Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **4(11),** 1-4, November **(2014)** *Res. J. Chem. Sci.*

From the Editor's Desk

Pilgrimage of Phthalocyanine Macromolecule (PART-VI)
Preparation of Pentamer Phthalocyanines (Through Nemi's Half Salt Method)

Jain N.C.
Our editor, Research Scientist, Department of Chemical Sciences, Maharaja Ranjit Singh College of Professional Sciences, Indore, INDIA

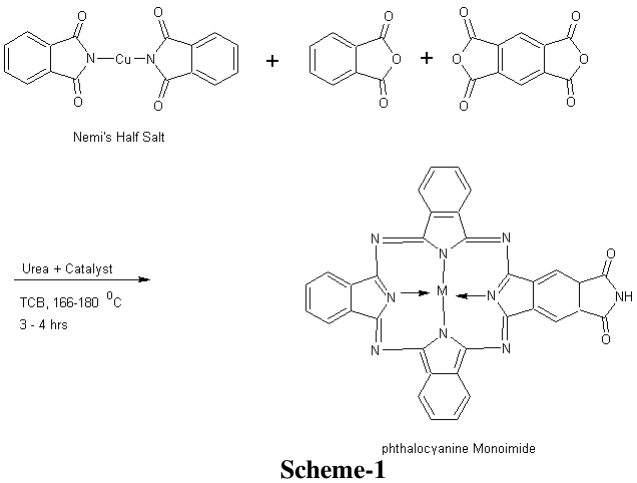
Available online at: www.isca.in, www.isca.me

Introduction

I have already described the preparation of some linear phthalocyanine derivatives in extension and conformation of our Nemi's half salt method (Part V). Presently me and my collogues, Dr. Dipak Sharma, and Dr. Lal kumar have prepared few pentamer sheet phthalocyanine derivatives. Here also, we have used our Nemi's half salt method to initiate our chemical steps in each of three preparative series.

Series I: Preparation of Unsubstituted pentamer phthalocyanine macromolecules: this preparation was done in two steps.

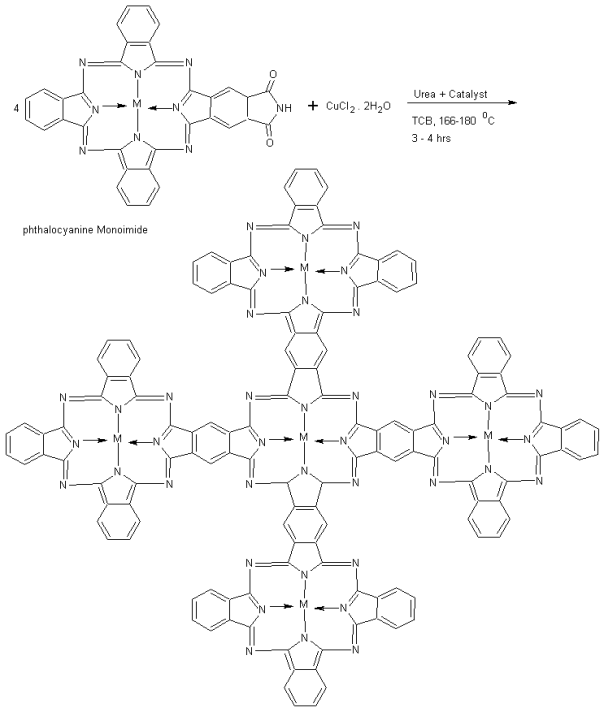
Step Ia: Preparation of phthalocyanine monoimide: One molar equivalent of Nemi's half salt was heated with one molar equivalent of Pyromellitic anhydride and one molar equivalent of phthalic anhydride in the usual Wyler's method of phthalocyanine



Scheme-1
Pc formation

After completion of the reaction, the phthalocyanine mono imide formed is filtered under suction on a Buckner funnel, washed with 10 ml of fresh TCB and 2 x 10 ml quantities of methanol, refluxed with 100 ml MeOH and filtered under suction to remove the remaining TCB and miner soluble material. The imide formed was used in the second steps without purification.

