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## 1. Introduction

Different types of phthalocyanine (Pc) dimers have been intensively studied in recent years, for example, clamshell dimers,<sup>1</sup> cofacial sandwich type lanthanide complexes<sup>2</sup> and doubledecker lanthanide(m) complexes.<sup>3</sup> Also the synthesis of a new class of Pc dimers, dinuclear ball-type metallophthalocyanines (MPcs), was reported for the first time by Zefirov and

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# Synthesis, characterization, oxygen electrocatalysis and OFET properties of novel mono- and ball-type metallophthalocyanines†

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Novel mono- and ball-type Co(II), Zn(II) and Cu(II) metallophthalocyanines (MPcs) were synthesized from 1,1'-p-anisylidenbis(2-naphthoxyphthalonitrile). The MPcs have been characterized by elemental analysis, UV/Vis, IR and <sup>1</sup>H-NMR spectroscopy and MALDI-TOF mass spectrometry. The performances of organic field effect transistors (OFETs) of the dinuclear ball-type MPcs have been compared to those of mononuclear counterparts. The ball-type MPc based OFETs showed a p-channel and typical ambipolar transport properties. On the other hand, it was not possible to measure the full transfer characteristics of the mononuclear MPc based devices. The best results were obtained in the case of dinuclear Cu<sub>2</sub>Pc<sub>2</sub>. In this case, the mobility value is  $\mu = 4.4 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and the threshold voltage is 27.6 volts. The reduction and oxidation characteristics of the mono-nuclear and ball-type MPcs have been compared by cyclic voltammetry, square wave voltammetry and controlled potential coulometry on platinum in nonaqueous media. The comparison suggested that the ball-type complexes form ring-based and/or metal-based mixed-valence species as a result of the remarkable interaction between the two Pc rings and/or metal centers. The stability of these species was confirmed by the mixed-valence splitting values for the complexes. The electrocatalytic performances of the mononuclear and dinuclear complexes for the oxygen reduction reaction were also studied. The compounds involving Co(II) at the phthalocyanine core, especially the ball-type one, showed much higher catalytic performances towards oxygen reduction than those of the other ones

> coworkers.<sup>4</sup> This new type of Pcs has four bridged substituents on the peripheral positions of each benzene ring of the two Pc monomers which are arranged cofacially.5 Recent studies suggested that these compounds exhibit very interesting gas sensing,<sup>6</sup> electrical,<sup>7</sup> nonlinear, optical<sup>8</sup> and electrochemical<sup>9</sup> properties depending on the wide range of interactions between the face to face Pc rings and/or the two metal centers. Thus, dinuclear ball-type MPcs have attracted increasing technological interest in various fields. For instance, ball-type cobalt Pcs displayed high catalytic activity toward dioxygen reduction which has vital importance in fuel cell applications.<sup>10,11</sup> Since bridging units with bulky substituents at the periphery may lead to changes in ball-type Pc characteristics, our studies to synthesize new examples of this type of compounds are still continuing and will be presented in forthcoming reports.

> The large conjugated  $\pi$ -system, excellent photoelectric characteristics, intriguing and unique optical properties, high thermal and chemical stability, molecular tolerability *via* chemical modification and compatibility with the flexible substrates of Pcs render them ideal organic semiconductor materials as active layers for organic field effect transistors



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(OFETs). Examples of reported Pc-based OFETs have good field-effect properties with field-effect mobilities ranging from  $9 \times 10^{-6}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> to 10 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, <sup>12,13</sup> the values depending upon the central metal atom, gate dielectric and the deposition techniques and parameters. It is well known that to be used as an active layer in OFET, the Pc materials are always prepared in thin film form. However, Pc compounds that carry no substituent on the ring system are essentially insoluble in organic solvents and are therefore not amenable to solution processing for deposition as thin films.

As compared to their parent monomers, ball-type Pcs display different and interesting electrochemical properties due to the wide range of interactions between the face-to-face Pc rings and/or two metal centres. The high catalytic activity of the ball-type cobalt Pcs toward dioxygen reduction has vital importance in fuel cell applications.<sup>14</sup> It is known that electron cloud overlap is important for strong interactions, mainly depending on the nature of the metal centres, bridging links and the presence or absence of axial ligands. The intermolecular and/or intramolecular interactions between the Pc rings and/or metal centers in dinuclear MPcs may be detected by spectroscopic and electrochemical measurements.<sup>10,11-15</sup>

In the present work, starting from a bulky electron donor 1,1'-*p*-anisylidenbis(2-naphthol) **1**, mono- and ball-type dinuclear Co(II), Zn(II), Cu(II) Pcs have been reported. The charge transport characteristics of Pc films have been investigated by preparing OFETs in which the active semiconductor layers were the spin-coated films of **7–9**. In addition, the redox and electrocatalytic properties of the novel mono-nuclear Pcs (**4**, **5** and **6**) and dinuclear ball-type Pcs (**7**, **8** and **9**) have been investigated and compared.

## 2. Results and discussion

## 2.1. Synthesis

Our key material 1,1'-*p*-anisylidenbis(2-naphthoxyphthalonitrile) **3** was synthesized by the reaction of **1** and **2**, in dry dimethylformamide (DMF) in the presence of K<sub>2</sub>CO<sub>3</sub>, with a yield 92%. The novel cobalt **4**, zinc **5** and copper **6** Pcs were prepared by the cyclotetramerization reaction of compound **3** with Co(OAc)<sub>2</sub>·4H<sub>2</sub>O, Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O and Cu(OAc)<sub>2</sub>·4H<sub>2</sub>O respectively in anhydrous DMF at 180 °C under a nitrogen atmosphere (Scheme 1). The conversion of **4**, **5** and **6** Pcs to the ball-type dinuclear Co<sub>2</sub>Pc<sub>2</sub> (7), Zn<sub>2</sub>Pc<sub>2</sub> (**8**) and Cu<sub>2</sub>Pc<sub>2</sub> (**9**) complexes was accomplished in anhydrous DMF and in the presence of excessive amounts of appropriate metal salts at 180 °C (Scheme 1). The yields were moderate and depended upon the metal ion.

Our novel MPcs are soluble in various solvents such as tetrahydrofuran (THF), acetone, dichloromethane (DCM), methanol, dimethylsulfoxide (DMSO), chloroform (CHCl<sub>3</sub>) and DMF. The intense solubility of these new MPcs in most of the organic solvents is probably due to methoxy (–OCH<sub>3</sub>) groups on the *para*-position of the benzene ring of the bulky starting compound. Characterization of the new Pc complexes was Elemental analysis, FT-IR, MALDI-TOF mass and UV/Vis spectra confirmed the proposed structures of the compounds. FT-IR spectra indicated the formation of 4, 5 and 6 clearly with the appearance of a sharp band at 2230 cm<sup>-1</sup> (-C $\equiv$ N), and additional bands at 1240–1245 cm<sup>-1</sup> (Ar–O–Ar), 1590–1670 cm<sup>-1</sup> (–C $\equiv$ C–), 1715–1730 cm<sup>-1</sup> (C $\equiv$ N) and 3050–3060 cm<sup>-1</sup> (aromatic CH). The main indicator of the formation of M<sub>2</sub>Pc<sub>2</sub> complexes 7, 8 and 9 was the disappearance of the sharp intense –CN stretching band at 2230 cm<sup>-1</sup> in the IR spectra. The IR-spectra of the CoPc 4, the ZnPc 5 and the CoPc 6 were very similar, as also IR-spectra of homo-dinuclear ball-type Pcs 7, 8 and 9.

