

## HEAT CAPACITIES AND THERMODYNAMIC PROPERTIES OF CoPc AND CoTMPP

S. J. Qiu<sup>1,2</sup>, H. L. Chu<sup>1,2</sup>, J. Zhang<sup>1,2</sup>, Y. N. Qi<sup>1,2</sup>, L. X. Sun<sup>1\*</sup> and F. Xu<sup>1</sup>

<sup>1</sup>Materials and Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences Dalian 116023, P.R. China

<sup>2</sup>Graduate School of the Chinese Academy of Sciences, Beijing 100049, P.R. China

The low-temperature molar heat capacities of CoPc and CoTMPP were measured by temperature modulated differential scanning calorimetry (TMDSC) over the temperature range from 223 to 413 K for the first time. No phase transition or thermal anomaly was observed in the experimental temperature range for CoPc. However, a structural change was found to be nonreversible for CoTMPP in the temperature range of 368–403 K, which was further validated by the results of IR and XRD. The molar enthalpy  $\Delta H_m$  and entropy  $\Delta S_m$  of phase transition of the CoTMPP were determined to be 3.301 kJ mol<sup>-1</sup> and 8.596 J K<sup>-1</sup> mol<sup>-1</sup>, respectively. The thermodynamic parameters of CoPc and CoTMPP such as entropy and enthalpy relative to reference temperature 298.15 K were derived based on the above molar heat capacity data. Moreover, the thermal stability of these two compounds was further investigated through TG measurements. Three steps of mass loss were observed in the TG curve for CoPc and five steps for CoTMPP.

**Keywords:** cobalt(II)phthalocyanine, cobalt(II)tetramethoxyphenylporphyrin, molar heat capacity, TG, TMDSC

### Introduction

Metallophthalocyanines (MPc) are paid much attention in molecular electronics [1], non-linear optics [2], liquid crystals [3, 4], gas sensors [5], catalysts [6–11], semiconductive materials [12], photovoltaic cells [13] and electrochromic displays [14, 15] over the last few decades. Especially, the cobalt(II) phthalocyanine (CoPc) and its derivatives are shown to catalyze reactions like the reduction of oxygen, carbon dioxide, formic acid, formaldehyde, trichloro acetic acid, and cysteine-containing proteins. For example, the CoPc-modified Au(111) electrode was found to enhance the electrochemical reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> [16]. Moreover, the CoPc–Pt/C as methanol-resistant oxygen-reduction electrocatalyst for direct methanol fuel cell (DMFC) exhibited an improved electrocatalytic activity when it was heated at a high temperature in high purity nitrogen environment [17]. In addition, metalloporphyrins are investigated extensively because they play an important role in biology due to their crucial function in many biological processes like photosynthesis, biological red-ox reactions, and transport of oxygen [18]. In recent years, metalloporphyrins are widely used as catalysts because of their extremely high selectivity in catalytic reactions [19]. Cobalt tetramethoxyphenylporphyrin (CoTMPP), a typical metalloporphyrin, was adopted as a catalyst in carbon particle-based air cathodes for application in the metal-air

fuel cell [20, 21]. Moreover, it was also applied as an electrocatalyst for the cathode reduction of hydrogen peroxide in fuel cells [22]. However, the thermodynamic properties of these substances were scarcely reported. For the theoretical research and practical application concerned with these substances, the thermodynamic data of CoPc and CoTMPP are urgently needed.

It is generally accepted that heat capacity is one of the most fundamental thermodynamic properties of substances and that it is closely related to other physical and chemical properties. Heat capacity determinations of various compounds have been focused by many researchers. Temperature modulated differential scanning calorimetry (TMDSC) is one of easier and more accurate methods for determining the heat capacity. In 1992, MDSC was initially proposed by Reading *et al.* [23], which applied a small sinusoidal modulation of temperature superimposed onto a linear underlying heating rate as an extension of the conventional DSC. The structure and principle of the calorimeter have been described in detail by the literatures [24–26]. Recently, this method has been greatly developed for directly determining heat capacities for various materials with isothermal and non-isothermal methods [27–31].

In the present paper, the low-temperature molar heat capacities of CoPc and CoTMPP were measured by TMDSC and the thermodynamic parameters such as entropy and enthalpy were also calculated. The ac-

\* Author for correspondence: lxsun@dicp.ac.cn

curacy of TMDSC is established by comparing the measured heat capacities of standard sapphire ( $\text{Al}_2\text{O}_3$ ) with previously reported values (NIST and NBS) [32, 33]. The thermal decomposition characteristics of these compounds were investigated by TG.

