

Supramolecular Phthalocyanine Aggregates



Thesis submitted towards partial fulfillment

BS-MS dual degree programme

by

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20091064

Under the guidance of

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CERTIFICATE

This is to certify that thesis entitled “**Supramolecular Phthalocyanine Aggregates**” which is submitted by **Vimlesh Kumar Bind** in partial fulfillment of the requirement for the award of BS-MS dual degree programme at Indian Institute of Science Education and research (IISER), Pune under the supervision of **Dr. Nirmalya Ballav**, Assistant Professor, Department of Chemistry, IISER Pune during the academic year 2013-2014.

Date:
Place

Dr. Nirmalya Ballav
Assistant Professor – Chemistry

DECLARATION

I hereby declare that the matter embodied in the report entitled “**Supramolecular Phthalocyanine Aggregates**” are the results of the investigations carried out by me at the Department of Chemistry, IISER Pune, under the supervision of Dr. **Nirmalya Ballav** and the same has not been submitted elsewhere for any other degree.

Date:
Place

Vimlesh Kumar Bind
BS-MS Dual Degree Programme, IISER Pune

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Introduction

Phthalocyanine is an intensely blue-green-coloured aromatic (18π -electrons) macrocyclic compound which is widely used in dyeing and its chemical structure closely related to the naturally occurring porphyrins. The cavity of phthalocyanine is capable of making coordination complexes with 63 different metal ions in the periodic table. Properties of phthalocyanine molecules are significantly influenced by three factors, (i) Functionalization (on molecular skeleton), (ii) Axial ligand (coordinated to metal ion perpendicular to the molecular plane) and (iii) Central metal ion (at cavity). For example functionalization with polar groups (SO_3^- , $-\text{COOH}$, etc.) increases the solubility in polar solvents as well as alters the π -electron density and thereby affects the optical and electrical conductivity properties. Oxidation state and number of unpaired electrons of metal ion strongly affects the optical and magnetic property. Insertion of diamagnetic metals increases the photoconductivity because of long-lived triplet state while the paramagnetic metal ions decrease the photochemical behaviour of phthalocyanine. Due to their high stability (chemical and thermal) and particularly interesting electronic properties render them to have diverse applications such as photodynamic therapy¹, optical data storage devices, nonlinear optics and photochemical cell etc. In photodynamic therapy, phthalocyanines are being utilized as photo-sensitizers (initiators of photochemical reactions) for the destruction of infected cells. Metalized phthalocyanines show better photosensitising activity compared to the metal-free phthalocyanines. The structural similarity of these molecules with chlorophyll makes them to be utilized in the synthesis of artificial photosynthesizers. Dye-sensitized solar cell uses phthalocyanine derivatives as dye in place of Rh (II)-dye because of relatively lower cost. Phthalocyanine molecules mimic some biological molecules (Hemoglobin, Myoglobin), so these can be used in vitro studies.

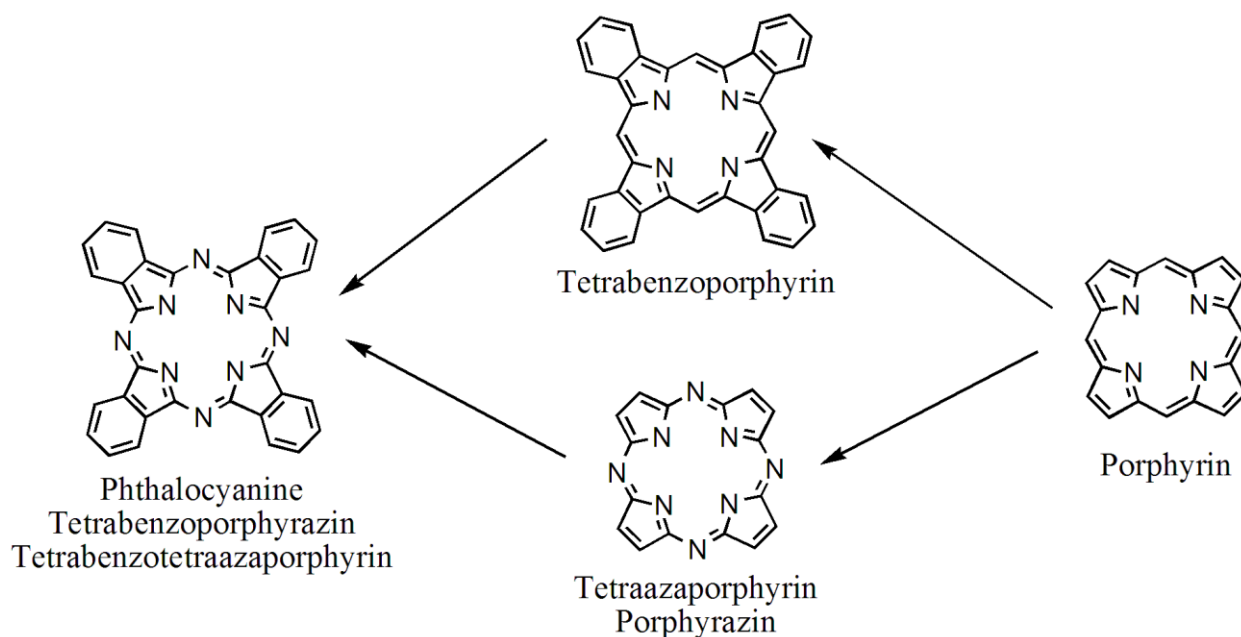


Figure 1: Pc-related compounds

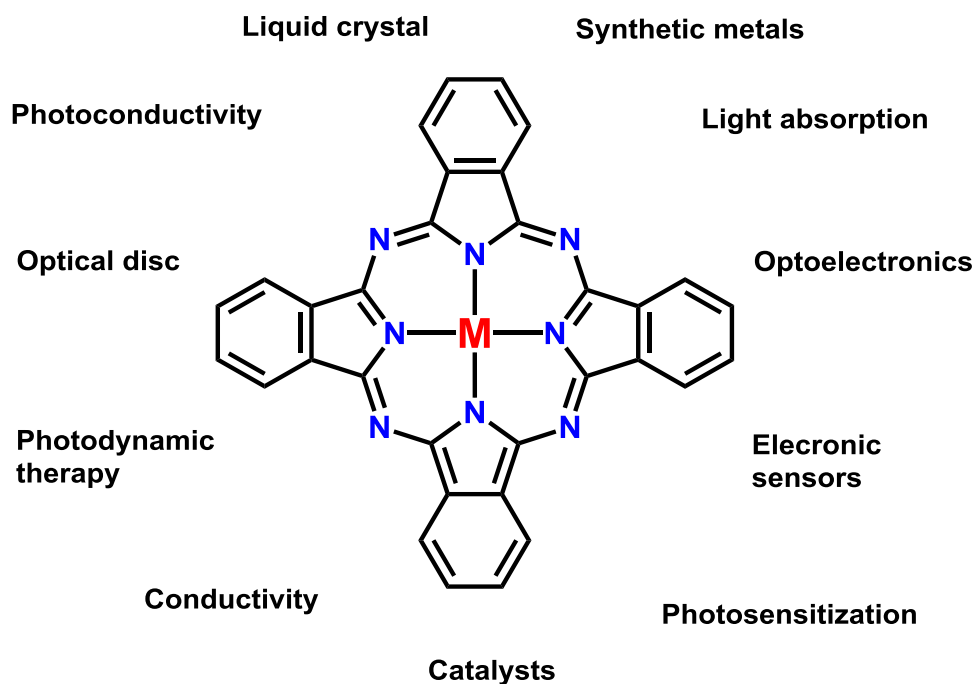


Figure 2: Typical functions of phthalocyanines/derivatives

Wet-chemical synthesis of Pcs and MPcs is well-established². So far It has been explored about the properties and application of isolated phthalocyanine molecules but not about their self-assembly. Therefore it is fundamentally interesting to study

about homo (same molecules) and hetero (different molecules) self-assembly of various kinds of phthalocyanine molecules.

Polymorphs of Phthalocyanines

If the same chemical species exhibit in different crystal lattice form is called polymorphism. Phthalocyanine molecules also exhibit polymorphism. Different polymorphs have different properties such as melting point, density and color. Different crystal lattice forms of phthalocyanine gives rise to reduction of the four fold symmetry which applies slight but significant distortion. These distortions lead to change in absorption properties of phthalocyanine. The unsubstituted phthalocyanines, metal free phthalocyanines and derivative of phthalocyanines occur in different crystal structures. To date maximum 10 polymorphs (α , β , γ , δ and ϵ etc.) of phthalocyanine have been recognized³.

