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## ARTICLE

# Microwave-assisted Synthesis of Novel Non-peripherally Substituted Metallophthalocyanines and Their Sensing Behaviour for a Broad Range of Lewis Bases

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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The synthesis of novel, symmetrical, tetrasubstituted metallophthalocyanines (cobalt, zinc, and manganese) bearing four 2-(4-methyl-1,3-thiazol-5-yl)ethoxy units was reported. The new compounds have been characterized using UV-Vis, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and mass spectroscopic data. Photophysical properties with zinc (II) phthalocyanine were found, including electronic absorption and fluorescence quantum yield. The fluorescence of the complexes was investigated in DMF and it was found that benzoquinone (BQ) was an effective quencher. The response and recovery behaviours of the spin coated films to different analytes, which span a broad range of Lewis base, have been investigated by means of conductivity measurements. It was observed that the operating temperature had a considerable effect on the gas sensing performance of the sensors investigated. The sensing behaviour of the films for a broad range of Lewis bases and the correlation between the sensor sensitivity and Lewis base enthalpies were investigated. Results show that sensitivity of the films may be correlated exponentially with binding enthalpy.

## Introduction

Phthalocyanines (Pcs) are a class of macrocyclic compounds which display remarkable properties like intensely high thermal, chemical stability, brightness, and high efficiency in electron transfer. Phthalocyanines (MPcs) could be modulated in a number of ways, for example, changing substitution, the central metal ion, and the axial ligands.<sup>1,2</sup> Phthalocyanines can be used in a number of applications in many areas because of these properties. Some technological applications include chemical sensors,<sup>3</sup> liquid crystals,<sup>4,5</sup> semiconductors,<sup>6</sup> non-linear optics,<sup>7</sup> and photosensitizers in photodynamic therapy (PDT).<sup>8</sup>

Thiazole is a heterocyclic compound that contains both sulfur and nitrogen in the ring. These rings are of planar and aromatic nature.<sup>9</sup> Thiazole group finds applications in different fields, such as antioxidant,<sup>10</sup> liquid crystals,<sup>11</sup> fluorescent dyes,<sup>12,13</sup> polymers,<sup>14</sup> photonucleases<sup>15</sup> and insecticides.<sup>16</sup> They play a prominent role in the nature. For example, the thiazole ring is a component of thiamine (Vitamin B<sub>1</sub>). Furthermore, their derivatives have been frequently synthesized to use as drugs in pharmaceutical industry. Thiazole derivatives are used in a number of pharmacological applications because of some biological features such as antimicrobial, antiviral, antifungal,

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antibacterial, antitumor, and anti-inflammatory activities.<sup>17</sup> As examples, the anticonvulsant riluzole, the antiparkinsonian talipexole, the antischistosomal miridazole, the antibacterial sulfathiazole, and the antiviral ritonavir can be cited.<sup>18</sup> According to our knowledge, there are very few articles in the literature on thiazole substituted phthalocyanine.<sup>19,20</sup> In our previous work, the synthesis and characterization of tetrasubstituted metallophthalocyanines carrying four 2-(4-methyl-1,3-thiazol-5-yl)ethoxy moieties on the periphery were described.<sup>21</sup> The wavelength of the absorption of the Q band and the aggregation properties of the compounds were also investigated.

Many recent experimental studies indicated that the electrical conductivity in MPc films depends strongly on atmospheric chemical species, which make them suitable for use as sensing element in gas sensors.<sup>22</sup> The growing interest in the use of Pc compounds in the production of miniaturized electronic devices to be able to act as chemical sensors is due to their capacity to satisfy a large number of electrical requirements. It is also well established that the sensitivity of MPc to gas molecules may be tuned by manipulation of the metal center and by substitution of functional groups on the organic ring.<sup>22-24</sup> The sensing behavior of many metal phthalocyanines to various gases have been studied in some detail by various workers.<sup>25-28</sup> However, little previous work has been performed on analyst with a broad range of binding strengths.

In this study, new phthalonitrile derivative bearing 2-(4-methyl-1,3-thiazol-5-yl)ethoxy substituent at non-peripheral positions have been synthesized. Novel non-peripheral cobalt, zinc and manganese phthalocyanines were synthesized and characterized for the first time. We report here the photophysical (fluorescence quantum yields and lifetimes) and quenching properties of zinc(II) derivative in DMF. In addition, the sensitivities of newly synthesized MPc (M = Co, Zn and Mn) are examined with respect to a series of analytes spanning a range of Lewis basicities.

## Results and discussion

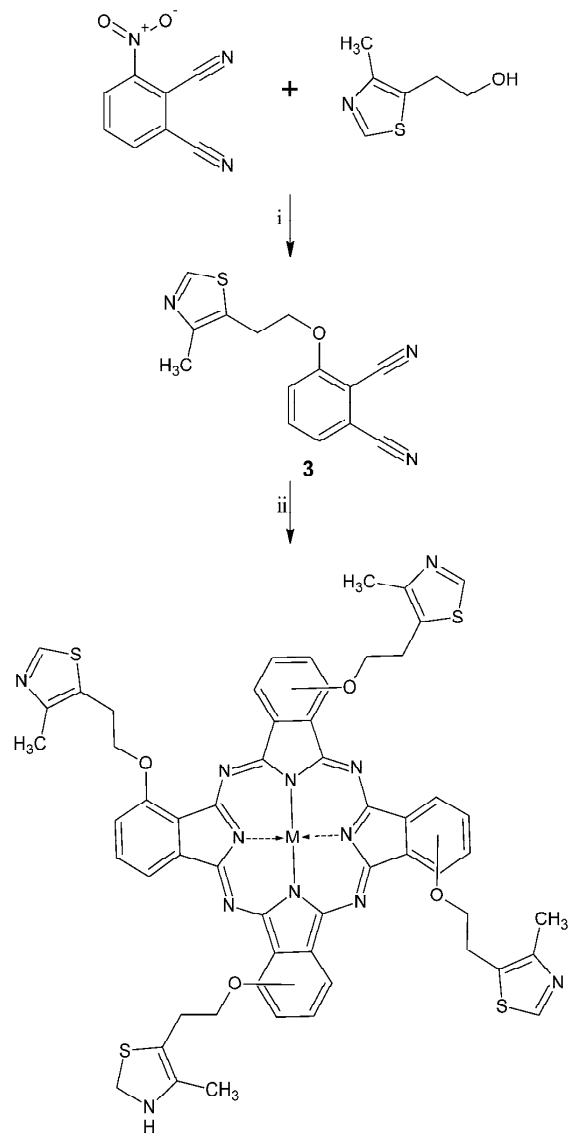
### Synthesis and structural characterizations

