COO)_2$ .  $H_2O$ , DBU, (iii) %20 KOH.

calculation of electronic structures of many-particle systems.<sup>8</sup> It could be helpful in the devise and syntheses of new molecules since the calculation of the energy levels of the frontier orbitals help to explain the reactivity and physicochemical properties of the molecules. Thus, DFT was employed to calculate the steric energies and heat of formations of **2–6**. The electrochemical and electrical properties of metallophthalocyanines (MPcs) **4–6** were also investigated.

#### **Results and discussion**

#### Syntheses and characterization

4-nitrophthalonitrile **1** was converted to **3** by the reaction of 1,1,2,2-tetrakis(*p*-hydroxy-phenyl)-ethane **2** in dry DMF as the solvent and  $K_2CO_3$  as the base with the method described previously in the literature.<sup>8</sup> Compound **3** was obtained in good yield (62%). For the synthesis of MPcs in this work, we modified the method described in the literature.<sup>9</sup> The MPcs **4**, **5** and **6** were synthesized by the reaction of compound **3** with Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O, Co(OAc)<sub>2</sub>·4H<sub>2</sub>O and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O, respectively, in penthanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 190 °C. Water-soluble Pcs **7**, **8** and **9** were obtained by boiling the suspensions of **4**, **5** or **6**, respectively, in aqueous KOH (20%) (Scheme 1).

The structures of compounds **4**, **5** and **6** were deduced from their IR, MALDI-TOF-mass and UV-vis spectroscopic data and elemental analysis. Compound **3** has satisfactory elemental analysis results. The IR spectrum of **3** displayed peaks of  $3427 \text{ cm}^{-1}$ (OH),  $3072 \text{ cm}^{-1}$  (Ar–C–H),  $2232 \text{ cm}^{-1}$  (C==N) and  $1280 \text{ cm}^{-1}$  (Ar– O–Ar) which confirms the formation of the compound. The C– OH peak at 3400 cm<sup>-1</sup> indicated the presence of hydroxyl groups, which do not attend in the formation reaction of compound **3**. The formation of compound **3** was also confirmed by the signals for the aromatic ring protons (in the region *ca*. 6.66 and 7.69 ppm), methyl protons (at *ca*. 4.65 ppm) and hydroxyl protons (at *ca*. 5.11 ppm) in its<sup>1</sup>H NMR spectrum.

Compound **3** was converted into the corresponding MPcs **4**–**6** in good yields (69.2–74.3%). Elemental analysis results for the compounds were good. Examination of the spectroscopic data for **4–6** indicated that <sup>1</sup>H NMR spectroscopy, coupled with IR, UV-vis and MALDI-TOF-mass spectroscopy, was potentially the best analytical technique to provide confirmatory structural evidence for their formation. The IR spectra of compounds **4**, **5** and **6** showed Ar–O–Ar peaks at 1230–1234 cm<sup>-1</sup>, C==C (in phenyl and naphthalene rings) peaks at 1616 cm<sup>-1</sup>, C==N peak at 1717 cm<sup>-1</sup>, Ar–CH peak at 2925 cm<sup>-1</sup> and the C–OH peak at 3400 cm<sup>-1</sup>. The absence of (C==N) stretches in the IR spectra of **4–6** is indicative of the completion of the reactions for the formation of these complexes.

The UV-vis spectra of **4–6** in DMSO showed typical absorptions between 672 and 682 nm in the Q band region (Fig. 1). The Q band absorptions of the complexes refer to the  $\pi \rightarrow \pi^*$  transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring. The B band absorptions of the complexes were observed within the UV region between 300 and 330 nm, due to the transitions from the deeper  $\pi$  levels to the LUMO. The ground state electronic absorption spectra of **4–6** showed monomeric behaviour evidenced by a single narrow Q-band, typical of MPc complexes (Fig. 1). Aggregation is usually depicted as a co-planar association and is dependent on the concentration.<sup>10</sup> In the aggregated state, the electronic structure of



Fig. 1 UV-vis spectra of 4–6 in DMSO.

the complexed Pc rings is perturbed resulting in alternation of the ground and excited state electronic structures.<sup>11</sup> This causes the broadening or the split of the absorption bands, especially at high concentrations. Fig. 2a shows the spectra of **4** in DMSO, 7 in DMSO and **7** in water to compare the differences of Pc and potassium phenolate Pc. The spectra of the structure taken in water and DMSO are clearly not similar because of the aggregation. Fig. 2b shows the spectra of **7** within the concentration range from  $4.6 \times 10^{-5}$  to  $5.5 \times 10^{-4}$  M in water as an example. As the concentration was increased, the intensity of absorption of the Q-band also increased linearly and there were no new blue shifted bands due to the aggregated species.