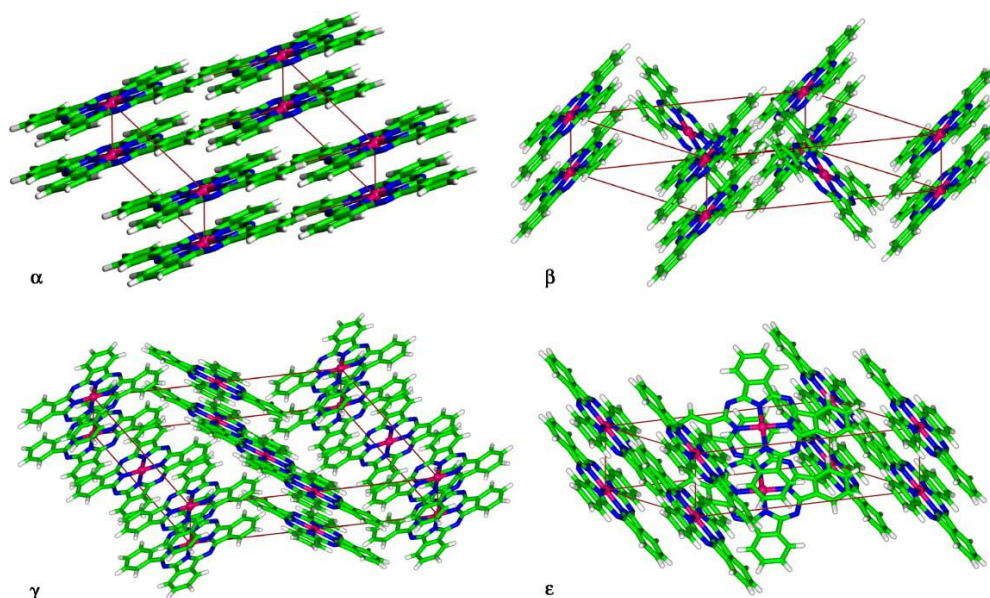


Figure 3: Packing diagrams of Copper Phthalocyanine polymorphs (taken from ref. [3])

Copper phthalocyanine exists in ten polymorphs but recently an eleventh polymorph has been grown under low gravity conditions in the space shuttle⁴. They can be distinguished by powder X-ray diffraction pattern and infrared spectroscopy. The raw Copper phthalocyanine comes in β -modification. Some of the phthalocyanine polymorphs can be prepared under the appropriate condition.

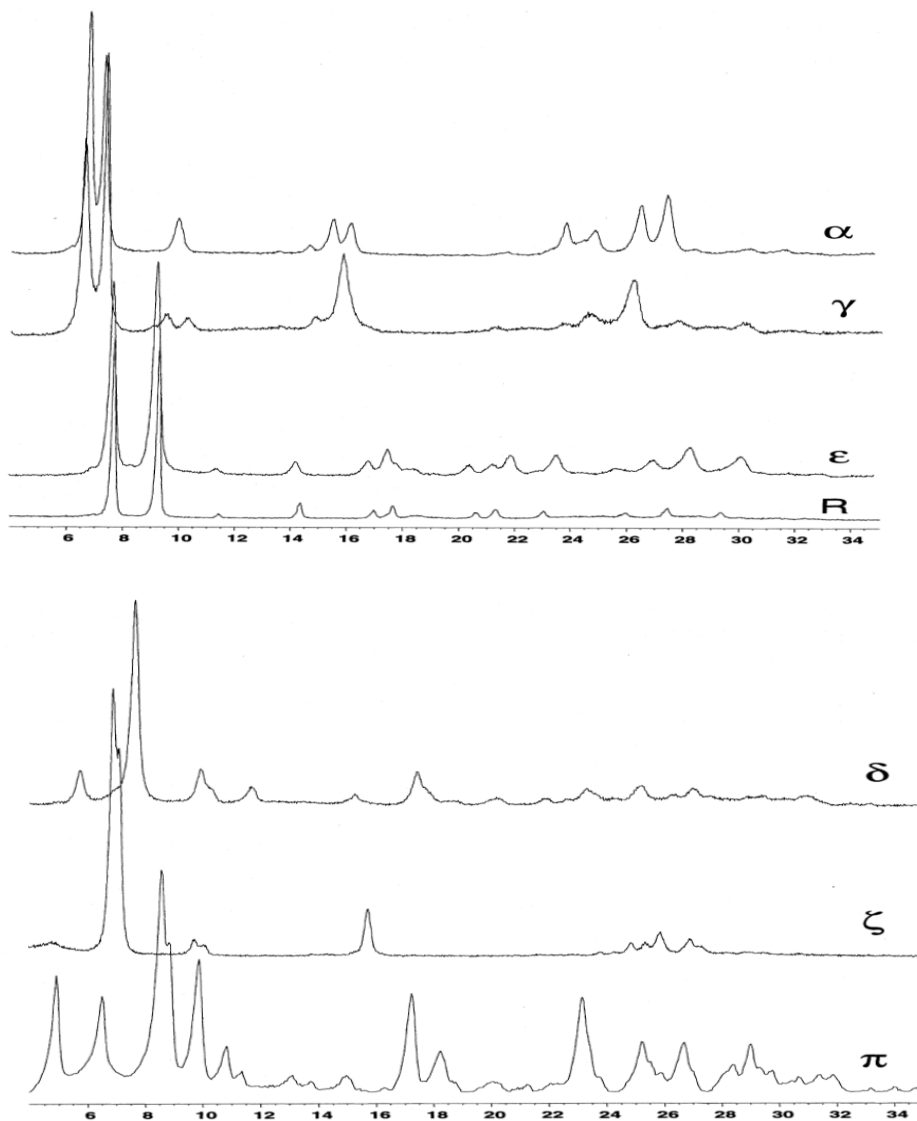


Figure 4: Powder XRD of Copper Phthalocyanine polymorphs (taken from ref.[3b])

Dry grinding of β -phase of Copper Phthalocyanine converts it into a partial α -phase modification. This is because of particle size reduce from 5-100 μ m to 10-50nm resulting in the mixture of α and β phase and the rate of alpha to beta transformation decrease with increasing the temperature. The enthalpy difference between α - and β -CuPc was found to be 10.75kJ/mol. α to β transformation has remarkable impact on size of unit cell of crystal lattice⁵.

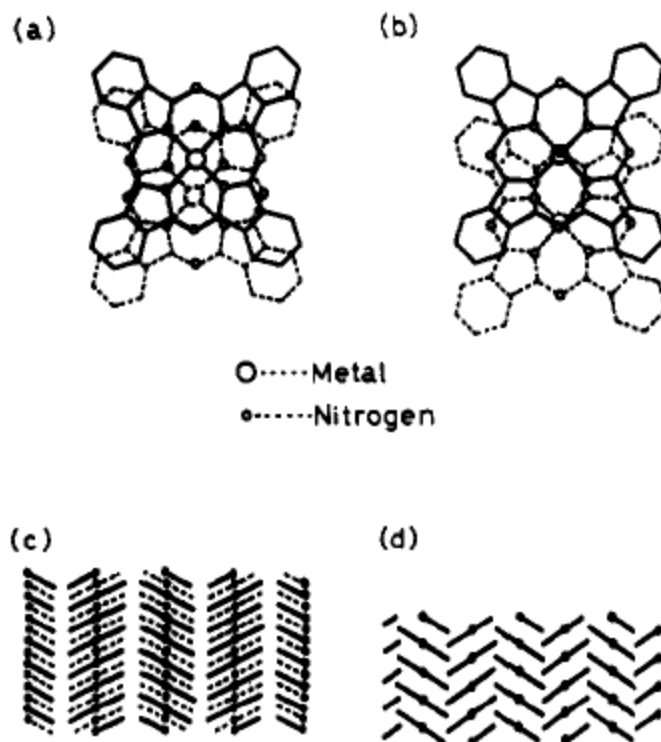


Figure 5: Superposition of successive phthalocyanine molecule in a molecular column along the b axis (a) alpha-polymorphs; (b) beta-polymorphs ; (c) projection on (100) plane in the alpha polymorphs; (d) projection on (100) in the beta polymorphs.(taken from ref.[3b])

Increasing order of thermodynamic stability⁶ of copper Phthalocyanine (CuPc) is $\alpha = \gamma < \delta < \epsilon < \beta$. Most thermodynamically stable β -phase of CuPc would be formed during the synthesis in aromatic solvent or at elevated temperatures in other solvent . All phases can be transferred into the most thermodynamic stable β modification by heating. Transformation takes place between temperature 200 to 300°C depending on the purity and crystallinity of material. At the temperatures above 540°C transformations into ϵ - phase have been reported⁷. Magnetic study has been mainly focused on MnPc single crystal which shows ferromagnetism below 10K⁸. The influences of crystal modification on magnetic properties have recently become apparent via pressure independent visitation⁹.

Supramolecular Chemistry of Pcs

Non-covalent interactions (plays an important role in biology as well as in material science) such as hydrogen bonding, halogen-halogen interaction, halogen-nitrogen, halogen-oxygen, electrostatic interaction and donor-acceptor, fluorine substituted aromatic – aromatic interaction is most thoroughly studied.

First time Tomas Torres and his co-workers¹⁰ showed that the hetero-association between electron-rich Zn(II)hexabutoxyphthalocyanine and electron-deficient Ni(II)hexa(alkylesulfonyl) phthalocyanine. They proposed that driving force for this kind of aggregation is acceptor-donor interaction.

