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Preparation and Characterization of Novel Octa-iso-Pentyloxymetallophthalocyanines(M= Pb,Ni,Cu) Gas Sensors

Li Zan[1,2], *Jiang WenRui*[2], *Wu Xiaohong*[2], *Shi Yunbo*[3,4]

[1] Harbin University, Harbin 150086, China)
[2] Harbin Institute of Technology, Harbin, Heilongjiang 150001, China)
[3] Mechanical Engineering Center for Post-doctoral Studies, Harbin Engineering University, Harbin 150001, China)
[4] School of Measurement Control Tech & Communications Engineering, Harbin University of Science and Technology, Harbin 150080, China)
*E-mail: lizan80@126.com

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Three kinds of high soluble phthalocyanine complexes were synthesized in cyclic tetramerisation reaction of a dicyano benzene component and different metal ions(Pb^{2+},Ni^{2+},Cu^{2+}) for the first time. The products were characterized by IR、GC/MS、^{1}HN MR and elemental analysis respectively. The electronic absorption spectra in solution of the complexes and the spin-coated films were compared. The thin films were characterized by AFM and SEM. The gas sensing properties of spin-coated films were determined to NO_2. The effects of central metal ions, film surface appearances and sensing temperature on gas sensing property have been studied. It can be concluded that 1,6,10,15,19,24,28,33-octa-iso-pentyloxy-2,3-phthalocyanine lead spin-coated film showed good gas sensitivity to NO_2.

Keywords: Phthalocyanine; Spin-coated film; Gas sensor

1. INTRODUCTION

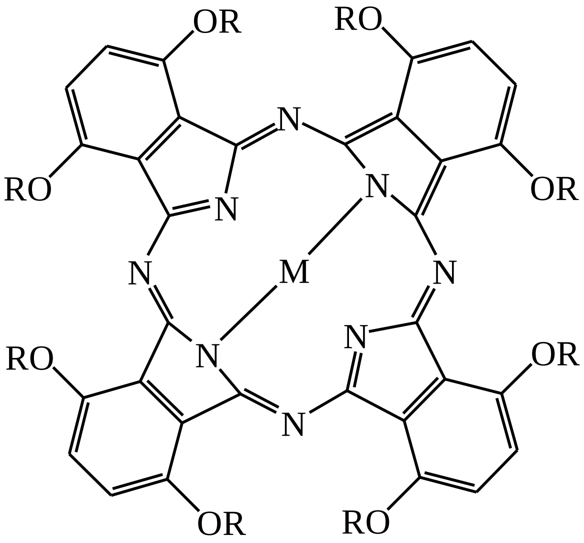
Phthalocyanine and its metal derivatives are a P-type semiconductor, which has attracted interest obviously as gas sensing materials[1]. The electronic properties of MPc thin films are known to be affected by the adsorption of oxidization or reducing gas, which has lead to the studies and application of these materials in the field of gas sensing [2]. One important feature of the MPc gas sensor, compared with that of inorganic metal oxide, is that it can be operated at much lower temperature[3].

A lot of researches on the gas sensitivity of CuPc and PbPc have been reported. Early in 1987 Burr et al. used PbPc as the gate material for FETs. Among the metals Pcs, PbPc is the one that has been most intensively studied [4–8].This material has been reported to be superior to other phthalocyanines. It had been reported that the response and reversibility of PbPc sensor can be improved by means of increasing the operating temperature [9]. CuPc films present similar features as that of PbPc films and the Pc material which is most intensively being studied [10-15].

Recently the sensing property of NiPc film towards NO gas was explored [16]. C.J. Liu et al. studied that the effect of surface morphology on the sensor current of a chemiresistor-type NO sensor based on the vacuum-deposited nickel phthalocyanine (NiPc) thin films[17].

To be used as a gas sensor, the MPc materials are always prepared in thin film form. Phthalocyanine thin films can be prepared in several ways, like spin coating technology, vacuum sublimation and Langmuir–Blodgett techniques. Among several methods, the spin coating technology is the easiest and feasible.

Solubility of phthalocyanines is a key impact factor in spin coating technology. MPcs with substituents express better solubility than that without substituents. Our team has been focusing on gas sensitivity of MPcs spin-coated films with alkoxy substituents, for as much their powders showed good soluble in common organic solvents. Based on this, we fabricated the spin-coated films (their chemical structures are shown in Fig.1)and studied their gas sensitivity to NO_2.



