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ARTICLE

Synthesis, characterization and gas sensing properties of novel homo and hetero dinuclear ball-type phthalocyanines

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The new ball-type homodinuclear Co(II)-Co(II) phthalocyanine (**2**) and ball-type heterodinuclear Co(II)-Fe(II) phthalocyanine (**3**) were synthesized from the corresponding [2,10,16,24-tetrakis(4,4'-cyclohexylidenebis(2-cyclohexyphenoxyphthalonitrile)phthalocyaninatocobalt(II)] (**1**). The novel compounds have been characterized by elemental analysis, IR, UV-Vis and MALDI-TOF mass spectroscopy. Gas sensing capability of the spin coated film of **2** and **3** were studied using amperometric technique at various temperatures. For a better understanding of the interaction of **2** and **3** films with organic compounds, two different groups of compounds (aromatics and alcohols) were selected as test analytes. It was observed that the operating temperature had a considerable effect on the gas sensing performance of the sensors investigated. The experimental results show that **3** film offers a promising perspective as sensing material for the detection of relatively low aromatic vapour even room temperature. This suggests that aromatics might be distinguished from alcohols. The obtained data were analysed using two different adsorption kinetic models; the pseudo first order equation and Elovich equation to determine the best fit equation for the adsorption of toluene vapor onto **2** and **3** films. The first-order equation was the best of the various kinetic models studied to describe the adsorption kinetic of toluene on Pc films at higher concentrations, as evidenced by the highest correlation coefficients. On the other hand, it was observed that Elovich equation generates a straight line that best fit to the data of adsorption of lower concentrations of toluene.

1. Introduction

Phthalocyanines (Pcs), thanks to properties such as strong delocalized 18 π -electron system, thermal stability and visible area optical properties, have been extensively studied due to their various technological applications, such as nonlinear optics,¹ gas sensors², liquid crystals,³ solar cells⁴ and photodynamic therapy⁵ and electrochromism.⁶ These compounds continue to be subject of the increasing research efficiency.

Ball-type Pcs, a new type of compounds, were reported in the literature for the first time in 2002.^{7,8} These Pcs have four bridged substituents on the periphery of each benzene rings of

the two Pc monomers which are arranged cofacially. In ball-type Pcs, such substituents also have a bridged nature and change not only the symmetry of the face to face Pcs depending on the size of the molecule and the distance of between two Pcs but also the properties of the compounds. In some cases all attempts at synthesis result in mono Pcs, which should be further refluxed in a solvent using excess of metal salts. However, this turns out to be an advantage for preparing hetero dinuclear ball-type Pcs as one can get different redox-active metal centers in the molecule.^{9,10} In recent years, our group has reported a number of papers on ball-type Pcs with various substituents, such as pentaerythritol,¹¹ *tert*-butylcalix[4]arene,¹²

1a,8b-dihydronaphtho[*b*]naphthofuro[3,2-*d*]-furan-7,10-diol,¹³ phenolphthalein,¹⁴ 3,3'-methylenebis(4-hydroxy-2*H*-chromen-2-one),¹⁵ bis[2-hydroxy-5-methyl-3-(1-methylcyclohexyl)phenyl]methane¹⁶ and 9*H*-fluorene-9,9-dimethanol.¹⁷ These Pcs, metal free or containing two homo- or hetero-metal centers, have attracted attention due to their interesting properties. These compounds show a wide range of interactions between the Pc rings due to metal centres. The chemical and physical properties of these complexes change significantly due to the distance between the two Pc monomers. The ball-type Pcs show different and interesting properties such as electrical,¹⁸ gas sensing,¹⁷ electrocatalytic^{19,20} and electrochemical²¹ in comparison to their parent monomers.

Recently, air quality contamination by many kinds of volatile organic compounds (VOCs) has become a serious problem for human life. Toluene is a neurotoxic volatile organic compound, widely used as a chemical reagent, which is known as the main nosogenesis of sick house syndrome.²² Therefore, there is an increasing demand for the detection of toluene vapour in the field of environmental analysis, industrial process control and work-place monitoring. Inorganic compounds, such as SnO₂-ZnO hollow nanofibers,²³ TiO₂ nanotubes,²⁴ Li and Ti co-doped NiO,²⁵ SnO₂ nanofibers²⁶ and SnO₂-Fe₂O₃ interconnected nanotubes²⁷ have been developed and used to detect toluene vapor. However, such materials have the disadvantages of low response and high operating temperatures which limit their practical application. Thus, the requirement for cheap, reliable and highly sensitive toluene sensors is urgent.

