

# Synthesis, purification and thermal behaviour of sulfonated metalloporphyrins

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Received: 10 May 2011 / Accepted: 21 September 2011 / Published online: 7 October 2011  
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**Abstract** A free-base tetra sodium meso-tetra (*p*-sulphonatophenyl) porphyrin (TPPS<sub>4</sub>) and its corresponding metalloporphyrins (MTPPS<sub>4</sub>), where M = Co, Ni and Zn were synthesized and characterized by UV–visible spectroscopy, infra red spectroscopy and <sup>1</sup>H nmr spectroscopy. Thermal studies of these porphyrins were conducted in synthetic air from room temperature to 800 °C. The residues of MTPPS<sub>4</sub> were qualitatively analyzed which showed the presence of corresponding metal oxides and Na<sub>2</sub>SO<sub>4</sub>. Further, the above porphyrins were subjected to TG-EGA-MS analysis in argon atmosphere to study the evolved gases/species during the thermal events. This information is useful to know the ring opening sequence of these porphyrins at corresponding temperatures.

**Keywords** Sulfonated metalloporphyrins · Thermogravimetry · Differential scanning calorimetry · Evolved gas analysis

## Introduction

Molecular engineering of porphyrins have become of great interest for use in molecular electronics, non-linear optics, optical data storage, sensors, electrochromic devices and electrocatalytic systems [1]. The number of sulfonated

porphyrins have exhibited excellent antiviral activity against the human immunodeficiency virus [2]. A free-base tetra sodium meso-tetra (*p*-sulphonatophenyl) porphyrin (TPPS<sub>4</sub>) and its corresponding metalloporphyrins (MTPPS<sub>4</sub>), where M = Co, Ni and Zn were synthesized and characterized by UV–visible spectroscopy, FTIR, <sup>1</sup>H nmr spectroscopy, mass spectrometry and elemental analysis. Further, TPPS<sub>4</sub>, CoTPPS<sub>4</sub>, NiTPPS<sub>4</sub> and ZnTPPS<sub>4</sub> are widely used in clinical experiments as potential sensitizers in photosensitized tumour therapy (PTT), and as colourant stabilizers in inks used in ink jet printers [3–5]. In this regard, it was felt necessary to study the sulfonated porphyrins with respect to the thermal stabilities, their decomposition temperatures and the sequence of cleavage of porphyrin rings.

## Experimental

The free-base TPPS<sub>4</sub> was synthesized by suitable method [6] and further it was subjected to purification by dry column chromatography using basic alumina as stationary phase. The mobile phase was comprised of gradient solution of water, methanol and acetone in the ratio of 7:2:1 [7]. During elution only purple fraction because of TPPS<sub>4</sub> was collected and other fractions were rejected.

Further, TPPS<sub>4</sub> was used to synthesize CoTPPS<sub>4</sub>, NiTPPS<sub>4</sub> and ZnTPPS<sub>4</sub> by independent method of synthesis as devised by us. The respective metal salt dissolved in ethanol and TPPS<sub>4</sub> were taken in stoichiometric quantities, added together with minimum amount of water and the reaction mixture was refluxed on steam bath for half an hour. It was also observed that if metal salts added were more than stoichiometric amount then concentration of green coloured dication [H<sub>4</sub>(TPPS<sub>4</sub>)<sup>2+</sup>] was correspondingly increasing. The purification of these metalloporphyrins was carried out

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using dry column chromatography as described above for TPPS<sub>4</sub>. During elution process three different coloured fractions were seen i.e. colourless fraction because of unreacted metal salt, green coloured fraction because of dication and blood red coloured fractions because of CoTPPS<sub>4</sub> and NiTPPS<sub>4</sub>, lastly violet coloured fraction for ZnTPPS<sub>4</sub> was collected. It was also observed that when metal salts used were in stoichiometric amounts then the yield of purified metalloporphyrin was in the range of 80–85%. On the contrary, when metal salts were taken more than stoichiometric quantities then the yield of the purified metalloporphyrin was around 50–60%. The purity of the above metalloporphyrins was checked on TLC using a mixture of methanol, ammonia and petroleum ether in the ratio 5:40:55.