The UV-Vis spectra of 4, 5 and 6 in DMSO  $(2 \times 10^{-5} \text{ M})$ (Fig. 2) showed characteristic absorptions between 600 and 700 nm in the Q-band region. The Q-band observed for the compounds was attributed 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 observed B bands within the range of 280-360 nm were due to the transitions from the deeper  $\pi$  levels to the LUMO. The comparison of UV-Vis spectra of mononuclear Pc compounds 4, 5, 6 with those of dinuclear ball-type ones 7, 8, 9 in DMSO  $(2 \times 10^{-5} \text{ M})$  (Fig. 2) implies that both groups of compounds display H-type aggregation, characterized by broadening of the Q-band absorptions for 4, 5, 7, 8 and splitting of the Q-band absorptions for 6 and 9. H-aggregation of mononuclear compounds 4, 5 and 6 resulted from intermolecular  $\pi$ - $\pi$  stacking interactions while the broadening or splitting of the Q-band absorptions for 7, 8 and 9 is probably due to intramolecular interactions between the two MPc units in these compounds. This interpretation is compatible with the theoretically determined highly planar structure of the molecule of 8 and the considerably small distance between the two MPc units in the molecule (Fig. 1). The fully optimized minimum energy structure in Fig. 1 was refined by performing an optimized geometry calculation in MOPAC using PM3 parameters.<sup>16</sup> This structure reflects very small geometrical constraints due to connectivity of the bulky substituents at the peripheral positions in comparison with that of a previously reported dinuclear ball-type M<sub>2</sub>Pc<sub>2</sub> model compound.<sup>15e</sup> In order to compare the bond distances and angles in the optimized structure, a 3D structure visualization software, Mercury 3.1, was also used.<sup>17</sup> In the present case, the distance between the two metal centers is 5.884 Å, comparatively shorter than that of 11.06 Å determined previously for the analogous molecule by the same method.<sup>15e</sup> The closest contact between the two rings is about 5.14 Å. These values reflect high planarity of the ring systems in the molecule. Furthermore, the N-Zn-N angles are also very close to 90°, which provides strong support for high planarity of the molecule. (ESI, Fig. S1<sup>†</sup>). The bulky naphthyl substituents are inclined at 66.69°, whereas the angle between these rings and the methoxyphenyl ring is about 75.81°. The bending of peripheral substituents causes the molecule to be



**Scheme 1** (i)  $K_2CO_3$ , DMF, 80 °C; (ii) 4,  $Co(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 5,  $Zn(OAc)_2 \cdot 2H_2O$ , 180 °C, 12 h; 6,  $Co(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; (iii) 7,  $Co(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 8,  $Zn(OAc)_2 \cdot 2H_2O$ , 180 °C, 12 h; 9,  $Co(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 7,  $Co(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 9,  $Co(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 7,  $Co(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 9,  $Co(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 7,  $Co(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 9,  $Co(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 7,  $Co(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 9,  $Co(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 7,  $Co(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 9,  $CO(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 9,  $CO(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 9,  $CO(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 9,  $CO(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 9,  $CO(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 9,  $CO(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 9,  $CO(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 9,  $CO(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 9,  $CO(OAc)_2 \cdot 4H_2O$ , 180 °C, 12 h; 9,  $CO(OAc)_2 \cdot 4H_2$ 



**Fig. 1** The space-filling presentation of the molecular structure of the ball-type homo-dinuclear zinc phthalocyanine (8). The structure was refined by performing an optimized geometry calculation in MOPAC using PM3 parameters.<sup>16</sup>

puckered as reflected by the  $N_{iso}$ -Zn- $N_{iso}$  angles of 171.2–172.2°. It is expected that the bending of peripheral substituents hinders strong intermolecular interactions between  $M_2Pc_2$ -type molecules. Thus, the foregoing attribution of the broadening or splitting of the Q-bands of dinuclear ball-type compounds to intramolecular interactions rather than intermolecular interactions is consistent with the bended peripheral substituents in the optimized structure.

In the <sup>1</sup>H-NMR spectra of 3 in CHCl<sub>3</sub>, the phenyl protons bearing nitrile groups appeared at 7.26 ppm (s), 7.01 ppm (d), 6.81 ppm (d) and the phenyl protons with methoxy groups at 6.62 ppm (br s), 6.53 ppm (br s), naphthalene protons at 7.85 ppm (d), 7.80 ppm (d), 7.66 ppm (d), 7.50 ppm (t) and 7.44 ppm (t), 6.50 ppm (d), aliphatic proton at 6.91 ppm (s), and a characteristic signal for  $-OCH_3$  protons at 3.59 ppm (ESI, Fig. S2–S4†). In the <sup>1</sup>H NMR spectra of **8**, the aromatic protons appeared at 8.95–6.11 ppm (m), Ar–OCH<sub>3</sub> peaks at 3.65–2.60 ppm and Ar–CH peaks at 2.89–2.77 ppm (ESI,



Fig. 2 UV/Vis spectra of mono (A) and ball-type (B) Pcs in DMSO.

Fig. S5<sup>†</sup>). MALDI-TOF mass spectra of the starting compound 3 and all MPcs 4-9 are shown in ESI (Fig. S6-S12<sup>†</sup>). For 4, the mass spectrum was obtained in high resolution mode showing only protonated molecular ions and also one and two water adducts to the protonated molecular ion. Although a protonated molecular ion peak was not observed in the case of 7, it was observed for the other complexes. Furthermore, the peaks characterizing matrix clusters and some fragmentations at different masses within the range of 670-780 Da were observed for all Pc complexes 4-9. These signals were found to have almost similar intensities, and the masses of the fragment ions were found to be identical. Additional water adduct peaks up to three were also observed for 8. For compound 7, the signals for the species of only sodiated at high intensity and potassiated and also water adduct were observed dominantly in the MALDI-TOF mass spectrum. This is because of the low proton affinity of the complex. When isotopic mass distributions of the experimental and theoretical four sodium adducts of the complex peaks were compared, it was noticed that the peaks overlapped each other perfectly. Also monoisotopic peak masses for the experimental and the theoretical values were found to be very close to each other. The comparison of the experimental and theoretical isotopic mass distributions of the protonated ions of 8 and 9 suggested that the peaks overlapped each other perfectly as 7. This showed the mass accuracy between the theoretical and experimental monoisotopic masses. In the mass range between 500 and 3500 Da, no signal representing impurity was observed during MALDI-TOF mass spectrometry measurements of the complexes.

#### 2.2. Characteristics of OFETs

It is well known that an OFET is a three-terminal device in which the gate electrode is electrically insulated from the active layer (semiconductor) through an insulating layer, and the source and drain electrodes are connected with the semiconductor. For a given drain-source voltage,  $V_{\rm DS}$ , the current flowing through the organic semiconductor shows a strong correlation with the applied gate-source voltage,  $V_{\rm GS}$ . In order to estimate the field effect mobility in **4-9** based OFETs, the drain-source current ( $I_{\rm DS}$ ) was measured as a function of the  $V_{\rm DS}$  by varying the applied  $V_{\rm GS}$ . It was observed that it was not possible to measure the full transfer characteristics of **4-6** based devices. Within the experimental range of  $V_{\rm DS}$ , a rather good linear relation was observed in **4-6** based devices including with a zero  $V_{\rm GS}$  voltage. Therefore, we focused on **7-9** based OFETs.