**Fig. 2** UV-vis spectra of **4** in DMSO (black), **7** in DMSO (red) and **7** in water (blue) (a), **7** at different concentrations within the range from  $4.6 \times 10^{-5}$  to  $5.5 \times 10^{-4}$  M in water (b).

Fig. 3a shows the fluorescence spectra of **4** in DMSO at different concentrations within the range from  $5.8 \times 10^{-6}$  to  $5.8 \times 10^{-5}$  M. Fluorescence emission peak was observed at 693.94 nm. The proximity of the wavelength of the component of the Q-band absorption to the Q-band maxima of the fluorescence spectra for the complex suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation.<sup>12</sup> The intensity of the fluorescence emission of **4** is directly proportional to its concentration. The fluorescence quantum yield ( $\Phi_F$ ) value of **4** was found 0.19 in DMSO. This value is slightly lower than that of unsubstituted ZnPc standard



**Fig. 3** (a) Fluorescence excitation spectra of **4** at different concentrations within the range of  $5.8 \times 10^{-6} - 5.8 \times 10^{-5}$  M in DMSO. (b) The correlation between time and fluorescence emission intensity of **4** at 693.94 nm in DMSO.

in DMSO ( $\Phi_{\rm F} = 0.20$ ).<sup>12</sup> It was also observed that the fluorescence emission of the compound decreased with time (Fig. 3b).

The optimized structure of 5, determined according to the molecular mechanics calculation is shown in Fig. 4. The molecular mechanics calculation of 2 and 3 were also carried out to understand the effect of their conformations on those of 4–6. The steric energies and heat of formations for 2–6 are listed in Table 1. Conformers 2 and 3 within the ten optimized ones have minimum steric hindrances and the lowest heat of formations, compared to the other conformers. Calculated steric energies of stable (-0.875 kcal mol<sup>-1</sup>) and unstable (-1.62 kcal mol<sup>-1</sup>) conformers of molecule 2 with HF theory at the B3LYP/3-21G level are in accordance with literature.<sup>7</sup> These results suggest that a central symmetrical conformation for 3 is in the formation of MPcs. The structure calculations indicated that the conformation



**Fig. 4** The optimized conformer of **5**, determined with HF theory at the B3LYP/3-21G level.

 Table 1
 Steric energies and heat of formations of 2–6, determined by HF theory at the B3LYP/3-21G level

Molecule	Steric energy/kcal mol <sup>-1</sup>	Heat of formation/kcal mol <sup>-1</sup>		
2	-0.875	73.46		
3	-2.741	151.52		
4	-80.287	432.21		
5	-96.106	402.89		
6	-85.862	402.97		

of **4**, **5** and **6** are not planar as shown in Fig. 4. The side groups diverge from linearity although the MPc rings seem nearly planar.

The MALDI-MS spectra of 4-6, recorded in α-cyano-4hydroxycinnamic acid, are shown in Fig. 5-8. For the high resolution spectra, reasonable peak intensities could not be obtained because of the short life times of the ions in reflection mode mass spectrometer. However, the complexes were more stable under the laser and MALDI-MS conditions in linear mode mass spectrometer. Thus, in linear mode positive ion mass spectra, reasonable resolution (about 1500) was obtained for 5 and 6. This allowed us to observe their resolved peaks resulted from isotopic distribution of the elemental composition of the elements existing in these complexes. Experimental and theoretical isotopic distributions of 5 and 6 matched properly each others. For 6, first isotopic peak mass started at 1367.35 and finished at 1373.37 Da in its theoretical isotopic mass distribution (Fig. 5 and 6). In the experimental data, first 6 peaks were observed in the similar masses but last one could not be observed because of the low intensity of the complex. For 5, all theoretical isotopic mass distributions



**Fig. 5** Positive ion and linear mode MALDI-TOF-MS spectrum of **5** in  $\alpha$ -cyano-4-hydroxycinnamic acid MALDI matrix using nitrogen laser (at 337 nm wavelength) accumulating 50 laser shots. Inset spectrum shows expanded molecular mass region of the complex.



**Fig. 6** Positive ion and linear mode MALDI-TOF-MS spectrum of **6** in  $\alpha$ -cyano-4-hydroxycinnamic acid MALDI matrix using nitrogen laser (at 337 nm wavelength) accumulating 50 laser shots.