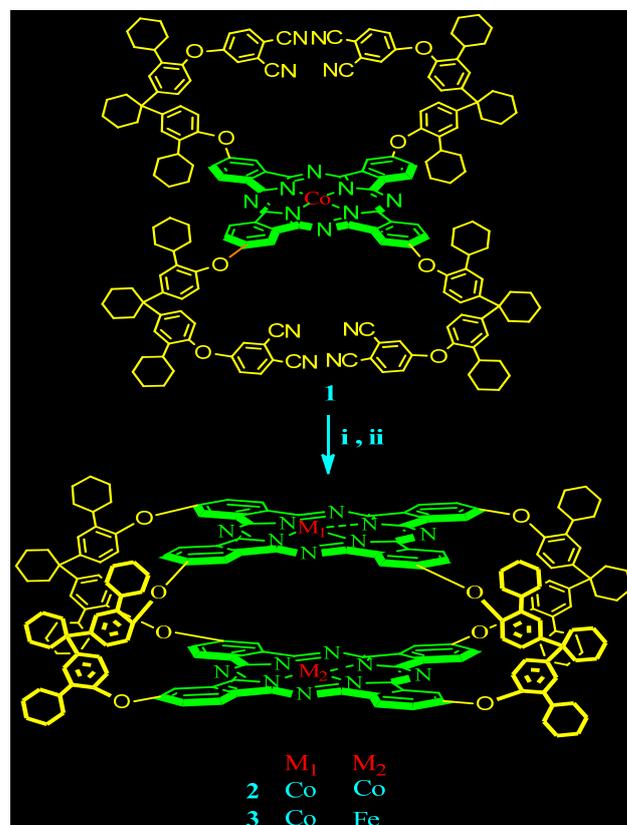
In this work, we describe two novel ball type Pcs starting from previously reported metallo mono Pc²⁸ using excess of the same and different metal salts as shown (Scheme 1). The organic vapor sensing performance of the newly synthesized compounds were studied as function of operating temperature and vapor concentration. This study also highlights the kinetics of toluene adsorption on the Pc surface. Kinetic models evaluated include the Elovich equation, and the first-order equation.

2. Results and discussion

2.1. Synthesis and characterizations

The starting compound **1** can be obtained via a reaction of [4,4'-cyclohexylidenebis(2-cyclohexylphenoxy)phthalonitrile] and Co(OAc)₂·4H₂O.²⁸ Next, the complexes **2** and **3** were synthesized by heating **1** with Co(OAc)₂·4H₂O, FeCl₂·4H₂O respectively, in a sealed tube under a N₂ atmosphere (Scheme 1). Both of the novel ball-type Pcs were characterized by elemental analyses, IR, UV-vis and MALDI-TOF mass spectrometer. The IR spectrum of compounds **2** and **3** showed Ar-O-Ar peaks at 1225-1260 cm⁻¹, an aromatic C=C peaks at 1590-1615 cm⁻¹, C=N peaks at 1715-1740 cm⁻¹ and aliphatic CH peaks at 2850-2925 cm⁻¹. Besides, they showed no nitrile peaks at 2230-2232 cm⁻¹. The UV-vis spectra of **2** and **3** in CHCl₃, show Q-band absorptions at 677 and 675 nm,

respectively which was attributed to the π→π* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring. The B-bands of these Pcs **2** and **3** in the UV region 300-330 nm were observed due transitions from the deeper π levels to LUMO (Fig.1).



Scheme 1. (i) Co(OAc)₂·4H₂O, DMF, 200°C, 72h; (ii) FeCl₂·4H₂O, DMF, 200°C, 72h.