Information concerning the performance of an organic field-effect transistor is provided by the most important parameters of these devices, namely the charge carrier mobility and the threshold voltage. Their value can be determined from the two typical characteristics obtained when characterizing these devices electrically, *i.e.* the output and transfer characteristics. To compare the effect of the active layer on the performance of an OFET device, a typical set of the output  $(I_{DS} - V_{DS})$ characteristics of the produced OFETs based on 7-9 for fixed gate voltage ( $V_{GS} = -50$  V) applied to the ITO electrode is shown in Fig. 3. The characteristics of the 7-9 based device exhibit an ideal  $I_{\text{DS}} - V_{\text{DS}}$  relationship in which the curves can be divided into two regions: a linear region and a saturated region. The curves match the behaviour of the traditional Pc based field-effect-transistor. On the application of a negative bias to the gate electrode, a typical hole accumulation (p-type) behaviour was observed for all devices. The maximum drainsource currents,  $I_{DS} = 0.64 \mu A$ , at gate-source bias  $V_{GS} = -50 V$ was observed for sample 9, while the maximum drain-source currents for sample 7 and for sample 8 were 0.41 µA and 0.53  $\mu$ A for the same gate-source bias ( $V_{GS} = -50$  V), respectively. A close investigation of these characteristics also shows that at low drain-source voltages  $V_{\rm DS}$ , the current  $I_{\rm DS}$  follows Ohm's law, and is proportional to  $V_{DS}$ . As  $V_{DS}$  approaches the gate voltage  $V_{\rm G}$ , the drain-gate voltage approaches zero. This results in the so-called pinch-off of the channel. Therefore it



Fig. 3 OFET characteristics of the films of 7–9 measured under ambient conditions.

The gate-source voltage dependence of the output characteristics of the produced OFETs was also investigated. In Fig. 4, the drain-source current IDS is plotted as a function of the drain-source voltage VDS by varying the applied gatesource voltage VGS for the 9 based OFET device. It is clear that the drain-source current IDS increases with increasing the gate-source voltage VGS negatively and the IDS current is also effectively modulated by gate-source voltage. This shows that the 9 based OFET typically works in a p-channel operational mode. The same types of output characteristics were observed for 7 and 8 based devices. The observed p-type channel operation indicates that an injection of holes from the metal electrode into the organic material takes place and there is a close match between the Fermi level (EF) of the metal electrode (source and drain electrode) and the HOMO energy level of the ball-type Pcs.

The most important parameter of the OFET is the fieldeffect mobility which indicates how easily the charge carriers can drift under the influence of the electric field. The relation between the  $I_{\rm DS}$  and the  $V_{\rm GS}$  in the saturation regions is given by eqn (1).<sup>18</sup>

$$I_{\rm DS} = \frac{W}{2L} C_i \mu_{\rm F} (V_{\rm GS} - V_{\rm t})^2 \tag{1}$$

where  $\mu_{\rm F}$  is the field-effect mobility, *W* and *L* are the channel width and length, respectively, *C<sub>i</sub>* is the insulator capacitance per unit area, and *V*<sub>t</sub> is the threshold voltage. The mobility of the transistors can be obtained in different ways. In this work, the values of the mobility for all devices were extracted from a plot of the square root of the drain–source current *versus V*<sub>GS</sub> by fitting data to eqn (1).

Fig. 5 shows the typical transfer characteristics ( $\sqrt{I_{\rm DS}} vs. V_{\rm GS}$  and  $I_{\rm DS} vs. V_{\rm GS}$ ) of 9 OFET with PVA gate insulators at a fixed  $V_{\rm DS}$  of -50 V. With the aid of eqn (1), from the slope of the linear portion of Fig. 5 the  $\mu_{\rm F}$  and  $V_{\rm t}$  values were determined



-V<sub>DS</sub> (V)

 $GS^{=0}V$ 

90 100

70 80



-V \_ (V)

Fig. 5 Transfer characteristics of 9 based OFET.

and summarized in Table 1. As can be seen from Table 1, the mobility value of the 9 based OFET transistor is higher than that of the mobilities of 7 and 8. It was also observed that the obtained mobility value of the studied Pc based OFET transistor is higher than that of the mobilities of CuPc based FET with the mobility of  $2.2 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> using PVA as a gate insulator<sup>19</sup> and CuPc organic thin film transistors (OTFTs) with the mobility of  $0.2 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> using a polymethyl methacrylate (PMMA) dielectric layer.<sup>20</sup> It seems that both the molecular shape and the central metal atom are important for OFET performance. It is well established that good match of energy level between the organic semiconductor and electrode for charge-carrier injection, large  $\pi$ -orbit overlap and short intermolecular distance are necessary for semiconductor materials in order to achieve high-performance OTFTs. It is also shown that the molecular orientation of the Pc molecules in the solid state is of great interest because it is thought to strongly affect the carrier mobility in electronic devices.<sup>21</sup> Therefore it is not easy to decide which mechanism is responsible for the observed higher mobility value in the case of 9. On the other hand the performance of OFETs is closely related to the packing mode of organic molecules in thin solid films. Several reports elucidated that  $\pi$ - $\pi$  stacking is a favored packing mode for OFET applications.<sup>22</sup> The  $\pi$ - $\pi$  stacking affords strong interactions between neighbouring molecules. Though the relationship between the mobility and film structure is not yet fully understood, we believe that the contribution from Pc ring stacking to the observed high mobility in the case of 9 might be significant.

Table 1 Summary of the electrical characteristics of the OFETs

Complex	$\mu_{\rm F}  ({\rm cm}^2  {\rm V}^{-1}  {\rm s}^{-1})$	$V_{\rm t}$ (v)
7	$5.2 \times 10^{-3}$	-2.5
8	$6.7 \times 10^{-3}$	-4.0
9	$4.4 \times 10^{-2}$	-27.6

10 20 30 40 50 60

1.0

0.8

0.2

Table 2	The electrochemical	data <sup>a</sup> for 4-9	in TBAP/DMSO
	The electrochemical		III IDAF/DM3C