Fig. 7 Positive ion and linear mode MALDI-TOF-MS spectrum of 4 in  $\alpha$ -cyano-4-hydroxycinnamic acid MALDI matrix using nitrogen laser (at 337 nm wavelength) accumulating 50 laser shots. Inset spectrum shows expanded molecular mass region of the complex.



Fig. 8 Positive ion and reflection mode MALDI-TOF-MS spectrum of  $C_{84}H_{48}K_4N_8O_8Zn$  complex was obtained in 1,8-dihy-droxy-9(10H)-anthracenone (dithranol) MALDI matrix using nitrogen laser (at 337 nm wavelength) accumulating 50 laser shots.

matched the experimental data exactly, with isotopic peak masses starting at 1363.35 and finishing at 1367.37 Da. For **4**, only a single peak with low resolution could be obtained (Fig. 7). This is because of more isotopic peaks of zinc compared to cobalt and copper. In the case of **4**, experimental molecular ion peak mass can be assigned to its theoretical average mass. MALDI-MS results showed that the complexes were synthesized truly in the experimental route and purified perfectly.

Positive ion and refection mode MALDI-MS spectrum of the synthesized complex was obtained and is given in Fig. 8. Some novel MALDI matrices were tried to find intense molecular ion peak at 1517.13 Da (monoisotopic) and low fragmentation under the MALDI-MS conditions for this complex. Only dithranol yielded the best MALDI-MS spectrum for the complex. Beside the protonated molecular ion peak of the complex, some potassium removed ion signals also observed. These ions were found to be  $[M - K + 2H]^+$ ,  $[M - 2K + 3H]^+$ ,  $[M - 3K + 4H]^+$  and  $[M - 4K + 5H]^+$ . These ions were occurred in acidified matrix solution as a normal processes in MALDI-MS during the salt analysis. MALDI-MS spectrum showed that complex was synthesized successfully and there was no impurity in the complex.

# Electrochemistry

The redox properties of the complexes **4–6** were examined by cyclic voltammetry on platinum in DMSO/TBAP. The voltammetric data is summarized in Table 2. The linear variation of peak currents

Complex	Redox process	<i>E</i> <sub>1/2</sub> <sup><i>a</i></sup> /V ( <i>vs</i> .SCE)	$\Delta E_{\rm p}\ ^{b}/{\rm V}$	$I_{\rm pa}/I_{\rm pc}{}^c$
ZnPc 4	$\mathbf{R}_1$	-0.66	0.10	1.00
	R <sub>2</sub>	-1.14	0.24	2.50
CoPc 5	0Î	0.29	0.12	1.00
	$\mathbf{R}_1$	-0.51	0.06	1.00
	$\mathbf{R}_2$	-0.98	0.18	2.85
CuPc 6	$\mathbf{R}_{1}$	-0.54	0.12	1.00

<sup>*a*</sup>  $E_{1/2}$  values were measured by cyclic voltammetry  $[E_{1/2} = (E_{pa} + E_{pc})/2]$ . <sup>*b*</sup>  $\Delta E_p = E_{pa} + E_{pc}$  at 0.050 V s<sup>-1</sup>. <sup>*c*</sup>  $I_{pa}/I_{pc}$  for reduction,  $I_{pc}/I_{pa}$  for oxidation processes at 0.050 V s<sup>-1</sup> scan rate.

with potential scan rate within the range of 0.010-0.500 V s<sup>-1</sup> for all redox processes of **4–6** showed that they are diffusion-controlled.

Complexes 4 and 6 displayed two reduction processes (Table 2). Fig. 9 shows typical cyclic voltammograms of 4 at 0.050 V s<sup>-1</sup> scan rate. It is clear from well-known redox properties of mononuclear MPcs and redox-inactive nature of Zn(II) and Cu(II) metal centers in Pc cavity that these redox processes are Pc-ring based.13 Cyclic voltammetric data and controlled-potential coulometry measurements suggested that the first reduction couples of 4 and 6 are one-electron quasi-reversible processes with anodic to cathodic peak separations of 0.100 V and 0.120 V, respectively. The cathodic peak currents of the second reduction processes of these complexes were much higher than those of the first reduction couples, as shown in Fig. 9 for 4. This implies that the second reduction processes of these complexes correspond to the reduction of 1,1,2,2-tetrakis(p-hydroxy-phenyl)-ethane-based peripheral hydroxy-phenyl groups. With the aim of clarifying this comment, we also examined the voltammetric behaviour of 1,1,2,2-tetrakis(p-hydroxy-phenyl)-ethane, 2 (Fig. 10). This compound displays an irreversible reduction signal at -1.70 V vs. SCE at the end of available potential window in DMSO/TBAP, providing support for the assignment of the second reduction processes of 4 and 6 to 1,1,2,2-tetrakis(p-hydroxy-phenyl)-ethanebased peripheral hydroxy-phenyl groups. The reduction of 2 occurs at relatively high negative potentials, compared to the second redox processes of 4 and 6. This can be attributed to the strong electronic