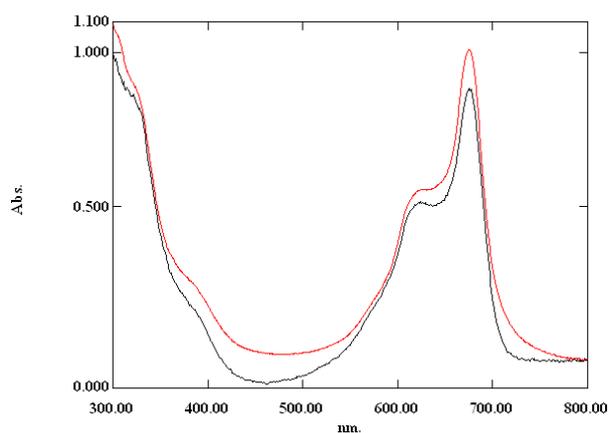


Fig.1 UV/Vis spectrum of **2** and **3** in CHCl₃ (Absorption spectra of **2** (black) and **3** (red))

For the complex **2** linear mode MALDI-TOF-MS spectrum was obtained in 2,5-dihydroxybenzoic acid MALDI matrix (Fig.2).

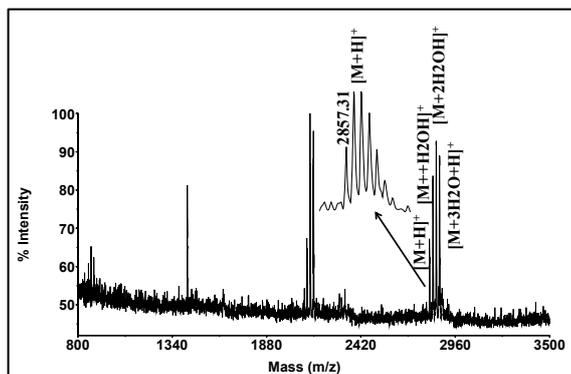


Fig. 2 Positive ion and linear mode MALDI mass spectrum of complex **2** was obtained in 2,5-dihydroxybenzoic acid MALDI matrix using nitrogen laser (at 337 nm wavelength) accumulating 100 laser shots

Reflectron mode MALDI-TOF-MS spectrum could not be obtained under the MALDI-MS conditions because of the less stability of this complex compared to complex **3**. Positive ion and reflectron mode MALDI-TOF-MS spectrum of complex **3** was obtained and is given in (Fig.3).

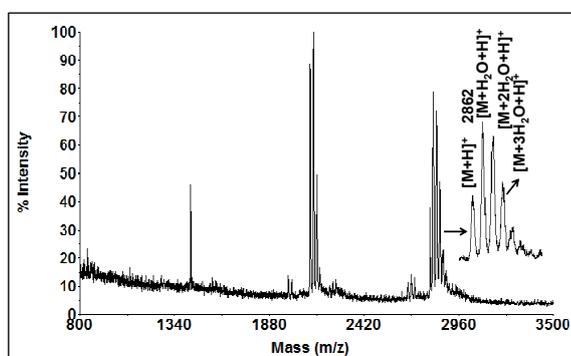


Fig. 3 Positive ion and reflectron mode MALDI mass spectrum of **3** complex was obtained in 2,5-dihydroxybenzoic acid MALDI matrix using nitrogen laser (at 337 nm wavelength) accumulating 100 laser shots.

Only 2,5-dihydroxybenzoic acid yielded intense molecular ion signal and low fragmentations under the MALDI-TOF-MS conditions for this compound. Mainly, complex **3** was yielded at low intensity protonated ion signals, and high intensity water adduct signals up to three water adduct signals in 2,5-dihydroxybenzoic MALDI matrix. For these two complexes, two intense fragment ion signals were obtained defining the some part of the complexes after the fragmentations. Mainly one core of complex was available in one fragment signal and the other core of complex was exist in the other fragment signal. But here fragmentation was found to be not symmetric nature.

2.2 Vapor sensing

It has been previously reported that the sensitivity of the MPCs to vapour molecules may be tuned by manipulation of the metal center and by substitution of functional groups on the organic ring.²⁹ It is also well known that the structure and morphology of phthalocyanine thin films can strongly influence

their gas sensing characteristics.³⁰ In this paper, the sensor sensitivity is defined as $S = \Delta I/I_0$, where ΔI and I_0 are the changes in current at a known concentration of analyte and the reference value of the Pc modified sensor exposed to carrier gas (N_2 in our case), respectively. The time taken to achieve 90% of the current variation is defined as the response time. After taking the sensor out of the target gas, the time that the sensor current returns 90% of the current variation is defined as the recovery time. In order to see the effect of the molecular structure of the sensing element especially, central metal, on the vapor sensing performance of the investigated Pc films the response characteristics of the films as a function of test duration for 100 ppm concentration of two different classes (aromatics and alcohols) of organic vapors is presented in (Fig.4). Comparison of the response-recovery characteristics for detecting two different organic families revealed that the sensors were significantly less sensitive for detection of alcohols compared to aromatic compounds. For both group of analytes, maximum sensitivity for the lower and upper limit of analyte concentrations were obtained with **3** coated sensor.

