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From the Editor's Desk

Pilgrimage of Phthalocyanine Macromolecule

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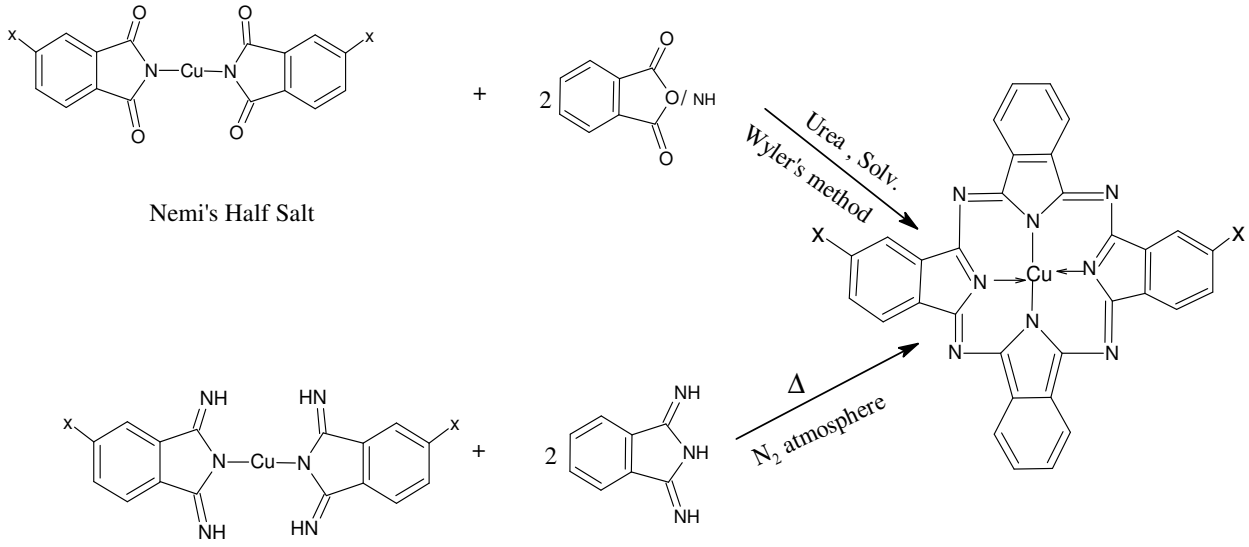
A New Era in the Preparation of Linear Phthalocyanine Macromolecule through Nemi's Half Salt Method (PART-V)

Right from the inceptions in 1930s, phthalocyanine macromolecules have gained very much importance as industrial pigments and dyes, because of their tinctorial superiority, fast colour and stability against heat, acids, alkalies, oxidation, reduction and other wear and tear activities. They have now extended their tentacles in variety of technical fields like solar absorption, solar photo cells, semiconductors, catalysts, anticancer drugs, TV tube and paints etc.

We, as mentioned below, have also now opened few new horizons for their newer utilities in the field of solar energy and textile activities by developing a new simple Nemi's half Salt Method for synthesizing specific phthalocyanine derivatives.

So far world's practice of synthesis of phthalocyanine molecules on both lab and industrial scale basis has been through a tetra cyclisation method. In one such important method, 4 moles of relevant phthalic acid derivatives like anhydride or imide are heated with/ without a metal salt (chloride/sulphate) with urea/ammonia in high boiling solvent(TCB, Nitrobenzene; 170-180 ^{0}C) in the presence of a catalyst (Am. Molybdate/boric acid). This method is known as Wyler's method (discoverer). Another tetracyclisation is done with 4 moles of phthlonitrile derivatives or 4 moles of 1, 3-diiminoisoindoline with/without solvent in N_2 atmosphere for obtaining phthalocyanine molecules (PC molecules) for specific endues.

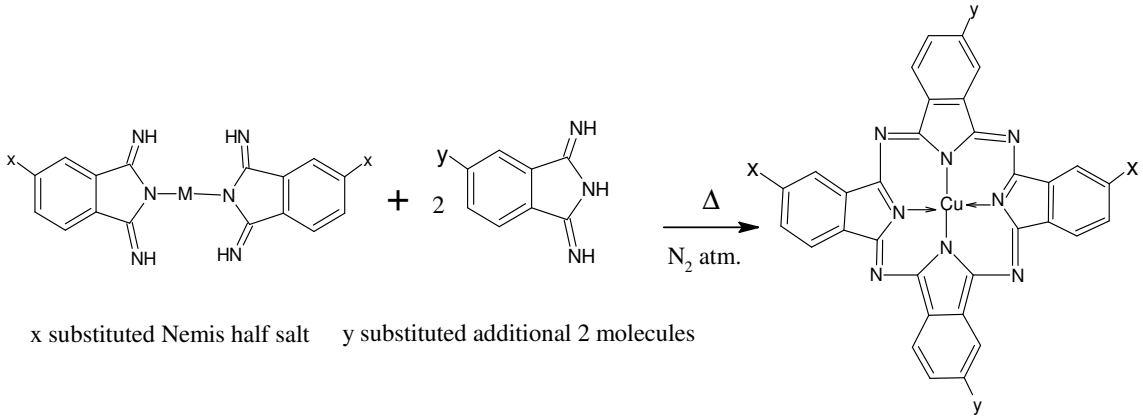
Very recently, with financial support from MPCST, Bhopal, India Project ref. No.2332/CST/R&D/2010 dated 9/9/2010 entitled "Modification and polymerization of Phthalocyanine macromolecules" our laboratory has developed a new simple Nemi's half salt method for entering in the PC molecule formation. In this method, an ionic salt of phthalimide or 1,3-diiminoisoindoline(one half of the total PC molecule along with central metal atom) is dimerized with another two similar molecules as in the tetracyclisation method as under.



Nemi's Half Salt

Nemi's Half Salt

Here, x substitutions on Nemi's half salts appear on the opposite side (para) benzene rings of the finished PC molecules after dimerization. If we also put y- substitution on some specific positions of the two additional similar molecules at the time of dimerizations, they are also bound to appear on the other two opposite benzene entities of the finished PC molecules as under.

