



Photoluminescence and photocatalytic degradation studies on some metallophthalocyanines

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ABSTRACT

This paper deals with the up-conversion intrinsic photoluminescence by exciting the Metallo-Phthalocyanine (MPC) prepared by melt method. MPCs were further characterized using UV visible spectrophotometer, FT-IR, and thermal analysis. The magnetic susceptibility, optical absorption and photoluminescence behavior of these compounds were studied. Photocatalytic degradation of amido black 10B dye using different MPCs at varying pH was done to see the efficiency of these compounds. High emission intensity and easy preparation makes these systems potential candidates for application as luminescent material.

1. Introduction

Metallo-Phthalocyanine (MPC) is a metal organic compound with four pyrrole like sub units linked to form symmetrical 18 π -electron aromatic macrocycle, closely related to the naturally occurring porphyrins. Like the porphyrins, the Pc macrocycle can play host to several different metal ions in its central cavity. MPCs are attractive as semiconductor catalysts for organic reactions like oxidations, coupling and ability to absorb oxygen as well as thermal stability [1-4].

The discharged wastes containing dyes, pigments, effluents etc are toxic to microorganism, aquatic life and human beings. Therefore, it is essential to degrade these wastes to safe fragmented products. Extensive research is underway to develop advance physicochemical and photocatalytic methods for the elimination of hazardous chemical wastes from water and soil. Semiconductor photocatalysis have attracted a special attention in the degradation of organic wastes and possible application to water pollution control using solar energy [5-8].

MPCs are highly photosensitive, trap light energy and this energy is used for the degradation of chemical wastes [9,10]. MPCs are excited on shining light and when anchored on TiO₂ or WO₃ are much more effective catalyst on irradiation [11,12]. The degradation of textile azo dyes has been studied by many investigators [13-16]. In the present work, the photocatalytic degradation of amido Black 10B over some MPCs and photoluminescence studies have been discussed. Photoluminescence properties make their application important in optical recording [17-19]. Different methods are reported for the synthesis of MPC [20-23] and here melt method for the preparation of the same was adopted. Different methods of preparations also bring about change in properties and photocatalytic activities.

2. Experimental

2.1. Instrumentation

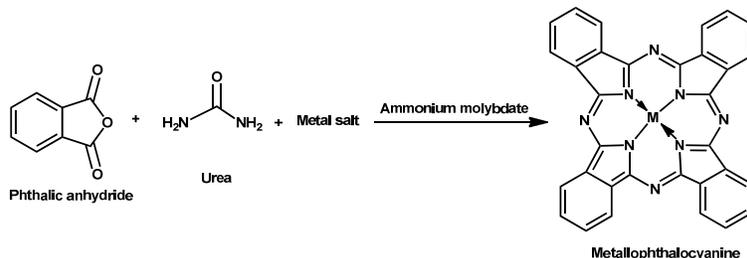
UV-visible spectra were recorded on Shimadzu UV-visible spectrophotometer (model UV/2450 UV). IR analysis of solid phthalocyanines was carried out using Shimadzu IR spectrometer (model Prestige/21 FTIR). TG-DSC measurements were done using NETZSCH-Geratebau GmbH Thermal Analyzer (STA 409 PC) to find out the thermal stability and the decomposition temperature at different stages. Magnetic susceptibility was done on a Gouy balance at room temperature employing a field of the order 8000 Gauss using Hg[Co(SCN)₄] as a standard material. Photoluminescence studies for the solid samples were carried out using Shimadzu Spectrofluorometer (model RF-5301PC) with xenon flash lamp. The samples were loaded on a powder sample holder. Photocatalytic degradation was studied using dye Amido Black 10B which has a λ_{max} 617-619 nm using MnPc, CoPc, NiPc, CuPc and ZnPc as photocatalysts. This study was carried out at different pH i.e. neutral (pH=7), alkaline (pH=8) and acidic (pH=6) in closed glass reactor.

2.2. Synthesis

All chemicals were of analytical grade and used without further purification. 7.50 g Phthalic anhydride, 15.00 g urea, 0.25 g ammonium molybdate and weighed amount of metal salt (one mole per 4 moles of phthalic anhydride) were taken in a clean and dry beaker. These chemicals were properly mixed and heated on sand bath for 1 hour. The hot product obtained was allowed to attain room temperature and was then heated for about 15-20 minutes on the water bath in presence of 1 N HCl, which was filtered and again heated on a water bath with

Table 1. Show UV-visible absorption (λ_{\max}), thermal decomposition temperature, magnetic susceptibility (χ_g), μ_{eff} and number of unpaired electrons.