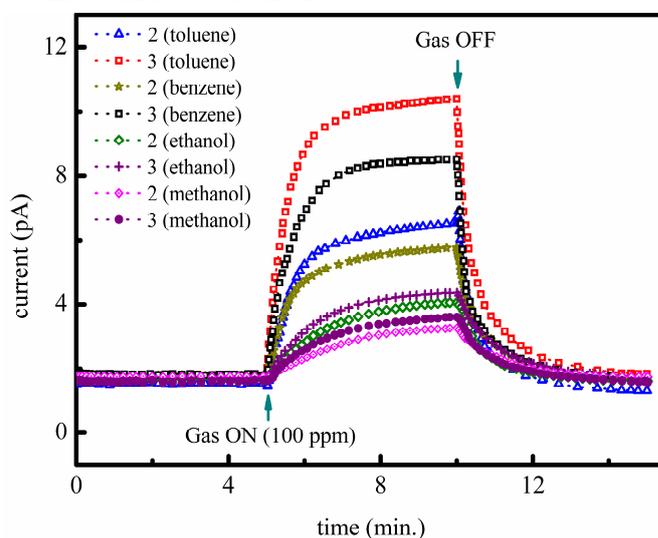


Fig. 4 The effect of 100 ppm analytes (toluene, benzene, ethanol and methanol) on the **2** and **3** coated sensor current.

Due to high sensitivity and quick response characteristics of **3** coated sensor toward toluene vapor, we concentrated on investigating the toluene sensing properties of spin coated film of **3**. The sensor response of **3** exposed to different concentrations of toluene between 50-250 ppm, following an increasing concentration order and then reverse concentration order were recorded (Fig.5). The same value of current on every time exposure of the film shows that the response curves are highly reproducible. As is clearly seen from the (Fig.5), the interaction of the toluene vapour with the spin coated film of the compound leads to a fast increases in its conductivity, which continue to raise until the vapour is turned off. After several minutes' exposure to toluene vapour, purging with dry nitrogen leads to an initial fast decrease followed by a slow drift and the current reaches its initial value after the toluene

vapour is turned off, and this proves that the adsorption processes are reversible. In fact, neither baseline drift nor time stability problems were detected during sensor testing. From data analysis, one can affirm that the **3** film presents a high sensitivity ($S = 4.9$) and short response time (80 s) to toluene vapour at room temperature. On the contrary, the **2** coated sensor present a lower sensitivity (3.8) and long response time (170 s) to the same concentration of toluene vapour. By the way, the sensitivities of the **2** and **3** coated sensors for methanol vapor were 0.8 and 1.1, respectively.

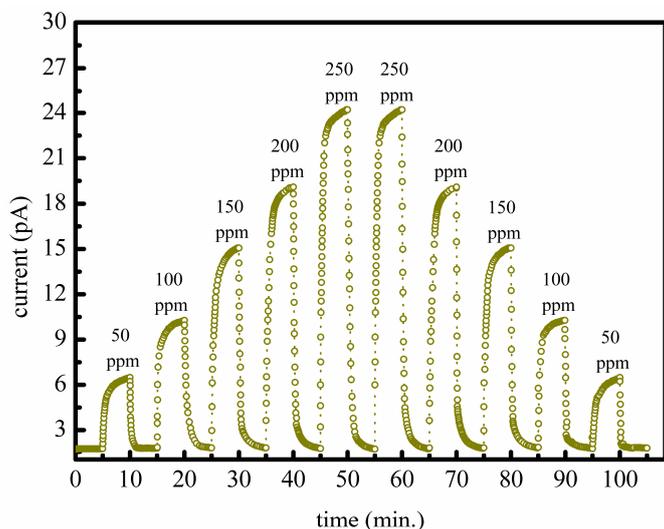
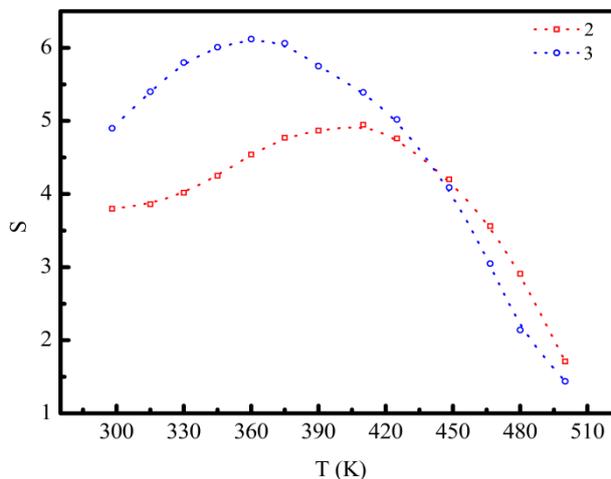