Step Ib: Preparation of pentamer phthalocyanine sheet polymer: Four molecular equivalent quantities of the above Pc imide were tetra cyclized with one molar equivalent of copper chloride by the Wyler's Urea Method of Pc formation

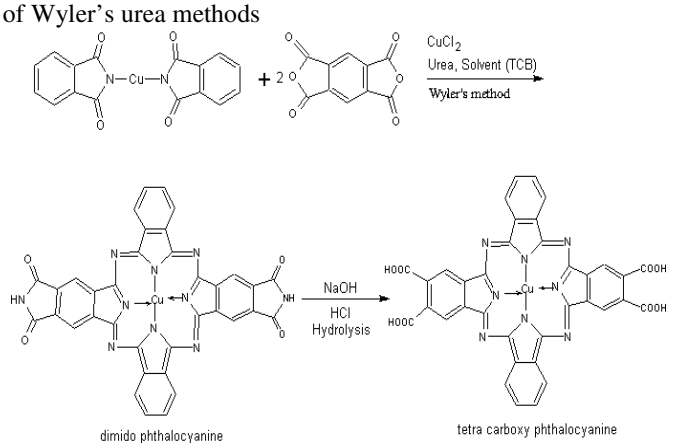


Scheme-2
Pentamer phthalocyanine macromolecule

The starting imide monomer phthalocyanine was dark green in colour while the pentamer phthalocyanine macromolecule gained a dark blue colour after completion of tetramerisation. Because there was no substitution on any of the benzenoid moiety of the pentamer phthalocyanine macromolecule, this was acid pasted by dissolving it in Conc. H_2SO_4. The thick solution in Conc. H_2SO_4 was then drowned in distilled water in a beaker with stirring. The blue pentamer phthalocyanine comes out in the form of a very shining picock blue material. The yields in the first and the second steps come around 80-85%.

Series II: Preparation of tetraimido symmetrical pentamer phthalocyanine (A): Preparation here was also done in two steps:

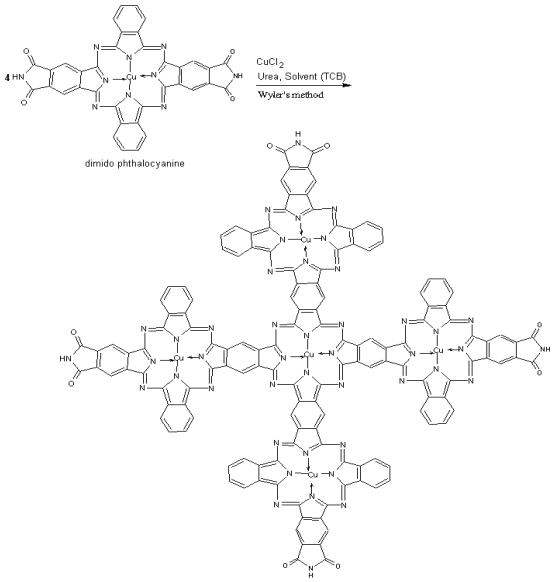
Step-I: Preparation of para di-imido phthalocyanine: One molar equivalent of Nemi's half salt and two molar equivalent of Pyromellitic anhydride were heated in Pc formation condition of Wyler's urea methods



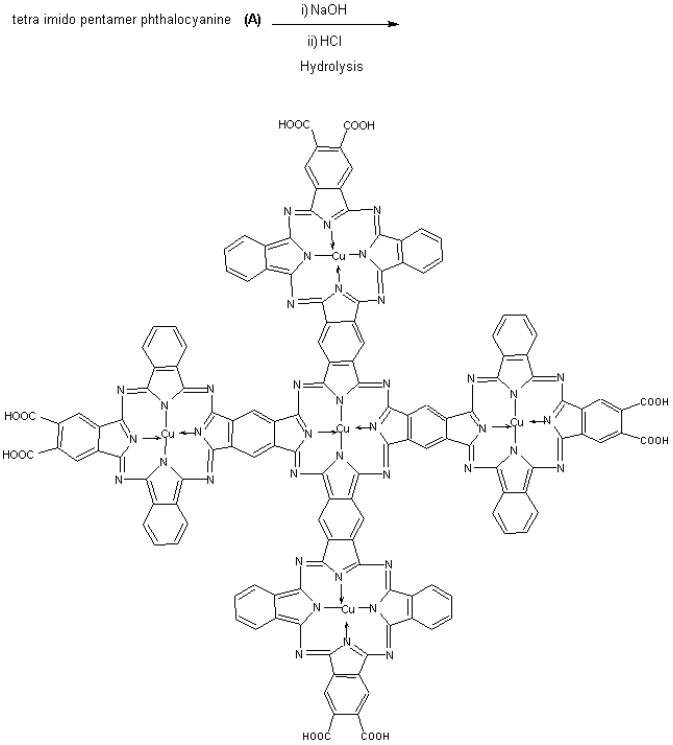
Scheme-3
Formation of tetra carboxy phthalocyanine