Complex	Redox processes		$E_{1/2}$ (V)	$\Delta E_{\mathrm{p}}\left(\mathrm{V}\right)$	$\Delta E_{1/2}$ (V)	$\Delta E_{\rm s}$ (V)
	[Co(III)Pc(-2)] <sup>+</sup> /Co(II)Pc(-2)	(O1)	0.40	0.08	0.73	
	$\operatorname{Co}(\mathbf{i})\operatorname{Pc}(-2)/[\operatorname{Co}(\mathbf{i})\operatorname{Pc}(-2)]^{-1}$	(R1)	-0.33	0.10		
	$[Co(1)Pc(-2)]^{-}/[Co(1)Pc(-3)]^{2-}$	(R2)	-1.37	0.06		
5	$\left[ Zn(\mathbf{u})Pc(-1) \right]^{+}/Zn(\mathbf{u})Pc(-2)$	(O1)	0.61	0.080	1.48	
	$Zn(II)Pc(-2)/[Zn(II)Pc(-3)]^{-1}$	(R1)	-0.87	0.060		
	$[Zn(II)Pc(-3)]^{-}/[Zn(II)Pc(-4)]^{2-}$	(R2)	-1.20	0.060		
	$[Zn(II)Pc(-4)]^{2-}/[Zn(II)Pc(-5)]^{3-}$	(R3)	-1.56	rev		
	Reduction of nitrile substituents	(R4)	-1.65	0.080		
5	$[Cu(\pi)Pc(-1)]^+/Cu(\pi)Pc(-2)$	(O1)	0.71	0.060	1.51	
	Си(п)Рс(-2)/[Си(п)Рс(-3)] <sup>-</sup>	(R1)	-0.80	0.080		
	$[Cu(\pi)Pc(-3)]^{-}/[Cu(\pi)Pc(-4)]^{2-}$	(R2)	-1.10	0.080		
	$[Cu(n)Pc(-4)]^{2-/}[Cu(n)Pc(-5)]^{3-}$	(R3)	-1.50	Rev		
	Reduction of nitrile substituents	(R4)	-1.70	0.080		
7	$[Co(II)Pc(-2)\cdot Co(II)Pc(-1)]^{+}/[Co(II)Pc(-2)]_{2}$	(O1)	0.38	0.080	0.78	
	$[\operatorname{Co(II)Pc}(-2)]_2/[\operatorname{Co(II)Pc}(-2)\cdot\operatorname{Co(I)Pc}(-2)]^-$	(R1)	-0.40	0.080		0.24
	$[Co(II)Pc(-2)\cdot Co(I)Pc(-2)]^{-1}/[Co(I)Pc(-2)]_{2}^{2-1}$	(R2)	-0.64	0.080		
	$[Co(1)Pc(-2)]_2^{2-}/[Co(1)Pc(-2)\cdot Co(1)Pc(-3)]^{3-}$	(R3)	-1.01	0.120		0.40
	$[Co(I)Pc(-2)\cdot Co(I)Pc(-3)]^{3-}/[Co(I)Pc(-3)]_{2}^{4-}$	(R4)	-1.41	0.06		
3	$[Zn(II)Pc(-1)]_2^{2+}/[Zn(II)Pc(-2)]_2$	(O1)	0.70	0.060	1.20	
	$[Zn(II)Pc(-2)]_2/[Zn(II)Pc(-3)]_2^2$	(R1)	-0.50	b		0.35
	$[Zn(II)Pc(-3)]_2^{2^-}/[Zn(II)Pc(-4)]_2^{4^-}$	(R2)	-0.85	b		
	$[Zn(II)Pc(-4)]_2^{4-}/[Zn(II)Pc(-5)]_2^{6-}$	(R3)	-1.11	b		0.39
	$[Zn(II)Pc(-5)]_2^{6-}/[Zn(II)Pc(-6)]_2^{8-}$	(R4)	-1.50	b		
Ð	$[Cu(\pi)Pc(-1)]_2^{2+}/[Cu(\pi)Pc(-2)]_2$	(O1)	0.65	0.060	1.13	
	$[Cu(\pi)Pc(-2)]_2/[Cu(\pi)Pc(-3)]_2^2$	(R1)	-0.48	b		0.32
	$[Cu(\pi)Pc(-3)]_2^{2-}/[Cu(\pi)Pc(-4)]_2^{4-}$	(R2)	-0.80	b		
	$[Cu(n)Pc(-4)]_2^{4-}/[Cu(n)Pc(-5)]_2^{6-}$	(R3)	-1.04	b		0.41
	$[Cu(\pi)Pc(-5)]_2^{6-}/[Cu(\pi)Pc(-6)]_2^{8-}$	(R4)	-1.45	b		

<sup>*a*</sup> Potentials are reported with respect to the SCE.  $E_{1/2}$  values were measured by cyclic voltammetry  $[E_{1/2} = (E_{pa} + E_{pc})/2]$  and/or differential pulse voltammetry. The peak separation values ( $\Delta E_p = E_{pa} - E_{pc}$ ) are reported at 0.050 V s<sup>-1</sup>.  $\Delta E_{1/2}$  is the potential difference between the first oxidation and first reduction potentials. It represents the HOMO-LUMO gap for 5, 6, 8 and 9, but the charge transfer transition for 4 and 7 involving redoxactive metal centers.  $\Delta E_s$  indicates mixed-valence splitting energy for the relevant split redox couple. <sup>*b*</sup> The peak separation values could not be monitored due to ill-defined cyclic voltammetry signals, but square wave voltammograms indicated the reversible or quasi-reversible nature of these redox processes.

#### 2.3. Electrochemistry

The cyclic voltammetry, square wave voltammetry and controlled-potential coulometry (CPC) measurements of 4-9 were carried out on platinum in DMSO using tetrabutylammonium perchlorate as a supporting electrolyte. The relevant data are presented in Table 2. It was concluded from the CPC measurements and well-known electrochemical behaviour of mononuclear phthalocyanine complexes<sup>23</sup> that compounds 4-6 gave ring and/or central metal-based stepwise one-electron reduction processes (except the last reduction process for 5 and 6) and a one-electron oxidation processes. The anodic to cathodic peak separations of these redox processes were within the range of 0.060-0.100 V which showed the reversible or quasi-reversible nature of these electron transfer processes.<sup>24</sup> For both 5 and 6, the difference between the half-peak potentials  $(E_{1/2})$  of the first oxidation and the first reduction processes ( $\Delta E_{1/2}$ ) is about 1.50 V, which is closely related to the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).<sup>25</sup> Fig. 6 shows cyclic and square wave voltammograms of 5 in TBAP/DMSO as an example. Approximate  $\Delta E_{1/2}$  values of 5 and 6 strongly suggest that the redox processes of these complexes are phthalocyanine ring-based.23 However, it should be noted that the peak currents for the last reduction



Fig. 6 Cyclic and square wave voltammograms of 5 on Pt in TBAP/ DMSO.

couple are much higher than those of the other reduction couples, probably due to the fact that the last reduction couples for 5 and 6 result from the reduction of nitrile substituents which are redox-active in this type of mononuclear phthalocyanine compounds.<sup>26</sup> On the other hand, both the first reduction and the first oxidation of 4 occur more easily than those of 5 and 6, and thus the  $\Delta E_{1/2}$  value of this complex

6

is 0.73 V (Table 2 and Fig. 7). This redox behaviour suggests that the first reduction and the first oxidation processes of **4** are metal-based.

Compound 8 displayed four reductions and a single oxidation within the potential limits of DMSO/TBAP medium (Table 2). The CPC studies showed that each redox process involves the transfer of one electron. Typical voltammograms for 8 are shown in Fig. 8. The transfer of one electron in each step, instead of two, indicates that the redox process of each ZnPc unit in 8 occurs at different potentials as a result of the interactions between the two ZnPc units and thus the splitting of the molecular orbitals. The strong interaction between the molecular orbitals of two ZnPc units in 8 causes remarkable changes in redox potentials, compared with the corresponding mononuclear phthalocyanine 5. It appears that the first reduction process of 8 shifts to less negative potentials and thus, the  $\Delta E_{1/2}$  value becomes smaller in comparison with 5. All redox processes of 8 are Pc ring-based since Zn<sup>II</sup> is redoxinactive in MPcs.<sup>23</sup> Similarly, the redox processes of mononuclear complexes 4 and 6 are split into two waves in 7 and 9, due to the interactions between the two MPc units (Table 2). Fig. 9 shows cyclic and square wave voltammograms of 7 in TBAP/DMSO as examples. The mixed-valence splitting,  $\Delta E_s$ ,



Fig. 7 Cyclic and square wave voltammograms of 4 at 0.050 V s<sup>-1</sup> scan rate on Pt in TBAP/DMSO.



Fig. 8 Cyclic and square wave voltammograms of 8 on Pt in TBAP/DMSO.



Fig. 9 Cyclic and square wave voltammograms of 7 at 0.050 V s<sup>-1</sup> scan rate on Pt in TBAP/DMSO.

values in V for the redox processes of **7–9** are presented in Table 2. These values give evidence of the delocalization of charge among the cofacial MPc units, and thus the formation of electrochemically stable oxidized and reduced mixed-valence species.