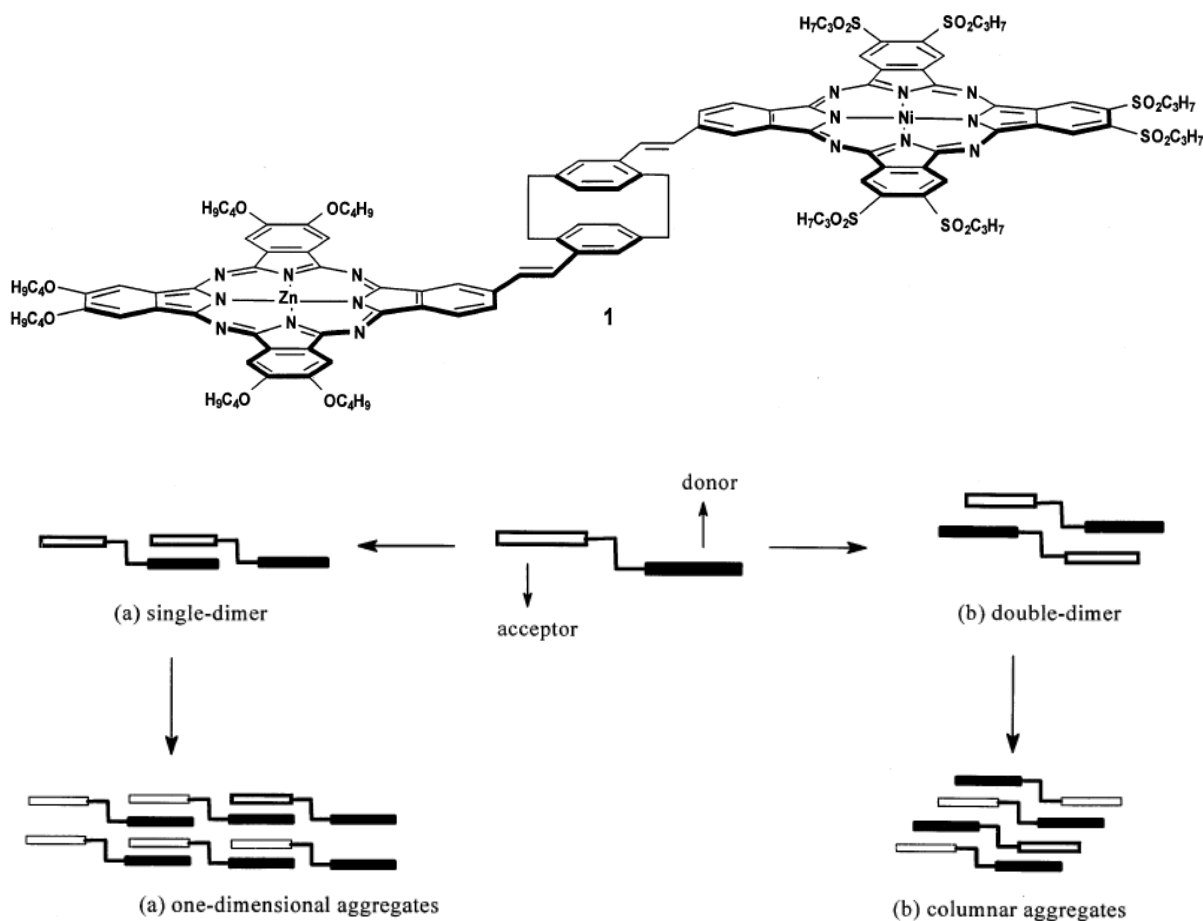


Figure 6: Representation of the type of form by donor-acceptor interactions: (a) one-dimensional aggregates (b) columnar aggregates (taken from ref [10]).

In 2002 K.W. Hipps and his co-workers¹¹ showed that the interaction between fluorinated cobalt phthalocyanine (CoF16Pc) and nickel tetraphenyl porphine (NiTPP) on the surface of Au(111), however that was unclear what is the driving force acting between phthalocyanine and porphine but they suggested various models like hydrogen bond C-H---F and attraction between dipole moment of phthalocyanine and porphine.

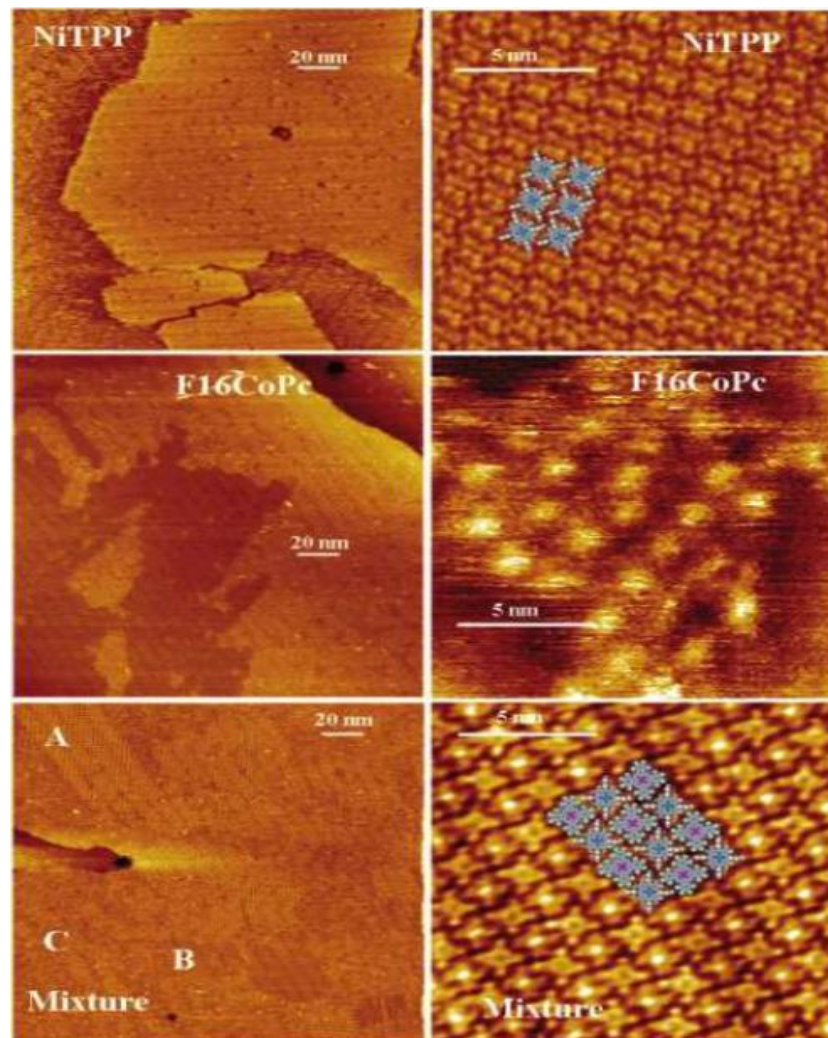


Figure 7: STM images of NiTPP, CoF16Pc and mixture on gold surface (111) (taken from ref.[11])

The resulting 2D surface of mixture shows entirely new crystalline structure which is more stable than parent compounds.

Recently Ballav and his co-workers presented two-dimensional supramolecular electron spin array using manganese phthalocyanine (MnPc) and fluorinated iron phthalocyanine (FeF₁₆Pc) as precursor molecules¹². Driving force for 2D supramolecular arrangement is intermolecular hydrogen bonding between phthalocyanines was mentioned to be predominantly due to C-H ... F hydrogen bond.

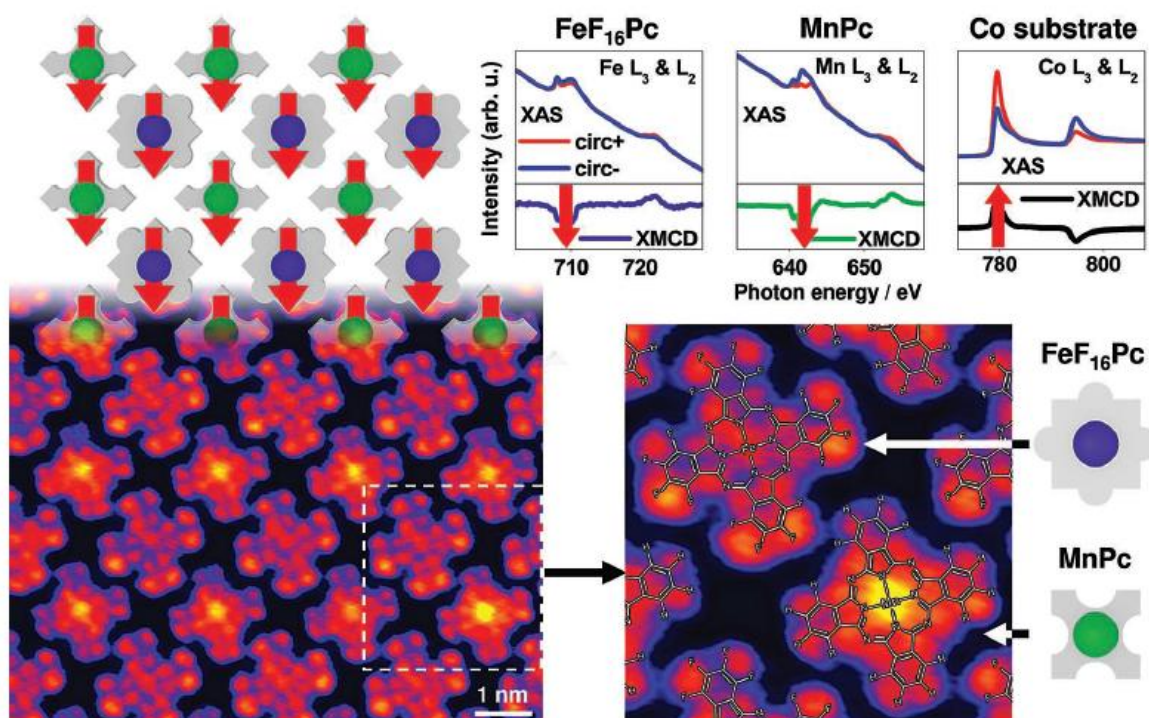


Figure 8: Bottom-up assembly of the supramolecular spin array. Chemical structures of FeF₁₆Pc and MnPc are superimposed on the scanning tunneling microscopy (STM) image which directly visualizes the supramolecular chessboard-like 2D lattice and the intramolecular electronic structure (taken from ref. [12]).