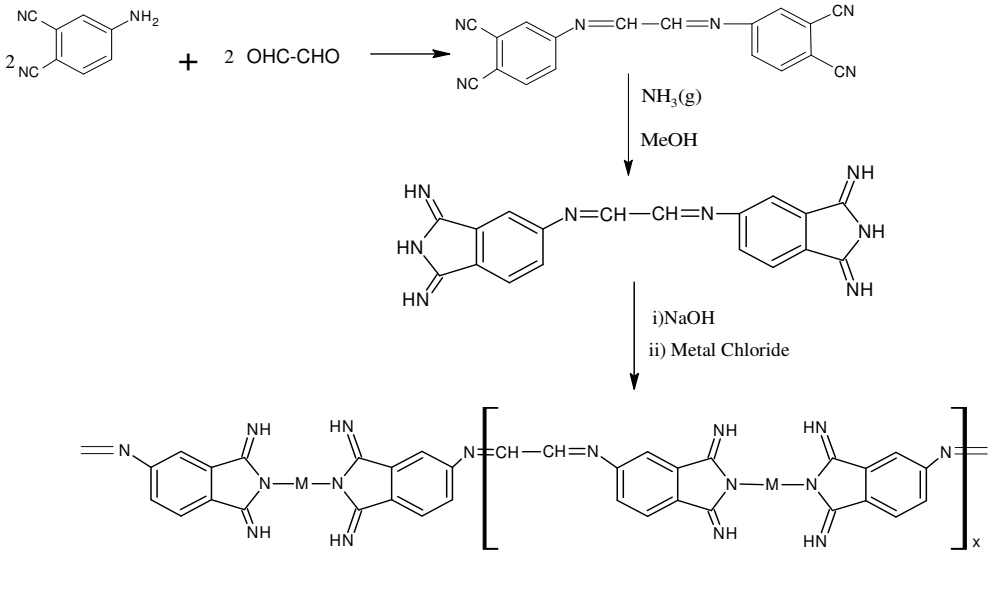


x substituted Nemis half salt y substituted additional 2 molecules

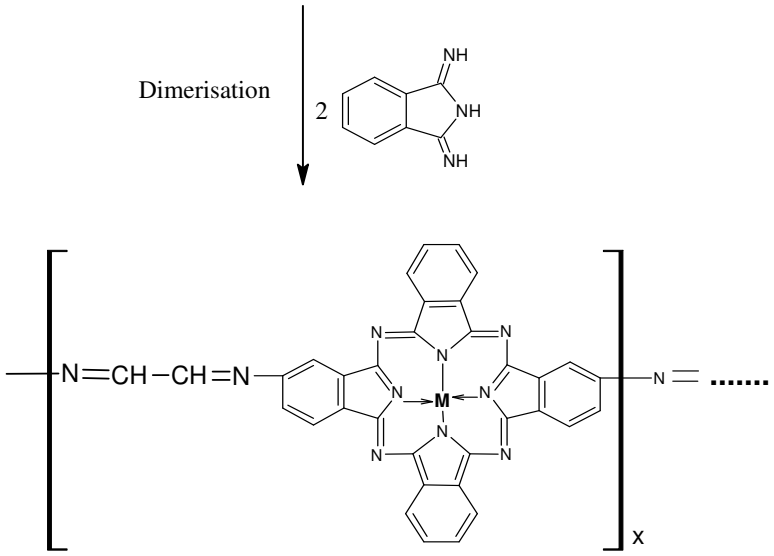
Here, x and y may be any auxochromic groups like SO_3H, NO_2, NH_2, COOH, $CONH_2$, COOMe etc.

Nemi's half salt method has made available these auxochromic groups on the para positions of the PC molecules for further reaction on either side of the PC molecules for the formation of the polymer compounds. Bimolar reacting molecules can react with these para substituted PC molecule for their extension on both sides to give rise to numerous coloured polymer compounds, because of their readily coloured mono starting molecules, Nemi's half salt method opens the possibilities of preparation of many coloured polymer molecules for solar energy, textile and other end-uses. Basic motto of our present project has been to synthesize variety of soluble, insoluble, conjugated and non-conjugated new coloured tougher polymers for different untouched superior applications including different coloured textile fibers (So far all natural and manmade fibers are almost white in coloured). Facing solubility, m.p. and purification difficulties in the handling of phthalocyanine series of compounds, we used the Nemi's half salt method in an altogether different way i.e., we plane to prepare the precursor of Nemi's half salt by known chemicals means and methods and convert them to different Nemi's half salts. From these half salts we prepare our desired coloured PC molecules by ours dimerization method. For the confirmation and extension of our Nemi's half salts method. We initiated to prepared few new compounds in the PC Series described as under. Reaction of 4-aminophthalonitrile with a bifunctional aldehyde gives a precursor Schiff base with two phthalonitrile end groups which are converted to Nemi's half salt through the following scheme. This half salt then is converted to the desired coloured polymer by our dimerization method as under:

Series 1: Scheme 1a



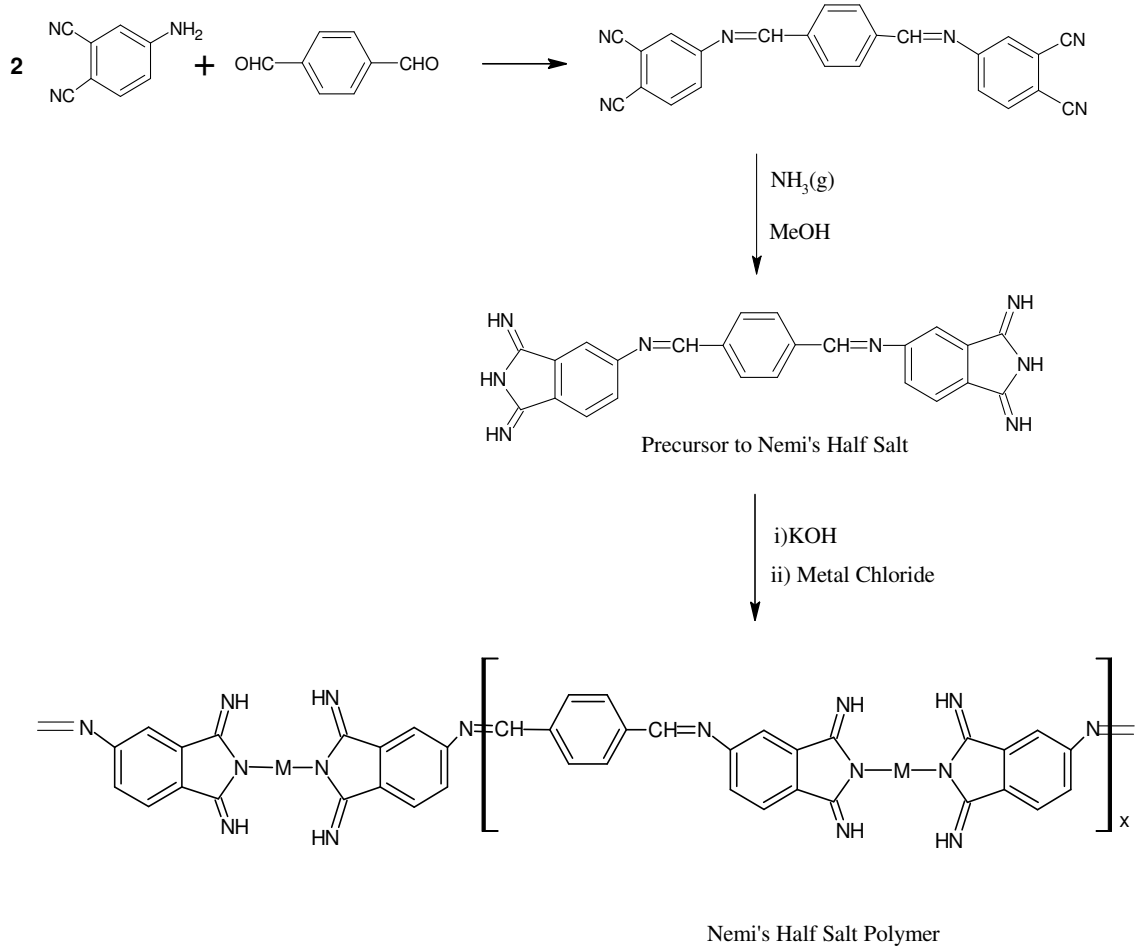
Nemi's Half Salt Polymer



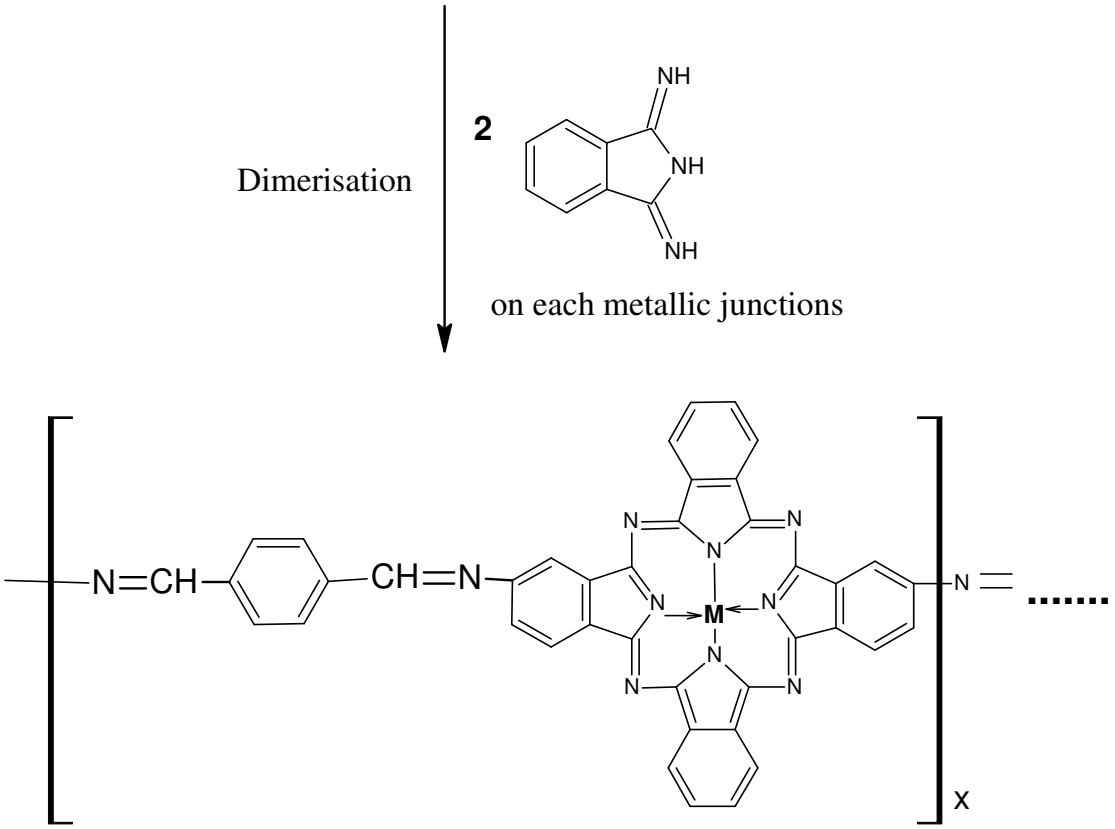
Conjugated Linear Polymer

(spacing group here is glyoxal)