In recent years, it was shown by our group that ball-type dinuclear metal phthalocyanines with various bridging units such as cyclopentyldisilanoxy-polyhedral oligomeric silsesquioxanes,<sup>10</sup> perfluorodecyl,<sup>15a</sup> pentaerythritol,<sup>11</sup> 1,1'-methylenedinaphthalen-2-ol<sup>15b</sup> and dithioerythritol<sup>15c</sup> show high catalytic activity towards oxygen reduction reaction (ORR), which is important for fuel cell applications. These bridging units link two metal phthalocyanine units cofacially at two sides with four arms. The relevant previous studies showed that the length of the bridging units, the main factor determining the suitable distance between the two metal centers for high catalytic activity, has vital importance. Thus, the electrocatalytic performance of each Pc complex towards ORR was tested in O2-saturated 0.5 M H2SO4 aqueous electrolyte solution (Fig. 10A). These measurements were performed by RRDE voltammetry with a glassy carbon disk electrode and a platinum ring electrode, and the glassy carbon electrode was modified by a mixture of the relevant Pc complex with carbon powder, Vulcan XC-72 (VC) and Nafion (Nf). The onset potential  $(E_{\rm o})$  where the current begins to increase, the limiting diffusion disk current density  $(J_L)$  and the half-wave potential  $(E_{1/2})$  for ORR were taken as the measure of catalytic performance. The disk potential at which the current density reaches 0.100 mA cm<sup>-2</sup> was taken as  $E_0$ . The electrocatalytic performances of the Pc-based catalysts are summarized in Table 3. The 7 (Co<sub>2</sub>Pc<sub>2</sub>)-based catalyst displayed the best catalytic activity with the most positive onset potential (0.44 V vs. SCE), the highest  $J_{\rm L}$  value (3.10 mA cm<sup>-2</sup> at 2500 rpm) and the most positive  $E_{1/2}$  value for ORR (0.06 V vs. SCE) (Table 3 and Fig. 10A). Complex 7 displays two reduction waves. The first wave probably produces water as the main product and some hydrogen peroxide as the side product. The second wave, appearing at considerably negative potentials presumably corresponds to the reduction of hydrogen peroxide to water. The

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**Fig. 10** (A) RRDE polarization curves for the electrocatalytic ORR at 0.005 V s<sup>-1</sup> on VC/Nf/metallophthalocyanine modified rotating (2500 rpm) glassy carbon disk electrodes in  $O_2$ -saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>, (B) the number of total electrons exchanged, (C) %H<sub>2</sub>O and (D) %H<sub>2</sub>O<sub>2</sub> produced in ORR as a function of disk potential ( $E_{ring}$  = 0.95 V vs. SCE) for VC/Nf/metallophthalocyanine modified electrodes.

Complex		<i>E</i> <sub>o</sub> <sup><i>a</i></sup> for ORR/V	$J_{\rm L}^{\ b}$ for ORR/mA cm <sup>-2</sup>	$E_{1/2}$ for ORR/V	Ref.
CoPc	4	0.23	2.78	-0.06	tw <sup>c</sup>
			0.40	-0.29	
ZnPc	5	-0.11	_	_	tw <sup>c</sup>
CuPc	6	0.04	_	_	tw <sup>c</sup>
$Co_2Pc_2$	7	0.44	3.10	0.06	tw <sup>c</sup>
			0.73	-0.30	
$Zn_2Pc_2$	8	0.07	2.45	-0.30	tw <sup>c</sup>
$Cu_2Pc_2$	9	0.03	0.50	-0.04	tw <sup>c</sup>
			1.95	-0.34	
$Zn_2Pc_2^{d}$	2	-0.15	1.06	-0.30	15f
$\operatorname{Co}_2\operatorname{Pc}_2^d$	3	0.06	2.54	-0.07	15f
$\operatorname{Co_2Pc_2}^{e}$		0.45	2.63	0.35	15d
			0.92	-0.20	
$\operatorname{Co}_2\operatorname{Pc}_2^f$		0.11	4.66	-0.15	15e
$\operatorname{Co_2Pc_2}^g$		0.10	3.30	-0.14	15 <i>c</i>
$\operatorname{Co_2Pc_2}^h$		0.68	4.27	0.41	10
-			2.17	-0.19	
$\operatorname{Co_2Pc_2}^i$		0.25	4.50	-0.09	15 <i>a</i>
$\operatorname{Co_2Pc_2}^j$		0.61	4.84	0.05	11

**Table 3**Electrocatalytic performances of 4-9 for ORR, and the com-<br/>parison with previously reported dinuclear metal phthalocyani-<br/>nes $^{10,11,15a,c-f}$ 

<sup>*a*</sup> The potential at which the current density reaches 0.100 mA cm<sup>-2</sup> was taken as the onset potential. <sup>*b*</sup> The limiting diffusion current density at 2500 rpm. <sup>c</sup> This work. <sup>d</sup> Octa substituted phenoxy-bridged. <sup>f</sup>4,4'-(Octahydro-4,7-methano-5H-inden-5-<sup>e</sup> Dicumarol bridged. ylidene)bisphenyl <sup>g</sup> Dithioerythritol-bridged. bridged. Cyclopentyldisilanoxy-polyhedral oligomeric silasesquioxanes <sup>*i*</sup> Pentaerythritol-bridged. <sup>j</sup> Pentaerythritol-bridged bridged. with heptadecafluorodecyl substituents.

absolute ring current decreases simultaneously while the disk current increases during the appearance of the second wave (Fig. 10A), which confirms that hydrogen peroxide produced at the first step as the side product is further reduced to water during the second wave. The 4(CoPc)-based catalyst also displayed much higher performance than those of the other phthalocyanine-based catalysts (Table 3 and Fig. 10A). ORR occurs at much more positive potentials at the VC/Nf/7 and VC/Nf/4 modified GCEs than that at the other Pc-based electrodes. In addition, the limit current densities for the VC/Nf/7 and VC/Nf/4 modified GCEs are much higher than those for the other Pc-based electrodes. These findings clearly indicate the higher catalytic activity of the formers relatively. Electrocatalytic reduction of oxygen on metallophthalocyanines takes place through a redox-catalysis type of process where oxygen binding ability and the redox potential of the central metal ions play a critical role.<sup>27</sup> The metal ion in the center of the Pc ring is oxidized by an oxygen molecule during its adsorption and thus reduces it. Therefore, the distinctive catalytic performance of 4- and 7-based catalysts can be attributed to the redox-active behavior of the  $Co(\pi)$  metal center. It appears that, in the case of a redox-active metal center, the interaction between the metal center and the O<sub>2</sub> molecule is enhanced. The catalytic performance of the 7(Co<sub>2</sub>Pc<sub>2</sub>)-based catalyst is better than that of the 4(CoPc)-based one (Table 3 and Fig. 10A). The better catalytic activity of the 7(Co<sub>2</sub>Pc<sub>2</sub>)-based catalyst, compared to the 4(CoPc)-based one, should also be

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related to its ability to bind a dioxygen molecule through peroxo species, Co-O-O-Co, the promotion of the O-O bond breakage and thus, the increase in the tendency of reduction directly to water via the four-electron path. It is known from the literature that even mononuclear metal Pcs with redoxactive metal centers have the ability to form peroxo species as a result of the interaction between the metal center and O2.<sup>28</sup> However, it appears that the presence of two redox-active faceto-face metal centers in 7 further promotes the formation of Co-O-O-Co species through the interaction of the two  $Co(\pi)$ centers with the O2 molecule. In terms of onset and half-wave potentials, and the limiting diffusion current densities for ORR, the catalytic performance of 7 is comparable to that of the recently reported dinuclear dicumarol-bridged<sup>15d</sup> cobalt phthalocyanine and better than those of previously reported dinuclear pentaerythritol-,<sup>15a</sup> dithioerythritol-,<sup>15c</sup> 4,4'-(octahydro-4,7-methano-5H-inden-5-ylidene)bisphenyl-15e and octa substituted phenoxy-bridged<sup>15f</sup> cobalt phthalocyanines while it is lower than those of cyclopentyldisilanoxy-polyhedral oligomeric silsesquioxane-bridged dinuclear cobalt phthalocyanine<sup>10</sup> and dinuclear cobalt phthalocyanine including pentaerythritol bridging units with heptadecafluorodecyl substituents.11