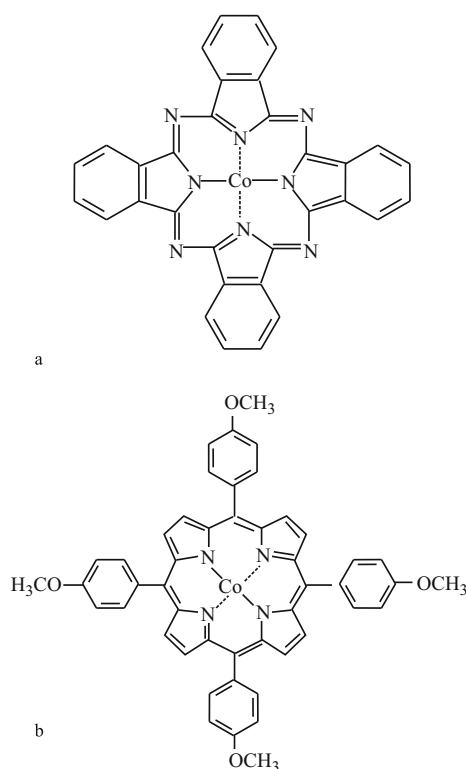
## Experimental

### Sample

Cobalt(II) phthalocyanine ( $\text{C}_{32}\text{H}_{16}\text{CoN}_8$ , CAS: 3317-67-7) and cobalt(II) 5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphine ( $\text{C}_{48}\text{H}_{36}\text{N}_4\text{O}_4\text{Co}$ , CAS: 28903-71-1) used in this study were provided by Aldrich Chemical Co. Their molar masses are 571.46 and 791.78  $\text{g mol}^{-1}$ , respectively. Their molecular structures are shown in Fig. 1. Before thermal experiments, these two samples were heated at 323.15 K in vacuum.

### Methods

FTIR spectra were recorded on a Bruker Equinox 55 FT-IR spectrometer using KBr pellet in the wavelength range of 4000–400  $\text{cm}^{-1}$ . Powder X-ray diffraction (XRD) experiments were carried out on a PANalytical X-ray Diffractometer (X'Pert MPD PRO,  $\text{CuK}\alpha$ , 40 kV, 40 mA).



**Fig. 1** Chemical structures of a – CoPc and b – CoTMPP

### Heat capacity measurement

Heat capacity measurements of the CoPc and CoTMPP were performed on DSC Q1000 (T-zero DSC-technology, TA Instruments Inc., USA). A liquid nitrogen cooling system was used for the experimental measurement. And dry nitrogen gas with high purity (99.999%) was used as purge gas ( $50 \text{ mL min}^{-1}$ ) through the DSC cell. The temperature scale of the instrument was initially calibrated in the standard DSC mode, using the extrapolated onset temperatures of the melting of indium (429.75 K) at a heating rate of  $10 \text{ K min}^{-1}$ . The energy scale was calibrated with the heat of fusion of indium ( $28.45 \text{ J g}^{-1}$ ). The heat capacity calibration was made by running a standard sapphire ( $\text{Al}_2\text{O}_3$ ) at the experimental temperature. The calibration method and the experiment were performed at the same conditions as follows: 1) sampling interval: 1.00 s/pt; 2) zero heat flow at 253.15 K; 3) equilibrate at 133.15 K; 4) modulate temperature amplitude of  $\pm 0.5 \text{ K}$  with period of 100 s; 5) isothermal for 5.00 min; 6) temperature ramp at  $5 \text{ K min}^{-1}$  to 413 K. The constants of heat capacity for the TMDSC:  $K_{\text{total}}=1.024$ ;  $K_{\text{reversible}}=1.019$ .

The masses of the reference and sample pans with lids were measured to within  $30 \pm 0.05 \text{ mg}$ . Samples were crimped in non-hermetic aluminum pans with lids. Sample mass was weighed on a METTLER TOLEDO electrobalance (AB135-S, Classic) with an accuracy of ( $\pm 0.01 \text{ mg}$ ).

### Thermal analysis

The TG curves of the CoPc and CoTMPP were performed on a thermogravimetric analyzer (Setaram Setsys 16/18, France) under nitrogen atmosphere (99.999%) from 350 to 1250 K. The heating rate was  $10 \text{ K min}^{-1}$  and the flow rate of nitrogen was  $100 \text{ mL min}^{-1}$ . The mass of the CoPc and CoTMPP were 15.9 and 15.4 mg, respectively. Two  $\text{Al}_2\text{O}_3$  crucibles were used (capacity: 100  $\mu\text{L}$ ). The reference crucible was filled with  $\alpha\text{-Al}_2\text{O}_3$ . The TG equipment was calibrated by the  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  (99.9%).