Scheme 1b



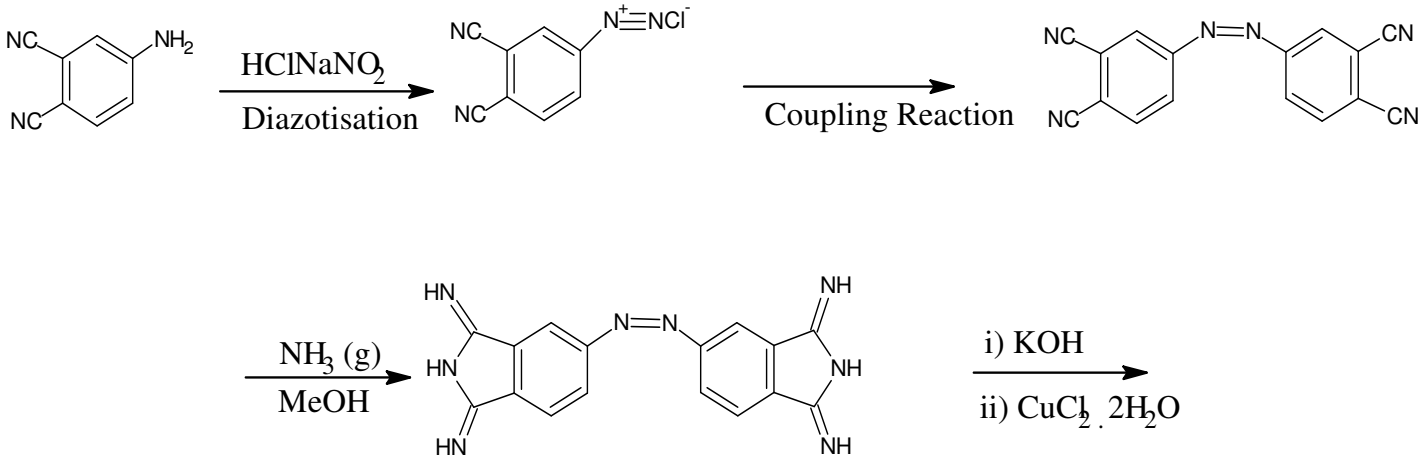
Nemi's Half Salt Polymer



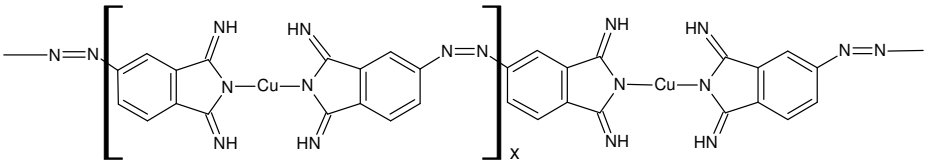
(spacing group here is terephthalaldehyde)

Conjugated Linear Polymer

Scheme 1c

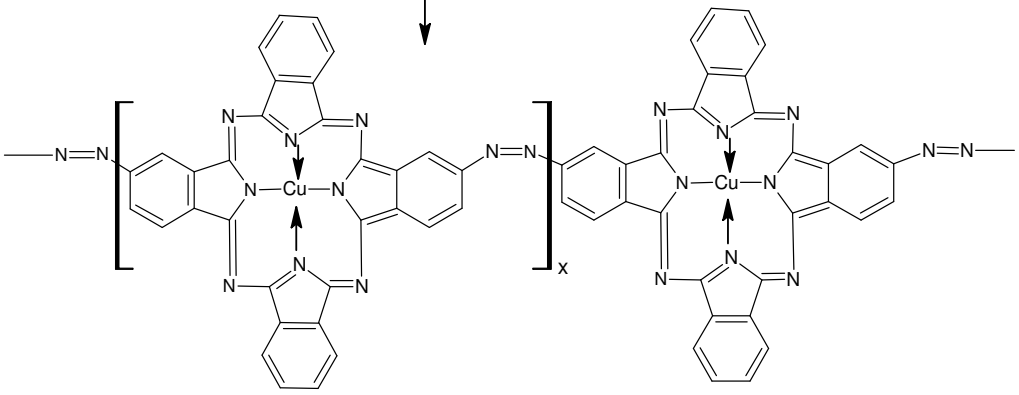


Precursor to Nemi's Half Salt



Nemi's Half Salt Polymer

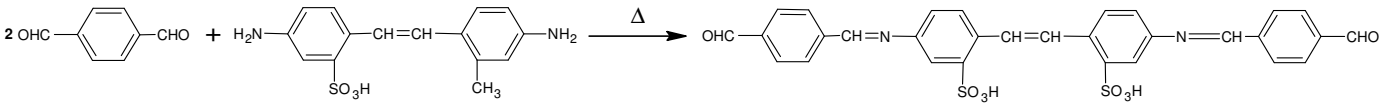
Dimerisation by two moles of 1,3-diaminoisoindoline
on each metallic junction of Nemi's Half Salt polymer

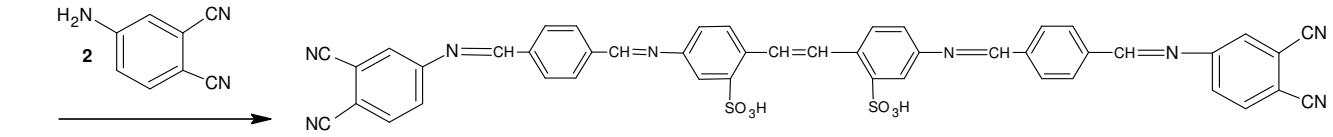


Coloured Conjugated Linear PC Polymer

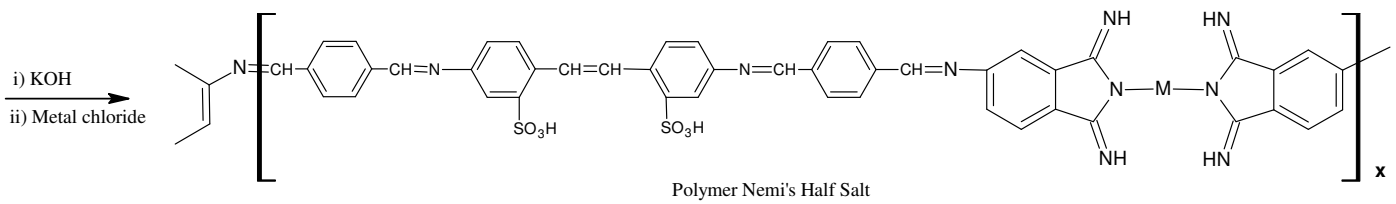
(spacing molecule - N=N -)