ORR in acidic medium can be reduced to water *via* a fourelectron process or hydrogen peroxide through a two-electron reduction. A complete reduction directly to water *via* a fourelectron transfer mechanism is desirable. However, it is possible in the case of low catalytic activity that oxygen gets reduced to hydrogen peroxide *via* a two-electron process, but the peroxide can still get reduced further *via* another two-electron process to form water. The number of electrons transferred,  $n_t$ , and the amount of generated hydrogen peroxide and thus water selectivity were determined by using the following equations.

$$n_{\rm t} = 4I_{\rm D} \left[ I_{\rm D} + (I_{\rm R}/N) \right]$$
 (2)

$$\% H_2 O_2 = 100(4 - n_t) \tag{3}$$

Here, N,  $I_D$ , and  $I_R$  are the collection efficiency, VC/Nf/phthalocyanine modified glassy carbon disk current and platinum ring (polarized at 0.95 V vs. SCE) current, respectively (Fig. 10B-10D). Reduction directly to water via a four-electron process occurs nearly in the case of all catalysts, together with reduction to hydrogen peroxide via a two-electron process. However, except the ones driven by VC/Nf/7 and VC/Nf/4 modified GCEs, all other ORRs occur at considerably negative potentials with high overpotential and usually produce higher amounts of water than that of hydrogen peroxide, *i.e.*, the numbers of exchanged electrons at different potentials on ORR waves are lower than 3 which corresponds to the formation of equal amounts of water and hydrogen peroxide. On the other hand, ORRs catalyzed by VC/Nf/4 and especially VC/ Nf/7 modified GCEs produce a higher amount of water than that of hydrogen peroxide ( $n_t$  is higher than 3). With the VC/ Nf/7 modified electrode, the  $n_t$  value increases with increasing overvoltage and becomes 3.64 (82%  $H_2O$  and 18%  $H_2O_2$ ) at the

limiting diffusion current plateau, leading to the production of water as the main product. The detection of hydrogen peroxide suggests that the first step of the series path, *i.e.*, oxygen reduction to hydrogen peroxide, is certainly operative. However, a direct path, *i.e.*, oxygen reduction to water *via* a four-electron process without the formation of hydrogen peroxide as an intermediate, is the main reaction to occur.

## 3. Experimental

#### 3.1. Materials

The starting material **2** was synthesized by methods described previously in the literature.<sup>29</sup> Compounds **1**,  $Zn(OAc)_2 \cdot 2H_2O$ ,  $Co(OAc)_2 \cdot 4H_2O$  and  $Cu(OAc)_2 \cdot 4H_2O$ , were obtained from commercial suppliers. All reactions were carried out under a nitrogen atmosphere. The Pc compounds were purified by column chromatography and washed with acetic acid, water, and ethanol. The purity of the products was tested in each step by TLC (SiO<sub>2</sub>). Chromatography was performed on silica gel 60.

#### 3.2. Equipment

UV-vis spectra were recorded on a Shimadzu UV-1601 UV-vis spectrometer. IR spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer as KBr pellets. Elemental analyses were performed by the Instrumental Analysis Laboratory of Tubitak-Ankara. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance DPX-400 MHz spectrometer. Mass spectra were acquired on a Voyager-DETM PRO MALDI-TOF mass spectrometer (Applied Biosystems, USA) equipped with a nitrogen UV-laser operating at 337 nm. Spectra were recorded in reflectron mode with the average of 100 shots. In MALDI matrix, 2,5-dihydroxybenzoic acid was prepared in a THF-H<sub>2</sub>O mixture in a 1:1, v/v, ratio at a concentration of 20 mg mL<sup>-1</sup> and acidified with trifluoroacetic acid (0.1%). MALDI samples were prepared by mixing sample solutions (2 mg mL<sup>-1</sup> in a THF-H<sub>2</sub>O mixture in a 1:1, v/v, ratio containing 0.1% trifluoroacetic acid) with the matrix solution (1:10, v/v) in a 0.5 mL Eppendorf<sup>®</sup> micro tube. Finally 1.0 µL of this mixture was deposited on the sample plate, dried at room temperature and then analyzed. MALDI-TOF mass spectra of all synthesized Pc complexes were recorded in 2,5dihydroxybenzoic acid with a better intensity than the other conventional MALDI matrices and the MALDI-TOF mass spectra are given in ESI, Fig. S6-S12.†

#### 3.3. Synthesis

**3.3.1. [1,1'-***p***-Anisylidenbis(2-naphthoxyphthalonitrile)] 3.** A mixture of **1** (0.69 g, 4 mmol) and 2 (0.90 g, 2 mmol) in 20 mL DMF was stirred at room temperature under argon.  $K_2CO_3$  (0.828 g, 6 mmol) was added into the mixture over a period of 2 h. After stirring the reaction mixture at 80 °C for a week, the undissolved salt was removed by filtration. The reaction mixture was poured into water (100 mL). The precipitate was filtered, washed with water and dried *in vacuo* (55 °C). The residue was fractionated on a silica gel column eluting with

CHCl<sub>3</sub>. Yield: 1.1 g (92%). Compound 3 is soluble in CHCl<sub>3</sub>, THF, acetone, DMSO, DMF, methanol, DCM and toluene. Mp: 248 °C. Anal. calc. for C<sub>44</sub>H<sub>26</sub>N<sub>4</sub>O<sub>3</sub>, calculated C, 80.23; H, 3.98; N, 8.51; found C, 80.41; H, 3.67; N, 8.23%; MS (MALDI-TOF): *m*/*z* 681.6 [M + Na]<sup>+</sup>, *m*/*z* 697.7 [M + K]<sup>+</sup>; IR (KBr pellet)  $\nu$ , cm<sup>-1</sup>: 521, 752, 821, 964, 1032, 1089, 1171, 1213, 1279, 1293, 1308, 1392, 1422, 1463, 1483, 1508, 1565, 1590, 2015, 2225, 2833, 2899, 3070; <sup>1</sup>H NMR (CHCl<sub>3</sub>)  $\delta$  7.85 (d, *J* = 7.10 Hz, 2H), 7.80 (d, *J* = 7.75 Hz, 2H), 7.66 (d, *J* = 6.85 Hz, 2H), 7.50 (t, 2H), 7.44 (t, 2H), 7.26 (s, 2H), 7.01 (d, *J* = 8.65 Hz, 2H), 6.91 (s, 1H), 6.81 (d, *J* = 8.70 Hz, 2H), 6.62 (br s, 2H), 6.53 (br s, 2H), 6.50 (d, *J* = 7.35 Hz, 2H), 3.59 (s, 3H) ppm.