The syntheses of substituted phthalonitrile derivatives constitute a critical step in phthalocyanine synthesis. Scheme 1 shows the synthesis of the target phthalocyanines **4–6**. 3-[2-(4-methyl-1,3-thiazol-5-yl)ethoxy]phthalonitrile (**3**) was prepared from the reaction between 3-nitrophthalonitrile and 5-(2-hydroxyethyl)-4-methylthiazole in DMF.  $K_2CO_3$  was used as the base for this nucleophilic aromatic displacement.<sup>29,30</sup> Ortho-disubstituted benzene derivatives, such as phthalimide, phthalic anhydride, phthalonitrile, and 1,3-diiminoisoindoline could be used to synthesize the resulting phthalocyanines. Generally speaking, 3- or 4- nitrophthalonitrile and 4,5-dichlorophthalonitrile are preferred because they can be easily converted to alkyl/aryl or thioether derivatives.<sup>31,32</sup> 3-Nitrophthalonitrile (**1**) are reacted with thiols or alcohols under basic conditions to form 3-substituted phthalonitriles, which are then converted to non-peripheral substituted phthalocyanines.<sup>33</sup> In the present study, cyclotetramerizations of the dicyano-derivative (**3**) to the metallo-phthalocyanines (**4–6**) were accomplished in *n*-hexanol in the presence of DBU and metal salts ( $CoCl_2$ ,  $Zn(CH_3COO)_2$ ,  $MnCl_2$ ). Elemental analyses and spectral data (EI-MS, MALDI-TOF,  $^1H$  NMR,  $^{13}C$  NMR, UV-Vis, and FT-IR) for all new products are consistent with the proposed structures. The results are given in the experimental section.

The mono-substituted phthalonitriles give a mixture of four constitutional isomers of tetra-substituted phthalocyanines ( $D_{2h}$ ,  $C_{2v}$ ,  $C_{4h}$ ,  $C_s$ ).<sup>34,35</sup> Isolation of one of these isomers needs more complicated separation techniques than crystallization and column chromatography. The scope of this work does not isolate pure isomers because of this reason it was not attempted to separate the constitutional isomers of the phthalocyanines. As expected the synthesized tetra-substituted Co(II), Zn(II) and Mn(III) phthalocyanines (**4–6**) were obtained as a statistical mixture of four four regioisomers ( $D_{2h}$ ,  $C_{4h}$ ,  $C_{2v}$  and  $C_s$ ) because of the various possible positions of the substituents relative to one another.

In the FT-IR spectrum of compound **3**, the absorption signals at 2228 and 3086  $cm^{-1}$  were assigned to the  $C\equiv N$  and the C–H stretching of the aromatic rings, respectively. The  $^1H$ -NMR spectrum of **3** in  $DMSO-d_6$  showed the signals at  $\delta = 8.63$  ppm as a singlet because of the aromatic proton belonging to the thiazole moiety. The aromatic protons were at  $\delta = 7.19–7.21$ ,  $\delta = 7.37–7.38$  and  $\delta = 7.64–7.66$  ppm as quartet, doublet and

doublet, respectively. The  $CH_2$  protons bonded to the thiazole entity and the other  $CH_2$  moiety were observed at  $\delta = 3.37–3.39$  and  $\delta = 4.28–4.31$  ppm as triplets, respectively. The singlet  $CH_3$  protons were at  $\delta = 2.49$  ppm. The molecular ion peak at  $m/z = 269$  was easily identified in the mass spectrum of **3**.



	M
<b>4</b>	Co
<b>5</b>	Zn
<b>6</b>	Mn(III)

**Scheme 1.** Synthesis of the phthalonitrile derivative (**3**) and the corresponding phthalocyanines **4–6**. (i)  $K_2CO_3$ , DMF, 50°C. (ii) Metal salts ( $CoCl_2$ ,  $Zn(CH_3COO)_2$ ,  $MnCl_2$ ), *n*-hexanol, DBU, 3–10 min., 350 W, 155°C.

A distinctive observation of the phthalocyanine formation from **3** is that the  $C\equiv N$  stretching peak in the FT-IR spectrum of the precursor compound. The FT-IR spectra of the phthalocyanines

4–6 are very similar. In the FT-IR spectra of the phthalocyanines (4–6), aromatic CH, aliphatic CH, and C–O–C vibrations were observed in the range of 3083–3067, 2926–2853 and 1239–1233  $\text{cm}^{-1}$ , respectively. In the  $^1\text{H-NMR}$  spectrum of compound 5, the  $\text{CH}_2$  protons bonded to thiazole ring and the other  $\text{CH}_2$  moiety were observed at  $\delta = 3.62\text{--}3.87$  and  $\delta = 4.93\text{--}5.11$  ppm, respectively. The aromatic protons were observed at  $\delta = 7.73\text{--}7.75$ ,  $\delta = 8.04\text{--}8.11$  and  $\delta = 8.75\text{--}8.76$  ppm, respectively. The aromatic proton which belongs to the thiazole ring was at  $\delta = 8.98\text{--}9.09$  ppm. The  $\text{CH}_3$  protons were present at  $\delta = 2.59$  ppm. The elemental analysis data and the mass spectra confirmed our structural assignment.