Scheme 1d

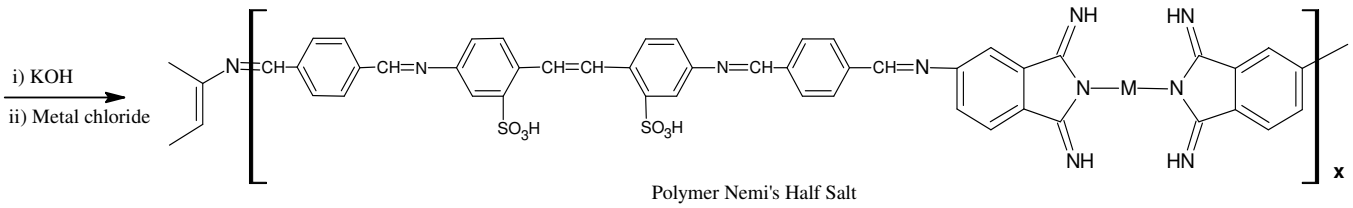




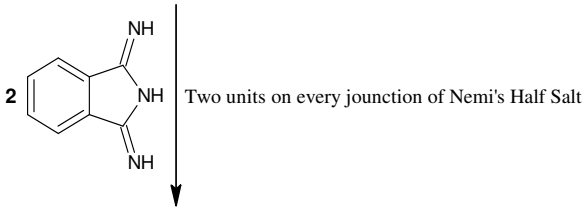
Precursor to Nemi's Half Salt

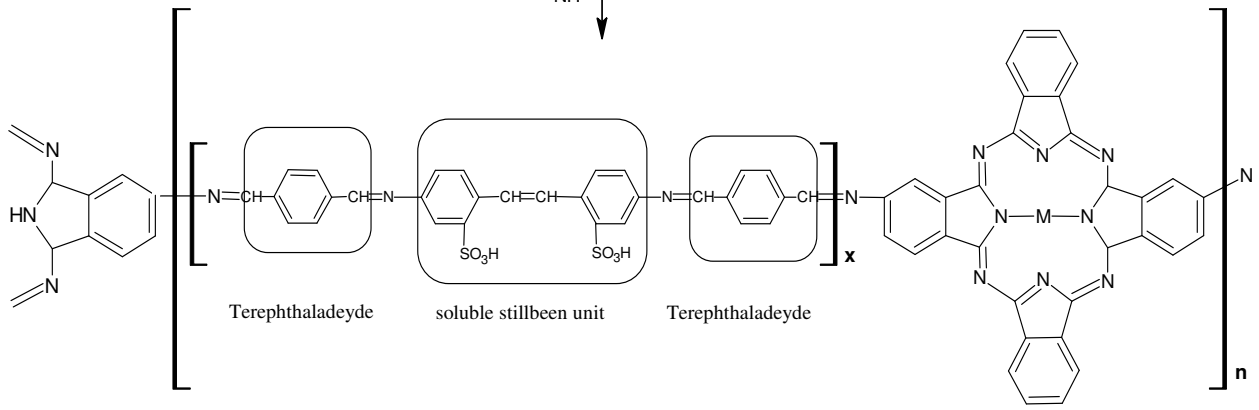


Polymer Nemi's Half Salt



Polymer Nemi's Half Salt





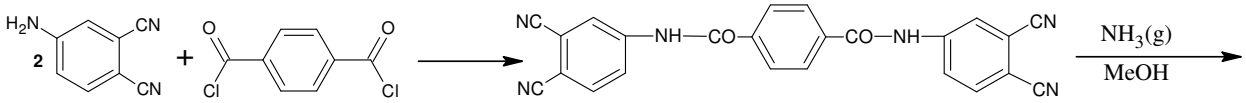
Terephthaladeyde soluble stillbeen unit Terephthaladeyde

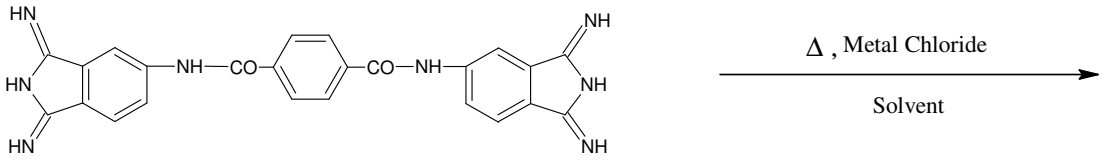
Coloured Conjugated PC Polymer

Since the PC unit molecules are joined here to each other by conjugated co-monomers, the whole coloured polymer chain cabl function as a conducting unit. Up till now we have prepared the basic dimer trimer, tetramer, pentamer units without substitution on the main PC units of the finished PC molecules or on the spacing chain molecules but we plan to continue our work to create some soluble derivatives by putting different long alkyl chains or auxochromic groups on these desired position also.

