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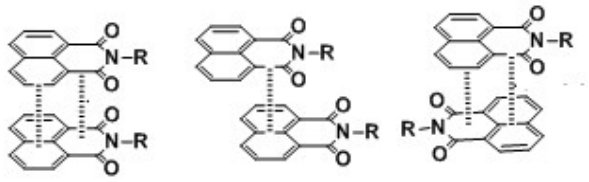
Graphical TOC:

Cyclic Aromatic Imides as a Potential Class of Molecules for Supramolecular Interactions



Prospects of stacking interactions of imides beneficial to generate new soft materials are projected by analysing examples of primary building blocks that provides basis for understanding at molecular level.

Jayanta Kumar Nath and Jubaraj B. Baruah

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Cyclic Aromatic Imides as a Potential Class of Molecules for Supramolecular Interactions

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Abstract: Cyclic aromatic imide based compounds can be a choice to meet the growing interests in soft materials as nano-dimensional materials. They serve as templates to build upon or act as host components to contribute to the knowledge of crystal engineering. Such compounds serve as the simplest building blocks of dipolar planar motifs and significantly contribute to assemblies through stacking effects of dipolar rings. The carbonyl groups of the imides provide extra stability to self-assemblies by participating in weak interaction scheme. Interactions of the carbonyl groups also provide directional effects to the supramolecular assemblies. Due to the concern of imide based compounds in biology, environment, non-conventional energy and material sectors, these units generate great impetus to use them as supramolecular systems and use of crystal engineering approach provides the answers to many important issues at the molecular level. In this article various aspects of aromatic imides focusing around their interactions with different substrates that could attract the interest of crystal engineering and supramolecular chemists is presented by taking representative examples.

General Introduction:

Cyclic aromatic imides and their derivatives exhibit various material properties. They find applications in semiconductor,[1] in organic light emitting diode,[2] liquid crystal display,[3] solar cell[4] and energy storage.[5] Moreover, due to fluorescence properties and good photostability, some imides have found extensive applications in sensing of cation[6] and anion,[7] fluorescent dyes for polymer materials[8] and as biological probes.[9] Imide derivatives have the capability to form host-guest chemistry,[10] can bind with DNA[11] and some imides also show anticancer activity.[12] Few illustrative examples of cyclic aromatic imides are shown in Figure 1.

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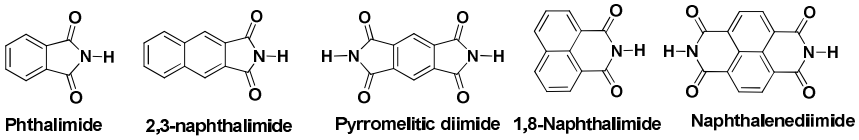

Figure 1: Representative examples of cyclic aromatic imides.

Structural skeleton of above examples are composed of two rings, one is an aromatic ring and other is imide containing ring. Thus, due to the presence of a relatively electron rich aromatic unit connected to an electron deficient imide ring, aromatic imides are dipolar. This allows them to arrange in different ways in the crystal lattices. Relative energies associated with each arrangement differ. Stacking contribution varies in energies in the range of about -12.5 to -16.5 Kcal/mol.[13] In a dipolar molecule such as 1,8-napthalimide, there can be different types of stacking interactions that may arise from the positions and arrangement of the dipoles. It has been established that the order of magnitude of interactions of two π- systems shown in Figure 2 are in the order π-deficient···π-deficient > π-deficient···π-rich > π-rich···π-rich[14a]. Such packing arrangements are guided by interplay of other weak interactions such as C-H···π, O-H···π, O···π and C-H···O which are comparable in energy.[14b-14d] Thus various self-assemblies can be generated from imide derivatives. Be a part of a coordination complex or a polymer or a discrete unit each may adopt interesting packing patterns which provides avenues for studying in domain of supramolecular chemistry.

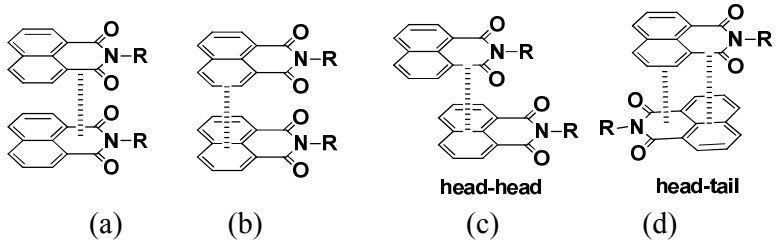

Figure 2: Different stacking arrangements in 1,8-naphthalimide derivatives: (a) π-deficient···π-deficient, (b) π-rich···π-rich and π-deficient···π-rich stacking interactions (c) head to head and (d) head to tail arrangements.

Supramolecular assemblies of cyclic imides:

Assembling of structural building blocks into regular arrays with new structural diversity and properties are one of the key features of supramolecular chemistry.[15] Host-guest chemistry[16] has tremendous potential to provide strategies to design and build these

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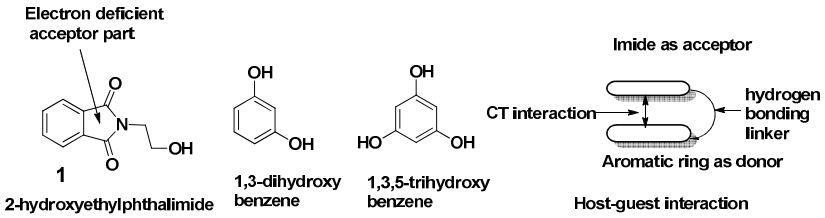
structures. Non-covalent interactions between π-donor and π-acceptor rings govern the self assemblies in solids or solution state.[16] Weak interactions such as π···π interactions, cation···π, dipole···dipole, ion···dipole also find special significances in assembling processes.[17] Stacking π···π interactions play important roles in packing of crystals containing aromatic moieties[18] Such interactions help to stabilize three-dimensional helical structures.[19] Cyclic imides generally exhibit face-to-face aromatic interactions because it contains electron deficient unit and their rigid, planar structure along with the ability to be easily functionalized with a wide variety of side groups help to tune their packing properties. Cyclic imides are widely studied to construct different host-guest systems using as precursor for intercalations,[20] foldamer,[21] ion channels,[22] catenanes[23] and rotaxanes.[24]

Structural and chemical properties make aromatic cyclic imides as ideal candidates for host-guest interactions in particular donor-acceptor charge transfer complexes. It has been shown earlier that 2-hydroxyethylphthalimide **1** forms 1:1 adduct with 1,3-dihydroxybenzene and 1,3,5-trihydroxybenzene[25] guided by hydrogen bonds and various other weak interactions leading to supramolecular-layered architecture (Scheme **1**).