Compound	λ_{\max} (nm)	Decomposition ($^{\circ}\text{C}$)	χ_g (cgs unit)	μ_{eff} (BM)	No. of unpaired electrons
MnPc	719	387	13.2×10^{-6}	4.2	3
CoPc	658	432	5.65×10^{-6}	2.8	2
CuPc	672	314	2.60×10^{-6}	1.9	1
NiPc	666	438	Diamagnetic	-	-
ZnPc	661	402	Diamagnetic	-	-

**Scheme 1**

1 N NaOH for 15-20 minutes and filtered. These washings were given in-order to remove any acid or base soluble impurities. The product obtained was thoroughly washed with distilled water to remove any traces of base if remaining. The final washing was done using little amount of methanol. The product obtained was dried in an oven for 2 h at 150°C . The product obtained was grounded to fine powder in agate mortar. The preparation of the compounds such as manganese phthalocyanine (MnPc), cobalt phthalocyanine (CoPc), nickel phthalocyanine (NiPc), copper phthalocyanine (CuPc) and zinc phthalocyanine (ZnPc) is given in [Scheme 1](#).

3. Results and discussion

3.1. UV-Visible spectroscopy

A sharp Q-band is observed between 600 to 700 nm and B bands are observed at around 350 nm. The λ_{\max} observed is shown in [Table 1](#).

3.2. FT-IR spectroscopy

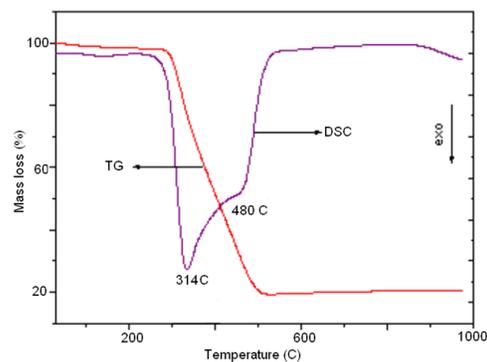
The energy required for the stretching vibration is more and the bands are seen in the region $4000\text{-}1600\text{ cm}^{-1}$ whereas the energy required for bending vibration is less and bands appear in the region from $1600\text{-}400\text{ cm}^{-1}$. $1121\text{-}1123$, $1090\text{-}1095$, $1067\text{-}1070$, $947\text{-}949$, $872\text{-}885$ and 754 cm^{-1} are due to phthalocyanine skeletal vibration. $1286\text{-}1290\text{ cm}^{-1}$ is due to C-N stretching, $900\text{-}905\text{ cm}^{-1}$ is due to C-N bending, $1332\text{-}1335$ and $1419\text{-}1425\text{ cm}^{-1}$ are due to aromatic phenyl ring, $1610\text{-}1616\text{ cm}^{-1}$ is due to C=C, C=N and ring stretching, $770\text{-}730\text{ cm}^{-1}$ is due to C-H out of plane bending, 1165 cm^{-1} is due to C-H in plane bending vibration. All these absorption bands were observed in these compounds.

3.3. Thermal analysis

MPCs are very well known for their good thermal stability compared to other metal organic compounds and this stability leads to their wide applications of these compounds. The thermal stability data is shown in [Table 1](#), they start decomposing above 300°C as seen in the representative [Figure 1](#).

3.4. Magnetic susceptibility

The magnetic measurements were done at room temperature. A field of order 8000 gauss was employed and sensitive analytical balance was used to measure the difference in weight. The field was recorded before and after the application of the magnetic field. The procedure was repeated for the other samples whose χ_g was determined. Manganese phthalocyanine, cobalt phthalocyanine and copper phthalocyanine were found to be paramagnetic with around 3, 2 and 1 unpaired electrons respectively, whereas nickel phthalocyanine, and zinc phthalocyanine are diamagnetic. The magnetic susceptibility data is given in [Table 1](#). Higher or lower values of μ_{eff} indicate the contribution of direct or super exchange intermolecular interaction to spin only value. Difference in magnetic moment values and their variation may be due to the difference in intermolecular interactions, spacing and inclination of the molecule in the crystal lattice.

**Figure 1.** TG/DSC thermogram of representative sample CuPc.

3.5. Photoluminescent studies

The luminescence properties of the materials were studied by analyzing the photoluminescence spectra of the material in the visible region from 400-800 nm. The photoluminescence spectra and the corresponding excitation spectra were recorded at the room temperature using Shimadzu RF-5301 PC Spectrofluorometer with Xe flash lamp. The sample was loaded on a powder sample holder.