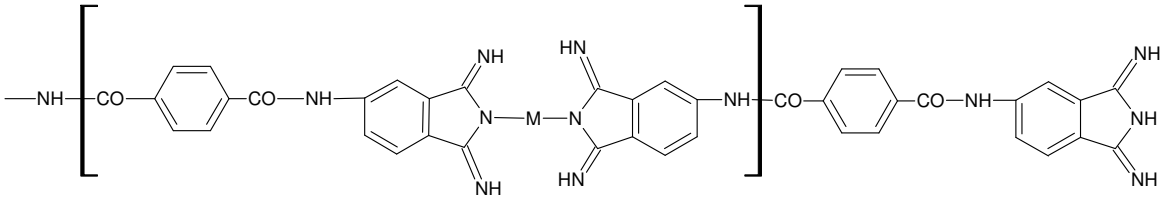
Series 2

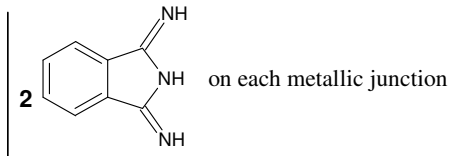
Scheme 2a



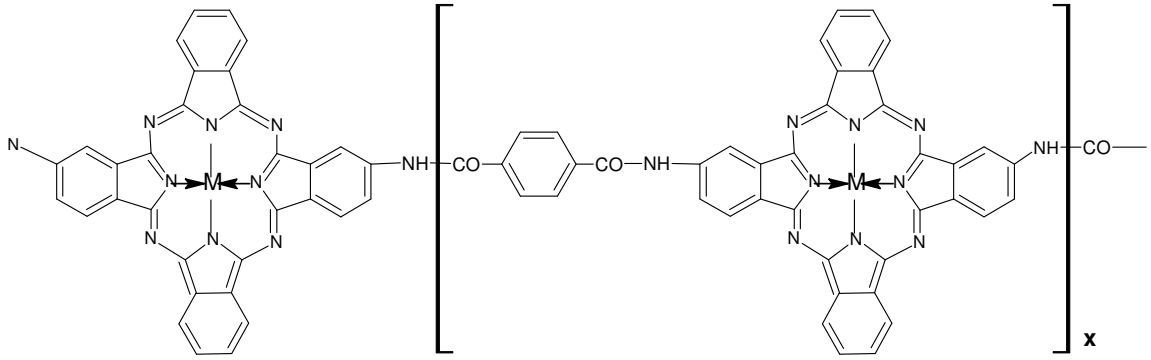


Precurosor for Nemi's Half Salt





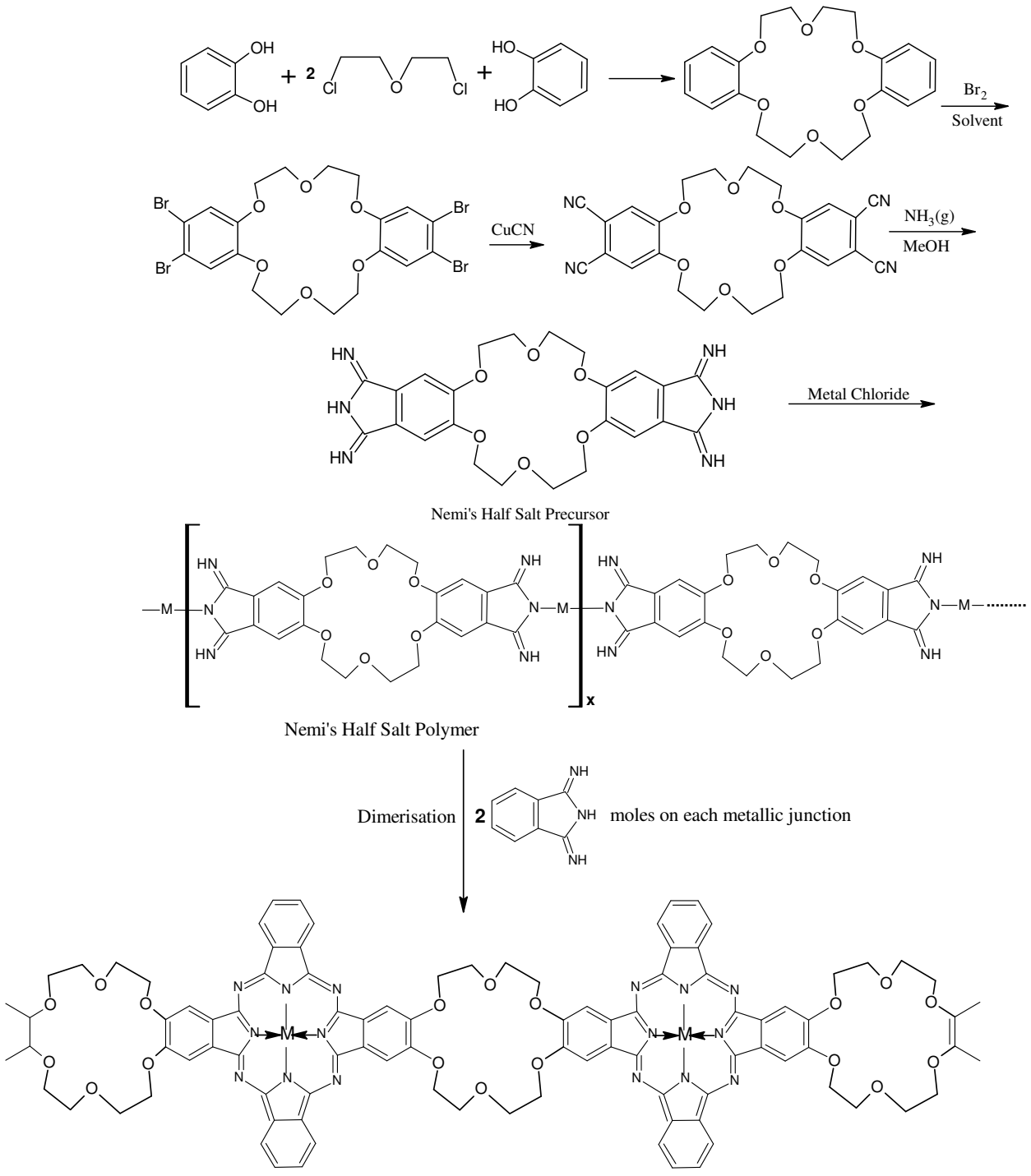
Nemi's Polymer Half Salt



Non-conjugated coloured linear polymer

Though conjugation in the spacing molecules is absent here but any bi-functional acid chloride can be used as copolymer to produce many polymer units. These units if contains long polymethylene chains in the acid/acid chloride co-monomer i.e., [ClOC$(CH_2)_x$COCl], the resulting coloured polymers may be soluble and of low melting points such polymers may be better suited for practical purposes.