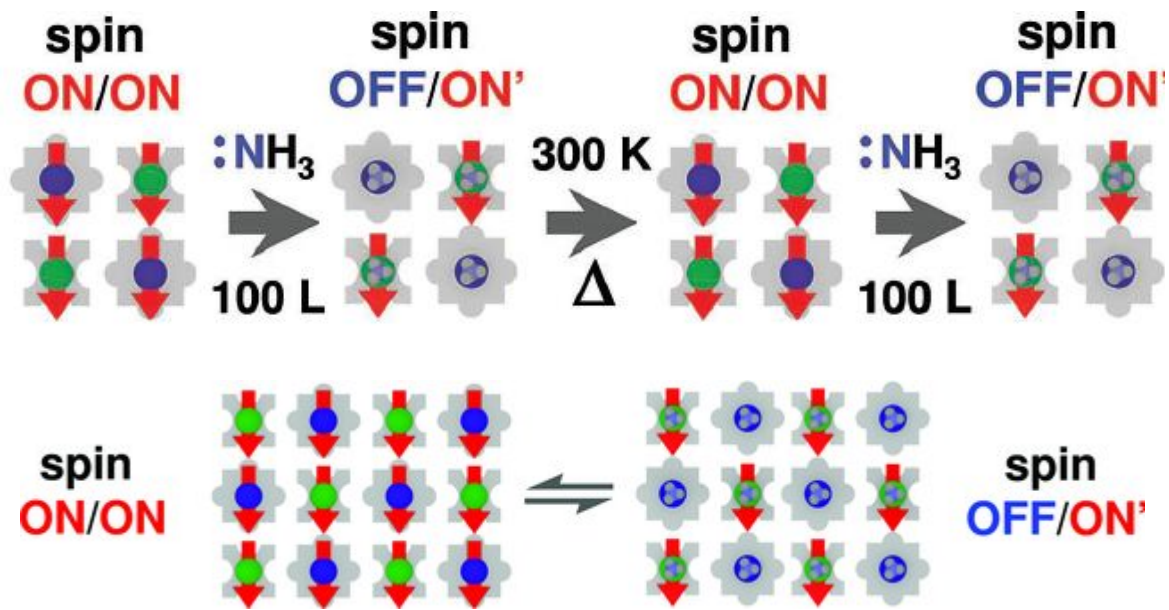


Figure 9: The spins in the bi-molecular array are controlled by consecutive ammonia (NH_3)-ligation (taken from ref.[12]).

Charge transfer in organic materials plays very crucial role in the fundamental and applied science. It has shown¹³ that charge transfer is taking place in hybrid state between phthalocyanines MnPc and F16CoPc at heterojunction. This charge transfer affects transition metals only and it is very sensitive to the distance between the molecules at interface. In conclusion they showed that MnPc and F16CoPc organic hetro-interface is characterized by interface reaction that lead to the formation of hybrid state and charge transfer between phthalocyanines right at the interface. This is important for application of such interfaces in organic electronic device because charge transfer affect the energy level alignment and the transport behavior of the respective heterojunction. Charge transfer is also connected to the spin transfer because if hybrid system has high spin such compound can also term as spintransfer material with the future application in the area of spintronics.

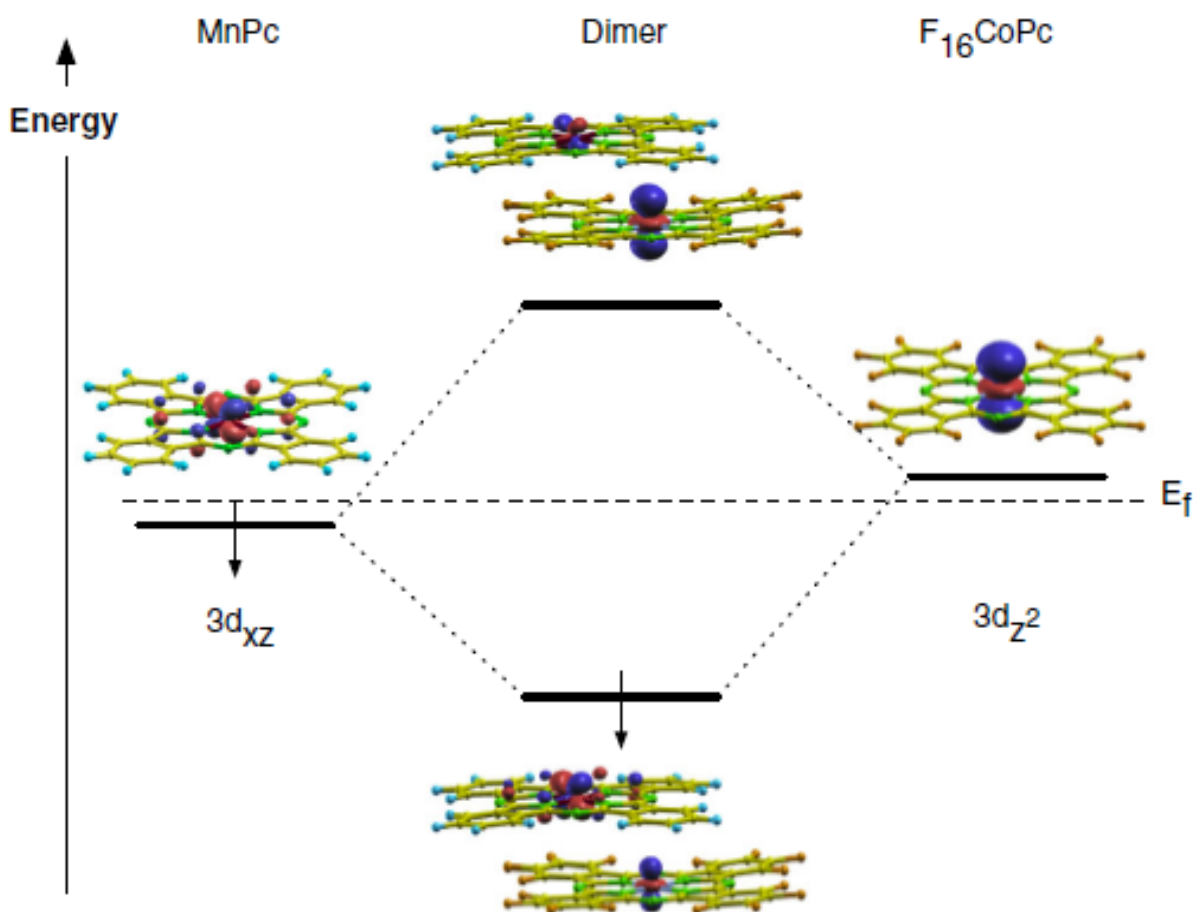


Figure 10: Interaction of the MnPc and F16CoPc state in the MnPc-F16CoPc dimer close to the Fermi level. Mn $3d_{xz}$ and the Co $3d_{z^2}$ orbital hybridize to form a two level system (taken from ref. [13])

Objective

During past years weak hydrogen bond has attracted more attention in scientific research. Hydrogen bonds are non-covalent which are very important in point of biological, nanoscale and engineering chemistry. Here we are trying to self aggregates of phthalocyanines in bulk with the help of C-H—F or C-H- π interaction because of this type of interaction has already shown on the surface. Keeping this results in mind we propose the interaction between two phthalocyanine molecules one is Ni(II)phthalocyanine other molecule Fluorinated Zinc(II)phthalocyanine (F16ZnPc) in bulk amount.

Experimental section

Hexadecafluorinated zinc phthalocyanine (ZnF₁₆Pc) and nickel phthalocyanine (NiPc) were purchased from sigma Aldrich. Millimolar solutions of ZnF₁₆Pc and NiPc were prepared in chloroform solvent. This two saturated solution are mixed together and within 24 hr solid insoluble product was obtained. This product was purified by filtration and washing of the residue with chloroform. The characterization of the insoluble mass was performed. Fourier transform infrared (FTIR) spectrums were recorded in NICOLET 6700 FTIR Spectrophotometer. The morphology of these materials was observed in Zeiss Ultra Plus field emission scanning electron microscope (FESEM). TEM images were recorded by using an FEI Tecnai T30 transmission electron microscope at an accelerating voltage of 200 kV. The powder X-ray diffraction data were recorded from a Bruker D8 Advance diffractometer at room temperature using Cu-K_α radiation ($\lambda=1.5406\text{\AA}$). UV-vis measurements were done using Perkin Elmer, Lambda 45 spectrometer. Fluorescence measurement was done in Fluoromax-4 spectrometer.