$R = CH_2CH_2CH_2(CH_3)_2$; M = Cu,Ni,Pb

Figure 1. The structure of $M(II)Pc(iso\text{-}PeO)_8$

2. EXPERIMENT

MPcs are synthesized from 1,2-dicyano-3-(2,2,4-trimethyl-3-pentyloxy) benzene and, anhydrous metal (Pb^{2+}, Ni^{2+}, Cu^{2+}) chloride in 1-pentanol solvent with 1,8-diazabicycio-[5.4.0]-

undec-7-ene (DBU) as the catalyst. The reaction mixture was refluxed for 6h in the presence of a nitrogen atmosphere. The reaction solvent was evaporated to half of the original volume by rotary evaporation. After the remained mixture was cooled to room temperature, methanol was added. The precipitated solid was collected by means of filtration and washed with methanol. The product was dried and purified by column chromatography.

The thin films were fabricated by spin-coating on interdigital aluminum electrode of 50 μm electrode spacing and 10 finger pairs, quartz, glass and CaF_2 substrates, respectively, in air (temperature 25℃, relative humidity 50-95%). MPcs films were prepared by spinning their benzene solution ($6.5 mg \cdot ml^{-1}$) onto cleaned substrates at 3000 rpm for 15s.

FT-IR spectra were recorded as KBr pellets over the range 4000– 400 cm^{-1} using a Bruker instrument system (Equinox 55). Elemental analyses were performed with an elemental analyzer (PE-2400). UV–VIS spectra were measured by means of using a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrometer with the resolution of 0.05nm. MALDI-TOF mass spectra were determined using LDI-1700 (Linear Scientific Inc). Themorphology of surface was examined with an atomic force microscope (Digital instrument Nanoscope IIIa).

The electrical resistance of the spin-coated film under various gas concentrations was measured with ZC 36 type high resistance meter at room temperature and 50℃, respectively. The temperature was controlled with a constant temperature-controlled instrument. In a typical run, nitrogen was first introduced into the test chamber at a flow rate of 500 ml/min for at least 30 mins. Then some amount of nitrogen dioxide was injected into the chamber by a microsyringe. Finally, the chamber was flushed with pure nitrogen until complete desorption. The sensitivity (S) is: $S = R_a/R_g$, where $R_a$and R_g are the resistance of the testing film measured in air and in a nitrogen diluted NO_2 gas, respectively.

3. RESULTS AND DISCUSSION

MPcs were synthesized in 1-pentanol by the cyclic tetramerisation reaction between different metal ions (Pb^{2+}, $Ni^{2+}$and Cu^{2+}) and 2,3-dicyano-1,4-di(iso-pentyloxy) benzene. These compounds were confirmed by elemental analysis, FT-IR spectra, MS spectra and UV-VIS spectra. The elemental analytical data identify well with their formulae: PbPc(iso-PeO)$_8$ for $C_{72}H_{96}N_8O_8Pb$: C, 61.38 ; H, 6.87 ; N, 7.95%; found: 61.42; H, 6.82; N, 7.90%; MS: m/e (1408.3), CuPc(iso-PeO)$_8$ for $C_{64}H_{80}N_8O_4Cu$: C, 68.35 ; H, 7.65 ; N, 8.86%; found: C, 68.40; H, 7.66; N, 8.82 %; MS: m/e (1263.0), NiPc(iso-PeO)$_8$ for $C_{64}H_{80}N_8O_4Ni$: C, 68.32 ; H, 7.68 ; N, 8.89%; found: C, 68.40; H, 7.62; N, 8.83%; MS: m/e (1258.0). MALDI-TOF mass spectra of the M(II)Pcs. The IR spectra of MPcs powders and films are summarized in Table. 1. It can be seen that the absorption bands of spin-coated films and films are similar in the main frequencies. It indicated molecules arrangement in spin-coated film was out of order. But, the relative intensity of certain absorption bands, such as $\upsilon_{C=C}$, $\upsilon_{C=N}$(macrocycle) changed obviously from the power and film. These phenomena indicate that molecules in spin-coating film are arranged more closely. The interaction forces among the molecules are increased and the macrocycle vibration can be decreased.