Fig. 9 Cyclic voltammogram of  $2.0 \times 10^{-4}$  M 4 at 0.050 V s<sup>-1</sup> scan rate on Pt in DMSO/TBAP (The inset shows the R<sub>1</sub> process over relatively high sensitive current scale).



Fig. 10 Cyclic voltammogram of 2 at 0.050 V s<sup>-1</sup> scan rate on Pt in DMSO/TBAP.

coupling between the Pc ring and peripheral 1,1,2,2-tetrakis(*p*-hydroxy-phenyl)-ethane-based peripheral moieties in **4** and **6**. The appearance of the second reduction potential of **5** at relatively less negative potentials, compared to the reduction potential of **2** was also observed (Table 2 and Fig. 10).

Voltammetric behaviour of 5 is different from those of 4 and 6. A typical voltammogram for 5 is shown in Fig.11. It displays an oxidation couple in addition to two reduction processes. The first reduction and the first oxidation couples are one-electron reversible and quasi-reversible processes with anodic to cathodic peak separations of 0.060 and 0.120 V, respectively. If the transition metal ion concerned has no accessible d orbital levels between the HOMO and the LUMO energies of a Pc species, then its all redox processes are Pc ring-based. The nickel, copper, zinc and some other MPcs behave in this fashion, with the M(II) central ion being unchanged as the MPc unit is either oxidized or reduced.13 However, the metal centre in some MPcs such as CoPc. FePc and MnPc are redox-active due to the presence of d orbital levels within the HOMO-LUMO gap of a Pc species. These species vary their electrochemical behaviour according to their environment in solution and thus their electrochemistry is split into two sections, that referring to donor solvents and that referring to non-donor



Fig. 11 Cyclic voltammogram of  $2.0 \times 10^{-4}$  M 5 at 0.050 V s<sup>-1</sup> scan rate on Pt in DMSO/TBAP.

solvents.<sup>13</sup> The main difference lies in whether metal or the ring is oxidized first. Donor solvents strongly favour Co(III)Pc(-2) by coordinating along the axis to form six coordinate species. If such donor solvents are absent, then oxidation to Co(III) is inhibited and ring oxidation occurs first. Thus, the first oxidation and the first reduction processes of 5 are probably metal-based and correspond to  $Co(II)Pc(-2)/[Co(III)Pc(-2)]^+$  and  $Co(II)Pc(-2)/[Co(I)Pc(-2)]^-$ , respectively, since the voltammetric measurements were carried out in DMSO/TBAP, while the second reduction corresponds to the reduction of 1,1,2,2-tetrakis(p-hydroxy-phenyl)-ethane-based peripheral hydroxy-phenyl groups. In order to provide additional support for the identification of the redox processes of 5, in situ spectroelectrochemistry of this complex was also studied. Fig. 12A shows the UV-vis spectral changes during the controlled potential electrolysis of 5 at a potential a bit more negative than the cathodic peak potential of R1' couple, -0.60 V vs. SCE Upon the first reduction at -0.60 V vs. SCE, the absorptions of the Q band at 673 nm and vibrational band at 606 nm decreases while two new bands at 454 and 710 nm appear. These spectral changes have welldefined isosbestic points at 391, 558 and 700 nm. The formation of a new band within the range of 400-500 nm and red shifting of the Q band indicate the formation of  $[Co(I)Pc(-2)]^{-}$  species, confirming that first reduction of 5 occurs at the metal center.<sup>14</sup> Fig. 12B shows the spectral changes during the oxidation process



**Fig. 12** In situ UV-vis spectral changed during the controlled-potential electrolysis of **5** at (A) –0.60 V and (B) 0.50 V vs. SCE in TBAP/DMSO.