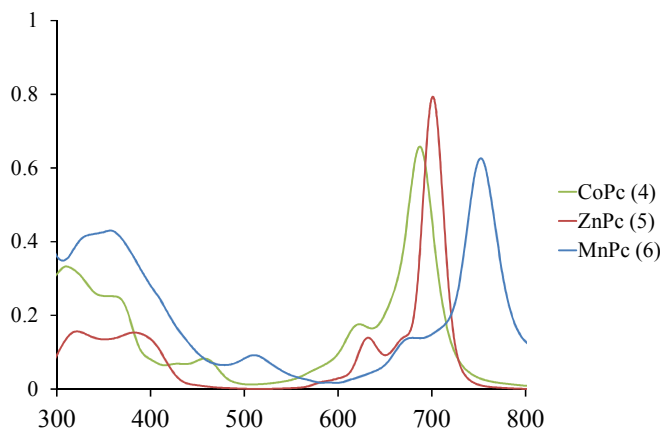


Fig. 1 Uv-Vis spectrum of 4-6.

#### Ground state absorption spectra and aggregation properties

The phthalocyanine macrocyclic system is characterized by, in the UV-Vis spectrophotometric spectral window, two strong absorption bands called Soret and Q bands, the former being at 300–350 nm and the latter observed in the visible region at 600–700 nm.<sup>36</sup> They are dominated by the  $\pi\text{--}\pi^*$  transitions within the heteroaromatic 18- $\pi$ -electron system. The absorption spectra of the non-peripherally substituted phthalocyanine complexes (4–6) showed exclusively monomeric behavior as evidenced by a single (narrow) Q band.<sup>37</sup> In the UV-Vis spectra of 4 and 5 in DMF, Soret bands were observed at 311 and 322 nm while the Q bands were found to be at 686, 708 nm, respectively. The UV-Vis spectrum of 6 in DMF exhibited the Soret band at 359 nm and the intense Q band at 751 nm. Further, the phthalocyanine (6) shows an absorption at 512 nm which was interpreted as charge transfer absorption (phthalocyanine  $\rightarrow$  metal, LMCT). The UV-Vis spectra of compounds 4–6 in DMF are shown in Fig. 1. The Q bands of the non-peripherally substituted phthalocyanines (4–6) are bathochromically shifted when compared to the corresponding peripherally substituted complexes in DMF. The bathochromic shifts are between 20–25 nm for non-peripheral and peripheral substituted derivatives.<sup>30</sup>

Aggregation behavior of phthalocyanines is described as the coplanar association of rings progressing from monomer to dimer and to higher order complexes. It depends on

concentration, nature of solvent, substituents, metal ions, and temperature. When the electronic spectra of phthalocyanines 4–6 are examined, there are weak peaks found at ca. 620–640 nm just on the higher energy side of the strong Q band. The identity of this band as to if they arise from aggregation or not can be explained by studying the absorption spectra in a series of compounds with different concentrations. The aggregative behaviour of the complexes 4–6 was examined at different concentrations in DMF. The intensity of absorption of the Q band also increased with an increase of concentration. It was observed that a new band did not occur due to the aggregated species.<sup>38,39</sup> The Beer–Lambert law was obeyed for all these compounds for the concentrations ranging from  $2.00 \times 10^{-6}$  to  $14.00 \times 10^{-6}$  M. The phthalocyanine derivatives 4–6 did not show a detectable aggregation in DMF.

In order to determine the band gap energy ( $E_g$ ) and to obtain information about direct or indirect interband transitions, the optical transmittances of the thin film of the compounds were also measured in the wavelength range of 300–800 nm. The band gap energy was calculated from the  $(\alpha h\nu)^2$  vs  $h\nu$  plot. The absorption coefficient  $\alpha$  is related to the photon energy  $h\nu$  by<sup>40</sup>

$$\alpha = \alpha_0 (h\nu - E_g)^n \quad (1)$$

where  $\alpha_0$  is an energy-independent constant,  $n$  is a constant which determines type of the optical transition ( $n = 1/2$  for allowed direct transitions and  $n = 2$  for allowed indirect transitions) and  $E_g$  is the optical band gap. The band gap energies of the thin films are 2.26, 2.33 and 1.98 eV for the 4, 5 and 6, respectively. It is evaluated that the optical band gap of the Pc films has a direct optical transition.

#### Fluorescence spectra and fluorescence quenching studies by benzoquinone

Fig. 2 shows the absorption, fluorescence emission, and excitation spectra for the zinc phthalocyanine (5) in DMF. Fluorescence emission peak was observed at 720 nm. The fluorescence quantum yields ( $\Phi_F$ ) of the complex were similar

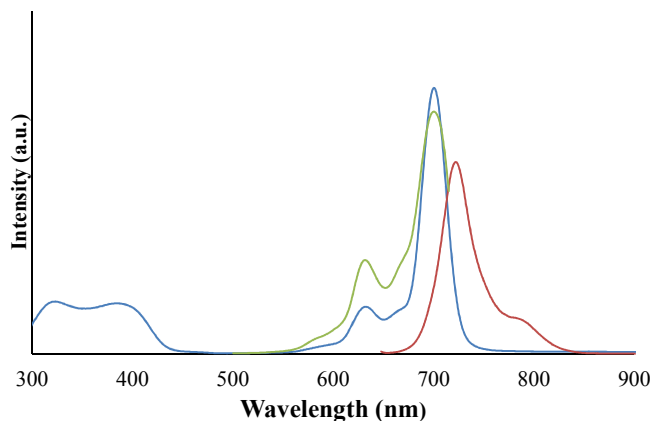
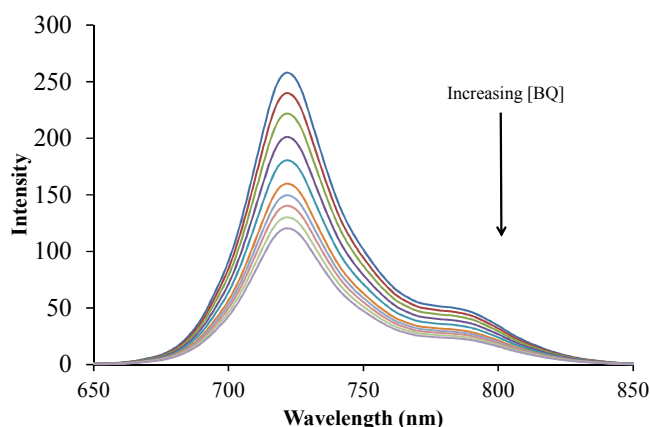


Fig. 2 Absorption, excitation, and emission spectra for compound 5 in DMF. Excitation wavelength=632 nm.