The electronic spectra of M(II) Pcs in chloroform solutions and the spin-coated films are given in Fig. 2. There are series of Soret-band in the ultraviolet region and Q-band absorption in the visible region in chloroform solution, which can be attributed to $\pi(a_{2u})$-$\pi^*(e_g)$ and $\pi(a_{1u})$-$\pi^*(e_g)$, respectively. The differences of Q-band can be observed in the spin-coated film and in solutions. It can be seen that the O_{max} of Q-band of the Pb(II)Pc(iso-PeO)$_8$, Cu(II)Pc(iso-PeO)$_8$ and Ni(II)Pc(iso-PeO)$_8$ in solution are at around 694, 707 and 702nm, which are red-shifted to around 708, 717 and 709nm and broadened in spin-coated films. It suggests that the phthalocyanine molecules form J-aggregate in spin-coated film according to the molecular excitation theory [18].

Table 1. The main IR frequencies and related assignment of MPcs compounds

R wavenumber(cm^{-1})						Assignment
Pb Cu Ni			Pb Cu Ni			
(KBr)			Spin-coating film			
3089	3186	3088				υ_{C-H} (benzene)
2953	2956	2951	2955	2954	2956	υ_{C-H} ($-CH_3$)
2925	2925	2917	2926	2920	2925	υ_{C-H} ($-CH_2-$)
2866	2870	2868	2869	2875	2870	υ_{C-H} ($-CH_3$)
			1729	1751	1731	$\upsilon_{C=O}$
1660	1645	1672				$\upsilon_{C=C,}\upsilon_{C=N}$
1593	1586	1604	1595	1601	1587	$\upsilon_{C=C}$ (macrocycle)
1484	1489	1498	1470	1499	1489	$\upsilon_{C=N}$ (macrocycle)
1384	1385	1385	1399	1382	1385	$\upsilon_{C=C}$ (pyrrole)
1365	1368	1363	1345	1363	1368	$\upsilon_{C=N}$ (pyrrole)
1329	1335	1328	1311	1314	1327	υ_{C-C}
1272	1279	1287	1252	1275	1279	υ_{C-C}
1244	1243	1261	1235	1210	1246	υ_{C-O-C}
1145	1136	1133	1116	1130	1136	β_{C-H} (benzene)
1063	1067	1071	1082	1070	1067	β_{C-H} (benzene)

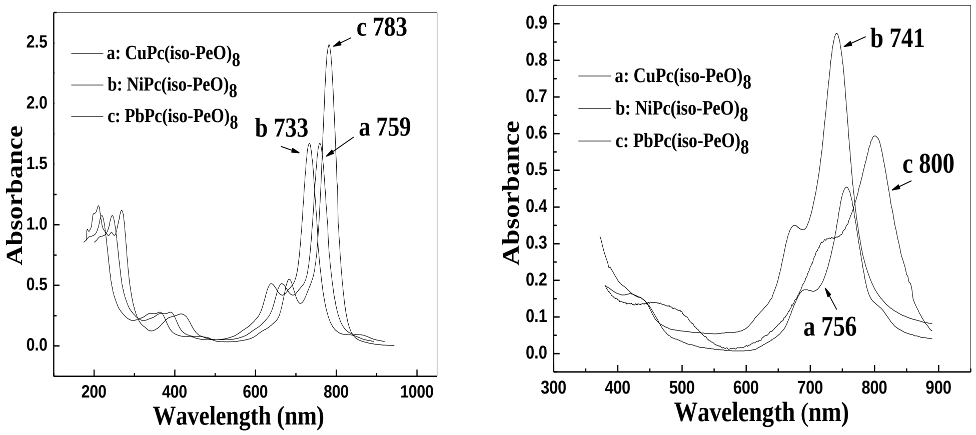
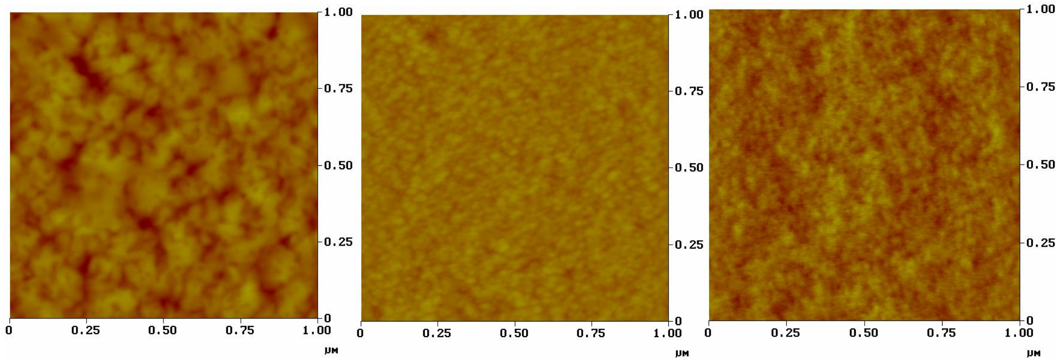