Results and Discussion

By mixing of two different Pcs, Nickel phthalocyanine and ZnF16Pc in chloroform gives precipitate in 5 minute which is further characterize by different instrument.

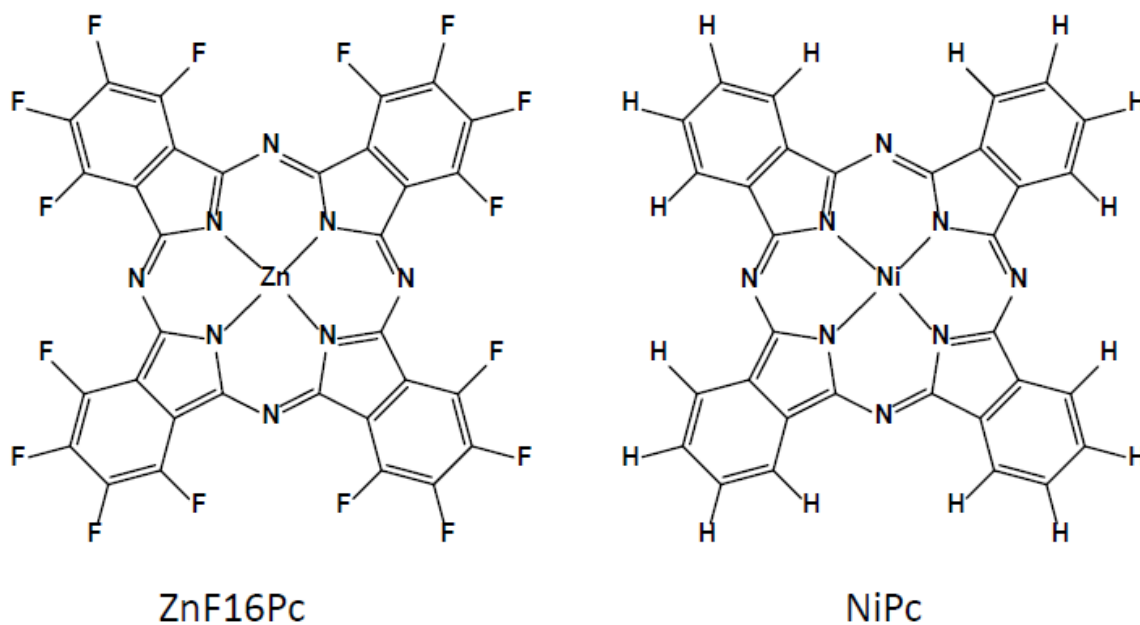


Figure 11: image of Zinc 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecafluoro-29H,31H-phthalocyanine(ZnF16Pc) and Nickel phthalocyanine(NiPc)

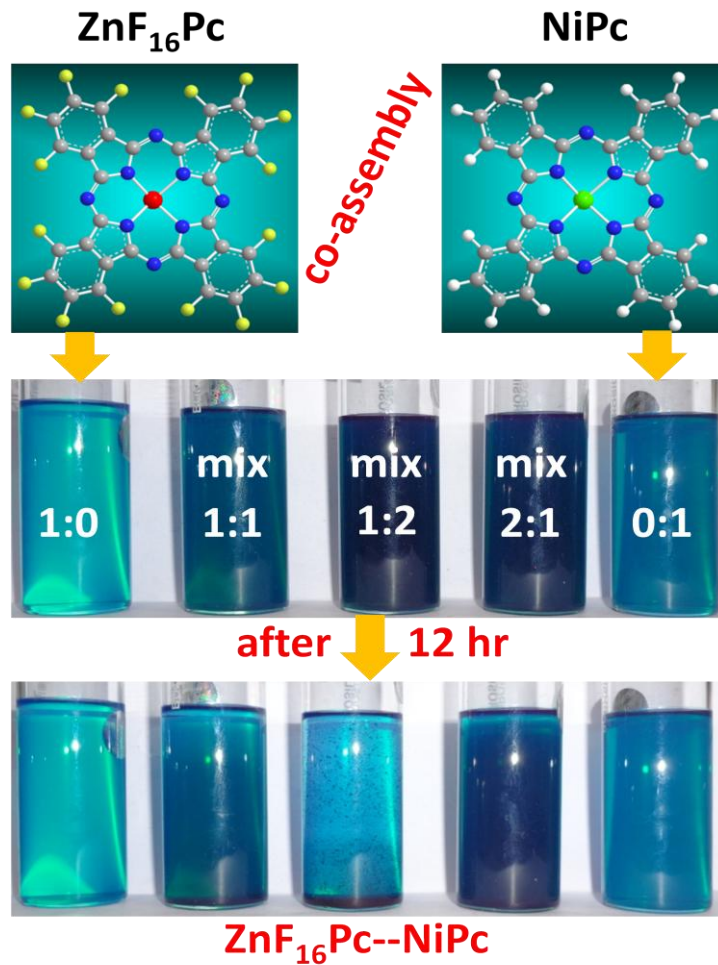


Figure 12: Solutions of ZnF₁₆Pc, NiPc and mixture ratios (1:1, 1:2 and 2:1) in chloroform

To check the composition of precipitated mixture of NiPc and ZnF₁₆Pc, three mixture of different molar ratio (1:1, 1:2 and 2:1) as well as individuals were allowed to get precipitate. Interestingly precipitate were coming in all mixture but not in case of individuals.

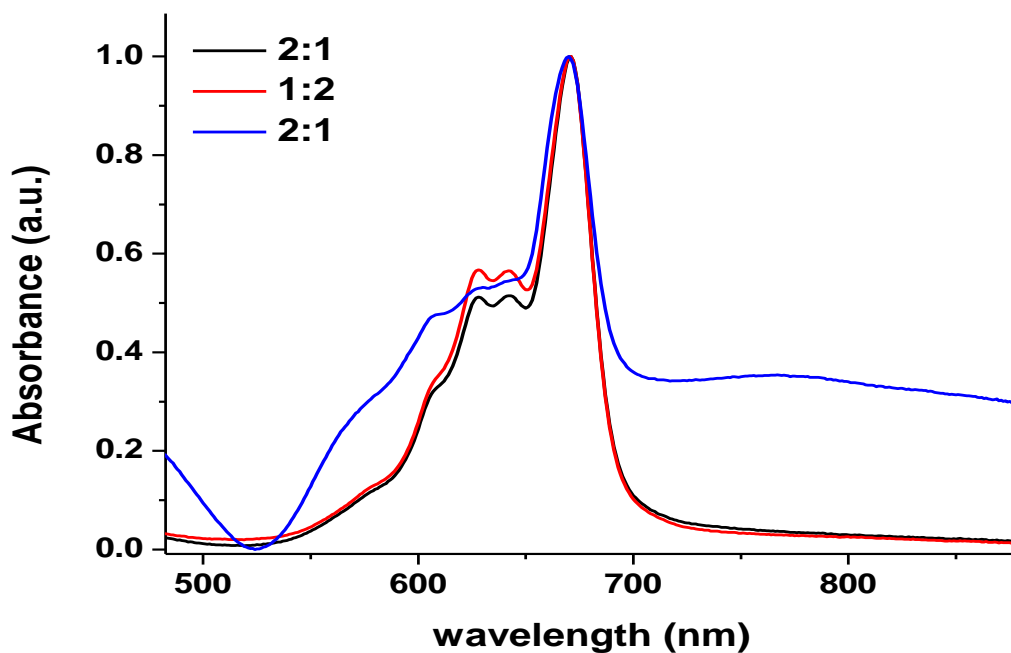


Figure 13: UV-Vis spectra for precipitated molar ratio of ZnF16Pc and NiPc

UV-Vis spectra of all molar ratios were taken in the THF solvent. The shape and location of the so-called Q-band is known to be a sensitive probe in determining the aggregation properties. All precipitates exhibit an intense Q-band absorption centered at 670nm. Interestingly spectra of all molar ratio composites showing similar absorption characteristics which imply that all the precipitate were similar from all molar ratios 1:1, 1:2 and 2:1.

Further all mixtures were characterized by Fourier Transform Infra-red (FTIR) spectroscopy.