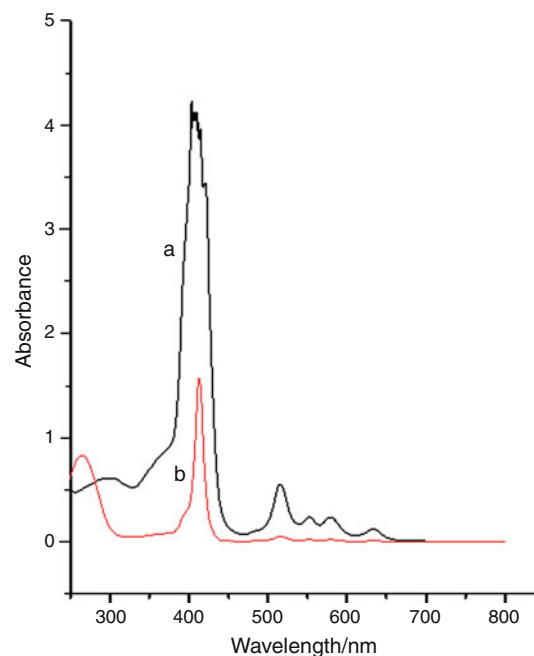
UV–visible spectra were recorded on Shimadzu visible spectrophotometer (model UV/2450 UV) using 10<sup>-4</sup> and 10<sup>-5</sup> M concentrations for each porphyrin. Infra red analysis of solid porphyrins was carried out using Shimadzu IR spectrometer (model prestige/21 FTIR). <sup>1</sup>H nmr spectra were recorded using Varian 300 MHz model. Elemental analysis were recorded on Prostar Varian C, H, N analyzer model Flash 1112 series EA. TG-DSC measurements were recorded in synthetic air from room temperature to 800 °C using NETZSCH-Geratebau GmbH Thermal Analyser (STA 409 PC) to find out thermal stability and decomposition temperature at different stages. The TG-EGA-MS results were recorded in argon atmosphere from room temperature to 900 °C. For detection of the gases and different species evolved from the sample, the mass spectrometer was calibrated for some desired gases/species as was expected from the structural information of a particular porphyrin. The temperature of the delivery tube which carries respective gases to the mass spectrometer was maintained below 125 °C.

## Results and discussion

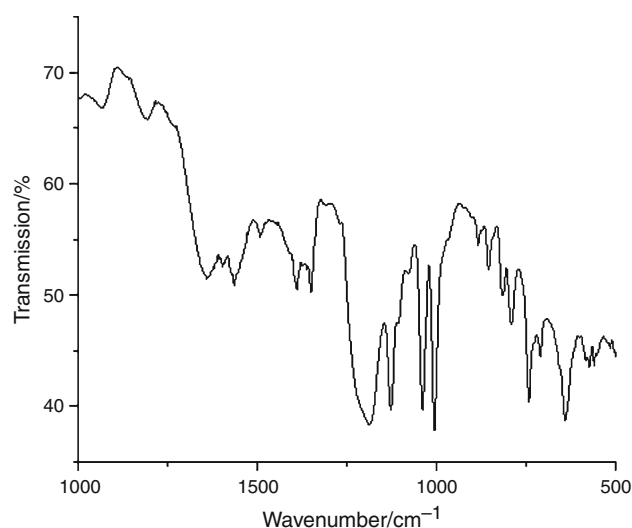
The above free-base porphyrin and metalloporphyrins were characterized by UV–visible spectrophotometry and the results were in good agreement with the literature values [8–10]. Since, the molar extinction coefficient values of porphyrins are high; therefore, very small quantity of the sample is required to prepare the solution for spectrophotometry. The concentrations of the solutions used were 10<sup>-4</sup> M and 10<sup>-5</sup> M for Q-band and Soret band, respectively. In free-base porphyrin like TPPS<sub>4</sub> the absorption band observed in Soret region is at 413 nm, others in Q-band region at 515, 552, 579 and 633 nm as shown in Fig. 1. When, free-base porphyrin TPPS<sub>4</sub> is metallated with different metals like Co, Ni and Zn number of

Q-bands are reduced to minimum because of symmetry changes from rectangular to square planar [9].