Scheme 1: A design principle for inclusion of hydroxyaromatic

Because of their carcinogenic and mutagenic properties polyaromatic hydrocarbons are hazardous to mankind.[26] For these reasons it is very much essential for their detections at low concentrations. Compound *N,N′*-bis(glycinyl)pyromellitic diimide (**2**) allows intercalation of aromatic hydrocarbons such as anthracene, phenanthrene and perylene as well as tetrathiafulvalene.[27] While forming such species, less directional π-deficient and π-rich stacking interactions have been observed. In these host-guest complexes, primary self-assemblies are governed by hydrogen bonds of the carboxylic acid groups to assemble the host molecules into 1D zig-zag chains. These chains are linked together to form sheets by π···π stacking interactions between aromatic π-donor guest molecules and electron deficient π-acceptor units of host molecules (Figure 3).

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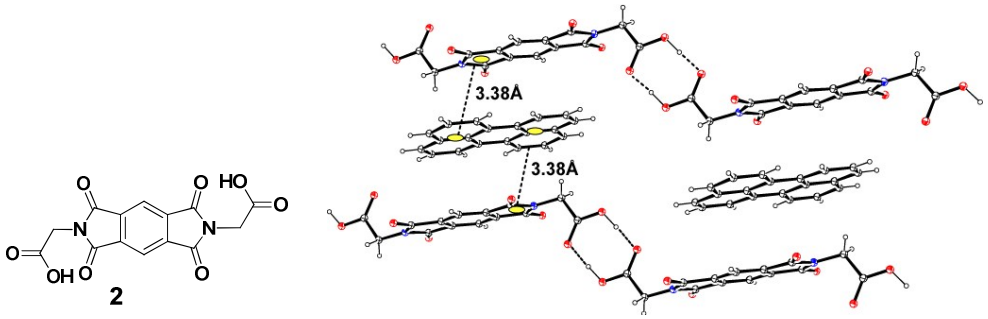
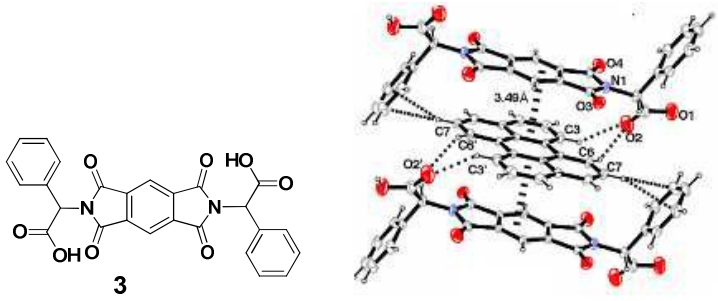


(a) (b)

Figure 3: (a) Structure of **2**, (b) π···π interactions between **2** and perylene molecules.

Introduction of phenyl group on the side chain of the host **2** changes the binding properties of the host. For example, it was observed that host **3** forms molecular host-guest assembly with polyaromatic guest molecules such as anthracene and perylene.[28] In these assemblies also π···π interactions play important role along with the conventional hydrogen bonds. The weak interactions such as C-H···π and π···π interactions guide the formation of host-guest complex between **3** and perylene which is shown in Figure 4(b).



(a) (b)

Figure 4: (a) Structure of compound **3**; (b) Host guest complex of **3** with perylene.

Rotello *et al.* have designed host systems for molecular recognition of naphthalimide through complementary hydrogen bonds in an elegant manner.[29] Based on specific binding ability of such host molecules they have developed three components molecular switches. In these examples, host molecules form three point hydrogen bonds with guest naphthalimide. The electrochemical studies on these adducts have revealed that while guest recognition takes place, the adducts show characteristic redox couples in cyclic voltamograms through their oxidised (N_{ox}) form or radical anionic (N_{rad}) form as illustrated as **4** and **5** respectively in Figure 5.[29]

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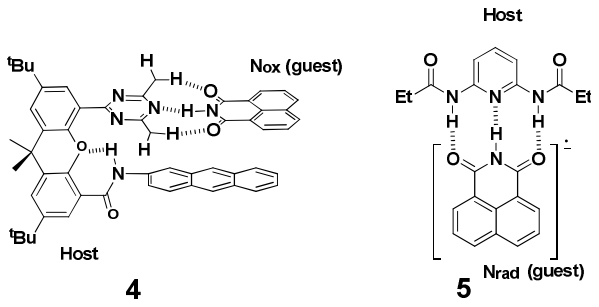

Figure 5: Recognition of oxidised form (**4**) and radical form (**5**) by host molecules.

A series of chiral amino acid functionalized naphthalenediimides derived from L-cysteine (**6**), L-lysine and their corresponding methyl esters derivatives were also reported. Sanders *et al*. have shown that these molecules exhibit molecular recognition through formation of host-guest assemblies. These molecules form supramolecular helical nano-tubes of different dimensions in aprotic solvents; one crystal structure of such a nano-tube is shown in Figure 6(b). In the given example shown in Figure 6(b) the dimension of the nano-tube is 115 nm. These nano-tubes are primarily formed by hydrogen bonds and are stabilized

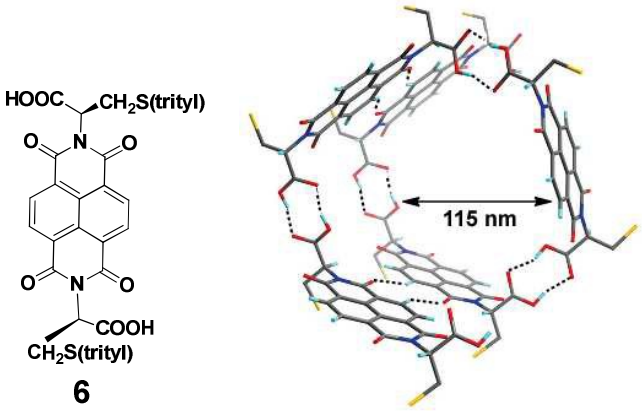

Figure 6: (a) Structure of the naphthalenediimide (**6**) derived from L-cysteine, and (b) supramolecular nano-tube formed by assemblies of **6**.

by other weak interactions. The dimensions of these nano-tubes are suitable to encapsulate polyaromatic compounds such as pyrene and their derivatives. Pyrene encapsulated nano-tubes show color in solution. Circular dichroism studies confirmed that the nano-tubes remain intact after encapsulation of guest molecules.[30] However, no significant color changes were observed if the larger analogues of pyrene were added to the nano-tubes as

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they do not fit into the cavities. Thus such assemblies are suitable for molecular recognitions.