Fig.5 Response–recovery characteristic of **3** coated sensor to various concentrations of toluene following an increasing and then reverse concentration order.

In order to find the optimum operating temperature, the toluene sensing tests are performed at different operating temperatures. The relationship between the different operating temperatures and the sensitivity of the sensors to 100 ppm toluene is shown in (Fig. 6). It is obvious that the sensitivity of the sensors controlled by the temperature, as expected. From the figure, we can see that the sensitivity value increases at first and reaches a maximum and then decreases dramatically in the range of the operating temperatures. This behavior of sensitivity can be interpreted as due to the temperature dependent contributions of the interaction sites. The value of temperature, at which the sensitivity of gas sensors attains the maximum indicates the strength of interaction between the film surface and the gas molecule. Up to a certain value of temperature depending on the toluene concentration, all the possible interaction sites 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 structure transformation. Passard et al.³¹ reported that the value of T_{max} varies with the sensing material, the crystal phase as well as the type of gas. 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.³² The result showed that the structure transformation cannot be avoided even at a temperature as low as 100 °C.

Fig.6 Effect of operating temperature on the sensitivity of **2** and **3** coated sensor after exposing 100 ppm toluene vapor.



2.3 Kinetic studies

In order to examine the mechanism of adsorption process, the experimental data were modelled using the first-order rate equation of Lagergren, Ritchie's equation and Elovich model. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2).

2.3.1 Pseudo-first-order process

The pseudo first-order equation is generally expressed as follows³³:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

After integration and applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the integrated form of Eq. (1) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

where q_e and q_t are the amounts of toluene adsorbed at equilibrium and at any time t , respectively, and k_1 is the first-order adsorption rate constant. By assuming that the sensor current is proportional to the amounts of adsorbed toluene (q_t), the plot of $\log(q_e - q_t)$ vs. t should give a linear relationship. To quantify the applicability of the first-order model the correlation coefficient, R^2 was calculated from these plots. Fig.7 shows a plot of linearized form of first-order model for all concentrations of toluene vapor. A Considerable deviation from the theoretical model is clear for low concentrations of toluene. On the other hand, it is obviously noticed that the linear regression analysis with respect to pseudo first order rate equation generates a straight line that best fit to the data of adsorption of gaseous toluene on **3** for the higher concentration (> 150 ppm) of toluene vapour.

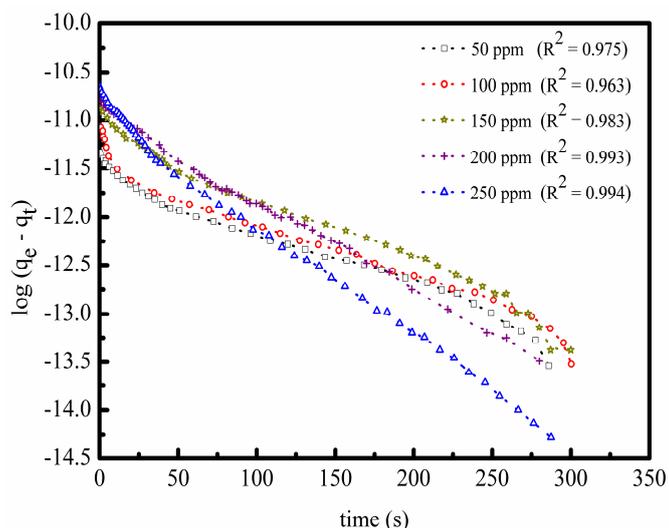


Fig.7 First-order sorption kinetics of toluene onto the compound **3** at room temperature.