The above synthesized porphyrins were then characterized by IR spectroscopy [6, 8] and it was found that TPPS<sub>4</sub> contains bands, such as 1041, 1128 and 1184/cm which confirms substitution of SO<sub>3</sub>Na group in each of the four phenyl rings at para position. The same trend is seen in the metalloporphyrins with above metals. The IR spectrum of representative sample NiTPPS<sub>4</sub> is given in Fig. 2. In



**Fig. 1** UV–visible spectra of TPPS<sub>4</sub> a 10<sup>-4</sup> M concentration b 10<sup>-5</sup> M concentration



**Fig. 2** IR spectra of NiTPPS<sub>4</sub>

TPPS<sub>4</sub>, the band because of N–H stretching is present which is absent in metalloporphyrins, confirming the metallation.

The <sup>1</sup>H nmr spectroscopy was further used to characterize the above porphyrins. TPPS<sub>4</sub> is selected as a representative compound for the proton nmr spectrum as seen in Fig. 3. In aqueous-porphyrins like TPPS<sub>4</sub>, it is seen that ortho-phenyl protons are shifted to more down-field value as compared to pyrrole protons signal. The reason may be because of the presence of SO<sub>3</sub>Na group at para position of the phenyl ring and the ortho protons may be deshielded. Therefore, in aqueous-porphyrins *o*-phenyl protons have maximum down-field signal than  $\beta$ -pyrrole protons. This was confirmed with the results of literature value and was found to be in good agreement [8].

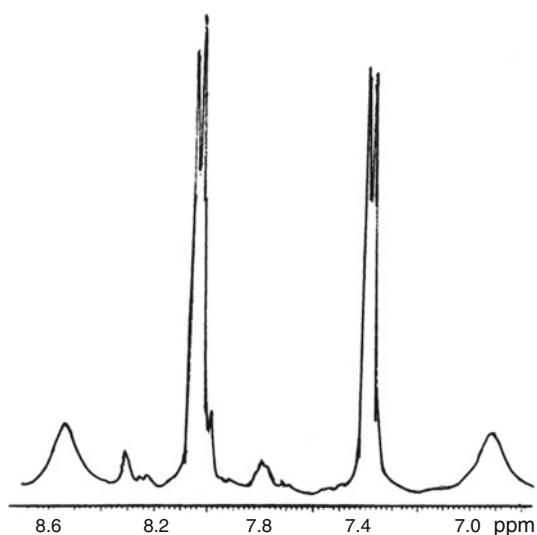


Fig. 3 Proton nmr spectra of TPPS<sub>4</sub>

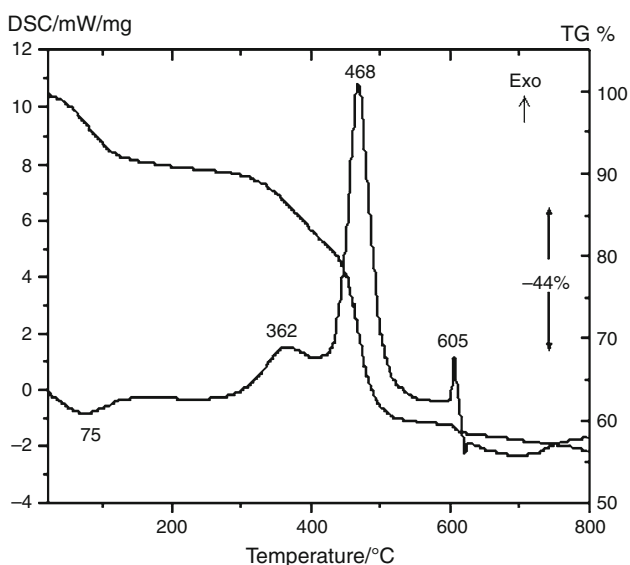


Fig. 4 TG-DSC curves of TPPS<sub>4</sub>

The molecular mass of TPPS<sub>4</sub> as a representative sample of the series was determined using High-resolution mass spectrometry. For the fixation of number of water molecules, elemental analysis for C, H and N was recorded on Prostar Varian C, H, N analyzer which gave 38.61% C, 3.62% H and 4.28% N as against 39.76% C, 3.65% H and 4.22% N expected results.

