

Thermal Studies of some non-Aqueous and aqueous porphyrins

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Abstract

A precursor of non-aqueous porphyrin i.e. a free-base tetra phenyl porphyrin (TPP) was synthesized. This was then subjected to sulphonation in such a way that sodium salt of sulphonic acid groups were substituted at the para position (4-position) of four phenyl rings in TPP to get tetra sodium meso-tetra (p-sulphonatophenyl) porphyrin (TPPS₄). Further, Co²⁺ was inserted in TPP and TPPS₄ and all compounds were characterized by UV- visible spectroscopy, IR spectroscopy and ¹H NMR spectroscopy. Subsequently, these compounds viz. TPP, CoTPP, TPPS₄ and CoTPPS₄ were subjected to TG-DSC analysis in synthetic air from ambient temperature to 800 °C. When sulphonic acid groups were substituted at the para- positions on the four phenyl rings of the aqueous porphyrins, it was observed that their thermal stability was reduced in comparison with non-aqueous porphyrins.

Introduction

Generally, it is seen that porphyrins, metalloporphyrins and their derivatives are non-toxic in nature and especially are used in molecular electronics. They possess remarkable oxidation and reduction chemistry that potentiates their use as wires, switches, transistors, junctions and photodiodes [1]. Further, synthetic porphyrin chemistry is extensively extended to homogeneous and heterogeneous photocatalysis [2, 3, 4]. Thermal analysis is used to verify the

thermal stabilities of these porphyrins so that they can be safely used for various catalytic or photocatalytic processes in the required temperature range.

Experimental

The non-aqueous free-base TPP was synthesized by suitable method [5] and a metal Co^{2+} was inserted in a porphyrin ring to get CoTPP by established method [6]. Both of these compounds were purified by dry column chromatography using silica gel as a stationary phase and AR grade CHCl_3 as a mobile phase.

The aqueous free-base porphyrin TPPS₄ was synthesized by suitable method [7] and a metal Co^{2+} was introduced in the porphyrin ring by independently devised method and CoTPPS₄ was obtained. These compounds were purified by dry column chromatography using basic alumina as a stationary phase and water, methanol and acetone in the ratio of 7:2:1 as mobile phase.

The porphyrins and metalloporphyrins synthesized above were characterized by UV-Visible spectroscopy, IR spectroscopy and ¹H NMR spectroscopy. The thermal studies of these compounds were carried out in synthetic air using NETZSCH-Geratbau GmbH thermal analyzer (STA 409PC) from ambient temperature to 800 °C.

Results and discussions

The above synthesized porphyrins viz TPP, CoTPP, TPPS₄ and CoTPPS₄ were characterized by UV-Visible spectroscopy, where Soret bands and Q-bands were compared with literature values and confirmed. Similarly, IR spectroscopy and ¹H NMR spectroscopy were used and the above synthesized compounds were confirmed.

When Fig.1 and Fig. 2 are compared it is observed that TPPS₄ loses its water of crystallization shown by broad endotherm at 74.5 °C and shows 7.7% loss which confirms its formula as TPPS₄.5H₂O. Further, when TPP and TPPS₄ are compared, it is evident that four exotherms in TPP at 432 °C, 472 °C, 546 °C and 719 °C and three exotherms in TPPS₄ at 362 °C, 468 °C, and 605 °C are observed. This reveals one fact that when sodium salt of sulphonic

acid is substituted at four para- positions of the four phenyl rings in TPP, then TPPS₄ is obtained. Thus due to substitution of SO₃Na, thermal stability of TPPS₄ has decreased as compared to TPP. The first reason for this may be attributed to the fact that due to SO₃Na group the molecule becomes bulky in nature and the bonds present between C – N are weakened. This further results in the fragmentation of pyrrole rings, with the evolution of species such as H₂, CH₂, C₂H₄ confirmed by TG-EGA-MS [8].