## Results and discussion

### Heat capacity of standard sapphire ( $\alpha\text{-Al}_2\text{O}_3$ )

The aim of this part is to assess the reproducibility and ensure accuracy of the measured data using TMDSC (Q1000). Heat capacity measurement of each compound is repeated three times under the same condition unless stated elsewhere. For heat capacity of sapphire ( $\alpha\text{-Al}_2\text{O}_3$ ) measurement (Table 1), the experimental standard deviation is within the range of  $\pm 0.0044$ , which shows that the testing system

**Table 1** The standard and experimental molar heat capacities of sapphire ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>)

<i>T</i> /K	$C_{p,m}/\text{J K}^{-1} \text{g}^{-1}$				Standard value [32]/ $\text{J K}^{-1} \text{g}^{-1}$	Standard deviation	RD/%
	<i>a</i>	<i>b</i>	<i>c</i>	average			
223	0.574	0.576	0.580	0.577	0.568	0.0030	1.5
233	0.598	0.600	0.604	0.601	0.600	0.0031	0.24
243	0.625	0.627	0.632	0.628	0.629	0.0032	-0.20
253	0.653	0.655	0.657	0.655	0.658	0.0020	-0.40
263	0.680	0.682	0.684	0.682	0.685	0.0021	-0.38
273	0.708	0.710	0.710	0.709	0.710	0.0013	-0.14
283	0.734	0.736	0.736	0.735	0.734	0.00087	0.12
293	0.760	0.762	0.762	0.761	0.757	0.0012	0.48
303	0.782	0.783	0.785	0.783	0.779	0.0016	0.54
313	0.803	0.805	0.807	0.805	0.800	0.0020	0.60
323	0.823	0.825	0.825	0.824	0.819	0.0014	0.61
333	0.841	0.842	0.843	0.842	0.838	0.00089	0.47
343	0.857	0.857	0.860	0.858	0.856	0.0016	0.27
353	0.873	0.873	0.875	0.874	0.872	0.0011	0.19
363	0.886	0.888	0.890	0.888	0.888	0.0019	-0.0080
373	0.900	0.900	0.904	0.902	0.903	0.0022	-0.14
383	0.913	0.913	0.916	0.914	0.917	0.0017	-0.32
393	0.924	0.924	0.929	0.926	0.930	0.0026	-0.47
403	0.936	0.936	0.941	0.938	0.943	0.0027	-0.57
413	0.946	0.945	0.951	0.947	0.955	0.0029	-0.81
423	0.957	0.956	0.961	0.958	0.967	0.0028	-0.89
433	0.967	0.965	0.971	0.967	0.978	0.0032	-1.0
443	0.976	0.975	0.982	0.978	0.988	0.0040	-1.1
453	0.986	0.985	0.991	0.987	0.998	0.0036	-1.0
463	0.996	0.992	1.00	0.996	1.01	0.0044	-1.1

of TMDSC is steady and the measurement data are creditable. Relative deviations have been calculated by the following equation:

$$RD(\%)=10^2[C_{p,m}(\text{exp})-C_{p,m}(\text{ref})]/C_{p,m}(\text{ref}) \quad (1)$$

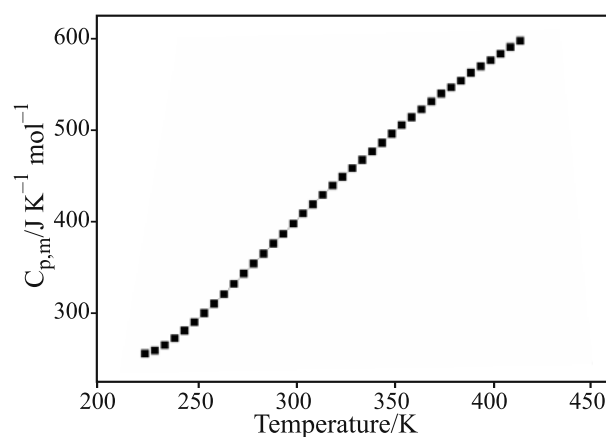
where  $C_{p,m}(\text{exp})$  is the experimental heat capacities and  $C_{p,m}(\text{ref})$  is the referenced heat capacities. The results show that the relative deviation of our calibration data from the recommended value (NIST) over the whole temperature range was within  $\pm 1.5\%$ .