and typical of MPc complexes.<sup>41</sup> The excitation spectrum of the zinc phthalocyanine was similar to absorption spectrum and both were mirror images of the emission spectrum in DMF. The proximity of the maximum wavelength of the absorption and the excitation spectra suggest that the nuclear configurations of the ground and excited states are similar and are not affected by excitation.<sup>42</sup> The observed Stokes shifts are 19 nm for **5** in DMF. The observed Stokes shift of the phthalocyanine compound is higher than standard ZnPc in both DMF.<sup>43</sup> Fluorescence quantum yields ( $\Phi_F$ ) were determined by the comparative method (Eq. (3)). Unsubstituted ZnPc was employed as a standard in DMF ( $\Phi_F = 0.17$ ).<sup>44,45</sup> The fluorescence quantum yield was calculated as 0.15. The  $\Phi_F$  value of the non-peripheral ZnPc complex is slightly higher than peripherally substituted ZnPc (0.14 ns) in DMF.<sup>21</sup> Fluorescence lifetime ( $\tau_F$ ) refers to the average time a molecule stays in its excited state before fluorescing; the longer the lifetime, the higher the quantum yield of fluorescence. Natural radiative lifetime ( $\tau_0$ ) was calculated using the Strickler–Berg equation. The fluorescence lifetime ( $\tau_F$ ) and natural radiative lifetime ( $\tau_0$ ) of the ZnPc were found to be 1.25 and 8.33 ns, respectively. The  $\tau_F$  values of the ZnPc complexes are slightly higher than unsubstituted ZnPc (1.03 ns) in DMF.<sup>44</sup>

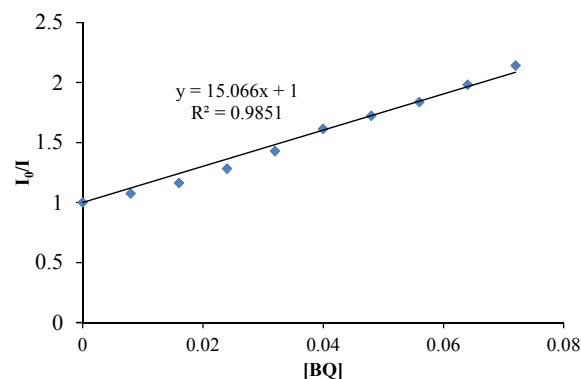


**Fig. 3** Fluorescence emission spectral changes of **5** ( $4.00 \times 10^{-6}$  mol dm<sup>-3</sup>) on addition of different concentrations of BQ in DMF. [BQ] = 0, 0.008, 0.016, 0.024, ..... mol dm<sup>-3</sup>.

The fluorescence quenching of the complex (**5**) was carried out by the addition of different concentrations of 1,4-benzoquinone (BQ) into the solution having the complex. BQ was used as the quencher. The concentrations of BQ in the resulting mixtures were from 0 to 0.072 mol dm<sup>-3</sup>. Fig. 3 shows the emission spectra of the ZnPc during quenching BQ as an example.

The linearity of Stern–Volmer plot ( $I_0/I$ ) versus the quencher's concentration ([BQ]) indicates that one type of quenching mechanism is predominant.<sup>46</sup> The fluorescence quenching of zinc phthalocyanine by benzoquinone (BQ) in DMF was found to obey Stern–Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions. The slope of the plot

shown at Fig. 4 gave a  $K_{SV}$  value ( $K_{SV} = 15 \text{ M}^{-1}$ ). The  $K_{SV}$  value of the ZnPc compound (**5**) is higher than the value of peripherally substituted zinc(II) phthalocyanine compound. The  $K_{SV}$  value of the ZnPc was lower than unsubstituted ZnPc ( $57.60 \text{ M}^{-1}$ ).<sup>47,48</sup> The bimolecular quenching constant ( $k_q$ ) values of the substituted zinc phthalocyanine ( $k_q = 12 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) was also lower than for unsubstituted ZnPc ( $5.59 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ).<sup>49</sup> Substitution of phthalocyanine framework with 2-(4-methyl-1,3-thiazol-5-yl)ethoxy groups seems to decrease the  $k_q$  values of the complex (**5**) in DMF. The  $k_q$  values are near  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  and in agreement with the theoretical Smoluchowski–Einstein approximation at 298 K.<sup>50</sup> The fluorescence quenching between Zinc Phthalocyanine and BQ was taken place via diffusion-controlled mechanism since bimolecular quenching rate constant was obtained to be close to the limits of  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . This property gives an indication of the potential of the compound as photosensitizer for PDT application.



**Fig. 4** Stern–Volmer plots for benzoquinone (BQ) quenching of **5** [ZnPc] =  $4.00 \times 10^{-6}$  mol dm<sup>-3</sup> in DMF. [BQ] = 0, 0.008, 0.016, 0.024, ..... and 0.072 mol dm<sup>-3</sup>

### Gas sensing

The gas sensing characteristics of the materials were investigated as a function of operating temperature and test gas concentration. Before gas sensing experiments, current–voltage (I–V) measurements were carried out on spin coated films of the compound. I–V measurements showed that the current is ohmic for low applied voltages (<2V) and then increases exponentially. A bias of 1 V was therefore chosen for the gas sensing measurements. Sensor responses were determined from time-dependent current plots at constant voltage. When the films were exposed to various concentrations of acetone vapour between 150 and 600 ppm, the room temperature dynamic current response of the sensors are shown in Fig. 5. It is clear from the Fig. 5 that the responses and recoveries generally exhibit an initial fast region, accounting for the largest change in sensor current, followed by a slow saturation region. The fast region of the response and recovery can be attributed to adsorption of analyte primarily at O<sub>2</sub> free metal centers, and the slow response region to competitive displacement of O<sub>2</sub> bound metal in all case, there is good linearity between the response



magnitude and the concentration of acetone vapour. The obtained linear relationship between the response magnitude and acetone concentration indicates that the sensors match with linear amplifying circuits for practical application in the detection range of 150 – 600 ppm. The correlation coefficient ( $R^2$ ) of the sensors fit curve was 0.98. It was reported that the delocalized  $\pi$ -electron system, the presence of heteroatoms and the central metal atom are important features in the volatile organic compound (VOC) vapour/MPc interaction mechanism.<sup>51</sup> The role played by the central metal atom in the sensing properties can be easily seen by comparing the response characteristics of the films. It is also clear from Fig. 5 that the 4 coated sensor shows the highest sensitivity ( $S$ ), which is defined as the ratio of the measured current after and before exposing to target gas. The order of sensitivities observed for these compounds are  $S_4 > S_6 > S_5$  at all temperatures investigated.