When Fig.3 and Fig. 4 are compared it is observed that CoTPPS₄ loses water of crystallization at around 74 °C and shows weight loss of 8.0 % , which confirms the formula of CoTPPS₄.5H₂O. It is also observed that CoTPP shows four decomposition exotherms at 413 °C, 435 °C, 502 °C, and 574 °C whereas CoTPPS₄ shows five decomposition exotherms at 351 °C, 366 °C, 520 °C, 612 °C, and 748 °C with 50% loss. As discussed above, in the similar way, decomposition temperatures of CoTPPS₄ are on lower range than CoTPP for the same reason. It can be also observed that TPP, CoTPP are nearing to the 95% – 100% loss whereas TPPS₄ and CoTPPS₄ show the per cent loss in the range of 43% - 50%. The reason is qualitative analysis of TPP and CoTPP has shown the presence of only respective metal oxides whereas TPPS₄ and CoTPPS₄ have shown presence of Na₂SO₄ in addition to the respective metal oxides. Fig.5 shows the first decomposition temperature of each of the porphyrin and Table 1 gives the details of the values of the first decomposition maximum temperature.

Conclusion

When SO₃Na group is substituted at four para - positions of the phenyl rings in free-base porphyrin(TPP) or metalloporphyrin (CoTPP), the decomposition temperature range of aqueous porphyrins (TPPS₄, CoTPPS₄) is lowered than non-aqueous porphyrins (TPP, CoTPP). The percent loss in weight of aqueous-porphyrins is far less than non-aqueous porphyrins, since in aqueous porphyrins Na₂SO₄ is formed in addition to respective metal oxides.

References

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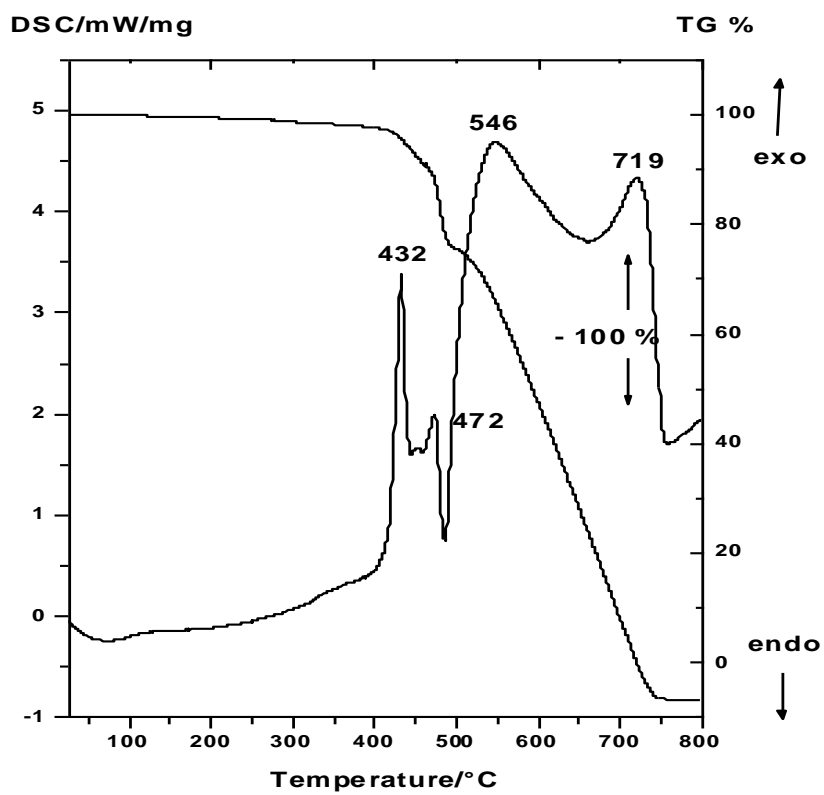