### TG-DSC measurements

Thermal studies of above porphyrins were carried out using thermogravimetry and differential scanning calorimetry in synthetic air from room temperature to 800 °C. The TG-DSC curves of TPPS<sub>4</sub>, CoTPPS<sub>4</sub>, NiTPPS<sub>4</sub> and ZnTPPS<sub>4</sub> are shown in Figs. 4, 5, 6 and 7.

TPPS<sub>4</sub> loses water of crystallization at around 75 °C and shows mass loss up to 8% as shown by broad endothermic peak given in Fig. 4. Further, it showed total mass loss up to 36% as seen by TG curve. The DSC curve of TPPS<sub>4</sub> showed first decomposition at 362 °C followed by 468 °C and 605 °C, respectively. Thus, it is seen that TPPS<sub>4</sub> decomposes in three stages. The qualitative analysis of the residue of TPPS<sub>4</sub> after thermal analysis was carried out which has shown the presence of Na<sub>2</sub>SO<sub>4</sub>. Thus, it is evident that when TPPS<sub>4</sub> is subjected to thermal analysis from room temperature to 800 °C, SO<sub>3</sub><sup>2-</sup> group from SO<sub>3</sub>Na in the compound gets oxidized to SO<sub>4</sub><sup>2-</sup> and therefore, Na<sub>2</sub>SO<sub>4</sub> is detected.

CoTPPS<sub>4</sub> showed first mass loss of 7% due to loss in water of crystallization at around 74 °C with a broad endotherm. Further, it shows 50% of mass loss due to rupture of porphyrin ring, which is shown by TG curve in

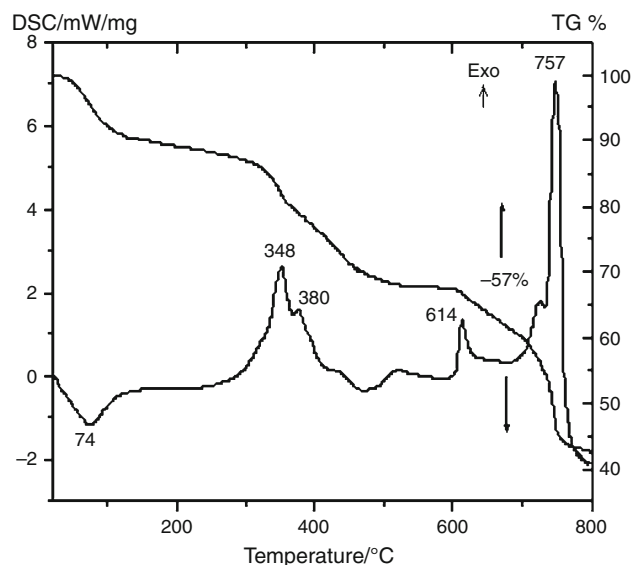
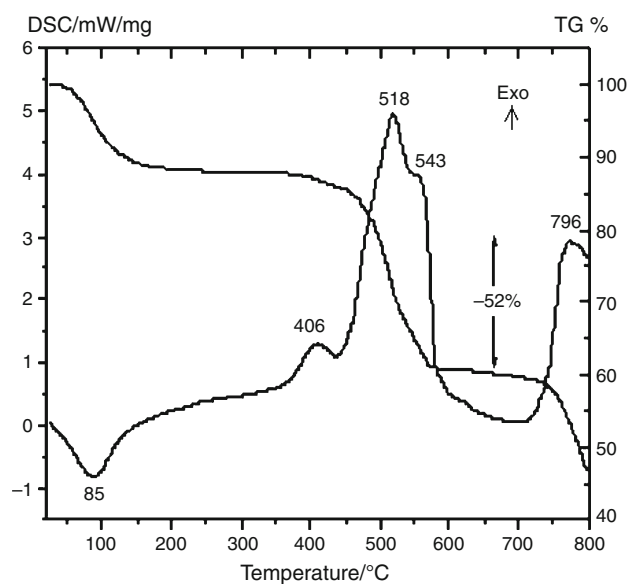
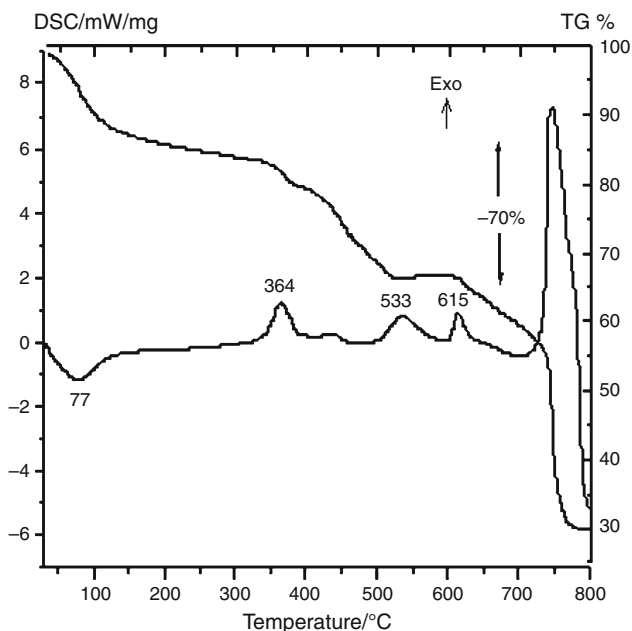