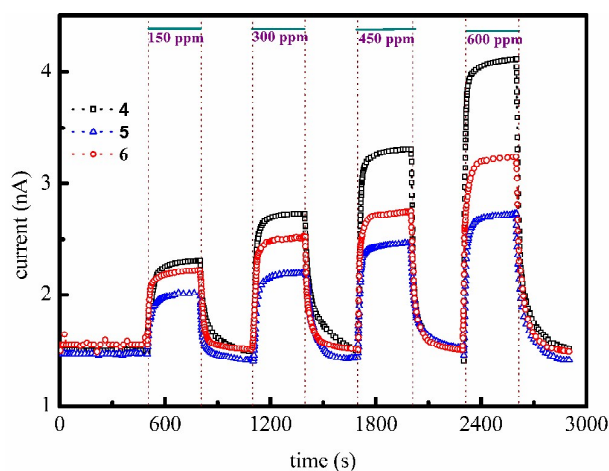


Fig. 5 The current response of the sensors during cyclic exposure to 5 min pulses with increasing concentrations of acetone vapor at room temperature.

Similar response-recovery characteristics were obtained for other analytes investigated. The kinetics of adsorption can be described in terms of a charge transfer interaction between the phthalocyanine and target vapours. The initial fast response and recovery can be attributed to the adsorption of analyte primarily at  $O_2$  free metal centers, and the slow response region to competitive displacement of  $O_2$  bound metal centres.<sup>52</sup>

The sensor sensitivities ( $S$ ), as conventionally used, is defined as;

$$S = \frac{\Delta I}{I_0} \quad (2)$$

where  $\Delta I$  is the changes in current at a known concentration of analyte,  $I_0$  is the reference value of the Pc modified sensor exposed to carrier gas ( $N_2$  in our case). As a representative result, the variation of sensitivity with temperature at a constant concentration (450 ppm) of acetone vapor for all sensors is shown in Fig. 6. Two distinct regions can be seen clearly in the sensitivity-temperature ( $S$ - $T$ ) graphs of the sensors. It is obvious that the sensors show increasing

sensitivity with the increase in temperature up to  $\sim 355$  K and then decreases with further increasing of operating temperature. It is expected that the sensitivity is proportional to the total number of the active oxygen free adsorption sites on the sensor surface. Therefore, the increase of the sensitivity with increasing temperature can be attributed to the increase in the total number of oxygen free adsorption sites on the film surface because of the removal of pre-adsorbed oxygen. In addition there are different mechanisms can lead to increase in sensor sensitivity with temperature. Up to a certain value of temperature, all the possible interaction sites, such as the conjugated  $\pi$ -electron system in the Pc ring, the substituents in macrocycle and the presence of heteroatoms contributes to the adsorption processes and results in an increase in sensitivity. The decrease in sensitivity with further increase in temperature can be attributed to the structural transformation. Recently, the effects of heat treatment, as well as the doping time of analyte molecules, on the sensing characteristics of CuPc films were investigated by Lee et al.<sup>53</sup> The result showed that the structure transformation cannot be avoided even at a temperature as low as  $100^\circ C$ . Hence, 355 K is the optimum operating temperature for the investigated sensors and is used in the following correlation experiments.

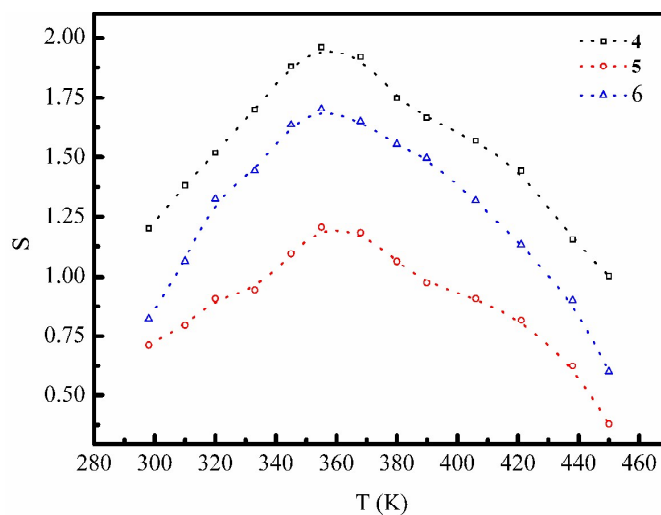


Fig. 6 The variation of the sensitivities with temperature.

To study the effect of the Lewis basicity ( $-\Delta H_{0BF3}$ ) of the analytes sensitivities of all sensors correlated with the  $-\Delta H_{0BF3}$  scale. Analytes were chosen to span a range of Lewis basicity. These included dichloromethane, acetone, nitromethane, dimethyl sulfoxide, N,N-dimethylformamide, and triethylamine (Table-1). Fig. 7 shows the variation of sensitivities of the sensors with analytes Lewis basicity at the maximum sensing temperature (355 K).

On close analysis of sensitivity versus Lewis basicity plots for the investigated sensors, it becomes clear that there are good exponential fits with the correlation coefficients ( $R^2$ ) between 0.970 and 0.987, above the threshold value of  $76.3 \text{ kJ mol}^{-1}$  there is a strong dependence of sensor response with Lewis basicity and the sensor is relatively insensitive to analytes with

$-\Delta H_{\text{BF}_3}^0$  values below this threshold. Comparison of sensor responses to bulk ligand parameters, such as vapor pressure and dipole moment, shows no such correlation.