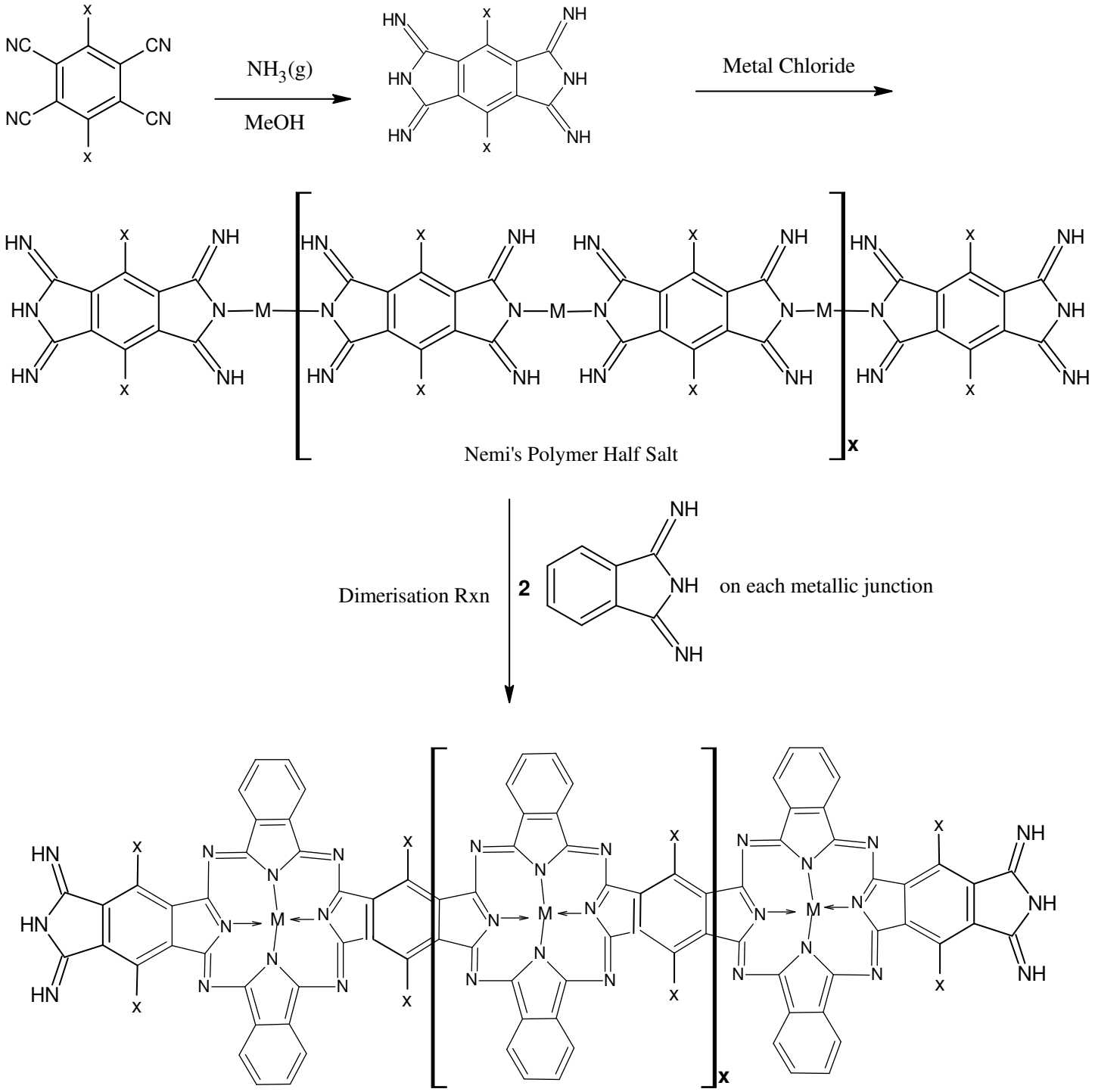
Scheme 2b



Conjugated Linear Coloured PC Polymer(Crown Ether Spacing Molecules)

Here, the crown ether spacing units in the final coloured PC polymer not only will push the total polymer molecule towards solubility and lower melting point but also create some special features related to chemical properties of crown ethers.