Fig. 5 TG-DSC curves of CoTPPS<sub>4</sub>



**Fig. 6** TG-DSC curves of NiTPPS<sub>4</sub>



**Fig. 7** TG-DSC curves of ZnTPPS<sub>4</sub>

Fig. 5. The DSC curve shows four decomposition temperatures at 348, 380, 614 and 757 °C, respectively. When NiTPPS<sub>4</sub> was subjected to thermal analysis, the TG curve shows total 52% of mass loss including that of loss because of water of crystallization at around 85 °C as shown in Fig. 6. The corresponding decomposition temperatures are seen in four different stages at 406, 518, 543 and 796 °C, respectively. The TG DSC curve of ZnTPPS<sub>4</sub> is shown in Fig. 7. It is seen that TG curve shows 10% loss because of water of crystallization and remaining 60% loss because of rupture of porphyrin ring. The DSC curve of ZnTPPS<sub>4</sub>

shows four decomposition temperatures at 365, 533, 615 and 748, respectively.

These exothermic peaks may be because of detachment and decomposition of sulphate group from phenyl rings, rupture and detachment of metal from pyrrole rings in case of metalloporphyrins, rupture of cleavage of phenyl rings and finally, the decomposition of remaining organic fragments. When the residues of all metalloporphyrins were subjected for qualitative analysis, they showed the presence of respective metal oxides and coal [11] in addition to Na<sub>2</sub>SO<sub>4</sub>. As the base line correction was not done every time or up to the mark, as a result instrument may show some error in the mass loss. The decomposition temperature varies based on bond strength, type of metal substitution and bond energy. Depending up on the first decomposition temperatures, the sequence of thermal stability for the above porphyrins obtained as NiTPPS<sub>4</sub> > ZnTPPS<sub>4</sub> > TPPS<sub>4</sub> > CoTPPS<sub>4</sub>. The magnetic measurements have shown that NiTPPS<sub>4</sub>, ZnTPPS<sub>4</sub> and TPPS<sub>4</sub> are diamagnetic in nature, whereas CoTPPS<sub>4</sub> is paramagnetic in nature. This indicates that characteristic role of each transition metal in assigning the different thermal stability to each type of porphyrins.