Bispyridyl based pyromellitic diimide **7**, shows selectivity to sense various aromatic diols (chart 1).[31] Receptor **7** is highly selective that forms charge transfer complexes with phenols and naphthols. These charge transfer complexes showing different colors and intensity of colors depends on the phenols and naphthols. The charge transfer band is useful to simultaneously report multiple characteristics about a guest such as size, recognition ability, and electronic structure.[32] Thus, the differences in colorimetric responses observed in this case are due to a combination of the abilities and the electronic structure of these guest molecules to form different hydrogen-bonded complexes. Host-guest complex **8** formed between **7** and 1,3-dihydroxybenzene is shown in Chart 1.

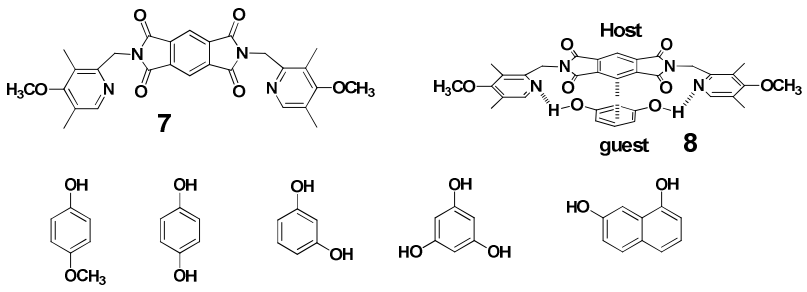

Chart 1: Host-guest complexes of imide derivatives.

Macrocyclic receptors bearing pyromelliticdiimide or naphthalenediimide, **9** and **10** bind to a wide range of electron-donor substrates (Figure 7).[33] Their bindings are assisted by π-stacking donor-acceptor interactions. These receptors are colorless but addition of π-electron donor molecules such as pyrene, perylene, 2,6-dimethoxynaphthalene, tetrathiafulvalene or pyren-1-ol to the solution of the receptor develops intense color. Such color changes are assigned to intermolecular charge-transfer absorptions. ^{1}H-NMR showed large ring-current-induced complexation shifts in each case during interactions at different proportions. Equimolar host-guest complex **11** was formed between macrocycle **10** and perylene was isolated and characterised by determining the crystal structure. In this study encapsulation of bis(8-quinolinolato)palladium(II) complex to one such macrocyclic host was shown.

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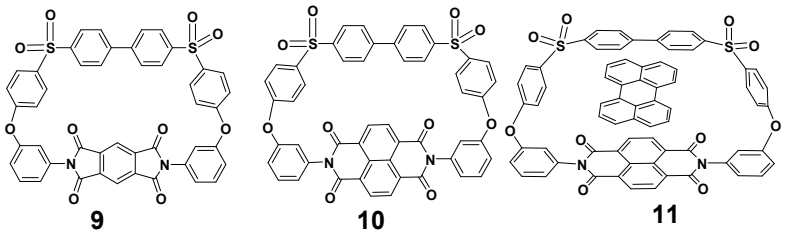

Figure 7: Macrocyclic hosts **9**, **10** and a host-guest complex **11**.

Pyromellitic diimide based cyclophane-type macrocycles with large ring size macrocyclic receptors (Figure 8) were reported by Shinmyozu *et al*. These receptors form tubular structures, those selectively encapsulate electron rich guest molecules like p-xylene and toluene.[34] High selectivity was observed to form 1:1 host-guest complex **13** between the electron-deficient host **12** and electron-rich guest. The structure of the host-guest complex was confirmed by X-ray crystallography and NMR spectroscopy. In this host-guest complex the pyromelliticdiimide moieties are arranged in parallel fashions with the benzene rings of the guest. This is an example to show the importance of a charge transfer type π···π interactions to form inclusion complex.

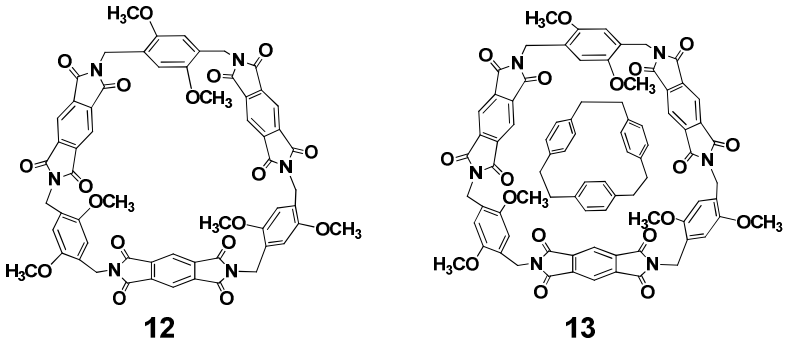

Figure 8: A macrocyclic host **12** and host-guest complex **13.**

Calix[4]arene based naphthalimide derivatives (**14)** were reported (Figure 9) and these receptors recognize aromatic molecules such as benzene, naphthalene, anthracene, pyrene and their derivatives. Guest binding properties were studied using fluorescence and UV-visible absorption spectroscopy.[35] Changes in fluorescence intensity was observed to be more in the case of compounds containing more numbers of aromatic rings. This was attributed to more π···π interactions present in such systems. An illustrative example **15** shows the binding of naphthaldehyde with **14** (Figure 9).

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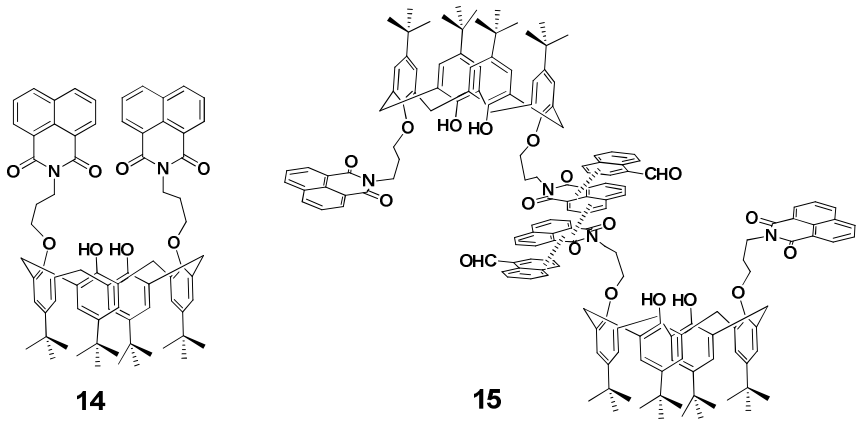
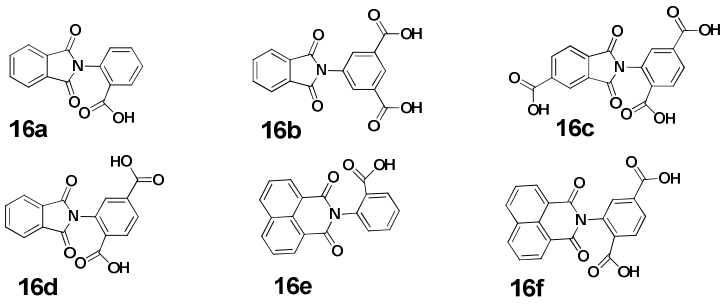


Figure 9: Structure of the host **14** and the host-guest complex **15.**

Several phthalimide and naphthalimide tethered carboxylic acids (**16a-16f**) were reported to form inclusion complexes with pyridine and quinoline. Crystal structures revealed that these complexes were formed by different hydrogen bonded motif. Depending on the assembly formed and methods of preparation, the host molecules accommodate guest molecules in different ratios.[36] In these examples pseudo polymorphs of such inclusion complexes were shown. For example **16a** can accommodate one pyridine molecule whereas **16c** can accommodate three pyridine molecules.