#### Molar heat capacities of CoPc and CoTMPP

The experimental molar heat capacity curve of CoPc vs. temperature is shown in Fig. 2. The experimental and simulated data are listed in Table 2. From Fig. 2, it can be seen that the heat capacity of the sample increases with increasing temperature in a smooth and continuous manner in the experimental temperature range. In this temperature range, no phase transition or thermal anomaly can be observed, which indicates

that this sample is stable in the experimental temperature range.

Figure 3 shows the experimental molar heat capacity curve of CoTMPP. The experimental and sim-

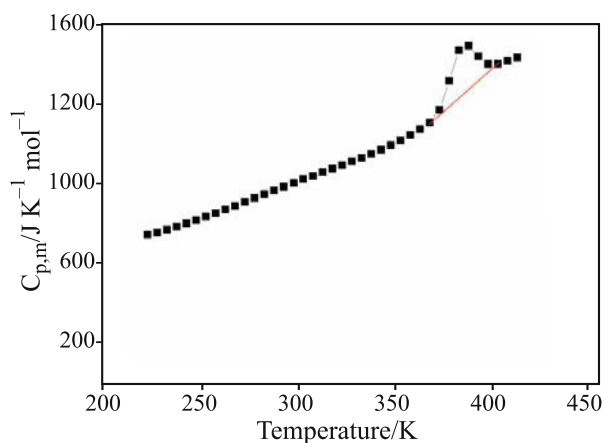


**Fig. 2** Molar heat capacities ( $C_{p,m}$ ) of CoPc as a function of temperature

**Table 2** The experimental and simulated molar heat capacities of CoPc

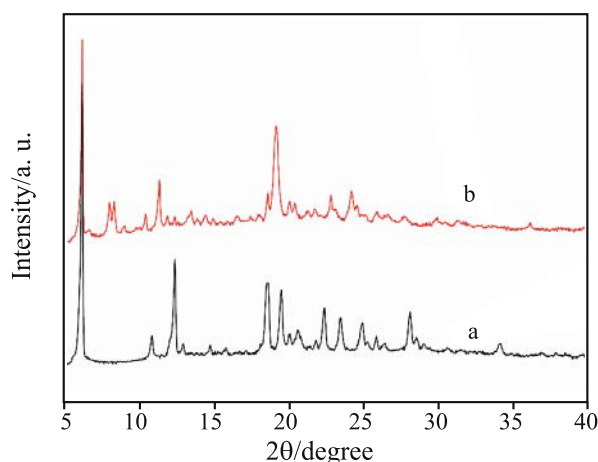
$T/K$	$C_{p,m}(\text{exp})/\text{J K}^{-1} \text{mol}^{-1}$	$C_{p,m}(\text{fit})/\text{J K}^{-1} \text{mol}^{-1}$	RD/%	$T/K$	$C_{p,m}(\text{exp})/\text{J K}^{-1} \text{mol}^{-1}$	$C_{p,m}(\text{fit})/\text{J K}^{-1} \text{mol}^{-1}$	RD/%
223	256.3	254.6	0.67	323	448.9	449.4	-0.11
228	259.6	259.8	-0.12	328	458.4	459.3	-0.18
233	265.5	266.3	-0.31	333	467.6	468.9	-0.28
238	273.0	273.8	-0.30	338	476.8	478.3	-0.32
243	281.3	282.1	-0.30	343	486.3	487.5	-0.25
248	290.6	291.2	-0.18	348	495.8	496.5	-0.13
253	300.6	300.8	-0.060	353	505.4	505.2	0.030
258	310.6	310.8	-0.070	358	513.8	513.8	-0.0042
263	321.2	321.2	-0.012	363	522.4	522.1	0.047
268	332.2	331.9	0.11	368	531.3	530.3	0.18
273	343.6	342.7	0.26	373	539.8	538.3	0.28
278	354.5	353.6	0.24	378	546.4	546.2	0.048
283	365.2	364.6	0.17	383	553.8	553.8	-0.014
288	376.1	375.6	0.14	388	562.4	561.4	0.18
293	386.8	386.6	0.068	393	569.4	568.8	0.096
298.15	397.9	397.7	0.043	398	575.9	576.2	-0.050
303	408.9	408.1	0.18	403	583.0	583.5	-0.077
308	419.0	418.7	0.067	408	590.3	590.7	-0.058
313	429.5	429.2	0.078	413	597.4	597.8	-0.079
318	439.5	439.4	0.017				

ulated data are listed in Table 3. From Fig. 3 it can be seen that the heat capacities of the sample increase with temperature in a smooth and continuous manner from 223 to 368 K and no phase transition or thermal anomaly was observed in this temperature range. This result suggests that the sample is stable in the above temperature range. However, a thermal anomaly was observed in the temperature range from 368 to 403 K before its decomposition temperature 427 K according to the TG curve in Fig. 6. The peak temperature of the thermal anomaly is 384 K. It can be concluded