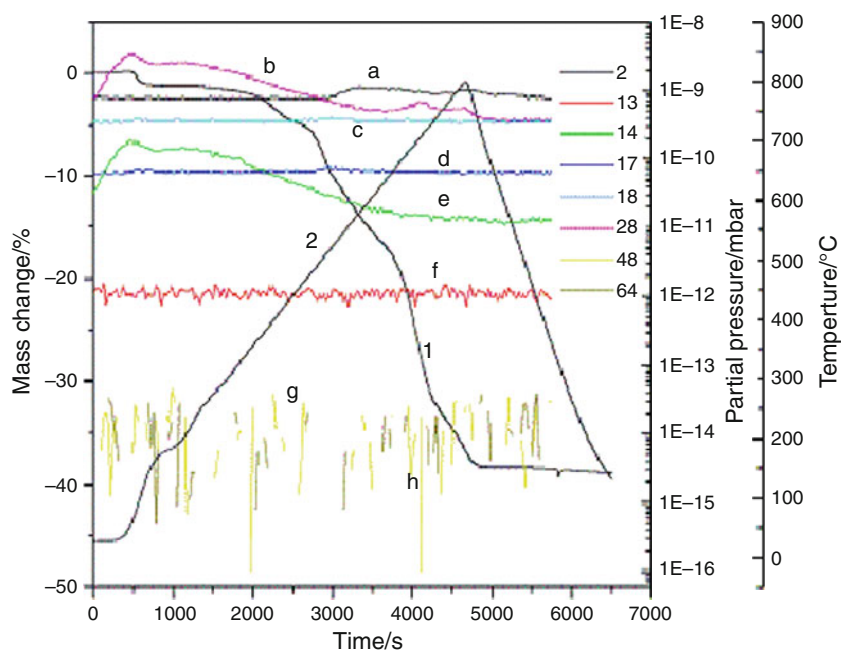
### TG-EGA-MS studies

In this type of study, thermogravimetry and consequently number of evolved gases or organic species which are recorded by mass spectrometer within a selected temperature range are detected [12]. Therefore, depending upon the structure of the selected compound, the mass spectrometer is calibrated for corresponding gases or organic species. With regards to this study, there is a possibility that because of condensation of some of the gases or species in the delivery tube they may not be recorded even though they are present. TG-EGA-MS studies of TPPS<sub>4</sub> and CoTPPS<sub>4</sub> were conducted in argon atmosphere from room temperature to 900 °C.

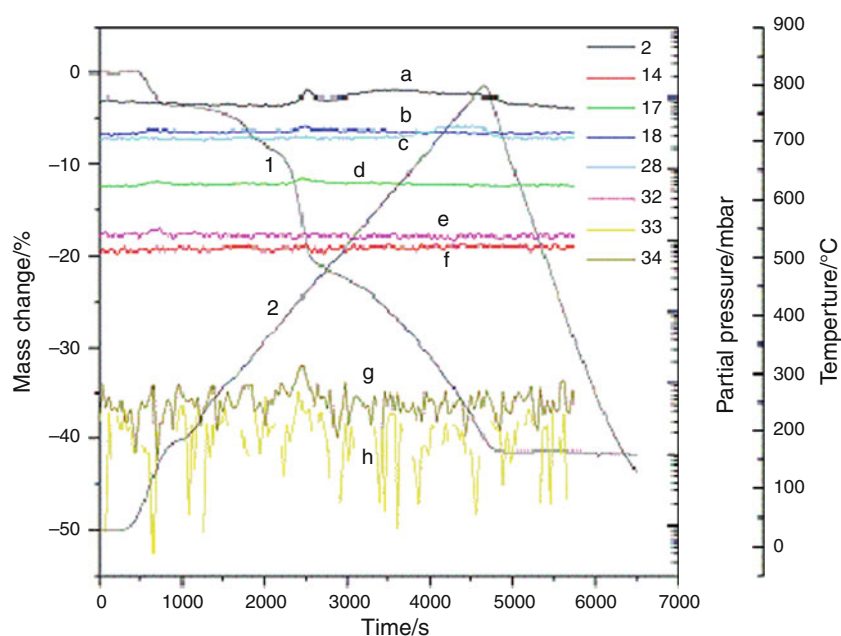
TG-EGA-MS curves for TPPS<sub>4</sub> are shown in Fig. 8. It is seen that various gases and species are evolving during the thermal events. The first species evolved is CH<sub>2</sub>/N within a temperature range of 50–250 °C. Subsequently, NH<sub>3</sub> and H<sub>2</sub>O are detected within 50–500 °C. Further, C<sub>2</sub>H<sub>4</sub>/N<sub>2</sub> is seen evolved from 50 to 750 °C followed by H<sub>2</sub> gas from 450 to 725 °C, respectively.