4-Amino-1,8-naphthalimide chromophore (**17)** were attached to cucurbit[6]uril and cucurbit[7]uril to generate different receptors with hydrophobic pockets of definite sizes. It was found that cucurbit[6]uril encapsulated a portion of the dye (Figure 10b) and such inclusion complexes have high binding constants. Strength of binding in such inclusion complexes was found to be invariant of pH of the media. Binding of dye is accompanied by fluorescence quenching and a bathochromic shift of charge-transfer absorption band of the dye. From quenching of fluorescence spectra, 1:1 host-guest complexation was established. Comparatively, cucurbit[7]uril derivative encapsulated the dye much less efficiently and it showed a significant fluorescence enhancement in contrast to fluorescence quenching shown while interacting with cucurbit[6]uril derivative. From

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such a study, dye-cucurbit[6]uril derivative has been identified as potential host for the detection of biogenic amines under physiological pH conditions and at low analyte concentrations.[37]

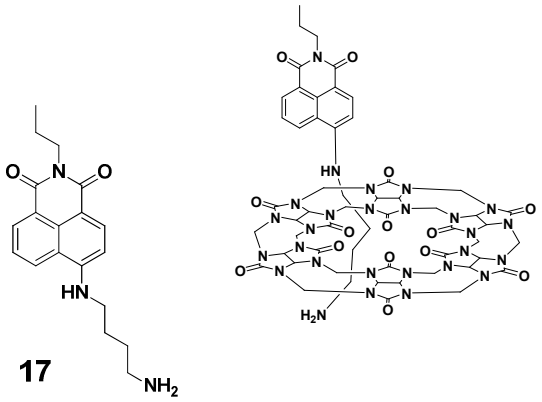

Figure 10: (a) Structure of the compound **17** and (b) the compound **17** encapsulated in cucurbit[6]uril.

From the above examples it is clear that π···π interactions in host-guest assemblies are prominent features and interplay of such interactions with other weak interactions such as C-H···O or C-H···π interactions help in the formation of these assemblies. Examples provided have clearly depicted that directional nature of the weak interactions and inherent dipolar nature of aromatic imides provide to be potential host molecules for binding to various neutral guest molecules thereby providing avenues to study molecular recognition properties.

Cyclic imides as sensors for anions:

Nature provides us many examples of anion binding motifs. Such motifs are primarily based on hydrogen-bonding interactions and they may be in charged or neutral states.[38] On the other hand, luminescent and colorimetric ion sensing is a rapidly developing field.[39] 1,8-Naphthalimide based structures connected to a receptor derived from molecules such as urea[40], thiourea[41] and amide[42] have been extensively used for anion recognition. Sensing as well as recognition is routinely carried out in organic, aqueous solutions, or within various polymeric networks. In such cases use of confined media such as hydrogels is of worth noting.[43] In the last decade, owing to many demonstrated examples of naphthalimide-based anion sensors,[44] versatility of this class of molecules within the fast

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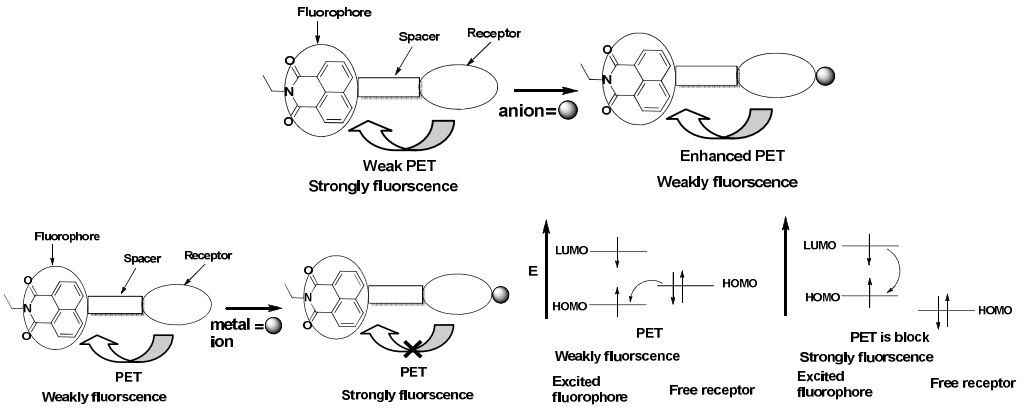
growing field of research has made a big impact. Structural modifications on an imide can be done easily on aromatic naphthalene moiety or at the N-imide site, which provide scopes to incorporate varieties of functional groups at these sites. UV-visible absorption and fluorescence emission spectra of naphthalimide can be easily tuned through judicious structural design. The optical properties of many naphthalimide derivatives depend on environments and more importantly on solvents. Thus they can either be solvochromic or solvatoemissive, which makes them advantageous to study as receptors in biological systems or for molecular recognitions. Their optical responses to different analytes are different but such changes occur in selective manner. Moreover, hydrogen-bonded receptors, as well as charged assisted anion receptors have been extensively used for anion recognition and sensing. Generally photo-induced electron transfer (PET) and internal charge transfer (ICT) are the most extensively studied processes to sense anions. Both these paths independently or in combined manner are effective to cause specific changes in optical spectra. In PET probes, a fluorophore is usually connected via a spacer to a receptor containing electronegative atoms such as nitrogen atom. Relatively high energy nonbonding electron pair presents in a receptor can transfer an electron to excited fluorophore, leading to the quenching of fluorescence. Upon binding to anion fluorescence emission gets quenched due to enhanced PET from the receptor to the excited state of the



Scheme 2: Schematic representations of PET with naphthalimide derivatives

fluorophore. However, upon coordination to a metal cation, reduction potential of a receptor increases so that corresponding energy of highest occupied molecular orbital is lower than that of fluorophore. As a consequence, PET process from receptor to