2.3.2 Elovich Model

In reactions involving adsorption of gases on a solid surface, the rate of adsorption decreases with time due to an increase in surface coverage. One of the most useful models to describe such type of activated sorption is the Elovich equation, which is expressed by³⁴:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (3)$$

where q_t is the quantity of gas adsorbed during the time t . α is the initial sorption rate and β is the desorption constant during any one experiment. The integrated form of Eq. (3) can be written in

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (4)$$

To simplify Elovich's equation, Chien and Clayton³⁵ assumed that $\alpha\beta t \gg 1$ and by applying the boundary conditions $q_t = q_t$ at $t = t$ and $q_t = 0$ at $t = 0$, the integrated form of Eq. (4) becomes,

$$q_t = \frac{1}{\beta} [\ln(\alpha\beta t + 1)] \quad (5)$$

Equation (5) will be used to test the applicability of the Elovich equation to the kinetics of toluene adsorption onto compound **2** and **3**. According to the Eq.(5), a plot of q_t vs. $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha\beta)$. A set of $\Delta I - \ln(t)$ plots, which are derived from (Fig.5), for room temperature adsorption of toluene with various concentrations on **3** surface are shown in (Fig.8).

It reveals that, the plots of ΔI versus $\ln(t)$ are linear for low concentrations of toluene (< 100 ppm), indicating that the interaction obeys the Elovich equation. However, at higher concentration levels the straight lines are discontinuous and change slope at one, two or three points. It can be concluded that Elovich equation is not appropriate to use as a model to

predict the adsorption kinetics of high concentration toluene onto the **3**.

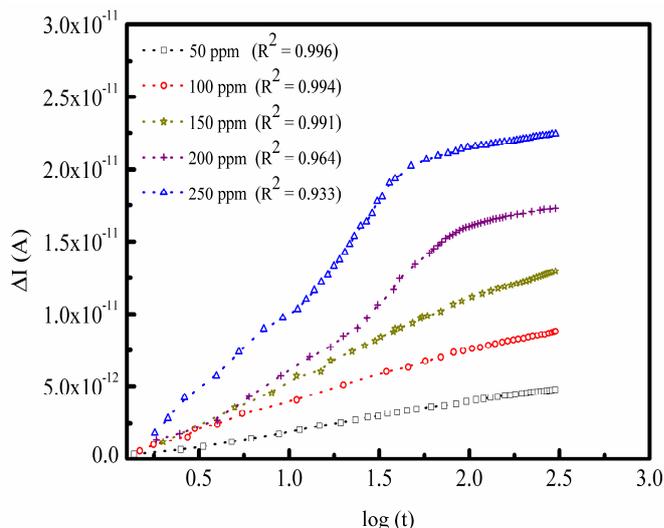


Fig.8 Elovich plots for toluene adsorption onto the compound **3** at room temperature

3. Experimental

The starting material **1** was synthesized by the method described previously in the literature.²⁸ IR spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer as KBr pellets. Electronic spectra were recorded on a Shimadzu UV-1601 spectrophotometer. 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 linear and also in reflectron mode with average of 100 shots. Elemental analyses were performed by the Instrumental Analysis Laboratory of TUBITAK-Ankara.

3.1. Synthesis

3.1.1. [2',10',16',24'-tetrakis(4,4'-cyclohexylidenebis(2cyclohexyphenoxy))phthalocyaninatodicobalt(II)] **2**

A mixture **1** (0.1 g; 3.6×10^{-2} mmol), $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (9.0×10^{-2} g; 0.36 mmol) and DMF (4 ml) were taken in a under N_2 atmosphere sealed tube, then the mixture was heated and stirred at 200°C for 72 h. After cooling room temperature, the reaction mixture was precipitated by adding methanol. The dark blue precipitate was filtered and washed hot water and methanol for 24 h in Soxhlet apparatus. The solid product was purified by column chromatography with silica gel using chloroform (CHCl_3) as eluent. This compound is soluble in CHCl_3 , dimethylformamide (DMF), dichloromethane (DCM) and tetrahydrofuran (THF). Yield : 57.4 mg (56%). Mp: $>350^\circ\text{C}$. IR (KBr pellet) ($\nu \text{ cm}^{-1}$) : 744, 882, 957, 1094, 1138, 1228, 1265, 1329, 1407, 1470, 1615, 1715, 2852, 2922. Anal. Calc. for $\text{C}_{184}\text{H}_{180}\text{O}_8\text{N}_{16}\text{Co}_2$: C, 77,23; H, 6,34; N, 7,83. Found: C,