The TG-EGA-MS curves for CoTPPS<sub>4</sub> are shown in Fig. 9. It is observed that the various gases and species evolved are matching with that of TPPS<sub>4</sub>. The amount of CH<sub>2</sub>/N seems to be a minor quantity from 50 to 250 °C, followed by NH<sub>3</sub> and H<sub>2</sub>O from 50 to 500 °C, respectively. Further, C<sub>2</sub>H<sub>4</sub>/N<sub>2</sub> show evolution within 50–750 °C and H<sub>2</sub> from 450 to 725 °C. Since, both the compounds viz. TPPS<sub>4</sub>

**Fig. 8** TG-EGA-MS of TPPS<sub>4</sub>, 1 TG curve, 2 Temperature curve, a H<sub>2</sub>, b C<sub>2</sub>H<sub>4</sub>/N<sub>2</sub>, c H<sub>2</sub>O, d NH<sub>3</sub>, e CH<sub>2</sub>/N, f CH g SO, i SO<sub>2</sub>



**Fig. 9** TG-EGA-MS of CoTPPS<sub>4</sub>, 1 TG curve, 2 Temperature curve, a H<sub>2</sub>, b H<sub>2</sub>O, c C<sub>2</sub>H<sub>4</sub>/N<sub>2</sub>, d NH<sub>3</sub>, e S, f CH<sub>2</sub>/N, g SH, h H<sub>2</sub>S



and CoTPPS<sub>4</sub> contain SO<sub>3</sub>Na groups, therefore, as a representative CoTPPS<sub>4</sub> was calibrated for S, SH and H<sub>2</sub>S for signals in mass spectrometer. It was observed that species S is evolved from 50 to 200 °C, SH from 50 to 450 °C and H<sub>2</sub>S from 50 to 450 °C, respectively.

The comparative study of TPPS<sub>4</sub> and CoTPPS<sub>4</sub> showed that the same species or gases evolve at the same temperature range in both the compounds. In the context of hydrogen gas, the first peak may be because of rupture of bonds between carbon and pyrrole protons whereas second peak may be because of phenyl protons. The reason is that as compared to phenyl ring, pyrrole ring is less aromatic

and it being heterocyclic ring can be comparatively easily ruptured. This makes pyrrole proton to detach first followed by phenyl protons. Thus, EGA-MS analysis is helpful in giving information of rupture of the porphyrin macrocycle sequentially.

## Conclusions

These porphyrins showed thermal stability up to around 350 °C. The free-base TPPS<sub>4</sub> do not show complete loss in mass in TG-DSC measurements because of formation

Na<sub>2</sub>SO<sub>4</sub> and coal. The metalloporphyrins of Co, Ni and Zn showed presence of respective metal oxides after TG-DSC measurements. The TG-EGA-MS analysis throws light on the evolution of gases and different organic species depending upon the structure of the respective porphyrins. In the above selected porphyrins, viz TPPS<sub>4</sub> and CoTPPS<sub>4</sub>, it is also seen that the evolution of gases or species such as H<sub>2</sub> (2), CH<sub>2</sub>/N (14), C<sub>2</sub>H<sub>2</sub>/N<sub>2</sub> (28), NH<sub>3</sub> (17) and H<sub>2</sub>O (18) are common and their corresponding evolution temperatures are also the same. All sulphur species are evolved from 50 to 450 °C. Therefore, this gives the information about the sequence of rupture of cleavages of the porphyrin ring during the course of thermal analysis.

**Acknowledgements** Authors are grateful to P.K. Ajikumar and Dr. A.K. Tyagi, IGCAR- Kalpakam, India, for TG-EGA-MS facility and UGC-New Delhi for the financial support.

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