3.3.2. [{2,10,16,24-Tetrakis-1,1'-p-anisylidenbis(2-naphthoxyphthalonitrile)} phthalocyaninatocobalt (II)] 4. A mixture of 3  $(0.263 \text{ g}, 0.4 \text{ mmol}), \text{ Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O} (0.025 \text{ g}, 0.1 \text{ mmol})$  and anhydrous DMF (3 mL) was mixed in a glass tube which was sealed under N<sub>2</sub>. The reaction mixture was stirred at 180 °C for 12 h. After cooling to room temperature, the dark blue mixture was diluted with acetic acid (10 mL) to precipitate the product and it was filtered. After it was washed successively with hot acetic acid ( $3 \times 20$  mL), hot ethanol ( $3 \times 20$  mL) and hot water to remove the unreacted organic materials, it was dried in vacuo (60 °C). The crude product was purified by column chromatography with silica gel eluting with CHCl<sub>3</sub>. Yield: 171 mg (65%). This compound is soluble in  $CHCl_3$ , methanol, acetone, toluene, DMSO, DCM, THF, and DMF. Mp >300 °C. Anal calc. for C<sub>176</sub>H<sub>104</sub>CoN<sub>16</sub>O<sub>12</sub>: C, 78.42; H, 3.96; N, 8.31%; found: C, 78.62; H, 3.76; N, 8.26%. MS (MALDI-TOF): m/z 2694.75[M + H]<sup>+</sup>, IR (KBr pellet)  $\nu$ , cm<sup>-1</sup>: 384, 443, 522, 649, 750, 818, 864, 968, 1032, 1059, 1091, 119, 1177, 1244, 1309, 1407, 1461, 1509, 1591, 1671, 1733, 2023, 2163, 2230, 2834, 2931, 3059; UV/Vis (DMSO), nm (log  $\varepsilon$ ): 671(4.60), 618(4.22), 312 (4.76).

3.3.3. [2,10,16,24-Tetrakis{1,1'-p-anisylidenbis(2-naphthoxyphthalonitrile)}phthalocyaninatozinc(II)] 5. A mixture of 3 (0.263 g, 0.4 mmol), Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.022 g, 0.1 mmol) and anhydrous DMF (3 mL) was mixed in a glass tube which was sealed under nitrogen. The reaction mixture was stirred at 180 °C for 12 h. After cooling to room temperature, the dark blue-greenish mixture was diluted with acetic acid (10 mL) to precipitate the product and it was filtered. The residue was washed successively first with hot acetic acid and then with hot ethanol and hot water before drying it in vacuo (60 °C). The residue was coarsely fractionated on a silica gel column eluting with CHCl<sub>3</sub> and a gradient of CHCl<sub>3</sub>-methanol up to 5% methanol. Yield: 176 mg (67%). This compound is soluble in CHCl<sub>3</sub>, acetone, DMSO, DCM, THF, and DMF. Mp >300 °C. Anal calc. for C176H104N16O12Zn: C, 78.23; H, 3.95; N, 8.29%; found: C, 78.03; H, 3.75; N, 8.17%; MS (MALDI-TOF): m/z 2699.75[M + H]<sup>+</sup>, IR (KBr pellet)  $\nu$ , cm<sup>-1</sup>: 386, 422, 440, 521, 540, 648, 744, 815, 862, 966, 1043, 1087, 1115, 1143, 1176, 1311, 1334, 1391, 1459, 1482, 1509, 1592, 1718, 1770, 2027, 2230, 2833, 3055; UV/Vis (DMSO), nm (log e): 689(4.65), 629 (4.13), 355(4.41).

3.3.4. [2,10,16,24-Tetrakis{1,1'-*p*-anisylidenbis(2-naphthoxyphthalonitrile)}phthalocyaninatocopper(II)] 6. The mixture of 3 (0.263 g, 0.4 mmol), Cu(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.020 g, 0.1 mmol) and anhydrous DMF (3 mL) was heated and stirred at 180 °C in a sealed glass tube for 12 hours under a dry N<sub>2</sub> atmosphere. After cooling to room temperature, the reaction mixture was precipitated by adding acetic acid. The dark-green product was filtered. Then, the crude product was washed with acetic acid, ethanol and water for 12 hours respectively in the Soxhlet apparatus. The residue was coarsely fractionated on a silica gel column eluting with CHCl<sub>3</sub> and a gradient of CHCl<sub>3</sub>-THF up to 100% THF. Yield: 189 mg (72%). This compound is soluble in acetone, CHCl<sub>3</sub>, DCM, THF, DMF and DMSO. Mp >300 °C. Anal calc. for C<sub>176</sub>H<sub>104</sub>CuN<sub>16</sub>O<sub>12</sub>: C, 78.28; H, 3.96; N, 8.30; found: C, 78.08; H, 3.75; N, 8.47%; MS (MALDI-TOF): m/z  $2698.76[M + H]^+$ , IR (KBr pellet), cm<sup>-1</sup>: 385, 398, 422, 440, 521, 539, 650, 747, 817, 863, 972, 1053, 1091, 1118, 1177, 1313, 1341, 1400, 1460, 1509, 1593, 1737, 1772, 2231, 2939, 3061; UV/Vis (DMSO), nm(log  $\varepsilon$ ): 686(4.52), 634(4.40), 338 (4.51).

3.3.5. [{2',10',16',24'-Tetrakis(1,1'-p-anisylidenbis-2-naphthoxy)}phthalocyaninatodicobalt(II)] 7. The mixture of compound 4 (0.119 g, 0.043 mmol) and Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.25 g, 1 mmol) was powdered in a quartz crucible and transferred into a reaction tube. 1 mL of DMF was added to this reaction mixture and the reaction mixture was heated in a sealed glass tube for 12 h under a dry N2 atmosphere at 180 °C. After cooling to room temperature, the reaction mixture was precipitated by adding acetic acid. The precipitate was filtered and washed with acetic acid, ethanol and water for 24 h respectively in the Soxhlet apparatus. The crude product was purified by column chromatography with silica gel eluting with CHCl<sub>3</sub> and a gradient of CHCl<sub>3</sub>-THF up to 5% THF. This compound is soluble in CHCl<sub>3</sub>, DMF, DMSO and THF. Yield: 71 mg (60%). Mp >300 °C. Anal. calc. for C<sub>176</sub>H<sub>104</sub>Co<sub>2</sub>N<sub>16</sub>O<sub>12</sub>: C, 76.79; H, 3.81; N, 8.14%; found: C, 76.89; H, 3.91; N, 8.20%; MS (MALDI-TOF): m/z 2839.67[M - 3H + 4Na]<sup>+</sup>; IR (KBr pellet)  $\nu$ , cm<sup>-1</sup>: 397, 422, 520, 644, 744, 813, 861, 969, 1032, 1089, 1117, 1176, 1312, 1393, 1458, 1508, 1594, 1713, 1770, 2160, 2826, 2951, 3055, 3391; UV/Vis (DMSO), nm(log ε): 678(4.55), 623 (4.24), 318(4.66).

3.3.6. [{2',10',16',24'-Tetrakis(1,1'-p-anisylidenbis-2-naphthoxy) **phthalocyaninatodizinc**(II) 8. The mixture of 5 (0.123 g, 0.044 mmol), Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.22 g, 1 mmol) and DMF(1 mL) was mixed in a glass tube which was sealed under nitrogen. The mixture was heated at 180 °C for 12 h. After cooling to room temperature, a blue-green reaction product was obtained, isolated and purified using the same procedure as explained above for 7. This compound is soluble in CHCl<sub>3</sub>, DMF, DMSO and THF. Yield: 60 mg (49%). Mp >300 °C. Anal. calc. for  $C_{176}H_{104}N_{16}O_{12}Zn_2$ : C, 76.43; H, 3.79; N, 8.10%; found: C, 76.28; H, 3.88; N, 8.01%; MS (MALDI-TOF): m/z 2761.66[M + H]<sup>+</sup>, IR (KBr pellet)  $\nu$ , cm<sup>-1</sup>: 388, 396, 421, 443, 520, 646, 744, 815, 861, 969, 1044, 1087, 1116, 1176, 1312, 1334, 1392, 1459, 1509, 1595, 1610, 1715, 1771, 2169, 2830, 2927, 3059; UV/Vis (DMSO), nm(log  $\varepsilon$ ): 689(4.66), 626(4.12), 354(4.44); 1H NMR (CHCl<sub>3</sub>): δ, ppm 8.95–6.11 (m, 88H, arom.), 3.65-2.60(m, 12H, Ar-OCH<sub>3</sub>), 2.89-2.77 ppm (m, 4H, Ar-CH).