This di-imido phthalocyanine was also used for the next step without any purification except removing the solvent (TCB) by refluxing in MeOH filtering and drying on water bath. The resulting p-di-imide phthalocyanine was also dark green in colour but when hydrolyzed with NaOH and acid treated with conc. HCl, the coloure of the resulting tetra carboxylic acid changed to dark-blue.

Step-II: preparation of tetra imido pentamer phthalocyanine polymer: The di imide was subjected to tetra cyclisation by Wyler's urea method.



Scheme-4
Formation of Tetra imido pentamer phthalocyanine (A)

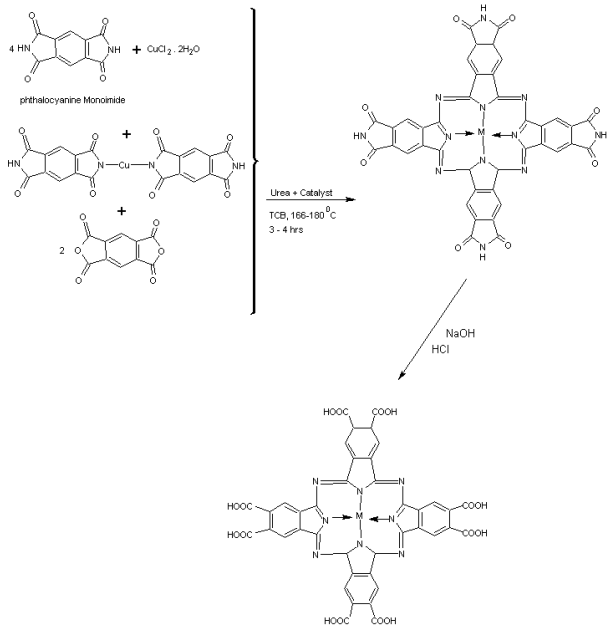


Scheme-5
Preparation of Octacarboxy pentamer phthalocyanine

The tetra imide pentamer phthalocyanine **(A)** was dark green in coloure but when hydrolyzed with 10 % NaOH at 80-90 ^{0}C on a water bath and acidified, the resulting octa carboxy pentamer phthalocyanine became dark blue in coloure. However, the octa acid was not acid pasted. The acid, when treated with NaOH, the neutral octa sodium salt was sparingly soluble in water. As such, neither the tetra imide nor the octa carboxy acid were soluble in most of the solvents, accept that both were soluble in the DMSO solvent to a very little extent. The analytical data for the resulting octa acid is still awaited.

Series III: Preparation of a multi substituted (12) imido or (24) COOH groups) pentamer Phthalocyanine sheet polymer

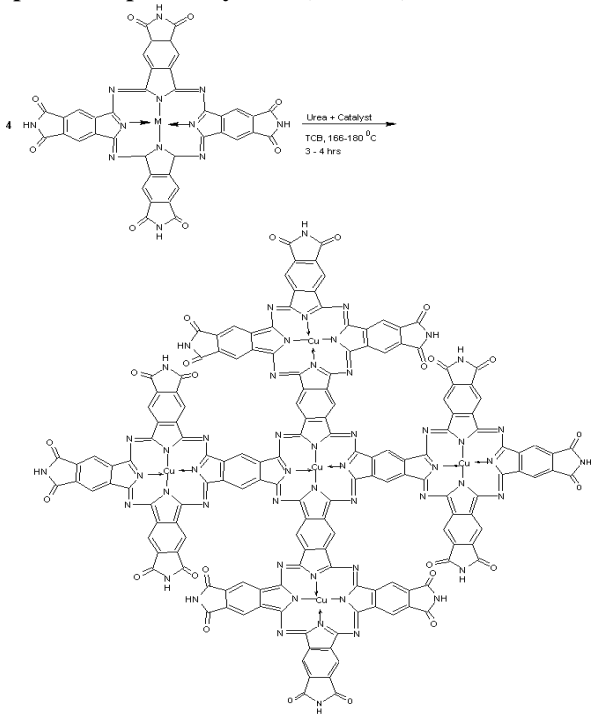
Step I: This series, we prepared tetra imido/ octa carboxy molecules in two ways i. By tetra cyclisation of 4 moles of Pyromellitic anhydride with 1 mole of cupper chloride ii. By forming a Nemi's Half Salt of Pyromellitic di-imide and then condensing with another 2 moles of the same Pyromellitic anhydride, formulated as under: We obtained the symmetrically oriented tetraimido and than subsequently the octa acid.