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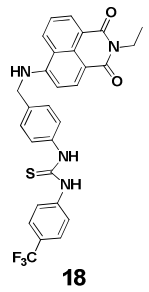
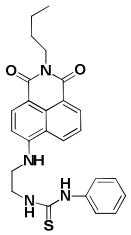
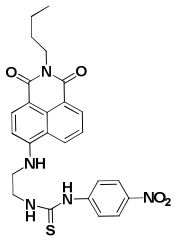
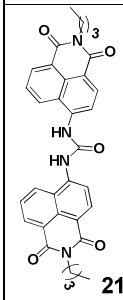
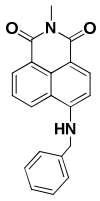
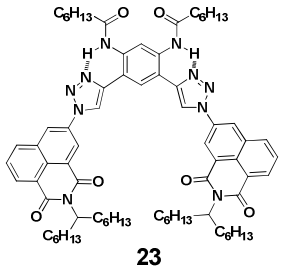
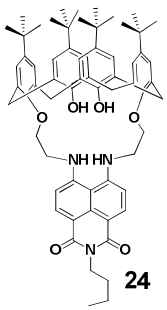
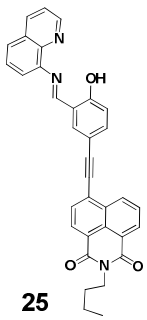
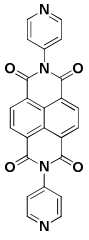
fluorophore is prohibited. In this process fluorescence intensity enhances. Polarity of a solvent can affect the oxidation potential of the receptor, thus use of highly polar solvent, PET-mediated quenching effect of the fluorescence occurs more quickly in polar solvent. There are many examples of sensors for detecting ions which are designed with sequence of arrangements of components as fluorophore-spacer-receptor, they operates through PET mechanism (Scheme 2).[45a-b] Thiourea functional unit connected to naphthalimide have been extensively reported as colorimetric anion sensors.[45c-e] Thiourea based naphthalimide receptor for anions have generated large interest due to ease to synthesize and handle at ambient conditions. In such sensors, thiourea parts act as anion receptors and naphthalimide moiety acts as a fluorophore. ^{1}H-NMR spectroscopy has been used as tool for detection of anions. Thiourea unit directly connected to naphthalimide unit has also been reported to recognize different anions.[46]

Table 1: Examples of some common naphthalimide based anion sensors.

Sensor	Anion	Sensor	Anion	Sensor	Anion
 **18**	F^- Ref. 47a	 **19**	$H_2PO_4^-$ Ref. 47b	 **20**	F^- and AcO^- Ref. 47c
 **21**	F^- and OH^- Ref. 47d	 **22**	F^- Ref. 47e	 **23**	Cl^- Ref. 47f
 **24**	F^- Ref. 47g	 **25**	F^- Ref. 47h	 **26**	F^- Ref. 50

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Receptors **18-26** behave as dual responsive chemosensor for selective detection of different anions such as F^-, Cl^-, $H_2PO_4^-$, AcO^-, OH^- ion.[47] These receptors display dual sensing actions for specific anion. Upon addition of an anion, they give rise to large changes in the UV-visible spectra (red shift) and show quenching of fluorescence intensity. Changes take place due to formation of 1:1 complex either through hydrogen bonds or through proton transfer of amino moiety. A few common naphthalimide based anion sensors are listed in the Table 1.

Anion-π interaction is a quadrupolar interaction that occurs between an appropriately placed anion over a π-cloud. Naphthalimide based compounds are well known for anion-π interactions which are reflected in their absorption and emission spectra.[48]

One illustrative interaction of chloride interacting cyano substituted naphthalenediimide derivative is shown in Figure 11. On the basis of such observations, naphthalenediimide based molecules were employed for selective anion recognition through anion-π interactions.[49a] Based on the type of anion-π interactions chloride or bromide anions can be differentiated from oxy-anions through changes in the respective fluorescence emission.[49b] Anion-π interactions and charge transfer or electron transfer involving F^- ions to naphthalenediimides are reflected in their emission and absorption spectra. Utilities of such effects were shown in π-electron deficient colorless naphthalenediimide receptors

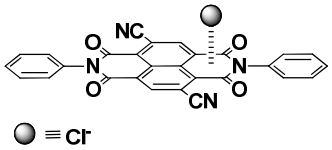

Figure 11: An example of Cl^--π interaction with naphthaenediimide derivative

bearing bis-pyridyl groups (**26)** shown in Table **1**. Strong electronic interactions between lone-pair electrons on F^- ions and π^*-orbitals of naphthalenediimide unit led to development of an orange color due to formation radical anion of naphthalenediimide. Further reduction of such radicals by another F^- ion, generate colored dianion of naphthalenediimide. Such color changes are useful to selectively detect F^- ions and they operate in a very specific manner over various other anions.[50]

Another methodology to detect anion by naphthalimide based sensors involve, uses of metal complexes containing naphthalimide units as a part of its ligand that serves as template for anion binding. While an anion interacts directly or indirectly with the metal ions, fluorescence properties of naphthalimide group changes leading to transducer signals. Based on such principle, both naphthalimide and naphthalenediimide based metal complexes or coordination polymers have been utilised to sense different anions.

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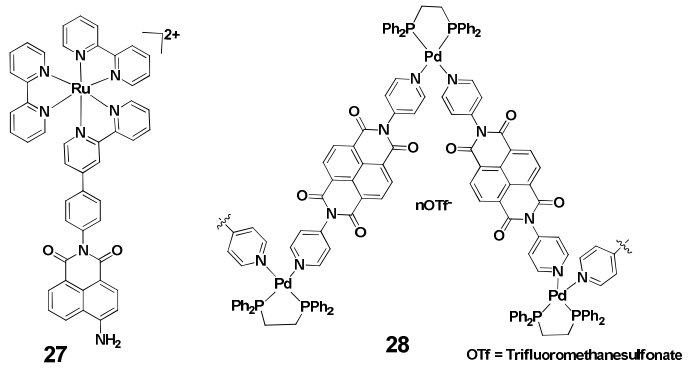

Ruthenium (II) based polypyridyl conjugate **27** was used as sensor for F^- ion in acetonitrile.[51] In this example, a metal to ligand charge transfer luminescence process is made use of to detect anions. This complex can effectively sense fluoride ion in presence of other anions such as acetate, phosphate and chloride. Palladium(II) coordination polymer **28** detects fluoride ions through anion-π interactions. Electrochemical studies showed that trifluoromethanesulfonate anions suppressed π-acidity of dipyridyl naphthalenediimide whereas in a palladium(II) coordination complex π-acidity of dipyridyl naphthalenediimide gets enhanced. Thus, enhanced ability of F^- ions to cause electron transfer to dipyridyl naphthalenediimide of the palladium (II) dipyridyl naphthalenediimide coordination polymer led to colorimetric sensing of F^- ions.[52]