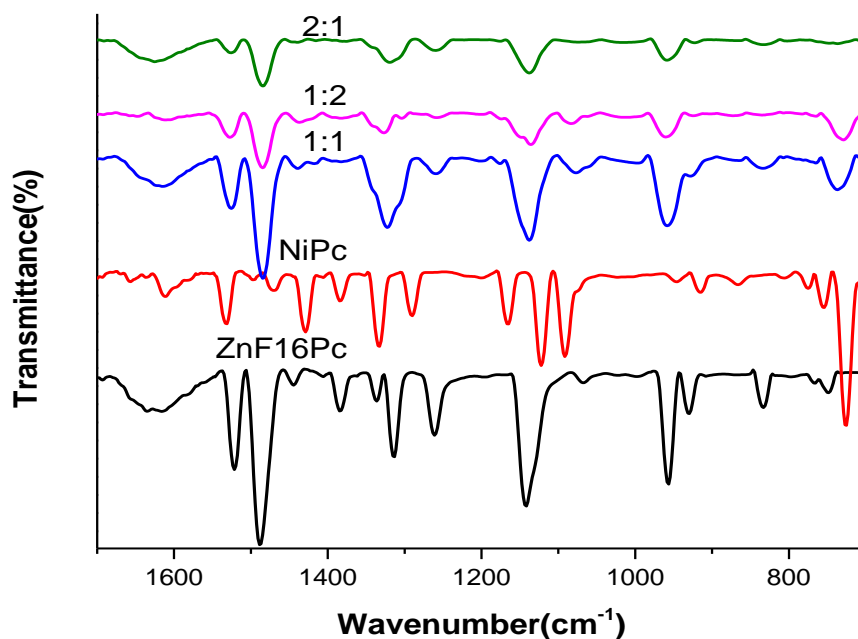


Figure 14: IR spectra of precipitate for different molar ratios and initial compounds.

FTIR spectrum of nickel phthalocyanine, fluorinated zinc phthalocyanine and different molar ratios (1:1, 1:2, 2:1) were measured in KBr pellets. Stretching vibration of C-H bond (3046-3060 cm⁻¹) has relatively low intensity¹⁴. C-C bond stretching frequency comes around 1580cm⁻¹ and spectra of frequency range around 1000-1300cm⁻¹ and 720-770cm⁻¹ also has been observed signature of inplane as well as out of plane bending mode of C_{ar}-H and C-H bond respectively. Since FT-IR spectroscopy also helps in determining the phase of metal phthalocyanine¹⁵, from FT-IR spectral feature it can be concluded that NiPc is attained neither alpha nor beta phase¹⁵ and ZnF16Pc attained alpha phase. Interestingly however, all precipitates are having the similar spectral features despite different molar ratios.

Effect of aggregation in phthalocyanine can be observed in NMR spectra. Mostly upfield can be seen in the aggregation due to the resonance of nuclei situated close to the 18- π electron macro cyclic ring with increasing concentration. Water soluble complex have been known for many years and used as NMR shift reagent¹⁶.

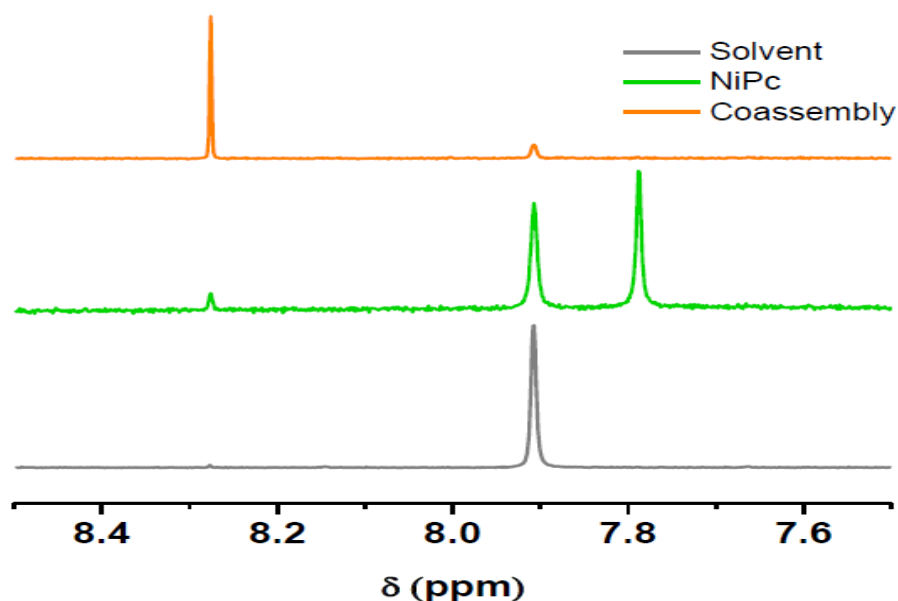


Figure 15: ¹H NMR of Nickel phthalocyanine and co-assembly (molar ratio 1:1)

Phthaloyanine ring protons in the range of 7.5 to 8.5ppm around DMSO d₆ solvent was used for ¹H NMR measurement. ¹H of Nickel phthalocyanine and 1:1 molar ratio were recorded, showing a downfield shift of aromatic hydrogen of NiPc from bare to mixture which is 7.7 ppm to 8.2 ppm¹⁰.

Scanning electron microscope (SEM) images were taken for zinc fluorinated phthalocyanine, nickel phthalocyanine and mixture of different molar ratios (1:1, 1:2, 2:1) on silicon wafer. Morphology of nickel phthalocyanine is having twisted rod shape. Length of this twisted rod is 1 to 10 μ m and width around 300 to 1000nm.

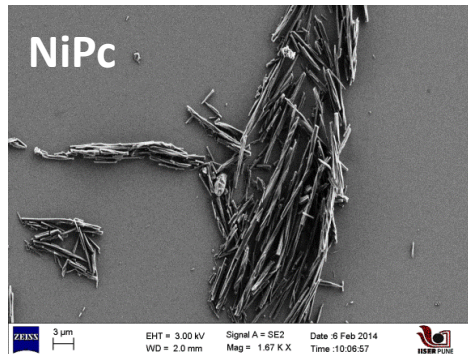
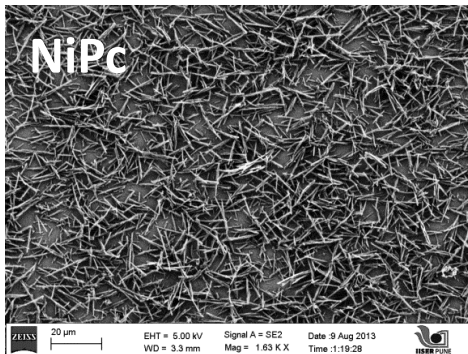
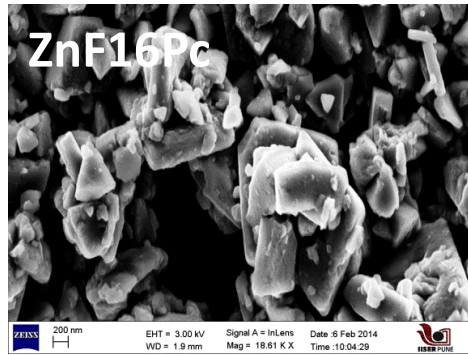
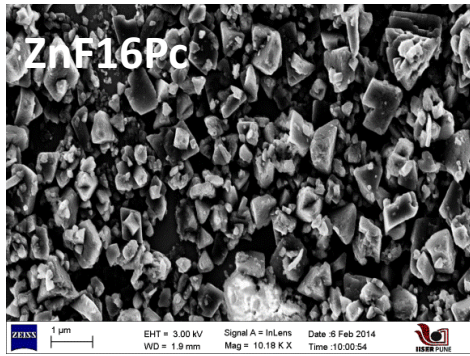
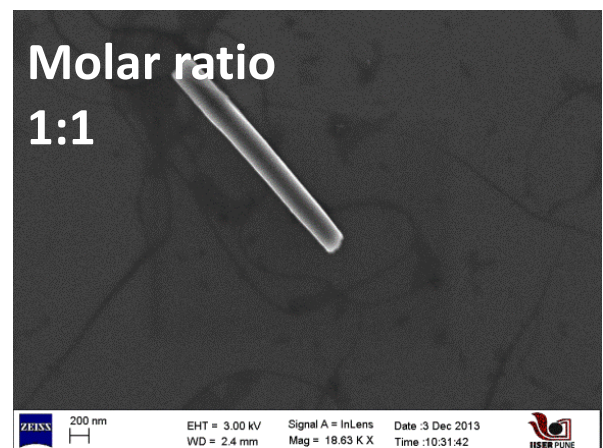
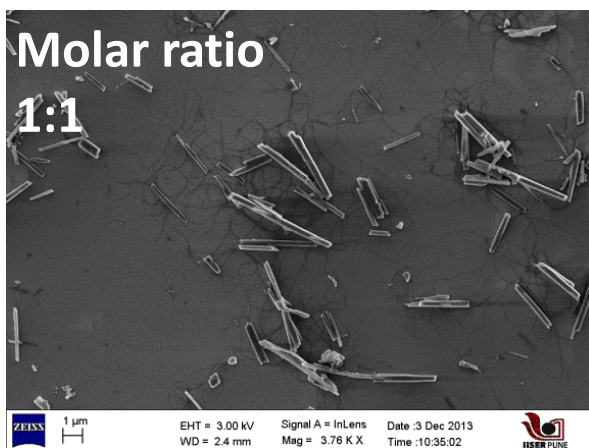


Figure 16: SEM image of Nickel phthalocyanine and Zinc fluorinated phthalocyanine

The morphology of zinc fluorinated phthalocyanine is completely different than nickel phthalocyanine which is triangular and rectangular and somewhat irregular morphology and the length varies from 200nm to 2μm.