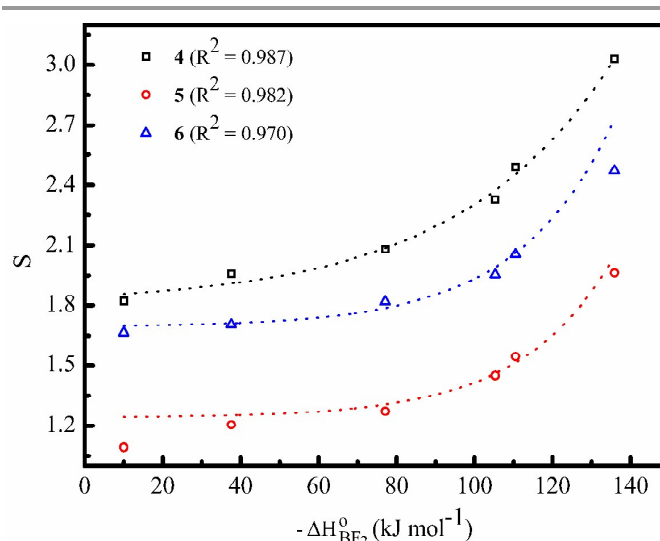
**Table 1** Lewis Basicities for Analytes Studied<sup>54</sup>

Analytes	$-\Delta H_{\text{BF}_3}^0$ (kJ mol <sup>-1</sup> )
Dichloromethane	10.0
Nitromethane	37.6
Acetone	76.0
Dimethyl sulfoxide	105.3
N,N-dimethylformamide	110.5
Triethylamine	135.9

Although the interaction of gas molecules with the surface of a solid is not fully understood, significant amount of published research is available to explain the adsorption of molecules onto surfaces with regards to catalysis and oxidation. It has been reported previously that the adsorption rates and coverages on uniform solid surfaces is strongly dependent on apparent Arrhenius parameters, including activation energy  $E_A$ ,<sup>55</sup> which is defined as the minimum amount of energy required to initiate a chemical reaction. According to Atkins,<sup>56</sup> the activation energy can also be considered as the Gibbs free energy of activation. Application of the Arrhenius behaviour to the interaction suggests that, at constant temperature  $T$ , the response will depend exponentially on binding enthalpy. Therefore, exponential fits would be consistent with standard models of surface coverage and binding energy.

As mentioned above, many elementary physicochemical processes must be considered to explain the dependence of sensor sensitivity on analyte Lewis basicity. The exponential dependence of the sensor sensitivity on the analyte Lewis basicity for the investigated compounds can be attributed to a transition from physisorption to chemisorption at relative analyte basicity. It can be proposed that for  $-\Delta H_{\text{BF}_3}^0$  greater than 76.3 kJ mol<sup>-1</sup>, chemisorption and coordination at the metal centre is the dominant mechanism of sensing. For weak binders, it is unclear whether chemisorption to the metal centre or physisorption on the organic ring is the dominant interaction. However, the weak sensor responses observed are consistent with limited charge transfer, whether it arises from weak coordination interactions or physisorption on the organic.<sup>25</sup>

It is well known that the polarity of analytes depends on their molecular structures with functional groups. In order to understand how the molecular polarity influence the charge transfer process between analyte molecules and Pc films. For this purpose For this purpose, a  $\tau_{90}$  parameter was defined as the time it takes for the film conductivity to reach to 90% of the final conductivity. It was observed that the response time and the dipole moment of the analyte molecules are strongly correlated. Molecules with higher dipole moments exhibit faster responses. The results suggest that the sensing response time is dominated by the dipole moment of the analyte molecules. On the other hand the sensitivity is dominated by the Lewis basicities of the analytes.



**Fig. 7** Sensitivities of the sensor plotted versus basicity for analytes.

## Conclusions

In this study, three new phthalocyanine compounds with non-peripheral substitution 4–6 were successfully prepared from the cyclotetramerization the precursor compound 3-[2-(4-methyl-1,3-thiazol-5-yl)ethoxy]phthalonitrile. Characterization of the products involved a common variety of methods including elemental analysis, <sup>1</sup>H-NMR, UV/Vis, FT-IR, and electron impact and matrix-assisted laser desorption ionization mass spectroscopy. The spectroscopic data of the new compounds were in accordance with the structures. This study has also presented a comprehensive investigation of concentration effects on the aggregation of the tetra-substituted phthalocyanines. No aggregation was demonstrated in DMF in a range of concentrations between  $2 \times 10^{-6}$  and  $14 \times 10^{-6}$  mol dm<sup>-3</sup>. The photophysical properties of the ZnPc compound were investigated in DMF. The fluorescence of the ZnPc compound is quenched by benzoquinone. The sensing behaviour of the compounds when exposed to analytes with different chemical groups (dichloromethane, acetone, nitromethane, dimethyl sulfoxide, N,N-dimethylformamide, and triethylamine) has been analysed. An analysis of the obtained data shows that these compounds could be used to monitor the presence of different analysts. The sensitivities of the sensors to vapour phase were found to correlate exponentially with binding enthalpy.

## Experimental

### Materials

Electronic spectra were recorded on a Scinco SD 1000 diode array, single-beam ultraviolet–visible (UV–Vis) spectrophotometer. FT-IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with ATR capability. A Perkin-Elmer LS55 fluorescence spectrophotometer was used for recording the fluorescence excitation and emission spectra. <sup>1</sup>H-NMR spectra of the synthesized compounds were recorded

on an Agilent VNMRS 500 MHz spectrometer. Mass spectra were performed on a Perkin-Elmer Clarus 500 GC-MS and a Bruker Microflex MALDI-TOF mass spectrometer. All the reagents and solvents were of reagent grade quality and were obtained from commercial suppliers.