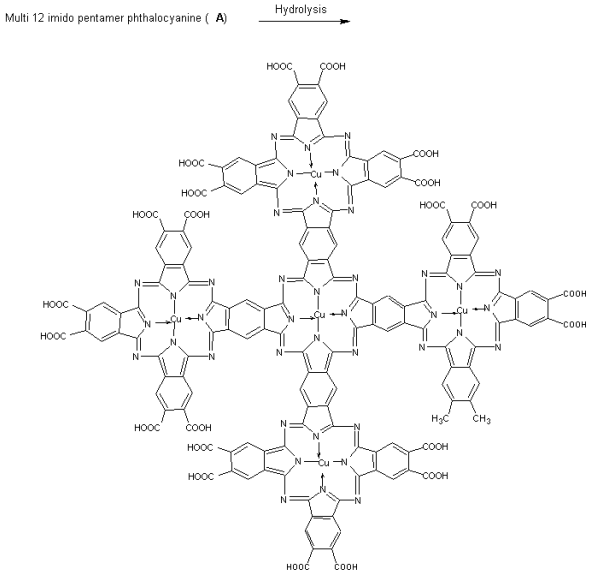
Scheme-6
Octacarboxy PC formation

From the above tetra imido product we were to prepare a multi imido (12 imido) or multi carboxy (24 COOH) products mentioned as under:

Step II: Preparation of Multi (12) imido and multi carboxy (24) pentamer phthalocyanine (A and B)



Scheme-7
Multi (12) imido pentamer phthalocyanine (A)



Scheme-8
Preparation of Multi (24) carboxy pentamer phthalocyanine (B)

But in this case, we are not getting the desired proper products. In our two attempts, we observed two separate products i.e., one in the powderous form and the other in a round ball like substance. We are trying to get the desired end products by improving our chemical procedures with different quantities of the reactants, temperature and time variations.

Conclusion

The pentamer phthalocyanine formation in all the above three series, though molecularly seems to be very complicated but their derivation with the help of Nemi's Half Salt is very facile. The few clear observations we noted that: All the imides in the first step or second step are dark green in colour. The acidification of all the imides in first step or second step in all the three series gives rise to corresponding carboxylic acids and they regain their dark blue colour back. The neutral sodium salts of the carboxy derivatives are very sparingly soluble in water. The solubility increases with successive increase in the number of carboxy groups.

Since, the solubility and melting point of all the monomer and pentamer phthalocyanines is a hard nut to be broken in ordinary conditions, we are facing difficulties in the determination of their analytical parameters. However, the utility of these pentamer sheet phthalocyanine polymers as resins and as conductive sheet layer for the hetero junction of photovoltic cells and panels seems to be very apparent. After collecting the analytical data we will try to find out their application part in such fields.

Acknowledgement

The idea of synthesis of this type of pentamer sheet polymer

phthalocyanine is very much related to our Nemi's Half Salt method of PC formation which we have invented in this chemical lab of Maharaja Ranjit Singh College of Professional Sciences, Indore (MP), India in the three years tenure of the Research Project entitled "Modification and Polymerization of Phthalocyanine Macromolecule" Reference: No. 2322 / CST/ R&D / 2010 Dated 9/9/2010. Our group is very much thankful to MPCST, Bhopal, (MP), India for the financial support and encouragement.