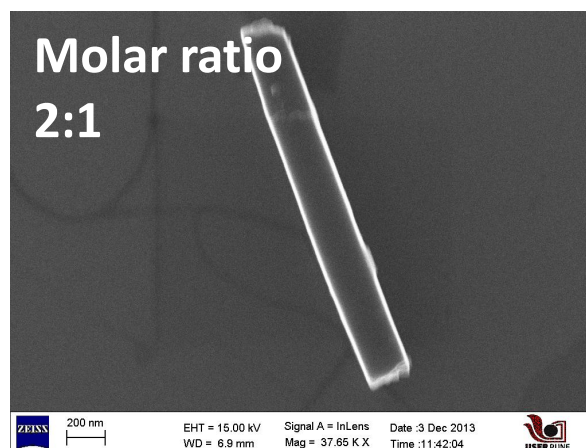
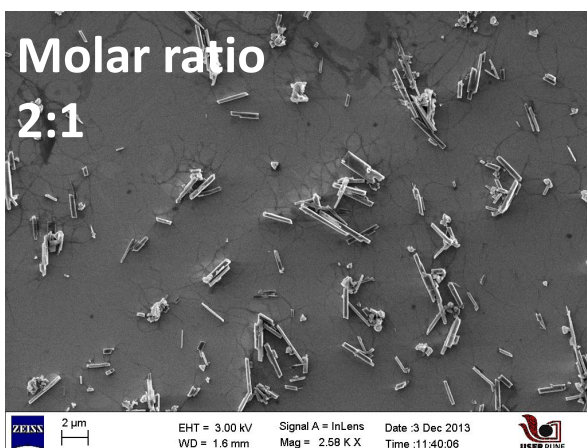
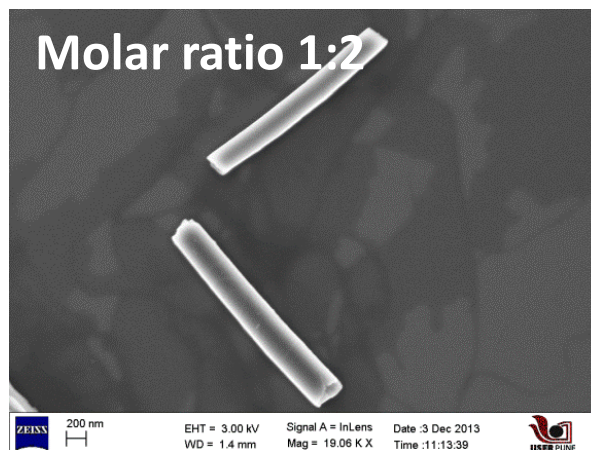
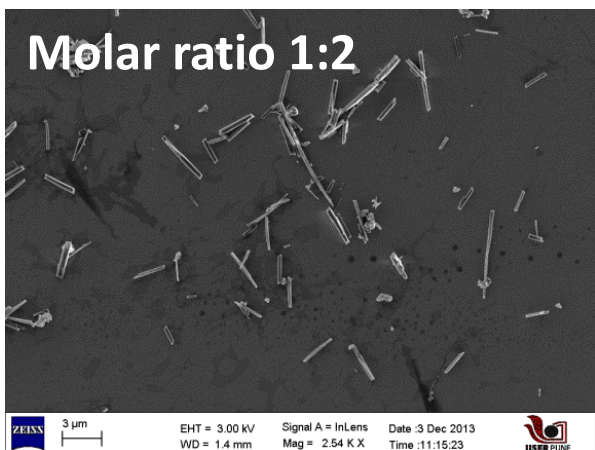


Figure 17: SEM images for precipitate of all molar ratios

SEM image of all precipitates from different molar ratios were taken and interestingly they were having same kinds of morphology (rod shape) but these are completely different from twisted rod shape of nickel phthalocyanine and irregular shape of zinc fluorinated phthalocyanine. However there are some impurities can be seen, which unreacted starting compounds because of washing problems are. Length of the rods is around 1 to 3 μm and width around 100 to 300 nm. As we can see on edge of the rod that it has layered structure which suggest that the mixture has head to head aggregation.

During the SEM imaging EDX (Energy Dispersive X-Ray) was taken for different molar ratio.

Table 1: EDX of Molar ratio 1:1

Molar ratio 1:1

Element	Weight%	Atomic%	Element	Weight%	Atomic%	Element	Weight%	Atomic%
N K	37.16	50.29	N K	36.36	50.79	N K	42.58	54.89
F K	44.18	44.09	F K	40.95	42.17	F K	43.13	40.99
Ni K	6.35	2.05	Ni K	7.16	2.39	Ni K	5.49	1.69
Zn L	12.31	3.57	Zn L	15.53	4.65	Zn L	8.80	2.43

Element	Weight%	Atomic%	Element	Weight%	Atomic%	Element	Weight%	Atomic %
N K	38.62	51.12	N K	37.47	50.11	N K	39.98	53.86
F K	45.23	44.14	F K	45.48	44.84	F K	40.59	40.31
Ni K	5.12	1.62	Ni K	5.00	1.60	Ni K	6.96	2.24
Zn L	11.02	3.13	Zn L	12.05	3.45	Zn L	12.48	3.60

In this table only four elements were taken and percentage of the metal Zn and Ni is in ratio of 1:1 respectively but sometime it was showing 2:1. However more interesting fact is that nitrogen comes from both initial compounds and fluorine come from ZnF16Pc only. Nitrogen and fluorine have same constant value individually (nitrogen in between 50 to 54% and fluorine 40 to 44%, average of nitrogen is 52%, fluorine is having 42%).

Table 2: EDX of molar ratio 1:2

Molar ratio1:2

Element	Weight%	Atomic%	Element	Weight%	Atomic%	Element	Weight%	Atomic%
N K	37.22	49.92	N K	35.56	49.64	N K	36.99	50.05
F K	45.28	44.78	F K	42.21	43.45	F K	44.59	44.48
Ni K	8.23	2.63	Ni K	7.47	2.49	Ni K	3.98	1.28
Zn L	9.27	2.66	Zn L	14.76	4.42	Zn L	14.44	4.19

Element	Weight%	Atomic%	Element	Weight%	Atomic%	Element	Weight%	Atomic%
N K	38.71	50.63	N K	34.91	48.51	N K	37.75	51.34
F K	46.89	45.22	F K	43.75	44.81	F K	42.57	42.69
Ni K	3.52	1.10	Ni K	9.81	3.25	Ni K	7.17	2.33
Zn L	10.88	3.05	Zn L	11.52	3.43	Zn L	12.51	3.65

In case of molar ratio 1:2, metal zinc and nickel are having 1:1 ratio except some cases which are having 2:1 ratio. Composition of nitrogen and fluorine are similar to the 1:1 molar ratio. The average percentage of nitrogen is 50% and fluorine is having 44%, which is approximately to the molar ratio 1:1.

Table 3: EDX for molar ratio 2:1

Molar2:1

Element	Weight%	Atomic%	Element	Weight%	Atomic%	Element	Weight%	Atomic%
N K	38.54	51.14	N K	37.28	49.02	N K	41.19	53.20
F K	45.07	44.10	F K	48.13	46.67	F K	44.93	42.78
Ni K	3.09	0.98	Ni K	6.16	1.93	Ni K	5.54	1.71
Zn L	13.30	3.78	Zn L	8.43	2.38	Zn L	8.35	2.31

Element	Weight%	Atomic%	Element	Weight%	Atomic%
N K	41.74	53.13	N K	39.01	51.91
F K	46.32	43.46	F K	43.82	42.99
Ni K	4.95	1.50	Ni K	6.29	2.00
Zn L	6.99	1.91	Zn L	10.89	3.10

EDX for molar ratio 2:1 is similar to the other molar ratio because the average of nitrogen is about 51% and fluorine is 42% and molar ratio is nearly equal to 1:1. After analyzing the EDX of mixture for all molar ratios, we can say that all the precipitates were appeared of similar materials. These results conclude that whatever molar ratio of mixture it is giving only one type of product.

Transmission electron microscopy (TEM) of molar ratio 1:1 mixture was taken and it showing layered structure and also suggest semi-crystalline nature of the material.