**Fig. 3** Molar heat capacities ( $C_{p,m}$ ) of CoTMPP as a function of temperature

that this transition is nonreversible due to a structural change during the melt. To confirm our conclusion, the XRD and IR of this sample heated at 408.15 K under nitrogen atmosphere for 30 min were performed. Figure 4 shows the XRD patterns of CoTMPP before and after heat treatment. From Fig. 4, it can be seen that the crystal type of CoTMPP changed evidently after it was heated at 408.15 K for half an hour, which indicated that the sample had a structural transition. The IR spectra of CoTMPP before and after heat



**Fig. 4** XRD patterns for CoTMPP a – before and b – after heat treatment

**Table 3** The experimental and simulated molar heat capacities of CoTMPP

$T/K$	$C_{p,m}(\text{exp}) / \text{J K}^{-1} \text{mol}^{-1}$	$C_{p,m}(\text{fit}) / \text{J K}^{-1} \text{mol}^{-1}$	$RD / \%$	$T/K$	$C_{p,m}(\text{exp}) / \text{J K}^{-1} \text{mol}^{-1}$	$C_{p,m}(\text{fit}) / \text{J K}^{-1} \text{mol}^{-1}$	$RD / \%$
223	664.8	666.8	-0.31	323	972.6	971.8	0.084
228	674.6	675.0	-0.063	328	988.7	988.3	0.038
233	687.3	685.9	0.22	333	1005	1005	-0.068
238	700.8	698.7	0.29	338	1022	1023	-0.090
243	715.0	713.0	0.27	343	1041	1042	-0.13
248	729.7	728.5	0.16	348	1061	1062	-0.13
253	744.8	744.6	0.019	353	1082	1084	-0.13
258	760.3	761.3	-0.12	358	1106	1107	-0.079
263	776.4	778.1	-0.22	363	1131	1132	-0.028
268	792.9	795.0	-0.27	368	1161	1158	0.23
273	810.0	811.9	-0.23	373	1217		
278	827.4	828.5	-0.14	378	1345		
283	844.3	845.0	-0.080	383	1480		
288	860.9	861.2	-0.031	388	1500		Phase transition region
293	877.3	877.2	0.014	393	1454		
298.15	894.2	893.4	0.084	398	1420		
303	910.5	908.6	0.21	403	1421	1421	0
308	925.3	924.2	0.12	408	1435	1435	0
313	941.7	939.8	0.20	413	1449	1449	0
318	957.3	955.7	0.17				

treatment shown in Fig. 5 further indicated that the structural change is nonreversible.

The molar heat capacities of the CoPc are fitted using the Shomate equation [34] of heat capacities ( $C_{p,m}$ ) with reduced temperature ( $t$ ) by means of the nonlinear least square fitting through the OriginPro 7.5 software:

$$C_{p,m} (\text{J K}^{-1} \text{mol}^{-1}) = -5048.9243 + 30943.76361t - 62578.75931t^2 + 46112.01723t^3 + 49.91217/t^2 \quad (2)$$

where  $t = T/1000$  and  $T/K$  is the experimental temperature. The correlation coefficient of the fitting is  $R^2 = 0.99995$ . The relative deviations of all the experimental points from the fitting heat capacity values are within  $\pm 0.67\%$ .

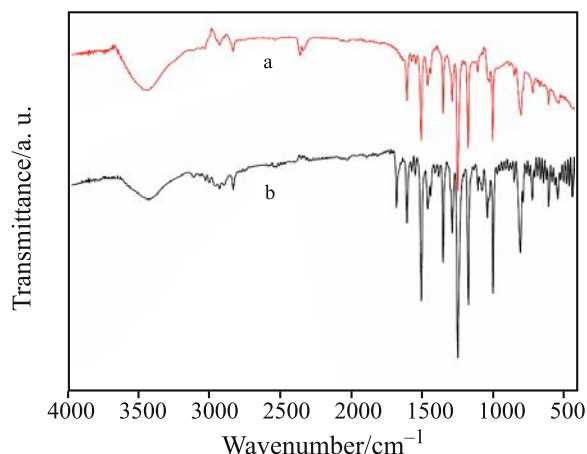
The molar heat capacities of the CoTMPP are also fitted using the Shomate equation.