of **5** at 0.50 V vs. SCE. The original Q band absorption at 673 nm increases and shifts to 686 nm. This spectral change is typical of metal-based Co(II)Pc(-2)/[Co(III)Pc(-2)]<sup>+</sup> redox process.<sup>14b,c</sup>

# **Electrical properties**

Arrhenius plots of  $\ln \sigma_{d.c.}$  vs. 1/T were plotted to understand the d.c. conduction mechanism of compounds **4–6** (Fig. 13). The d.c. conductivity values for the films of compounds were calculated from the slopes of the measured I-V characteristics by using the following equation (eqn (1)),

$$\sigma_{d,c} = \frac{I}{V} \frac{d}{(2n-1)\mathbf{l}.\mathbf{h}} \tag{1}$$

where, I is the measured current, V applied voltage, d distance between the finger pair, n number of the finger pair, l overlap length and h thickness of the electrodes. It is well known that, the electrical conduction processes in Pc compounds depend on several factors that include the chemical nature of Pcs, the polymorphic phase of the microcrystallites comprising the film, the film thickness, the presence of impurities or molecular doping and the electrode materials. It is clear from the figure that  $\ln \sigma_{dc}$  vs. 1/Tcurves are straight lines for all compounds showing the validity of equation  $\sigma_{d.c.} = \sigma_0 \exp(-E_A/kT)$  in the present case. Where  $E_A$ is the activation energy, T the temperature, k the Boltzmann's constant and  $\sigma_0$  is the constant of proportionality. The values of the activation energies which are determined from the slope of the ln d.c. conductivity vs. 1/T graphs, are  $E_A = 0.68$ , 0.75 and 0.70 eV for compounds 4, 5 and 6, respectively. The general trend, for the order of electrical conductivities, observed in the whole temperature range for these compounds are  $\sigma_{dc}(6) > \sigma_{dc}(5)$  $> \sigma_{dc}(4)$ . This result is significant because it strongly suggests that the central metal atom plays a major role in the electrical conduction behaviour.



Fig. 13 Temperature dependence of d.c. conductivity for the films of 4-6.

The a.c. electrical conduction behaviour of the films was also investigated. A.c. measurements were carried out in the frequency range 40–105 Hz. at temperatures between 300 and 452 K. As a representative result, the temperature dependence of the measured a.c. conductivity of  $\bf{6}$  as a function of frequency at indicated temperatures is shown in Fig. 14. In organic and many inorganic



Fig. 14 The variation of a.c. conductivity with frequency for the film of 6 at different temperatures.

materials, the frequency dependent part of the total conductivity,  $\sigma(\omega)$ , is given by the power law of the form shown in eqn (2):

$$\sigma(\omega) = A\omega^s \tag{2}$$

where A and s are temperature dependent parameters.

Various models such as quantum mechanical tunnelling (QMT) and correlated barrier hopping (CBH) has been proposed to explain this type of behaviour. But, it is not easy to decide which of those mechanisms is responsible for the observed conduction mechanism. However, the behaviour of the exponent s with temperature can help in determining the possible conduction mechanism. The frequency exponent, s, were calculated from the slope of the  $\ln \sigma_{a.c.}$  vs.  $\ln f$  graphs and were generally found to decrease with increasing temperature. The behaviour of s with temperature cannot be explained by the QMT model. This model, which is based on phonon assisted tunnelling of electrons, predicts temperature independent frequency exponent s with a constant value around 0.8. According to the CBH model, the a.c. conductivity which can be expressed in terms of the density of localized states, the permittivity, the effective relaxation time and the electronic charge. This model suggests a temperature dependent s parameter which is given by the following equation (eqn (3)):

$$s=1-6\frac{kT}{W_{m}}$$
(3)

where  $W_m$  is the optical band gap. Unlike QMT model the CBH model predicts a temperature dependent s parameter which decreases with increasing temperature. It was observed that the calculated s parameters decrease with increasing temperature. These results are quantitatively consistent with the prediction of the CBH model.

To get more detailed information about the electrical properties of the compounds, impedance spectra measurements in the frequency range of  $40 - 10^5$  Hz were also carried out on spin coated film of the compounds. The measured impedance spectra, when plotted in a complex plane plot, appears in the form of a succession of semicircles representing the contributions to the electrical properties due to bulk material, grain boundary effect and interfacial polarization phenomena. So, the impedance spectra technique enables us to separate the effects due to each component. At low temperatures, the impedance spectra consist of a quasi-vertical line. The existence of semicircular shaped curves in the Nyquist plot means that the impedance becomes capacitive even at relatively high frequency. The effect of temperature on the impedance spectra of the films becomes clearly visible with rise in temperature. On the complex plane plot at high temperatures, only a depressed semicircle with different radius were observed for all at higher temperatures, indicating deviation from the Debye dispersion relation (Fig. 15). In the case of a depressed semicircle in the impedance spectra, the relaxation time is considered as a distribution of values, rather than a single relaxation time. The same type of behaviour was observed for other films.