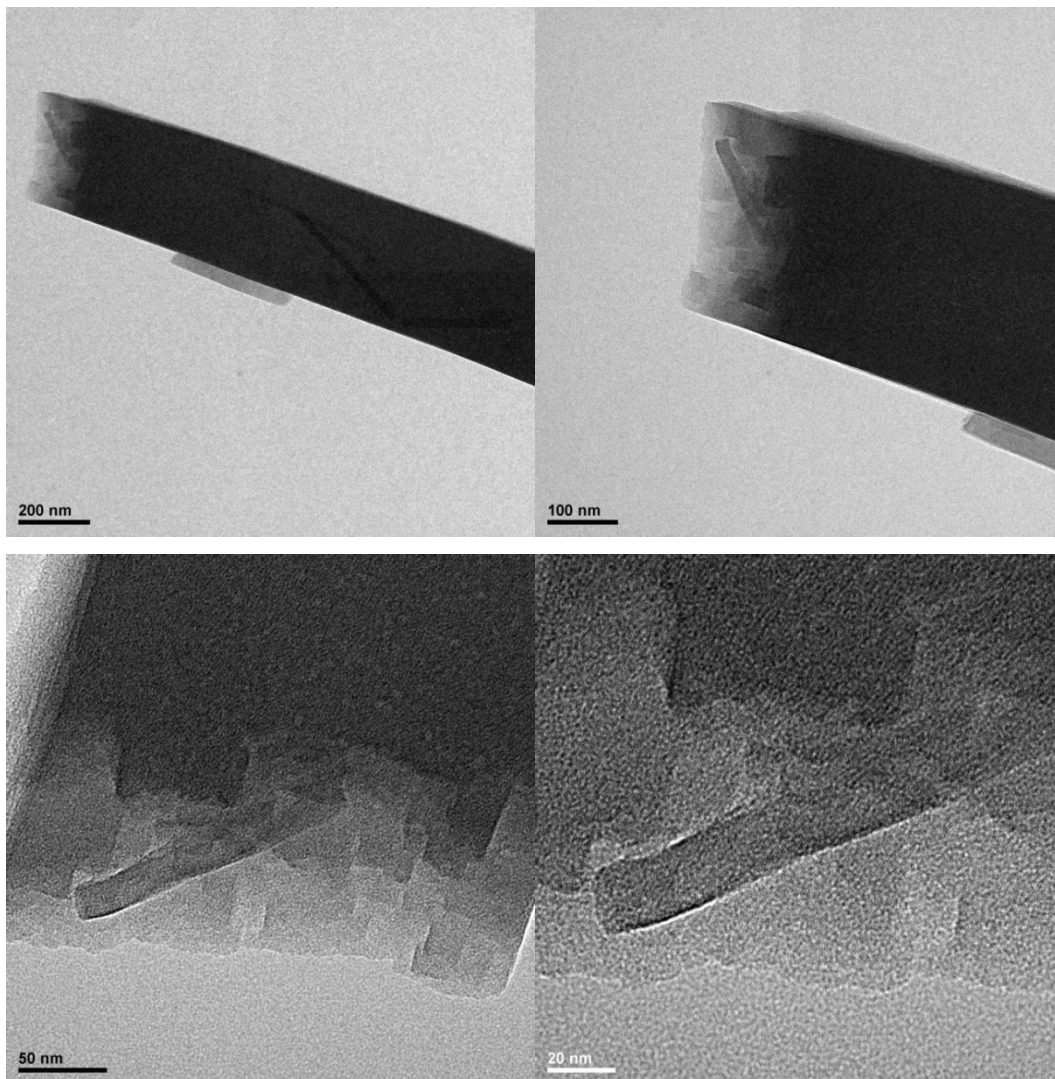


Figure 18: TEM image of mixture (molar ratio 1:1) at different scale

Powder XRD of all molar ratios and initial compounds shown in the figure. PXRD of precipitated materials were performed under room temperature. As we know that various polymorphs or crystals form can be recognize by X-ray diffraction pattern. Crystal modification leads to different intermolecular interaction in different crystal lattice therefore specific electronic and vibronic properties for each crystal.

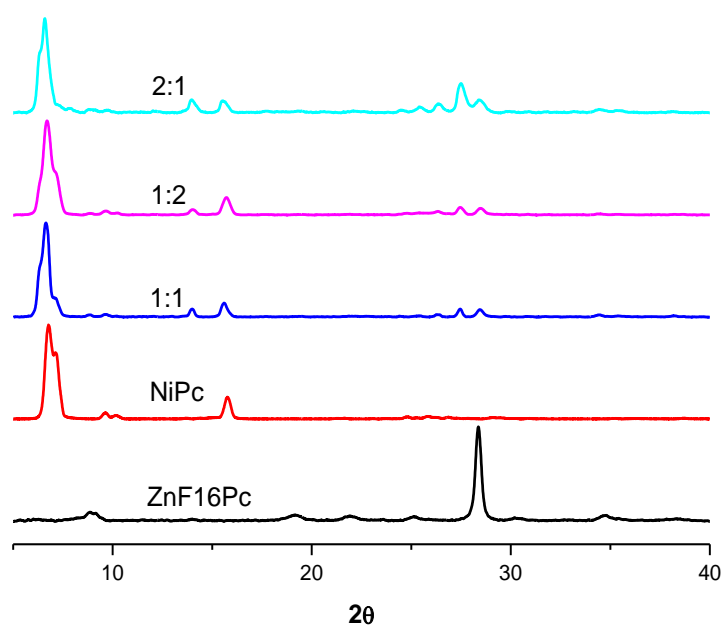


Figure 19: PXRD Pattern of initial and different molar ratios

Characteristic signature of ZnF16Pc in PXRD come at 28° and this semi crystalline and metastable and this is suggesting that it is having α -crystal modification¹⁷. Nickel phthalocyanine seems to be not having α or β -modification¹⁸ but it could be other stable phase. Initial compounds are having different phase however in mixture we are getting a completely different crystal modification. Interestingly in all the mixture of molar ratio, XRD patterns are similar. This is suggesting that in all molar ratios precipitated materials are same. Phase of mixture might having both the phases from initial compound or it is having ζ -phase⁵ or γ phase³.

Molecular weight of nickel phthalocyanine is 571.22 for zinc fluorinated phthalocyanine is 865.76. MALDI-Tof of precipitate of all the molar ratios were performed, interestingly we were getting similar mass distribution at four spot (571, 866, 1142, 1420) for all molar ratio. At mass 1142 is dimer of NiPc, 1420 is composite of NiPc and ZnF16Pc in equimolar amount.

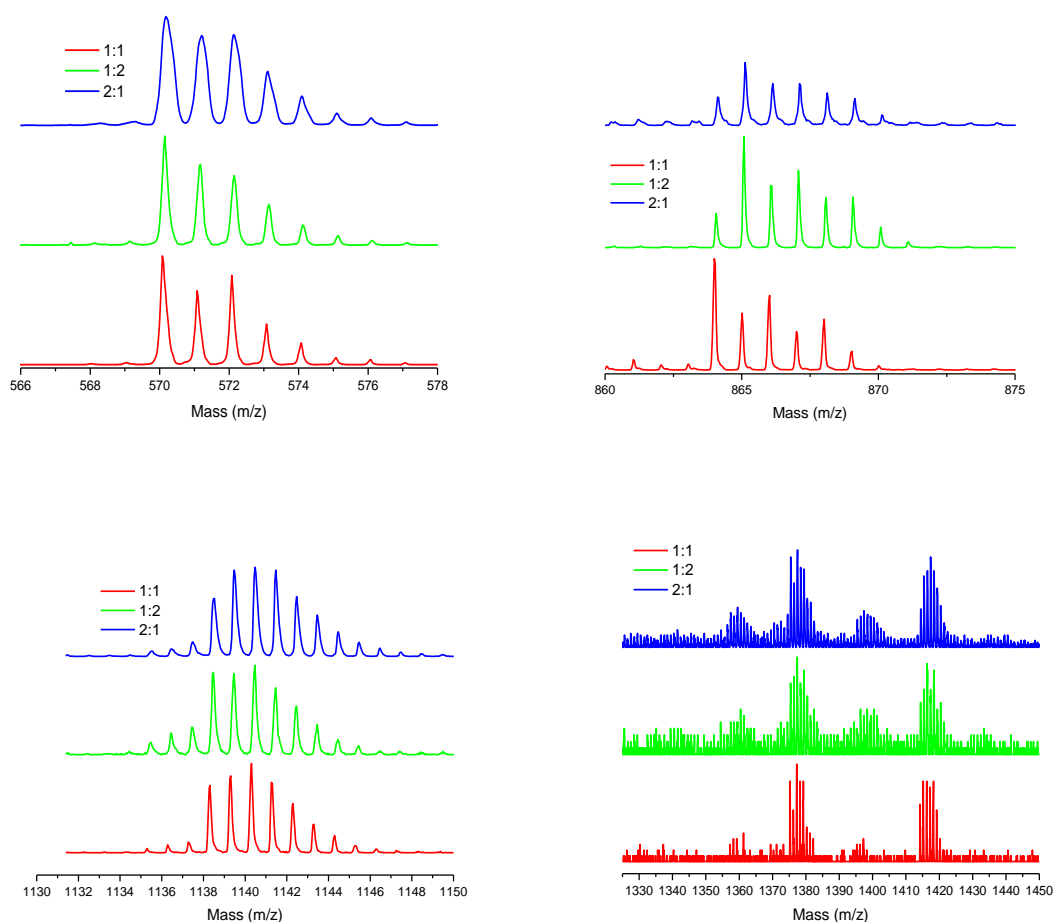


Figure 20: MALDI-TOF of all molar ratios

Conclusion

In conclusion heteroassociation between electron rich Ni(II)phthalocyanine and electron deficient 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecafluoro Zn(II)phthalocyanine for long range order has been observed first time. This heteroassociation does not depend on the molar ratio (mixture) of initial compounds; in all cases we got one product. Aggregated material is having different crystal modification than initial compounds. We proposed that driving force for this aggregation is C-H...F hydrogen bond and/or C-H... π interaction(s).

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