Fig.1 TG/DSC curve for TPP

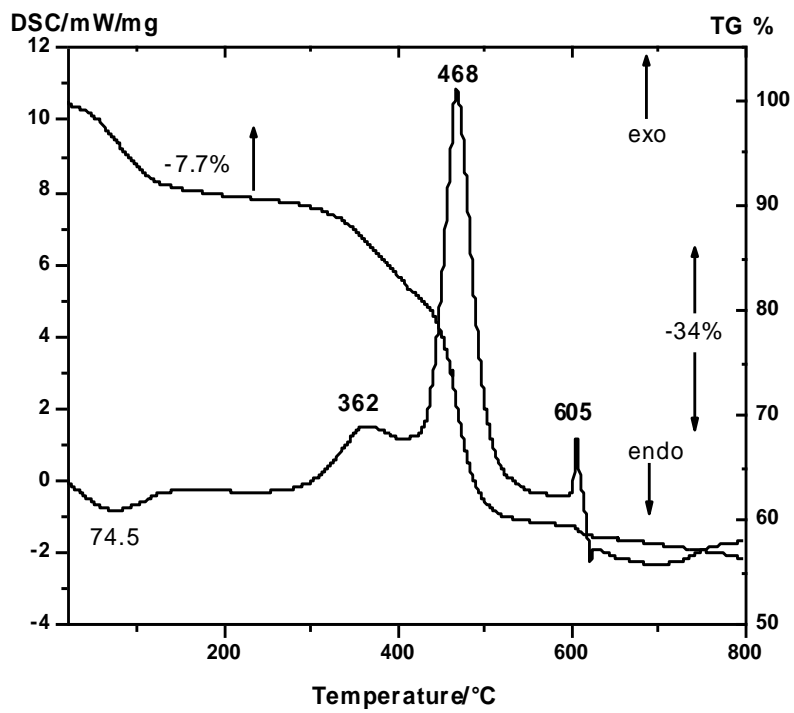


Fig.2 TG/DSC curve for TPPS₄

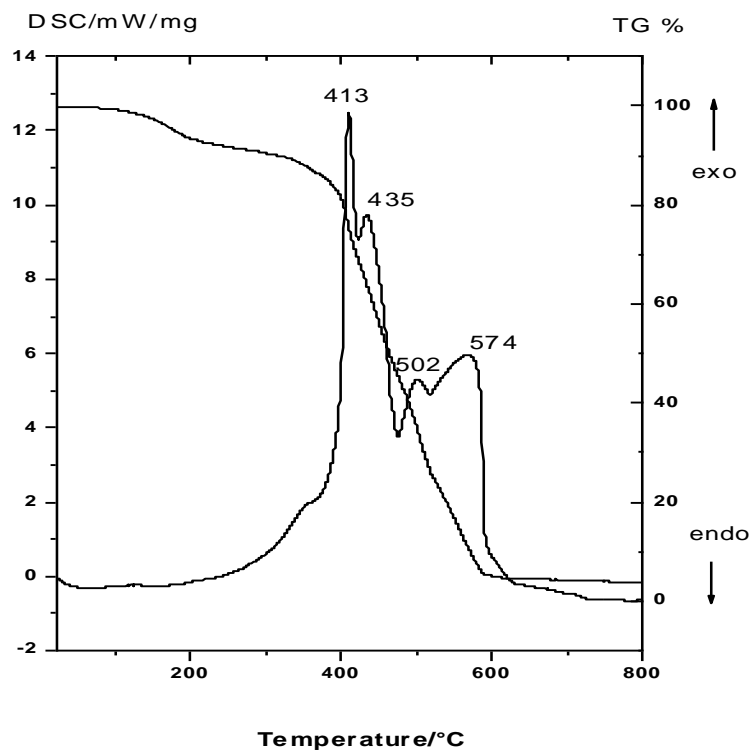


Fig.3 TG/DSC curve for CoTPP

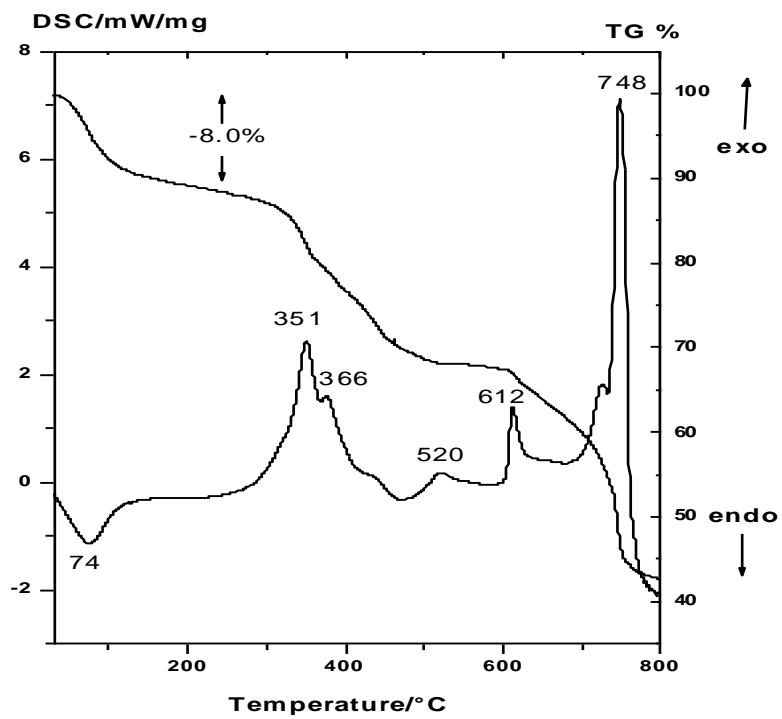


Fig.4 TG/DSC curve for CoTPPS₄