Figure 2. Electronic spectra of M(II)Pcs (left: Chloroform solution, right: spin-coating film)

We also studied the influence of different metal ions on the O_{max} of Q-band in solution. From Fig. 2, it is clearly shown that the absorption peak was red-shifted from nickel(II) and copper (II) to lead (II). The results in our experiments can be explained as followed: the metal ion was connected with the nitrogen atom of macrocycle. According to the modern molecule orbit theory [19], if the electron clouddensity of molecule internal nitrogen atom of phthalocyanine is increased, that will lead to the red shift of absorption peak of the Q-band. This ability increases along with the decrease of the positive electricity ability of metal ion. The positive electricity ability of metal ion is in the order of nickel (II) > copper (II)> lead (II), so the maximum absorption of M(II)Pcs is lead(II) > copper(II) > nickel(II).



a b c

Figure 3. AFM images of spin-coated films.(a) Pb(II)Pc(iso-PeO)$_8$; (b) Cu(II)Pc(iso-PeO)$_8$; (c) Ni(II)Pc(iso-PeO)$_8$

The solubility of M(II)Pcs in some organic solvents, such as benzene, chloroform and dichloromethane is > 2 % (wt).

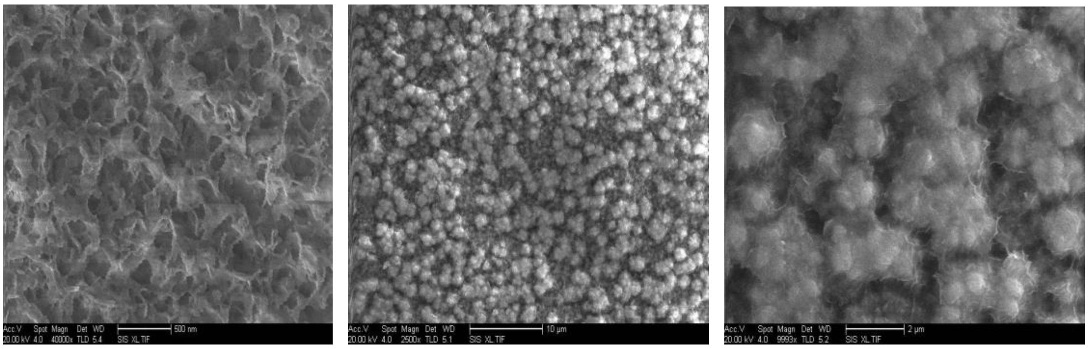


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Figure 4. SEM images of spin-coated films.(a) Pb(II)Pc(iso-PeO)$_8$; (b) Cu(II)Pc(iso-PeO)$_8$; (c) Ni(II)Pc(iso-PeO)$_8$

These results showed that the M(II)Pcs were highly soluble, which gave these M(II)Pcs potential application for gas sensor by using spin-coating technique. Further interesting results have obtained by means of AFM and SEM measurements (Fig. 3 and Fig. 4). The AFM micrographs indicate that spin-coated films of Pb(II), Cu(II) and Ni(II)(iso-PeO)$_8$ were uniform, smooth and dense on glass. with a mean roughness of 0.324 nm, 0.165 nm and 0.256 nm, respectively. The porous structure which is in favour of absorbing small gas molecules can be seen in Fig. 4. Moreover, the spin-coated films of PbPc(iso-PeO)$_8$ produced films with aggregate structure analogous to films of PbPc obtained from the vacuum deposited by J.C. Hsieh.[6].

The gas sensitivity of MPcs is based on their electronic conductivity, namely the difference of energy level between valence band and conduction band. Central metal ions have many influences on the HOMO, LUMO and energy level structure of the complexes, sequentially do the gas sensitivity. In order to discuss this influence, we chose the metal(II) phthalocyanines with the same substituent(pentyloxy) and different metal ions(Pb,Cu,Ni).To fabricate the spin-coated films the same concentration solvent were chosen. The gas sensitivity were determined at different temperature to NO_2.Gas sensitivity as a function of operating temperature of MPc(iso-PeO)$_8$ films to NO_2 is in Fig.5.