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**3.3.7.** [{2',10',16',24'-Tetrakis(1,1'*p*-anisylidenbis-2-naphthoxy)}phthalocyaninatodicopper(u)] **9.** The mixture of compound **6** (0.132 g, 0.047 mmol), Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.20 g, 1 mmol) and DMF (1 mL) was heated and stirred at 180 °C in a sealed glass tube for 12 h under N<sub>2</sub>. After cooling to room temperature, a dark green reaction product was obtained, isolated and purified using the same procedure as explained above for 7. This compound is soluble in CHCl<sub>3</sub>, DMF, DMSO and THF. Yield: 69 mg (52%). Mp >300 °C. Anal. calc. for C<sub>176</sub>H<sub>106</sub>Cu<sub>2</sub>N<sub>16</sub>O<sub>12</sub>: C, 76.54; H, 3.80; N, 8.11%; found: C, 76.39; H, 3.89; N, 8.05%; MS (MALDI-TOF): *m/z* 2759.68 [M + H]<sup>+</sup>, IR (KBr pellet)  $\nu$ , cm<sup>-1</sup>: 385, 439, 519, 645, 744, 814, 861, 970, 1048, 1088, 1116, 1143, 1176, 1313, 1396, 1458, 1508, 1594, 1715, 1770, 2161, 2834, 2927, 3056; UV/Vis (DMSO), nm(log  $\varepsilon$ ): 688(4.49), 639(4.25), 333(4.47).

## 3.3. OFET fabrication

The field effect transistors were prepared using indium tin oxide (ITO) coated glass substrate as the gate electrode. The OFET devices were fabricated with the bottom-gate and top source-drain contact geometry configuration. Before using, the ITO coated substrates were cleaned by ultrasonic treatment in acetone, isopropyl alcohol, and deionised water in that order. The gate insulator layer was PVA, obtained commercially and used as received. The PVA gate insulating film was spincoated from a solution of PVA in distilled water at 2500 rpm for 45 s. After drying the PVA film in a vacuum oven at 90 °C for 15 min to evaporate the solvent remaining in the film, a solution of Pcs in chloroform, with a concentration of  $5 \times 10^{-3}$ M, was spun on top of the PVA film rotating at 3500 rpm. Subsequently, the deposited films were thermally annealed at 120 °C for 45 min to evaporate the solvent. The ellipsometric technique was used to measure the thickness of the dielectric layer and the Pc films. The source and drain electrodes were deposited onto the semiconducting layer with a shadow mask to produce top contact OFETs. Au was used for the sourcedrain contact metal, at a thickness of 100 nm. The channel length and width of the OFETs were 80 µm and 4 mm, respectively. The electrical characteristics of these devices were measured in air. For electrical measurements a Keithley 617 programmable electrometer and a Keithley 2400 source-meter were used.

### 3.4. Electrochemical measurements

Electrochemical and in situ spectroelectrochemical measurements were achieved by a Gamry Ref. 600 potentiostat combined with an Ocean Optics HR2000 UV/vis spectrophotometer. A Pt disc, a Pt spiral wire and a saturated calomel electrode (SCE) were employed as the working, counter and reference electrodes, respectively, for cyclic voltammetry and square voltammetry measurements. Ferrocene was used as an internal reference, but all potentials were presented as the ones vs. SCE. Electrochemical grade tetrabutylammonium perchlorate (TBAP) in extra pure DMSO was employed as the supporting electrolyte at a concentration of 0.20 mol dm<sup>-3</sup>. High purity N<sub>2</sub> was used for deoxygenating the

Ultra-pure water and sulfuric acid were used to prepare the electrolyte solution in electrocatalytic measurements. Vulcan XC-72 (VC) (Cabot Co), 5% Nafion (Nf) solution (Aldrich), extra pure ethyl alcohol (Merck), and the Pc compounds were used in catalyst preparation. A glassy carbon disk electrode, a platinum ring-glassy carbon disk electrode and a polishing kit for these electrodes were purchased from Pine Instruments. Two Gamry Ref. 600 potentiostats were connected as a bipotentiostat to control the ring and disk potentials and to collect the respective currents during rotating ring-disk electrode (RRDE) experiments. A Pine Instrument Company AFMSRCE modulator speed rotator was employed in RRDE experiments. A Pine Instrument Company AFMSRCE modulator speed rotator was employed in RDE RRDE experiments. RRDE measurements were performed with a glassy carbon disk (5 mm dia.) in O<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution under quasi-stationary conditions (0.005 V s<sup>-1</sup> sweep rate) at 25 °C. For RRDE experiments, the working electrode was a glassy carbon disk (5.61 mm dia.) and a platinum ring leading to a collection efficiency, N = 37%. These experiments were carried out at 2500 rpm in oxygen saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte solution at 25 °C. The disk potential was swept at 0.005 V  $s^{-1}$ whereas the ring potential was held at 0.95 V vs. SCE. In order to disperse the catalysts on a carbon support for RRDE experiments, a mixture of the Pc compound, VC and 5 wt% Nf solution in absolute ethanol was prepared and ultrasonically homogenized for half an hour. A micropipette was used to load a suitable amount of the catalyst ink onto a freshly polished glassy carbon electrode. The amount of Nf in the ink was adjusted so that the catalyst film was sufficiently thin, and thus its diffusion resistance was negligible. In order to obtain a total coverage of the glassy carbon surface, the deposited drop of ink was dried with pulsed air at ambient temperature to evaporate the solvent quickly. Each voltammogram was recorded with a freshly prepared electrode due to the possible catalyst degradation in acidic medium. The counter electrode was a Pt spiral and the reference electrode was a SCE.

# 4. Conclusions

The novel mono-nuclear **4**, **5** and **6**, and ball-type **7**, **8** and **9** have been synthesized from **3**. The complexes were characterized by elemental analysis, UV-vis, IR, <sup>1</sup>H NMR and MALDI-TOF mass spectroscopies.

By choosing an appropriate metal electrode (drain and source electrode), high field effect mobility in OFETs consisting of spin coated **7–9** film was successfully demonstrated and characterized. It was observed that the field-effect mobility and the threshold voltage, which are the main OFET performance

parameters, using spin coated film of **9** as organic channels are much higher than the values of the respective devices using **7** and **8**. One of the reasons why, unlike the ball-type Pc based OFETs, the mono-nuclear based OFETs are incapable of exhibiting a satisfactory saturation area of the drain currentdrain voltage curves, is that in the film during the spin coating, stacking structures are rapidly formed. The results suggest that ball-type films, especially **9** are promising materials for the fabrication of OFETs with low threshold voltage and high mobility.

The comparison of the voltammetric behaviour of the novel dinuclear ball-type phthalocyanines (7, 8 and 9) with their mononuclear homologues (4, 5 and 6) suggested that these compounds form Pc ring-based and/or metal-based mixedvalence species as a result of the interactions between the two cofacial MPc units. Novel cobalt phthalocyanines, 4 and 7, displayed high catalytic activity towards dioxygen reduction. The high catalytic performance of these compounds was attributed to the redox-active nature of the CoII metal center which enhances the interaction with dioxygen. On the other hand, the further enhanced catalytic performance of 7  $(Co_2Pc_2)$  in comparison with that of 4 (CoPc) was attributed to its distinctive coordinating properties due to the presence of two interacting redox-active metal centers and thus its ability to bind a dioxygen molecule through peroxo species, Co-O-O-Co, the promotion of the O-O bond breakage and thus the increase in the tendency for reduction directly to water via the four-electron path.

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