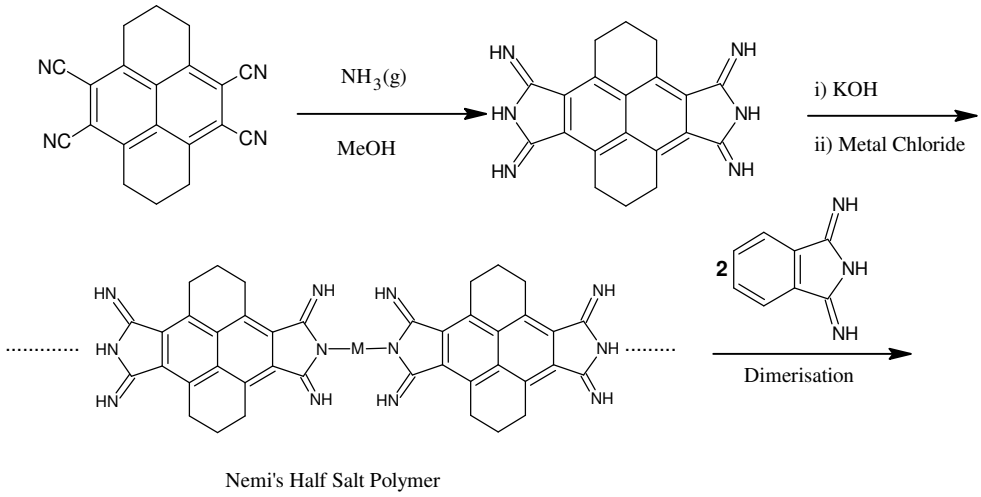
Series 3



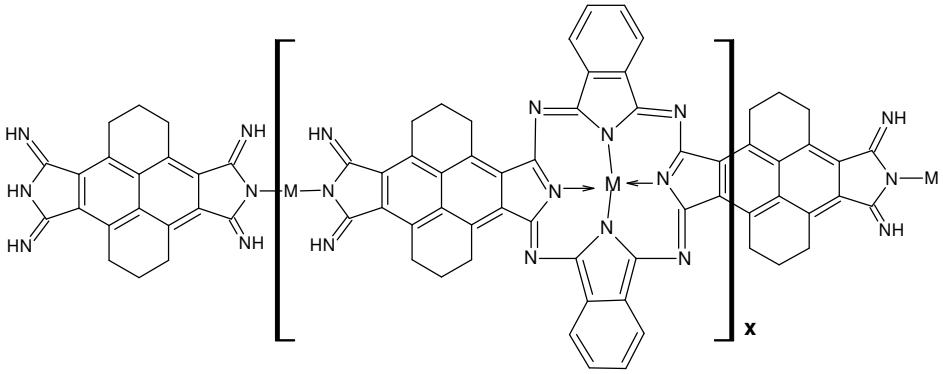
Unintrupted coloured Linear PC Polymer

We are trying to prepare this type of continuous linear polymer molecules. Though, putting few 100 / 1000 monomers units in such compound has not been successful because of many technical hindrances but we hope to solve this problem in a very near future. This type of polymers will not only serve as tough coloured fibers but they will proved to be very good solar absorbing materials.

Series 4
Scheme 4a



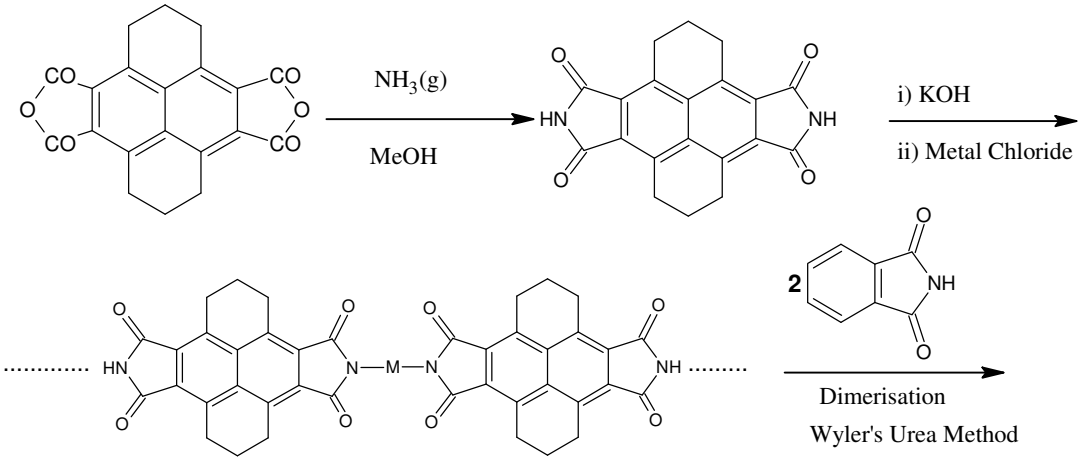
Nemi's Half Salt Polymer



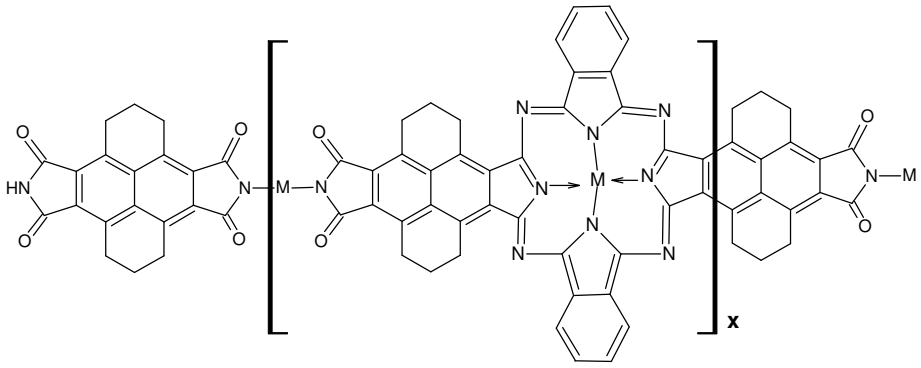
Substituted naphthalene (spacing molecule)

Coloured Linear PC Polymer

Scheme 4b



Nemi's Half Salt Polymer



Substituted naphthalene (spacing molecule)

Coloured Linear PC Polymer

Conclusion

Linear alongation of Nemi's half salt on both sides by any spacing molecules can very well give rise to a long linear coloured polymer or specific desired activity. i. The conjugation throughout the linear coloured polymer will make it conductive for conductivity appliances. ii. If polymerization reaches up to few thousand molecule stage resulting coloured polymer will be used as coloured fibers for textile purposes. iii. If some solublising groups are put on PC portion or spacing portion, this attempt may give rise to soluble and crystalline polymers as well. iv. Though chlorophyll is the natural product for solar energy absorbing agent, these compounds may be good solar energy absorbing agents and can be manufactured on large scale. v. Coloured PC Polymers interrupted by molecules like crown ether may give rise to polymers which may be used as tough textile fibers such tough fibers may be woven for unique clothing and other uses. vi. Along with extension of Nemi's half salt on both sides we can also extend our end polymers on the other right angle direction to give rise to sheet polymers also. Sheet polymer formation by tetra cyclisation has not been very successful because of some stearic or purity reasons. Our method can eliminate these drawbacks.

The above synthetic routes are the preliminary attempts for the utilization of the Nemi's half salt method. We are continuing our PC Polymer activity in the lab of chemical sciences of Maharaja Ranjit Singh College, Indore, (M.P.) India. We also wish to modify the natural polymers like oil, rubber, polyacetylene, etc. in continuation to our half salt method.

Acknowledgement

I along my team member investigators Dr. Anjani Phadnis and Dr Dipak Sharma are very much thankful to our funding agency M. P. Council of Science and Technology, Bhopal (M.P.) India for granting us the research project entitled "Modification and polymerization of Phthalocyanine macromolecules" Reference: No 2322 /CST/R&D/2010 for completing the activities described in this report.

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