### Synthetic part

**3-[2-(4-methyl-1,3-thiazol-5-yl)ethoxy]phthalonitrile (3)** 3-Nitrophthalonitrile (**1**) (0.591 g, 3 mmol) was dissolved in 20 mL of dry DMF and 5-(2-hydroxyethyl)-4-methylthiazole (**2**) (0.48 mL, 4 mmol) was added and the mixture was heated at 45°C. After stirring for 15 min, 0.62 g of finely ground anhydrous K<sub>2</sub>CO<sub>3</sub> (4.5 mmol) was added in small portions over 2 h with efficient stirring. The mixture was stirred under nitrogen stream for 3 days. Then the mixture was poured into crushed ice-water mixture. The resulting yellowish solid was collected by filtration and washed with water until the pH of the washings were neutral. After drying in vacuo at 75 °C, the pure product was obtained by chromatography on silica gel using chloroform/ethyl acetate (5:1) mixture as eluent. Yield: 0.525 g, (65%), mp 153°C, FT-IR  $\nu$  (cm<sup>-1</sup>): 3086 (aromatic C-H); 2960–2924 (aliphatic C-H); 2228 (C≡N); 1579; 1461; 1286; 1054. GC-MS (EI)  $m/z$  (C<sub>14</sub>H<sub>11</sub>N<sub>3</sub>OS) found= 270 (calcd. for [M+1]<sup>+</sup> 270.07, 269 (calcd. for [M]<sup>+</sup> 269.06), 268 (calcd. for [M-1]<sup>+</sup> 268.06). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  ppm 2.49 (3H, s, CH<sub>3</sub>), 3.37–3.39 (2H, t, CH<sub>2</sub>), 4.28–4.31 (2H, t, O-CH<sub>2</sub>), 7.19–7.21 (1H, d, Ar-H), 7.37–7.38 (1H, d, Ar-H), 7.64–7.66 (1H, d, Ar-H), 8.63 (1H, s, S-CH-N). <sup>13</sup>C NMR (500 MHz; DMSO-d<sub>6</sub>):  $\delta$  ppm 15.22 (CH<sub>3</sub>), 25.81 (CH<sub>2</sub>), 70.13 (O-CH<sub>2</sub>), 103.29 (aromatic C), 114.03 (aromatic C), 115.92 (C≡N), 116.23 (C≡N), 118.98 (aromatic C), 126.35 (aromatic C), 127.20 (aromatic C), 136.30 (S-C), 150.13 (N-C), 151.48 (aromatic C), 161.02 (S-C-N). Calcd. for C<sub>14</sub>H<sub>11</sub>N<sub>3</sub>OS: C 62.43, H 4.12, N 15.60%; found C 62.19, H 4.24, N 15.38%.

**1, 8 (11), 15 (18), 22 (25) - Tetrakis [2- (4- methyl - 1, 3 - thiazol-5-yl) ethoxy] phthalocyaninatocobalt(II) (4)** 3-[2-(4-methyl-1,3-thiazol-5-yl)ethoxy]phthalonitrile (**3**) (0.135 mg, 0.5 mmol) and anhydrous CoCl<sub>2</sub> (16 mg, 0.13 mmol) were ground together in a microwave oven and 1-hexanol (2 mL) and a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were added. The reaction mixture was irradiated in microwave reaction oven at 160°C, 350 W for 5 min. After cooling to room temperature, methanol: water (1:1) mixture (50 mL) was added. The precipitated blue solid product was filtered off, and then dried. The obtained blue product was purified from the column chromatography which is placed silica gel using ethyl acetate as eluent to remove the impurities. The chromatographic column was then eluted with THF. Yield: 41 mg, (30%), FT-IR  $\nu$  (cm<sup>-1</sup>): 3083 (aromatic C-H); 2926–2869 (aliphatic C-H); 1585; 1487; 1234; 1037. UV-Vis (DMF,  $c = 6 \times 10^{-6}$  mol dm<sup>-3</sup>)  $\lambda_{\max}/\text{nm}$  (log  $\epsilon$ ): 311 (4.87), 686 (5.17). Calcd. for C<sub>56</sub>H<sub>44</sub>CoN<sub>12</sub>O<sub>4</sub>S<sub>4</sub>: C 59.20, H 3.90, N 14.79%; found C 59.01, H 3.93, N 14.65%. MS (MALDI-TOF):  $m/z$  (C<sub>56</sub>H<sub>44</sub>CoN<sub>12</sub>O<sub>4</sub>S<sub>4</sub>) found= 1139.255 (calcd. for [M+4H]<sup>+</sup> 1139.18).

**1,8(11),15(18),22(25)-Tetrakis [2-(4-methyl-1,3-thiazol-5-yl)ethoxy] phthalocyaninatozinc(II) (5)** A mixture of the dinitrile **3** (0.135 g, 0.5 mmol) and anhydrous zinc acetate (23 mg, 0.13 mmol) were ground together in a microwave reactor tube. 1-hexanol (2 mL) and a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were added. The reaction mixture was irradiated in a microwave oven at 160°C, 350 W for 5 min. The resulting green suspension was cooled to room temperature and the crude product was precipitated by the addition of methanol: water (1:1) mixture. The precipitate was collected by filtration and washed successively with ethanol and methanol and dried. The product was chromatographed over silica gel with ethyl acetate as eluent to remove the impurities. The chromatographic column was then eluted with THF. The solvent was evaporated, thus affording the phthalocyanine derivatives. Yield: 30 mg, (22%). FT-IR  $\nu_{\max}$  (cm<sup>-1</sup>): 3067 (aromatic C-H); 2922–2861 (aliphatic C-H); 1584; 1487; 1233; 1038. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  ppm 2.59 (12H, s, CH<sub>3</sub>), 3.62–3.87 (8H, br d, CH<sub>2</sub>), 4.93–5.11 (8H, br d, O-CH<sub>2</sub>), 7.73–7.75 (4H, m, Ar-H), 8.04–8.11 (4H, m, Ar-H), 8.75–8.76 (4H, m, Ar-H), 8.98–9.09 (4H, br d, S-CH-N). <sup>13</sup>C NMR (500 MHz, DMSO-d<sub>6</sub>)  $\delta$  ppm: 15.42 (CH<sub>3</sub>), 26.53 (CH<sub>2</sub>), 68.73 (O-CH<sub>2</sub>), 105.34 (aromatic C), 105.67 (aromatic C), 117.66 (aromatic C), 123.37 (aromatic C), 125.36 (aromatic C), 128.13 (aromatic C), 139.63 (aromatic C), 146.10 (S-C), 149.98 (N-C), 151.40 (aromatic C), 159.79 (S-C-N). UV-Vis (DMF,  $c = 6 \times 10^{-6}$  mol dm<sup>-3</sup>)  $\lambda_{\max}/\text{nm}$  (log  $\epsilon$ ): 322 (4.90), 708 (5.58). Calcd. for C<sub>56</sub>H<sub>44</sub>N<sub>12</sub>O<sub>4</sub>S<sub>4</sub>Zn: C 58.86, H 3.88, N 14.71%; found C 58.80, H 3.93, N 14.50%.