Anion-π interactions of naphthalenediimide have also relevance in ion-transport in biological systems. Important applications of anion-π interaction of such molecules are developed to study transport of anions across lipid bilayer membranes.[53,54] These kinds of studies are important as variety of diseases or channelopathies, most notably cystic fibrosis, arises when anion transport across biological membranes gets disrupted.[55] A range of compounds that function as discrete molecular carriers or as synthetic channels allowing anions to pass through a lipid bilayer are developed. Such molecules also provide an approach for modelling synthetic ion transporter which can mimic different biological activities such as trans-membrane anion transport and also to photosynthetic activity in system having anion-π interactions[56] for selectivity and multi-ion hopping across lipid bilayer membranes.[57] Naphthalenediimide group were derivatized to generate hydrophobic rigid-rod like structural backbones. Such rods were designed such that they are long enough to span width of phospholipids bilayer. Matile *et al.* correlated theoretical

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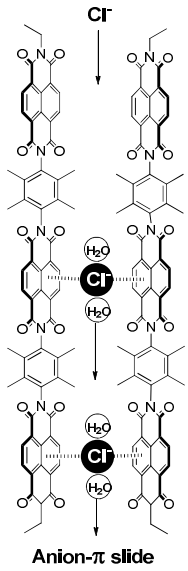

Figure 12: Concept of anion- π slide in naphthalenediimide derivative

and experimental findings of anion-π slides for chloride-selective multi ion hopping across lipid bilayer by synthesizing shape-persistent oligo-p-phenylene-N,N'-naphthalenediimide as π-rods. The concept of anion-π slide in lipid bilayer is shown in Figure 12.[58] These compounds were shown by spectroscopic to be assays for measuring pH and ion concentrations inside phospholipid vesicles. It was also found that these hydrophobic and π-acidic rods can selectively transport anions across lipid membranes.

Cyclic imides as sensors for cations:

Design of chemo-sensors for transition metal ion is actively investigated, as this metal ion is a significant environmental pollutant and an essential trace element in biological systems. Cyclic imides are also frequently used for colorimetric and ratiometric chemosensors for metal ions. Depending on design principles, absorption and emission spectra of imide can be highly modulated by binding to cations. To recognize metal cations, the receptors should have some pre-organized binding sites. This criterion is fulfilled easily by functionalization with different units which has metal binding sites. Imide functional group contributes to supramolecular architecture of metal complexes, as well as they may be fluorescent or electroactive, such properties can be easily modulated and studied to design cation sensors. These compounds exhibit fluorescence responses to an analyte via Photo induced electron transfer (PET),[59] Intramolecular charge transfer (ICT),[60] Fluorescence resonance energy transfer (FRET)[61] and exciplex[62] mechanisms.

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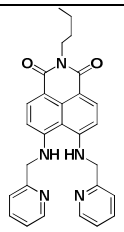
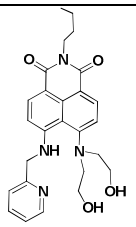
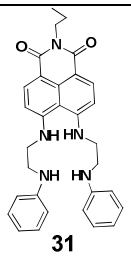
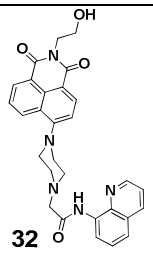
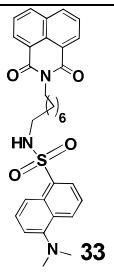
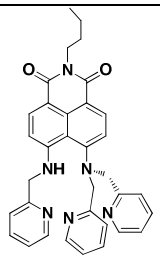
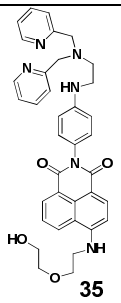
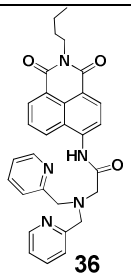
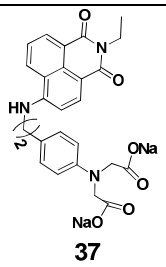
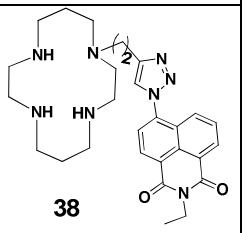
4-amino-1,8-naphthalimide derivatives have been reported by various group as a colorimetric and ratiometric sensors for different transition metal ions. In these classes of compounds addition of metal ion changes in both UV-visible spectra and fluorescence spectra are observed due to the binding of receptor to the metal ion through N and O atom. In some cases deprotonation of secondary amine also takes place which facilitate the formation of metal conjugate and as a result of which internal charge transfer takes place from metal complex to fluorophore. The proposed mechanism for the detection of M^{2+} is generally based on the binding of donor atoms to metal ions or M^{2+}-induced deprotonation of the secondary amine directly conjugating with the 4-amino-1,8- naphthalimide

Table 2: Cu^{2+} and Zn^{2+} ion sensors based on naphthalimides.

M^{2+}	Sensor				
Cu^{2+}	 **29** Ref. 63a	 **30** Ref.63b	 **31** Ref. 63c	 **32** Ref. 63d	 **33** Ref. 63e
Zn^{2+}	 **34** Ref. 63f	 **35** Ref. 63g	 **36** Ref 63h	 **37** Ref. 63i-j	 **38** Ref. 63k

chromophore and changes in fluorescence spectra are due to photo induced electron transfer or internal charge transfer mechanism. A few common metal ion sensors (**29-38**) for Cu^{2+} and Zn^{2+} ions are shown in the Table 2.[63]

Naphthalimide based fluorescence ratiometric probes **39-42** were reported for selective detection of trivalent ions such as Cr^{3+}, Fe^{3+} and Al^{3+} over other metal ions (Table 3). In

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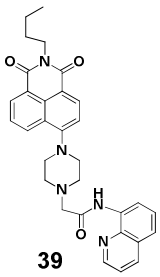
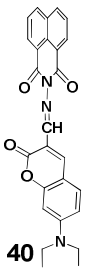
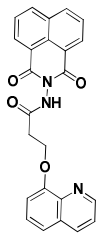
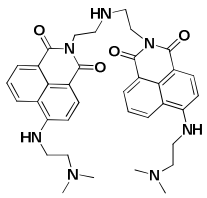
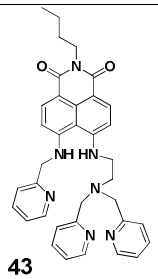
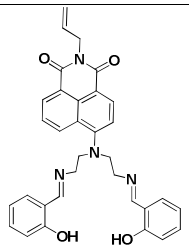
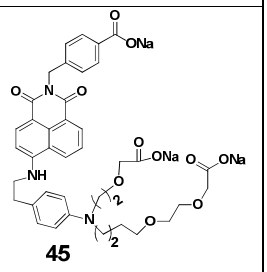
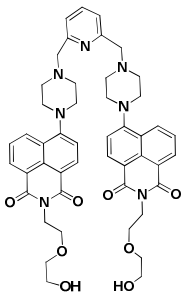
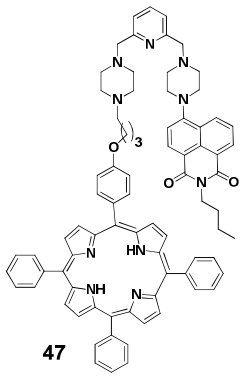
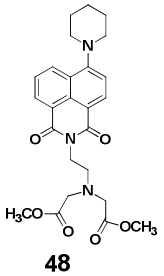
Table 3: Some naphthalimide sensors for trivalent metal ions.