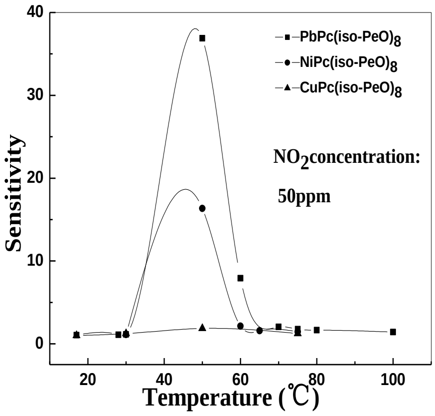

Figure 5. Gas sensitivity as a function of operating temperature of MPc(iso-PeO)$_8$ films to NO_2

From Fig 5 it can be seen the sensitivity(R_a/R_g) of the spin-coated films of PbPc(iso-PeO)$_8$ and NiPc(iso-PeO)$_8$ increased firstly, then declined during the experiment temperature range to NO_2(50ppm),reached the highest point at 50 ℃ .The relationship between temperature and the sensitivity showed the peak shape. The reason is probably that adsorb NO_2 molecules needs an activation energy. The temperature is higher, the amount of the current carrier is bigger. It amounts to potential energy barrier of electronic transition fell, the conductivity strengthened. At the same time, the higher temperature, the bigger the amount of desorption .The decrease in the number of electron holes resulted in the decrease in number of the current carrier and it amounts to that the potential energy barrier is increased the conductivity is weakened. Besides, the spin-coated films at different temperature are very sensitive to contribution of electron-phonon interactions crucial role is played by contribution of electron subsystem electively interacting with the particular molecule and principal here is the values of the ground state dipole moments of the chromophore determined by cations[20,21]. Additionally these films may be promising as materials for light emitting devices and photovoltaics.

It can also be seen that the gas sensitivity of MPc(iso-PeO)$_8$ films varied with the metal ion , with an order of lead(II) > nickel (II)>copper(II) in Fig. 5 , which is consistent with the date obtained for LB films by F. Armand [22] (Zinc>Nickel >Copper>Cobalt),and does not correlate with the date obtained for sublimed films by T.A. Jones [23](cobalt>copper>Zinc>Nickel). These results demonstrate that the structure has influence on the gas sensitivity to some extent, and at the same time, the surface morphologies of thin films also have many influences on the gas sensitivity. Moreover, the principal roles for the properties of films give also film-substrate interfaces determining nano-tapping levels[24].

The response-recovery curves characteristic of MPc(iso-PeO)$_8$ films at room temperature and 50℃ is in Fig.6 and Fig.7. The same point is that when the thin films exposed to NO_2, the resistance decreased dramatically, namely, the conductivity increased and all manifested obvious P-type conductor characteristic. The different point is that at room temperature, the spin-coated films of MPc(iso-PeO)$_8$ showed a poor sensitivity and reversibility in NO_2. The reason is probably the desorption of chemisorbed NO_2 molecules needs an activation energy [6,20]. No matter at room temperature or 50℃ the spin-coated film of PbPc(iso-PeO)$_8$ expressed the best gas sensitivity to NO_2. Even at room temperature the spin-coated film of PbPc(iso-PeO)$_8$ shows sensitivity to minimum concentration 5ppm of NO_2. It can be seen that the gas sensitivity of MPc(iso-PeO)$_8$ films varied with the metal ion , with an order of lead(II) > nickel (II)>copper (II) in Fig. 6 or 7. From CuPc(iso-PeO)$_8$ to PbPc(iso- PeO)$_8$, although the metallic apparent value is the same, the net charge number on the whole shows accretion current. Thus, with the increase of central metal ion number, the capability of the ring of phthalocyanine donor electrons enhances. These complexes present to be oxidized easily. NO_2 is a planar-π electron accepter, with the increase of d electron of the central metal, the sensitivity should increase in accordance with the order of experiment result. Besides, Pb(iso-PeO)$_8$ molecule possess unique structure, lead ion stands out of conjugated phthalocyanine π-system. Most other phthalocyanine molecules are in the same plane. The special structure leads to the special semiconductor property. On the other hand, eight pentyloxy substituents have some influences on the electron density of phthalocyanine macrocycle, and sequentially affect the gas absorption and electron transfer. Pentyloxy is an intense donor, which strengthened the chemisorption with facile production of ionized states and charge carriers which are formed from strong charge transfer interactions between phthalocyanine macrocycle and NO_2. Meanwhile the molecular configuration change for the large substituents. The steric effect of the substituents makes the space larger among molecules, which makes molecule plane anamorphic. The difference of energy level between valence band and conduction band take place changes, which result in the change of conductance. The gas sensitivity has been improved. Moreover the dissolvability of the complexes has been improved because of the introdudtion of large substituents, which is beneficial to fabricate spin-coating films. The interspace induced by the steric effect of the substituents is propitious to adsorption and desorption to NO_2.It is also found in AFM and SEM pictures. The porous structure is in favor of adsorption, diffusion and desorption of gas molecules. Therefore the response-recovery ability of the spin-coated film of PbPc(iso-PeO)$_8$ is the best of three.