76,81; H, 6,21; N, 7.68. MS (MALDI-TOF): m/z 2860 [M+H]⁺. UV-Vis (CHCl₃), λ_{\max} nm (log ϵ): 677(4,442), 622(4.205), 318(4.424)

3.1.2. [2',10',16',24'-tetrakis(4,4'-cyclohexylidenebis(2cyclohexoxy))phthalocyaninato cobalt(II)-iron(II) 3

Compound **3** was synthesized using the same procedure explained above for **2** by starting from compound **1** (0.1 g; 3.6×10^{-2} mmol), FeCl₂·4H₂O (7×10^{-2} g; 0.36 mmol) and DMF (4 ml). The dark blue product is soluble in CHCl₃, DMF, CH₂Cl₂ and THF. Yield : 68,4 mg (67%). Mp: > 350 °C. IR (KBr pellet) (ν cm⁻¹) : 752, 882, 957, 1095, 1139, 1230, 1267, 1309, 1408, 1471, 1615, 1715, 1740, 2852, 2925. Anal. Calc. for C₁₈₄H₁₈₀O₈N₁₆CoFe: C, 77,32; H, 6,35; N, 7,84. Found: C, 76,74; H, 6,23; N, 7,70. MS (MALDI-TOF): m/z 2859 [M+H]⁺. UV-Vis (CHCl₃), λ_{\max} nm (log ϵ): 675(4,304), 625(4.046), 325 (4.248).

3.2. MALDI sample preparation

MALDI matrix, 2,5-dihydroxybenzoic acid was prepared in THF-DMSO (1:1, v/v) containing 0.1% trifluoroacetic acid at a concentration of 10 mg/mL. MALDI sample was prepared by mixing sample solutions (0.2 mg/mL in THF-DMSO mixture (1:1, v/v) having 1% trifluoroacetic acid) with the matrix solution (1:10, v/v) in a 0.5 mL eppendorf® micro tube. Finally 0.5 μ L of this mixture was deposited on the sample plate, dried at room temperature and then analyzed.

3.3. Electrical measurements

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 extra pure grade chloroform at concentrations of 7.5×10^{-2} M for all compounds. 25 μ 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 toluene 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 toluene vapour were prepared by mixing the reference gas (dry air) with the target gas (toluene). The concentration of the target gas was varied from 50 to 250 ppm by using mass flow controllers (MKS Inst. Co.). A typical gas sensing experiment consisted of repeated exposure to toluene vapour and subsequent purging with dry air to reset the baseline. Each cycle of exposure lasted for 5 min, followed by recovery in dry air for another 5 min. 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 toluene diluted in dry air, starting from an equilibrium state in air. Gas sensing data were recorded using an IEEE-488 data acquisition system incorporated to a personal computer.

4. Conclusions

The novel ball-type homo- and hetero-dinuclear Pcs **2-3** were obtained from compound [2,10,16,24-tetrakis(4,4'-cyclohexylidenebis(2cyclohexoxy)phthalonitrile)phthalocyaninato cobalt(II)] **1**. The new ball-type complexes were characterized by elemental analysis, UV-vis, IR and MALDI-TOF mass spectroscopies. The vapor sensing properties of the spin coated films of **2** and **3** were studied as a function of temperature and gas concentrations. The selectivity of the sensors was studied by exposing the sensors to various groups of organic vapors such as, aromatics (toluene and benzene) and alcohols (ethanol and methanol) and it was found that the sensors are more sensitive to aromatic vapors compared to alcohol vapors. This suggests that aromatics might be distinguished from alcohols. All the observations demonstrated that superior toluene sensing can be achieved by the film of **3** even at room temperature. Pseudo-first order and the Elovich equation were applied to experimental data. Although the adsorption of toluene on the thin films of **2** and **3** can be explained by the Elovich equation for low concentrations of toluene vapour, a deviation from the Elovich model is observed for high concentrations of toluene. Comparing the regression coefficients R² shows that the Elovich model and first-order models best describes the experimental data on the adsorption of toluene with studied samples at low and high concentrations of toluene, respectively.

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Notes and references

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