M^{3+}	Sensor	M^{3+}	Sensor	M^{3+}	Sensor	M^{3+}	Sensor
Cr^{3+}	 **39** Ref. 64a	Fe^{3+}	 **40** Ref. 64b	Cr^{3+} Fe^{3+} Al^{3+}	 **41** Ref. 64c	Cr^{3+} Fe^{3+}	 **42** Ref. 64d

case of sensor **40,** it can specifically recognizes Fe^{3+} over other monovalent, divalent and trivalent metal ions through changing the conformation of naphthalimide moiety.[64]

Heavy metal ions and first row transition-metal ions usually play important roles in various biological systems or have toxic impacts on the environment. In particular, cadmium and mercury ions are considered to be very dangerous environmental pollutants by bio-accumulating through the food chain when they are ingested or inhaled by human

Table 4: Examples of naphthalimide based sensors for cadmium and mercury ion.

M^{2+}	Sensor		
Cd^{2+}	 **43** Ref. 65a	 **44** Ref. 65b	 **45** Ref. 65c
Hg^{2+}	 **46** Ref. 65d	 **47** Ref. 65e	 **48** Ref. 65f

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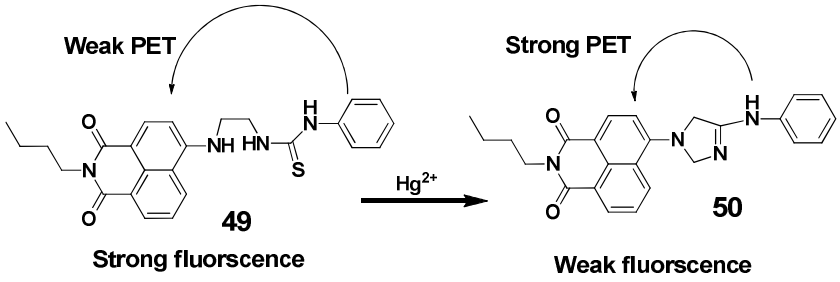
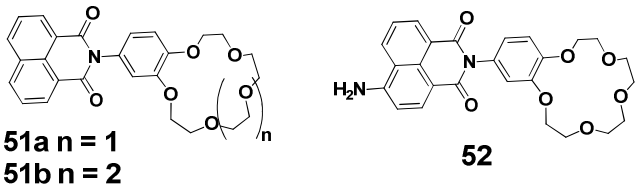
beings. Due to issues of environmental health hazard, a large numbers of chemo sensors for detection of cadmium and mercury have been reported till date. A few naphthalimide based ratiometric and highly fluorescence sensors (**43**-**48**) for cadmium (II) and mercury (II) ions are shown in Table 4.[65]

Thiourea based naphthalimide derivative **49** was used for detection of mercury (II) ions. Addition of mercury (II) ion to a solution of **49** causes quenching of fluorescence; quenching occurs through photo induced electron transfer mechanism present in a chemically transformed species. Mercury (II) ion facilitates desulfurization cum cyclization to form a phenyl imidazole derivative **50** (Scheme **3**). The chemical transformation generates a species which has the aniline part at a closer proximity than the parent compound, thus facilitates photo induced electron transfer in this case much efficiently. The receptor is highly selective in detecting mercury (II) ion in presence of other divalent metal ions. In order to improve practical applicability of such sensors in aqueous environment, gold-nanoparticle are also used to immobilize naphthalimide receptor to generate characteristic optical signals.[66]



Scheme 3: Enhancement of fluorescence through PET mechanism.

Crown effect of cyclic ethers tethered to naphthalimide leading to molecules such as 15-crown-5 (**51a**) and 18-crown-6 (**51b**) receptor for Na^+ and K^+ ions were reported. This class of molecules are highly soluble in water act as OFF-ON, dual fluorescent probes for



alkali metal ions. Depending upon the size of cations **51a** selectively binds Na^+ over K^+, whether **51b** displays higher sensitivity to K^+ relative to Na^+ ions.[67] Introduction of amine group at 4 position of **51a,** receptor **52** show specific binding towards Ba^{2+} ions.[68]

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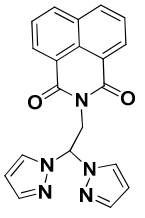
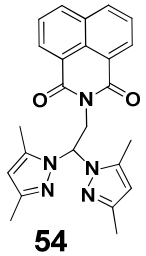
Coordination chemistry/polymers with cyclic imides and related compounds:

Cyclic imides derivatives containing different functional groups having suitable binding sites have been used to synthesize different metal complexes with diverse structures. Such ligands are extensively used in ion detections and are discussed partially in earlier section. Imides can be deprotonated to form metal complexes in which N-M bond prevails. In another class of reactions they may be used as precursors to result in amide or carboxylate ligands through ring opening reactions. This class of compounds are useful for synthesis of coordination polymers.[69] N-substituted cyclic imide derivatives are often used to construct highly organized structures with different metal ions. These organized structures are formed especially from 1,8-naphthalimide or naphthalenediimide derivatives through a large range of bonding forces like classic M-donor atom bonds, to strong halogen or hydrogen bonds to much weaker forces such as weak hydrogen bonds and π···π stacking of small aromatics leading to various supramolecular architectures. Naphthalimide derivatives have been utilized as building blocks in metal based supramolecular architectures due to their π-deficient nature and ability to be readily functionalized. This nature has been exploited giving rise to systems in which extension of the structures occur through π-stacked interactions giving rise to new structures with new material properties. This type of work has largely been pioneered by Reger and co-workers over last decade, where they functionalized 1,8-naphthalimide moiety with various functional groups such as carboxylates, pyrazoles and other coordinating groups at the imide nitrogen site.[70] These functionalities have been used to construct various MOFs by reacting with transition metal ions as well as group 1 and group 2 metal ions and studied their structural aspects.

1,8-Naphthalimide group incorporated into a bis(pyrazolyl)methane ligand system (**53-54**) are useful in the formation of silver complexes. In these complexes depending on the compositions and substituent, different supramolecular structures formed through π···π stacking interactions were observed.