From 223 to 368 K,

$$C_{p,m} (\text{J K}^{-1} \text{mol}^{-1}) = -25319.77476 + 181113.07363t - 467506.84596t^2 + 434653.33207t^3 + 200.25556/t^2 \quad (3)$$

The correlation coefficient of the fitting is  $R^2 = 0.99991$ . The relative deviations of all the experimental points from the fitting heat-capacity values are within  $\pm 0.31\%$ .

From 403 to 413 K,



**Fig. 5** IR spectra of CoTMPP a – before and b – after heat treatment

$$C_{p,m} (\text{J K}^{-1} \text{mol}^{-1}) = -23450.75404 + 185042.2906t - 466617.71795t^2 + 397949.46855t^3 + 5.9286/t^2 \quad (4)$$

Correlation coefficient  $R^2$  of least square fitting is 1.0000.

#### Thermodynamic functions of CoPc and CoTMPP

The molar enthalpy  $\Delta H_m$  of phase transition of CoTMPP were derived by the integration of  $C_p - T$

**Table 4** Calculated thermodynamic function data of CoPc

$T/K$	$H_T-H_{298.15}/$ $\text{kJ mol}^{-1}$	$S_T-S_{298.15}/$ $\text{J K}^{-1} \text{mol}^{-1}$	$T/K$	$H_T-H_{298.15}/$ $\text{kJ mol}^{-1}$	$S_T-S_{298.15}/$ $\text{J K}^{-1} \text{mol}^{-1}$
223	-23.99	-91.68	323	10.54	33.91
228	-22.71	-85.98	328	12.81	40.90
233	-21.40	-80.28	333	15.13	47.91
238	-20.04	-74.55	338	17.50	54.97
243	-18.65	-68.77	343	19.91	62.06
248	-17.22	-62.93	348	22.37	69.18
253	-15.74	-57.03	353	24.87	76.33
258	-14.21	-51.04	358	27.42	83.49
263	-12.63	-44.98	363	30.01	90.68
268	-11.00	-38.83	368	32.64	97.88
273	-9.312	-32.60	373	35.31	105.1
278	-7.571	-26.28	378	38.03	112.3
283	-5.776	-19.87	383	40.78	119.5
288	-3.925	-13.40	388	43.56	126.8
293	-2.020	-6.833	393	46.39	134.0
298.15	0	0	398	49.25	141.2
303	1.954	6.502	403	52.15	148.5
308	4.022	13.27	408	55.09	155.7
313	6.141	20.10	413	58.06	163.0
318	8.313	26.98			

**Table 5** Calculated thermodynamic function data of CoTMPP

$T/K$	$H_T-H_{298.15}/$ $\text{kJ mol}^{-1}$	$S_T-S_{298.15}/$ $\text{J K}^{-1} \text{mol}^{-1}$	$T/K$	$H_T-H_{298.15}/$ $\text{kJ mol}^{-1}$	$S_T-S_{298.15}/$ $\text{J K}^{-1} \text{mol}^{-1}$
223	-58.05	-222.7	323	23.17	74.60
228	-54.70	-207.8	328	28.07	89.65
233	-51.29	-193.0	333	33.05	104.7
238	-47.83	-178.4	338	38.12	119.8
243	-44.30	-163.7	343	43.29	135.0
248	-40.70	-149.0	348	48.55	150.2
253	-37.02	-134.3	353	53.91	165.5
258	-33.25	-119.6	358	59.39	180.9
263	-29.41	-104.8	363	64.98	196.5
268	-25.47	-89.98	368	70.71	212.1
273	-21.46	-75.13	373		
278	-17.35	-60.24	378		
283	-13.17	-45.33	383		
288	-8.905	-30.39	388		
293	-4.559	-15.43	393		
298.15	0	0	398		
303	4.370	14.54	403	74.01	220.7
308	8.952	29.54	408	81.15	238.3
313	13.61	44.55	413	88.36	255.9
318	18.35	59.57			

curve from 368 to 403 K. The entropy  $\Delta S_m$  of phase transition of CoTMPP was derived according to the following equation:

$$\Delta S_m = \Delta H_m / T_m \quad (5)$$

where  $T_m$  is the peak temperature.