[Figures 2, 3](#) and [4](#) show the photoluminescence spectra. Samples on excitation with the wavelength of 220 nm show emission in blue-green region i.e. from 430-550 nm. All the

samples showed same spectra with several emission lines in blue green region showing maximum emission at 468 nm. Presence of several intrinsic levels in the conduction bands gives this complex spectrum. Influence of transition metals resulted in different intensities. The emission intensity of cobalt phthalocyanine is maximum followed by zinc phthalocyanine, copper phthalocyanine, nickel phthalocyanine and manganese phthalocyanine. Presence of 2 unpaired electrons may be the probable reason for cobalt phthalocyanine showing the highest intensity. Zinc phthalocyanine, copper phthalocyanine and nickel phthalocyanine show low intensity because non radiative processes occurring are more than the radiative processes. Manganese phthalocyanine shows the least intensity in blue-green region and also it shows emission in the green region (550-600 nm). This observation may be attributed to presence of manganese in more than one oxidation state and also the unpaired electrons are shared by two oxidation states which results in decrease in the intensity.

The excitation pattern observed is in the range of 220-240 nm and the intensity is similar to that observed as in emission spectra.

Up-conversion is observed in all the samples by keeping the slit width same. Sample was excited with different wavelength in the range 580-650 nm, of which 625 nm showed the up-conversion at 440-550 nm with maximum intensity. The up-conversion pattern was similar to that of excitation at 220 nm emission pattern indicating that in both the cases emission centers are same. The up-conversion process may be explained by anti stokes two photon theory i.e. when the samples are irradiated at 625 nm the first photon pumps the electron from the conduction band to the intermediate level and the second photon ionizes it to the conduction. When the electrons are recaptured or transfer energy in the valence band, intrinsic emission occurs and while the recombination or transfer of energy in the intermediate level gives the emission at lower wavelength.

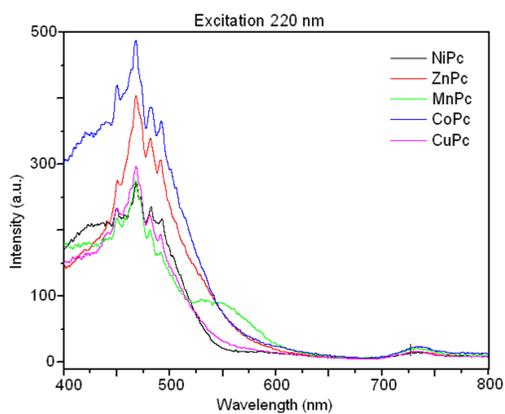


Figure 2. Emission spectra keeping excitation at 220 nm.

3.6. Photocatalytic studies

A 100 mL 10^{-5} M solution of the dye was prepared and oxygenated by bubbling with oxygen for 5 minutes. The 20 mg of the MPc catalyst was added to that 100 mL solution and then transferred to air tight glass reactor for photolysis. The solutions were then irradiated under solar radiation between 11.00 to 15.00 hours. The degradation of each solution was recorded at different time interval i.e. irradiation after 1 h, 2 h, 3 h, and 4 h using UV-visible spectrometer by monitoring the absorbance of the dye solution.

Similar procedure was repeated in alkaline medium wherein dye solution was made alkaline by adding drop wise 0.5 N NaOH till pH=8. Similarly, dye solution was made acidic by adding 0.5 N HNO_3 till pH=6. Figures 5, 6 and 7 represent the

degradation of dye Amido Black10B in neutral, alkaline pH=8 and acidic pH=6 respectively at different interval of time.

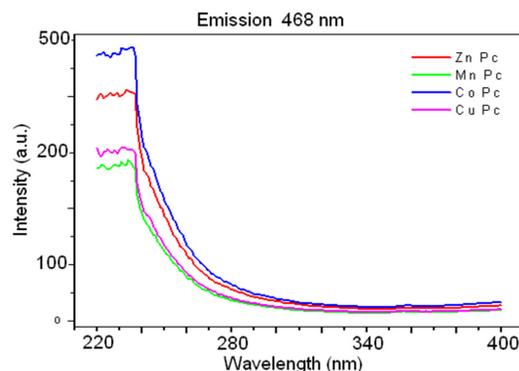


Figure 3. Excitation spectra keeping emission at 468 nm.

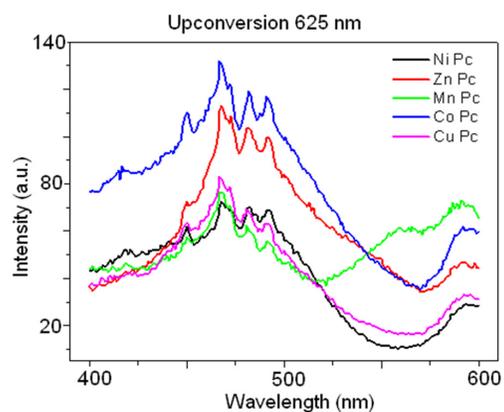


Figure 4. Up-conversion luminescence with excitation wavelength at 625 nm.