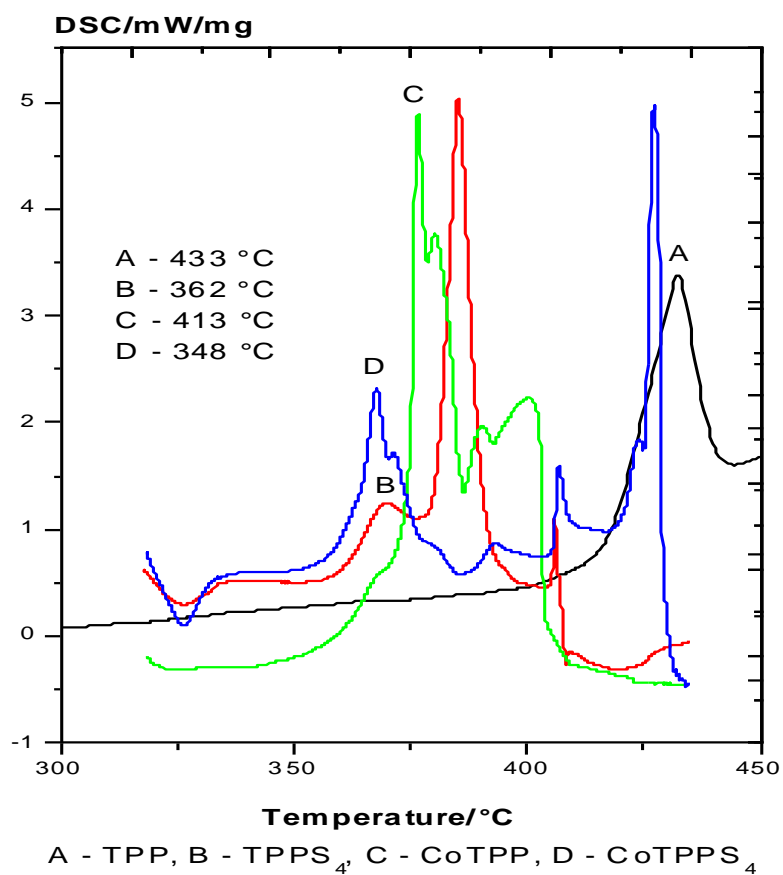


Fig.5 First decomposition temperatures of porphyrins

Table 1 First decomposition onset temperatures for porphyrins

Compound	First decomposition maximum temperature (°C)
TPP	432
TPPS ₄	362
CoTPP	413
CoTPPS ₄	351