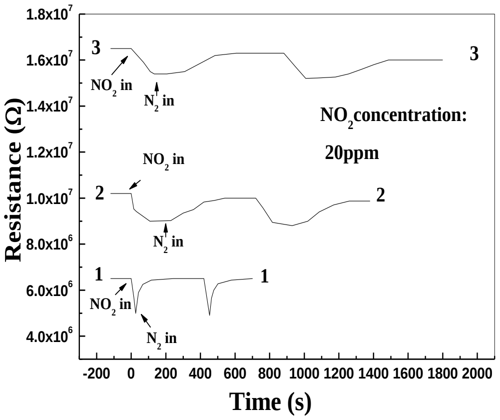

Figure 6. Response-recovery curves characteristic of MPc(iso-PeO)$_8$ films at room temperature:(1) PbPc(iso-PeO)$_8$; (2) NiPc(iso-PeO)$_8$; (3) CuPc(iso-PeO)$_8$

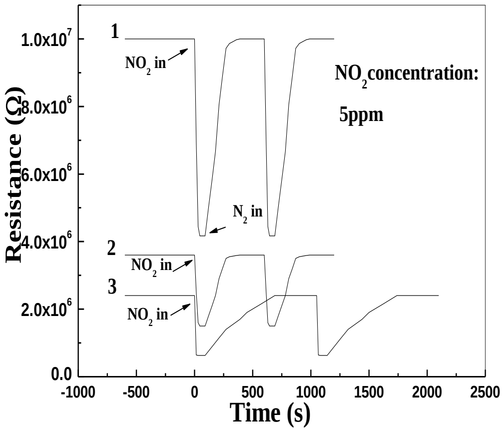

Figure 7. Response-recovery curves characteristic of MPc(iso-PeO)$_8$ films at 50℃:(1) PbPc(iso-PeO)$_8$; (2) NiPc(iso-PeO)$_8$; (3) CuPc(iso-PeO)$_8$

In order to discuss the selectivity of the spin-coated film of PbPc(iso-PeO)$_8$, gas sensitivity were determined to CH3CH2OH, CH3COCH3 and NH_3. The data showed in Table 2 including the sensitivity to NO_2. We can find out the gas sensitivity to NO_2 is the best in four.

Table 2. The main IR frequencies and related assignment of MPcs compounds

Concentration/40ppm	CH_3CH_2OH	CH_3COCH_3	NH_3	NO_2
Sensitivity	0.87	0.92	0.76	3.75

4 CONCLUSION

Three kinds of MPc(iso-PeO)$_8$(M=Pb,Ni,Cu) complexes with good solubility in organic solutions were synthesized for the first time. The relative thin films were prepared by spin-coating method. The influence of different metal ions and the testing temperature on NO_2 gas sensitivity were studied. M(II) Pcs complexes had potential application as a gas sensor by means of using spin-coating due to their good solubility, fast response and recovery characteristics at 50℃, and PbPc(iso-PeO)$_8$ would be suitable for gas sensor to NO_2 because of its high sensitivity, good reversibility and linear relationship between sensitivity of PbPc(iso-PeO)$_8$ spin-coating films and the concentration of NO_2. They also may be promising as materials for light emitting devices and photovoltaics.

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Author: Li Zan（1980-）a doctor in Harbin Institute of Technology, teacher of School of Science in Harbin University.