Fig. 15 Impedance spectra of the 4 at different temperatures.

# 3. Experimental

#### Syntheses and characterization

Melting points (mp) were determined using a Sanyo Gallenkamp apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrophotometer as KBr pellets. Electronic spectra were recorded on a Shimadzu UV-3150 UV-vis-NIR Spectrophotometer. Fluorescence spectra were recorded on the Varian Eclipse Fluorescence Spectrophotometer. Elemental analyses were performed on an Elementar Vario EL III instrument. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance DPX-400 spectrometer, operating at 400.13 MHz for proton. <sup>1</sup>H NMR spectra were measured for *ca.* 25–30% solutions in DMSO, unless otherwise indicated and all chemical shifts are expressed relative to Me<sub>4</sub>Si. Mass spectra were acquired on a Voyager-DE<sup>™</sup> PRO MALDI-TOF-mass spectrometer (Applied Biosystems, USA), equipped with a nitrogen UV-laser operating at 337 nm. Spectra were recorded in linear mode (1500 resolution) with average of 50 shots.

4,4'(Ethane-1,1-p-phenol-2,2-p-phenoxy)phthalonitrile3.Compound 1 (1.384 g, 8 mmol) and compound 2 (1.593 g,4 mmol) were dissolved in dry DMF under argon. After stirringfor 15 min, finely ground anhydrous  $K_2CO_3$  (1.655 g, 12 mmol)was added portion wise in 15 min with efficient stirring. Thereaction mixture was heated and stirred at 90 °C for 24 h under

argon. After cooling to room temperature, it was treated with water and the product filtered off and washed with water and ethanol. This compound is soluble in pyridine.

Yield: 1.612 g, 62%. Mp: 174 °C. Anal. calcd for  $C_{42}H_{26}N_4O_4$ : C 77.53, H 4.03, N 8.61. Found: C 77.57, H 4.08, N 8.66%. IR (KBr pellet)  $\nu/\text{cm}^{-1}$ : 3427 (C–OH), 3072 (Ar–H), 2232 (C=N), 1563– 1591 (C=C), 1240–1280 (Ar–O–Ar); <sup>1</sup>H NMR (DMSO)  $\delta$ /ppm: 7.69 (m, 2 H), 7.27 (m, 4 H), 7.02 (m, 8 H), 6.88 (m, 4 H), 6.66 (m, 4 H), 5.11 (brs, 2 H), 4.65 (m, 2 H).

3,9,17,23-Bis(ethane-1,1-*p*-phenol-2,2-*p*-phenoxy)phthalo-cyaninatozinc(II) (4), [3,9,17,23-bis(ethane-1,1-*p*-phenol-2,2-*p*phenoxy)phthalocyaninatocobalt(II)] (5) and [3,9,17,23-bis(ethane-1,1-*p*-phenol-2,2-*p*-phenoxy)phthalocyaninato-copper(II)] (6). A mixture of compound 3 (0.325 g, 0.5 mmol), and Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.096 g, 0.6 mmol) in 5 mL of DMF was refluxed in a sealed tube under Ar for 24 h. After cooling to room temperature the reaction mixture was treated with water to precipitate the product and then filtered. The crude product was washed with common organic solvents. This compound was soluble in pyridine and DMSO.

Yield (4): 0.508 g, 74,3%. Mp: > 300 °C. Anal. calcd for  $C_{84}H_{58}N_8O_8Zn$ : C 73.82, H 3.83, N 8.20. Found: C 73.85, H 3.85, N 8.18%. MS (MALDI-TOF), m/z: 1367 [M + H]<sup>+</sup>. IR (KBr pellet)  $\nu/cm^{-1}$ : 3100 (C–OH), 2925 (arom. –CH), 2853–2780 (aliph. – CH<sub>2</sub>), 1616 (C=C), 1230 (Ar–O– Ar). UV-vis(DMSO)  $\lambda/nm$  (log  $\varepsilon$ ): 681 (4.30), 617 (3.74).

Pc, **5** was synthesized using a similar procedure to that as described above for **4**. Compound **5** was soluble in DMSO, ethanol and methanol.