**1,8(11),15(18),22(25)-Tetrakis [2-(4-methyl-1,3-thiazol-5-yl)ethoxy] phthalocyaninato (chloro)-manganese(III) (6)** Compound **3** (0.135 g, 0.50 mmol) was dissolved in 2 mL of hexanol, and anhydrous manganese (II) chloride (16 mg, 0.13 mmol) was added to this solution. The reaction mixture was irradiated in a microwave oven at reflux temperature, for 5 min. The brown mixture was cooled to room temperature and precipitated with a mixture of water/methanol. It was filtered off. The precipitate was washed with hot water, methanol, acetone. The purity of the Pc was checked using thin layer chromatography (TLC). The pure phthalocyanine dried in vacuo. Yield: 57 mg (42%). FT-IR  $\nu_{\max}$  (cm<sup>-1</sup>): 3067 (aromatic C-H), 2924–2853 (aliphatic C-H), 1589, 1461, 1239, 1056. UV-Vis (DMF,  $c = 6 \times 10^{-6}$  mol dm<sup>-3</sup>)  $\lambda_{\max}/\text{nm}$  (log  $\epsilon$ ): 359 (5.20), 751 (5.42). Calcd. for C<sub>56</sub>H<sub>44</sub>ClMnN<sub>12</sub>O<sub>4</sub>S<sub>4</sub>: C 57.60, H 3.80, N 14.39%; found C 57.55, H 3.99, N 14.65%. MS (MALDI-TOF)  $m/z$  (C<sub>56</sub>H<sub>44</sub>ClMnN<sub>12</sub>O<sub>4</sub>S<sub>4</sub>): 1170.167 (calcd. for [M+4H]<sup>+</sup> 1170.15).

### Photophysical parameters

**Fluorescence quantum yields and lifetimes** Fluorescence quantum yields ( $\Phi_F$ ) were calculated using the comparative method (Eq. (3)). Unsubstituted ZnPc ( $\Phi_F = 0.17$  in DMF) was used as a standard<sup>57,58</sup>

$$\Phi_F = \Phi_F(\text{std}) \frac{F_{\text{Std}} A_{\text{Std}} \eta^2}{F_{\text{Std}} A_{\text{Std}} \eta^2} \quad (3)$$



$F$  and  $F_{\text{Std}}$  are the areas under the fluorescence emission curves of the zinc phthalocyanine and the standard, respectively.  $A$  and  $A_{\text{Std}}$  are the respective absorbances of the samples and standard at the excitation wavelength.  $\eta$  and  $\eta_{\text{Std}}$  designate the refractive index of the solvent employed ( $\eta_{\text{DMF}} = 1.430$ ) for the sample and standard.

PhotochemCAD software was used to calculate natural radiative lifetimes ( $\tau_0$ ).<sup>59</sup> The fluorescence lifetimes ( $\tau_F$ ) were evaluated using Eq. (4).

$$\Phi_F = \frac{\tau_F}{\tau_0} \quad (4)$$

**Fluorescence quenching by benzoquinone (BQ)** Fluorescence quenching experiments of ZnPc (**4**) were achieved by the addition of different concentrations of BQ. The fluorescence spectra of ZnPc (**2**) at each BQ concentration were recorded.

$$\frac{I_0}{I} = 1 + K_{SV}[BQ] \quad (5)$$

$I_0$  and  $I$  are the fluorescence intensities of ZnPc in the absence and presence of quencher, respectively.  $[BQ]$  is the concentration of the quencher. The ratios of  $I_0/I$  were calculated and plotted against  $[BQ]$  according to Eq. (5), and Stern-Volmer constant ( $K_{SV}$ ) is determined from the slope.<sup>60</sup>

$K_{SV}$  is the product of the bimolecular quenching constant ( $k_q$ ) and the  $\tau_F$  (Eq. (6)):

$$K_{SV} = k_q \times \tau_F \quad (6)$$

**Sensor fabrication and gas sensing experiments** Interdigital array of metal (Au) electrodes (IDE) photolithographically patterned on glass substrates were used as transducers. Coating of the transducers with the sensitive material was achieved using the spin coating technique. Coating solutions were prepared by dissolving the Pcs in an appropriate solvent at concentrations of  $5 \times 10^{-2}$  M for all compounds. 25  $\mu\text{L}$  of such solutions were added with a glass pipette onto the IDE structure held on the spinner (Speciality Coatings Systems Inc., Model P6700 Series). The substrate was spun at 1500 rpm for 45 s and the solvent had evaporated during this period, producing a homogeneous film of phthalocyanine derivatives. The substrate temperature was kept constant at 298 K during deposition of the materials over the electrodes. The sensing properties of the coating material were tested in a cylindrical chamber of Teflon, 8 cm long and 4 cm diameter, which a gas could be passed. Well-defined concentrations of target vapor were prepared by mixing the reference gas (dry nitrogen) with the target gas. The reference gas used in the experiments had purity level of 99%. The concentration of the target gas was varied from 150 to 600 ppm for all vapours investigated by using mass flow controllers (MKS Inst. Co.). A typical gas sensing experiment consisted of repeated exposure to target vapor and subsequent purging with dry nitrogen to reset the baseline. Each cycle of exposure lasted for 5 min, followed by recovery in nitrogen for another 5 min. The flow rate of the  $\text{N}_2$  gas was adjusted as 100 standard cubic

centimeter (sccm) during the purging experiments. One volt dc voltage bias was applied and the dc current in the layer was measured with a Keithley 617 electrometer. The current variations were recorded as a function of time on exposures to target vapour diluted in dry nitrogen, starting from an equilibrium state in  $\text{N}_2$ . Gas sensing data were recorded using an IEEE-488 data acquisition system incorporated to a personal computer.

## Acknowledgements

This work was supported by Research Funds of Istanbul Technical University.

## Notes and references

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