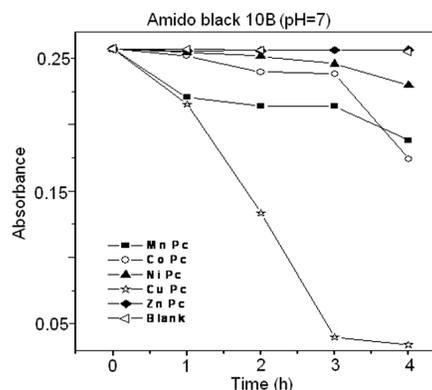


Figure 5. Absorbance of Amido Black 10B on photocatalytic degradation with time at neutral pH in aqueous media.

In neutral pH=7 copper phthalocyanine showed good catalytic activity as compared to other phthalocyanines. Manganese phthalocyanine and cobalt phthalocyanine showed less photo-catalytic activity whereas zinc phthalocyanine and nickel phthalocyanine did not show any appreciable degradation of the dye.

In alkaline pH=8 copper phthalocyanine retained its activity as that in neutral pH. The catalytic activity of manganese phthalocyanine and cobalt phthalocyanine increased in alkaline medium but no degradation of dye was

observed in presence of nickel phthalocyanine and zinc phthalocyanine.

In acidic pH=6, copper phthalocyanine showed the good rate of dye degradation. Manganese phthalocyanine showed increase in activity than in neutral pH but cobalt phthalocyanine showed less activity. There was no effect of pH on nickel phthalocyanine and zinc phthalocyanine as it did not show any activity. The CuPc, MnPc and CoPc are paramagnetic with unpaired electrons and show photocatalytic activity for dye degradation in all three pH values, whereas ZnPc and NiPc did not show activity. The ZnPc and NiPc are diamagnetic which have no unpaired electrons as a result may not generate sufficient electrons in conduction band and holes in valence band suffering degradation process.

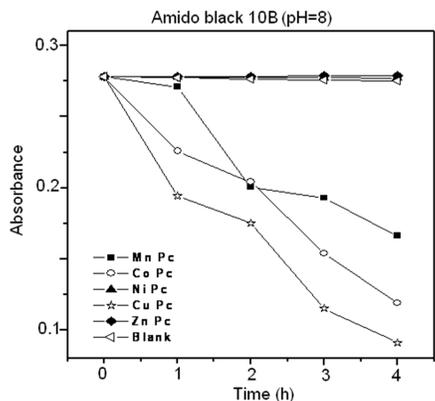


Figure 6. Absorbance of Amido Black 10B on photocatalytic degradation with time at pH 8 in aqueous media.

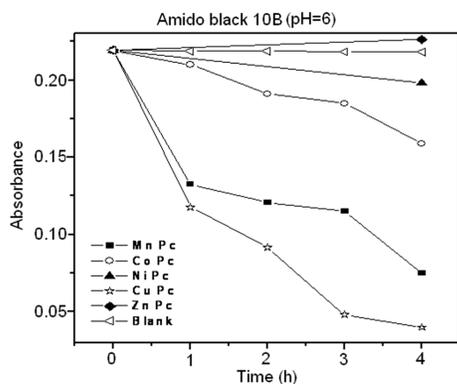
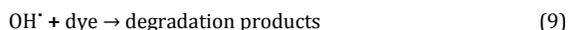
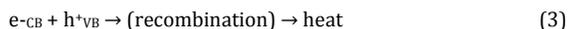


Figure 7. Absorbance of Amido Black 10B on photocatalytic degradation with time at pH 6 in aqueous media.

These compounds are known to be wide band gap semiconductors. Equation 1-9 shows the probable photocatalytic reaction pathways similar to reported by others [13,24,25]. Solar light when shines on MPC molecule get excited to MPC* and electron transfer takes place from valence band to conduction band (e_{-CB}) and hole is created in the valence band (h^+_{VB}). The e_{-CB} is the active site for O_2 adsorption because of force of attraction, whereas the h^+_{VB} is the site for adsorption for electron rich species such as OH^- ion. This electron (e_{-CB}) is then trapped by O_2 forming O_2^- as seen in equation (4). This O_2^- reacts with water to generate OH^- ions which attack the positive holes (h^+_{VB}) to give OH^\cdot radicals as indicated in equations (5) and (6). These OH^\cdot radicals attack the adsorbed dye leading to the degradation of the dye.



4. Conclusion

Magnetic susceptibility studies showed manganese phthalocyanine, cobalt phthalocyanine and copper phthalocyanine to be paramagnetic whereas nickel phthalocyanine, and zinc phthalocyanine to be diamagnetic. Photoluminescence studies suggested up-conversion at 468 nm by exciting with 625 nm. The intensity of the spectra is influenced by the transition metal. The phenomenon called as diamagnetic quenching is observed in phthalocyanines, which decrease the intensity of the spectra. Up-conversion observed confirms phthalocyanines to be good photosensitive. In photocatalytic studies of dye degradation at different time interval and in different pH conditions, copper phthalocyanine showed very good photo-catalytic activity as compared to other phthalocyanines.

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