Yield (5): 0.470 g, 69.20%. Mp: > 300 °C. Anal. calcd for  $C_{84}H_{58}N_8O_8Co$ : C 74.17, H 3.85, N 8.24. Found: C 74.20, H 3.87, N 8.22%. MS (MALDI-TOF), m/z: 1360 [M + H]<sup>+</sup>. IR (KBr pellet)  $\nu/cm^{-1}$ : 3434 (C–OH), 2925 (arom. –CH), 1614 (C=C), 1231 (Ar–O–Ar). UV-vis (DMSO)  $\lambda/nm$  (log  $\varepsilon$ ): 673 (4.40), 606 (3.85).

Pc, 6 was synthesized using a similar procedure to that as described above for 4. Compound 6 was soluble in DMSO, ethanol and methanol.

Yield (6): 0.479 g, 70.40%. Mp: > 300 °C. Anal. calcd for  $C_{84}H_{58}N_8O_8Cu$ : C 73.92, H 3.84, N 8.21. Found: C 73.94, H 3.87, N 8.20%. MS (MALDI-TOF), m/z: 1363 [M + H]<sup>+</sup>. IR (KBr pellet)  $\nu/cm^{-1}$ : 3435 (C–OH), 2927 (arom. –CH), 1615 (C=C), 1232 (Ar–O–Ar). UV-vis (DMSO)  $\lambda/nm$  (log  $\varepsilon$ ): 682 (4.33), 617 (3.89).

3,9,17,23-Bis(ethane-1,1-*p*-phenol-2,2-*p*-phenoxy)phthalo-cyaninatozinc(II) tetrapotassium (7), 3,9,17,23-bis(ethane-1,1-*p*phenol-2,2-*p*-phenoxy)phthalocyaninatocobalt(II)] tetrapotassium (8) and [3,9,17,23-bis(ethane-1,1-*p*-phenol-2,2-*p*-phenoxy)phthalocyaninatocopper(II)] tetrapotassium (9). Pc, 4 (0.027 g, 0.02 mmol) was suspended in aqueous KOH solution (20%, 5 mL) and boiled for 10 min. The solution of the compound 7 was cooled, and the mixture poured into ethanol (100 mL). The performed precipitate was filtered off, dissolved in water and re-precipitated in ethanol several times until the solution was neutral. The product was then washed with ethanol and diethyl ether, and dried *in vacuo*. The compound is soluble in water at room temp. Yield (7): 0.021 g, 70%. M.p. > 300 °C. Pc, **8** was synthesized using a similar procedure to that as described above for **7**. Yield (**8**): 0.023 g, 76%. M.p. > 300 °C.

Pc, 9 was synthesized using a similar procedure to that as described above for 7. Yield (9): 0.024 g, 78%. M.p. > 300 °C.

#### **MALDI** sample preparation

MALDI matrix,  $\alpha$ -cyano-4-hydroxycinnamic acid (ACCA) was prepared in ethanol–water mixture in 1 : 1, v/v ratio at a concentration of 10 mg mL<sup>-1</sup>. MALDI samples were prepared by mixing sample solutions (2 mg mL<sup>-1</sup> in DMSO:ethanol mixture, 1 : 1 v/v ratio) with the matrix solution (1 : 10 v/v) in a 0.5 mL Eppendorf<sup>®</sup> micro tube. Finally 0.5 µL of this mixture was deposited on the sample plate, dried at room temperature and then analyzed.

For molecule 7 MALDI matrix, 1,8-dihydroxy-9(10H)anthracenone (dithranol) was prepared in tetrahydrofuran at a concentration of 10 mg mL<sup>-1</sup>. MALDI samples were prepared by mixing sample solutions (1.5 mg mL<sup>-1</sup> tetrahydrofuran–water mixture (1:1, v/v)) with the matrix solution (1:10 v/v) in a 0.5 mL Eppendorf<sup>®</sup> micro tube. Finally 0.5  $\mu$ L of this mixture was deposited on the sample plate, dried at room temperature and then analyzed.

#### **Theoretical calculations**

Geometric and electronic structure of compounds **2–6** were examined by *ab initio*/DFT quantum mechanical calculations. These calculations were performed by the Gaussian 03 program,<sup>15</sup> using HF theory at the B3LYP/3-21G level. For complex **4**, including atoms over 150, the smaller basis set was selected. The molecular structure was energetically optimized to reach the stable structure using HF/3-21G level theory. After optimization, we investigated the steric energies and heat of formations of the compounds.