The values of peak temperature  $T_m$ , molar enthalpy  $\Delta H_m$  and entropy  $\Delta S_m$  of phase transition of the sample were determined to be 384 K, 3.301 kJ mol<sup>-1</sup> and 8.596 J K<sup>-1</sup> mol<sup>-1</sup>, respectively. Enthalpy and entropy of substances are basic thermodynamic functions. In terms of the polynomials of molar heat capacity and the thermodynamic relationship, the  $[H_T - H_{298.15}]$  and  $[S_T - S_{298.15}]$  of CoPc and CoTMPP were calculated in the temperature ranges from 223 to 413 K with an interval of 5 K relative to the temperature of 298.15 K. The thermodynamic relationships are as follows:

$$H_T - H_{298.15} = \int_{298.15}^T C_{p,m} dT \quad (6)$$

$$S_T - S_{298.15} = \int_{298.15}^T (C_{p,m} / T) dT \quad (7)$$

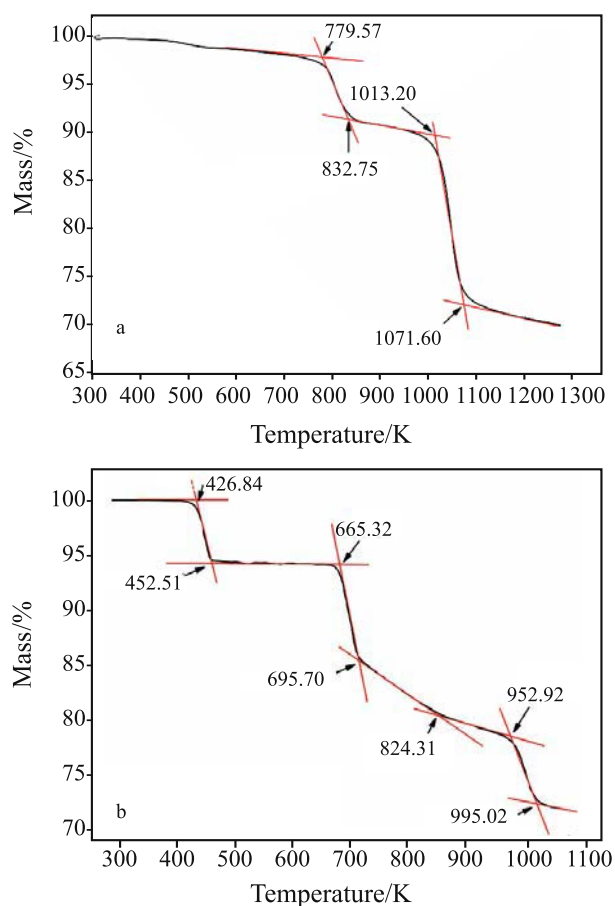


Fig. 6 TG curves of a – CoPc and b – CoTMPP

The calculated thermodynamic functions  $[H_T - H_{298.15}]$  and  $[S_T - S_{298.15}]$  are shown in Table 4 for CoPc and Table 5 for CoTMPP.

### TG analysis

TG curves of CoPc and CoTMPP are shown in Fig. 6. TG analysis showed that the three-step mass loss occurred in the temperature range of 350–1250 K for CoPc. The mass loss is 2.26, 6.31 and 17.53%, respectively. The results are in agreement with literature [17]. However, the five-step mass loss was observed in the temperature range of 300–1100 K for CoTMPP. The mass loss is 4.59, 7.24, 5.22, 2.74 and 5.29%, respectively.

### Conclusions

The molar heat capacities of cobalt(II) phthalocyanine (C<sub>32</sub>H<sub>16</sub>CoN<sub>8</sub>, CoPc) and cobalt(II) 5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphine (C<sub>48</sub>H<sub>36</sub>N<sub>4</sub>O<sub>4</sub>Co, CoTMPP) were measured by MDSC in the temperature range between 223 and 413 K. It was found that a nonreversible transition is observed for CoTMPP in the temperature range from 368 to 403 K, while there was no thermal anomaly for CoPc in the experimental temperature range. The thermodynamic function data relative to the reference temperature (298.15 K) were calculated based on the heat capacities measurements. Moreover, the thermal stability of these two compounds was further investigated by TG.

### Acknowledgements

The authors gratefully acknowledge the National Nature Science Foundation of China for financial support to this work under Grant No. 20473091, 20573112 and 50671098.

### References

- 1 W. Göpel, *Synth. Met.*, 41 (1991) 1087.
- 2 M. A. Diaz-Garcia, I. Ledoux, J. A. Duro, T. Torres, F. Agullo-Lopez and J. Zyss, *J. Phys. Chem.*, 98 (1994) 8761.
- 3 H. Eichhorn, D. Wohrle and D. Pressner, *Liq. Cryst.*, 22 (1997) 643.
- 4 D. Lelievre, M. A. Petit and J. Simon, *Liq. Cryst.*, 4 (1989) 707.
- 5 J. D. Wright, P. Roisin, G. P. Rigby, R. J. M. Nolte, M. J. Cook and S. C. Thorpe, *Sens. Actuators B*, 13 (1993) 276.
- 6 J. H. Zagal, *Coord. Chem. Rev.*, 119 (1992) 89.