#### **Electrochemical measurements**

The electrochemical measurements were carried out with a Princeton Applied Research Model VersoStat II potentiostat/galvanostat controlled by an external PC and utilizing a threeelectrode configuration at 25 °C. A platinum disk, a platinum spiral wire and a saturated calomel electrode (SCE) served as the working, the counter and the reference electrodes, for cyclic voltammetry measurements. The reference electrode was separated from the bulk of the solution by a double bridge. Electrochemical grade tetrabutylammonium perchlorate (TBAP) in extra pure dimethylsulfoxide (DMSO) was employed as the supporting electrolyte at a concentration of 0.10 M. High purity N2 was used for deoxygenating the solution at least 20 min prior to each run and to maintain a nitrogen blanket during the measurements. For controlled potential coulometry studies, Pt gauze working electrode (10.5 cm<sup>2</sup> surface area), Pt wire counter electrode separated by a glass bridge, and SCE as a reference electrode were used. In situ spectroelectrochemical measurements were carried out by an Agilent Model 8453 diode array spectrophotometer equipped with the potentiostat/galvanostat and utilizing an optically transparent thin layer (OTTLE) cell with three-electrode configuration at 25 °C. The working electrode was transparent Pt gauze. Pt wire counter electrode and a SCE reference electrode separated from the bulk of the solution by a double bridge were used.

#### 3.5 Electrical measurements

Spin coated thin film of compounds were prepared on the glass substrate fitted with interdigitated (IDT) gold electrodes for the d.c. and a.c. measurements. Prior to vacuum evaporation, glass substrates were thoroughly cleaned by ultrasonically and then coated with 100 Å of chromium followed by 1200 Å of gold in a Edwards Auto 500 coater system. The film patterned photolitographically and etched to provide 10 fingers pairs of electrodes having a width of 100 µm, spaced 100 µm from the adjacent electrodes. The finger overlap distance was 5 mm. Gold was selected as the electrode material, since it is well-known that it forms ohmic contact to the Pc. The film of each compound was obtained by spin-coating DMF solutions of the compounds over the electrode arrays to obtain devices suitable for electrical measurements. The substrate temperature was kept constant at 300 K during deposition of the materials over the electrodes. D.c. conductivity measurements were performed between 300 K and 452 K by using a Keithley 617 electrometer. Impedance spectroscopy measurements were carried out with a Keithley 3330 LCZ meter in the frequency range, 40-10<sup>5</sup> Hz, and in the temperature range from 300 K to 452 K. All measurements were carried out on the same sample to avoid the effect of the film thickness and substrate on the d.c. and impedance properties of the Pc films, and performed under vacuum ( $\leq 10^{-3}$  mbar) and in the dark. Both the d.c. conductivity and impedance data were recorded using an IEEE-488 data acquisition system incorporated to a personnel computer.

## Conclusions

In this work compound **3** was designed, synthesized and well characterized to obtain novel ball-type Pcs. But all attempt resulted the same mononuclear Pc in high yield, instead of expected of ball-type Pc. Probably because of the conformation of the starting material of **2** other isomers of the Pcs either are not formed or are formed very few not to be detected and isolated [**3**]. Four free phenol hydroxy groups of Pcs in %20 KOH solution are easily turned phenolate which are soluble in water. In some advance reactions have showed that four hydroxy groups are very functional to obtain unprecedented Pcs, *e.g.* joined two fluorinated two PcTi(IV) oxide to give three nuclear Pc, building phthalocyano-crown, dendirimer and even rotaxane and catenane. Our continuing work is concentrated now to overcome the solubility problem of some those compounds and to measures their intrinsic properties.

Electrochemical measurements showed that complexes 4 and 6 displays one-electron reversible or quasi-reversible Pc ring-based reduction processes while complex 5 exhibits one-electron quasi-reversible metal-based redox couples. The comparison of the redox behaviour of 4–6 with that of 1,1,2,2-tetrakis(*p*-hydroxy-phenyl)-ethane suggested clearly that peripheral hydroxy-phenyl groups of these complexes are redox-active. The effect of temperature on the d.c. conductivity and impedance spectra of spin coated films of compounds were also investigated at the temperatures between 300 K and 452 K and in the frequency range of  $40-10^5$  Hz. Thermally activated conductivity dependence on temperature was observed for all compounds. A.c. results indicated that

conduction mechanism can be explained by classical hopping barriers mechanism for all films.

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