- 7 P. Janda, N. Kobayashi, P. R. Auburn, H. Lam, C. C. Leznoff and A. B. P. Lever, *Can. J. Chem.*, 67 (1989) 1109.
- 8 N. Kobayashi and W. A. Nevin, *Appl. Organomet. Chem.*, 10 (1996) 579.
- 9 W. J. Todd, F. Bailly, J. Pavez, P. W. Faguy, R. P. Baldwin and R. M. Buchanan, *J. Am. Chem. Soc.*, 120 (1998) 4887.
- 10 M. K. Halbert and R. P. Baldwin, *Anal. Chem.*, 57 (1985) 591.
- 11 E. Karmann, D. Schlettwein and N. I. Jaeger, *J. Electroanal. Chem.*, 405 (1996) 149.
- 12 R. Zhou, F. Josse, W. Gopel, Z. Z. Ozturk and O. Bekarolu, *Appl. Organomet. Chem.*, 10 (1996) 557.
- 13 D. Wöhrle, L. Kreienhoop, G. Schnurpfeil, J. Elbe, B. Tennigkeit, S. Hiller and D. Schlettwein, *J. Mater. Chem.*, 5 (1995) 1819.
- 14 N. Toshima, T. Tominaga and S. Kawamura, *B. Chem. Soc. Jpn.*, 69 (1996) 245.
- 15 B. Lukas, J. Silver, D. R. Lovett and M. J. Cook, *Chem. Phys. Lett.*, 241 (1995) 351.
- 16 S. Yoshimoto, A. Tada, K. Suto and K. Itaya, *J. Phys. Chem. B*, 107 (2003) 5836.
- 17 Y. H. Lu and R. G. Reddy, *Electrochim. Acta*, 52 (2007) 2562.
- 18 X.H. Wei, X.H. Du, D.H. Chen and Z.P. Chen, *Thermochim. Acta*, 440 (2006) 181.
- 19 R. Huszank and O. Horvath, *Chem. Commun.*, (2005) 224.
- 20 S. Sathyanarayana and N. Munichandraiah, *J. Appl. Electrochem.*, 11 (1981) 33.
- 21 M. Maja, C. Orecchia, M. Strano, P. Tosco and M. Vanni, *Electrochim. Acta*, 46 (2000) 423.
- 22 N.A. Savastenko, V. Brüser, M. Brüser, K. Anklam, S. Kutschera, H. Steffen and A. Schmuhl, *J. Power Sources*, 165 (2007) 24.
- 23 M. Reading, D. Elliot and V. L. Hill, *Proc. of the 21<sup>st</sup> North American Thermal Analysis Society Conference*, (1992) 145.
- 24 B. Wunderlich, Y. Jin and A. Boller, *Thermochim. Acta*, 238 (1994) 277.
- 25 R. L. Danley, *Thermochim. Acta*, 402 (2003) 91.
- 26 B. Wunderlich, *J. Therm. Anal. Cal.*, 85 (2006) 179.
- 27 S. Heidenreich, T. Langner and H. Rohm, *J. Therm. Anal. Cal.*, 89 (2007) 815.
- 28 Z. A. Mohd Ishak, P. P. Shang and J. Karger-Kocsis, *J. Therm. Anal. Cal.*, 94 (2006) 637.
- 29 M. Varma-Nair and B. Wunderlich, *J. Therm. Anal. Cal.*, 46 (1996) 879.
- 30 J. Majumdar, F. Cser, M. C. Jollands and R. A. Shanks, *J. Therm. Anal. Cal.*, 78 (2004) 849.
- 31 B. Wunderlich, *J. Therm. Anal. Cal.*, 48 (1997) 207.
- 32 D. G. Archer, *J. Phys. Chem. Ref. Data*, 22 (1992) 1441.
- 33 D. C. Ginnings and G. T. Furukawa, *J. Am. Chem. Soc.*, 75 (1953) 522.
- 34 P. J. Linstrom, W. G. Mallard, Eds, *NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg MD, July 2001, p. 20899* (<http://webbook.nist.gov>).

---

Received: July 11, 2007

Accepted: September 14, 2007

---

DOI: 10.1007/s10973-007-8625-3