53



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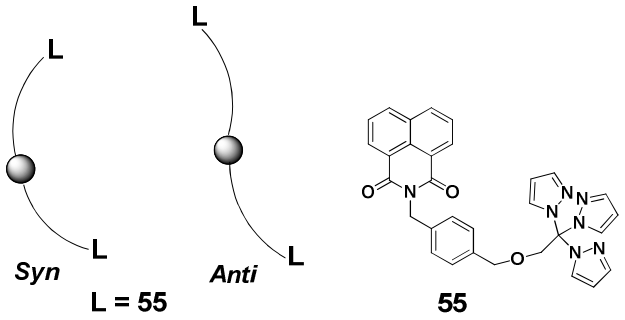
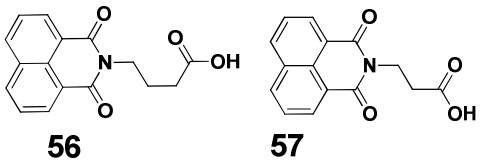
These examples provides viable means for studying interplay of weak interactions contributing to the organization of the basic building blocks into higher dimensionality architectures.[71]



Scheme 4: Conformational isomers from naphthalimide derivative **55**.

Hetero-bifunctional ligand, **55** forms *syn* and *anti* conformations (Scheme 4) by complexing with copper (II), iron (II) and cadmium (II) metal ions. Strong π···π stacking of the 1,8-naphthalimide functional groups dominates noncovalent structures of these four complexes.[72]

Naphthalimide containing aliphatic carboxylic acids **(56-57)** formed dimeric copper (II) complexes in the presence of either pyridine or 4,4′-bipyridine having dimeric cores of paddlewheel type structure. Strong π-stacking interactions of 1,8-naphthalimide groups organize these structures into sheets and 3D structures.[73]



Trifunctional ligand, **58** contains a carboxylate donor group, a homochiral center which are derived from L-alanine and a strong π-stacking, 1,8-naphthalimide synthon. This ligand has been used to form copper (II) complexes in which packing patterns are guided by strong π···π stacking interactions. Such interactions lead to the formation of homochiral, helical, 3D supramolecular metal-organic framework. These complexes show conventional paramagnetic properties of copper (II) complexes in the temperature range 20 K to 300 K. Possibility of intermolecular magnetic couplings below 20 K was suggested.[74] A tetrameric copper (II) metallacycle, $[Cu_4(\mathbf{59})_8(py)(MeOH)]$ was formed from L-aspargine containing naphthalimide, **59** that shows optical activity**.** The methanol

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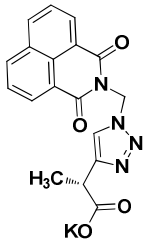
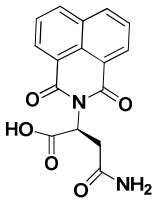


58



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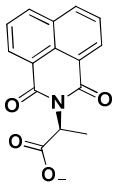

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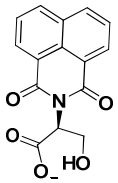

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ligand in this complex is located in a chiral pocket. Guest molecule can be replaced by exposing it to racemic ethyl-lactate vapour to form enantioselective optical isomer [Cu_4(**59**)$_8$(py)((S)-ethyl-lactate)]. This change can occur in a single-crystal to single crystal transformation.[75] Chiral amino acids tethered naphthalimide ligands of L-alanine and L-serine (**60-61**) were found to form homochiral metal-organic frameworks of group 1 and group 2 metal ions.[76] Ligand **60** forms tetrameric zinc (II) [Zn_4(**60**)$_6$$(OH)_2$$(MeOH)_4$]·3($CH_2Cl_2$)·2(MeOH) whereas a dimeric cadmium (II) complex ([Cd_2(**60**)$_4$$(DMF)_3$(MeOH)] was formed on reaction with cadmium ions. Strong π-stacking 1,8-naphthalimide organize tetramers into a 3D architecture that contains linked, homochiral helical chains. Same ligand formed a dimeric cadmium complex with a 2D sheet structure. Both these complexes show luminescent properties in solid state.[77]

A series of enantiopure metal complexes of calcium (II) and strontium (II) with optically active ligands **60** and **61** were reported. In these complexes π-stacking interactions between 1,8-naphthalimide rings link adjacent rod like units of secondary building blocks into two and three-dimensional structures.[78] Interestingly, group 1 and group 2 metal ions bound to the carbonyl oxygen atoms of naphthalimide unit contribute to formation of complex structures. In all such cases, strong π···π interactions dominates in constructions of supramolecular architecture.

Zaworotko *et al*. reported imide ligand formed by condensation of 4-amino-pyridine and trimellitic anhydride **62**. This ligand generates a series of isostructural porous metal-organic complexes when coordinated to cobalt (II), nickel (II), copper (II), and cadmium (II) ions. These isostructural metal-organic materials were found to exhibit a porous structure having square channels. They are capable to efficiently store hydrogen gas.[79a] Another phthalimide derivative of benzene-1,3-dicarboxylic acid **63** forms two supramolecular isomers with [Cu_2(**63**)$_4$]. Distinctions in their structures are very prominent; although in both cases paddlewheel dimeric copper carboxylate units are reflected as repeat units, but the final patterns in one case is Kagome lattice and in other is

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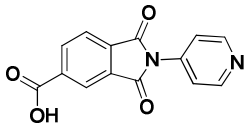
NbO net topology.[79b] Formation of these supramolecular isomers are guided by solvents used during synthesis.



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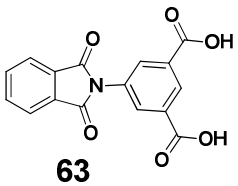
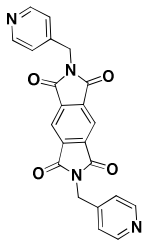


63

Su *et al* have reported a series of manganese (II), cadmium (II), and cobalt (II) complexes with semi-rigid ligands **64-67.** Characteristic feature of these ligands is that they have two relatively flexible pyridyl arms at two ends of diimides. Thus various conformations across imide are possible depending on the orientation of the pyridyl groups. These ligands generate discrete zero-dimensional to polymeric three-dimensional coordination polymers though self assemblies. In solid state the packing patterns of these coordination polymers are guided by hydrogen bonds and π-interactions. Some of these coordination polymers are used as photoactive materials.[80]

A series of complexes of mercury (II), cadmium (II), zinc (II) and cobalt (II) with ligand **66**, were synthesized. Due to flexibility of the ligand, they adopt different conformations



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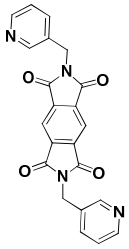

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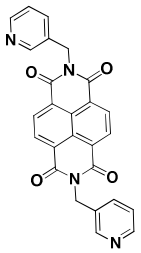

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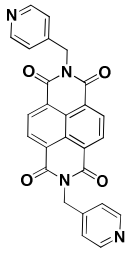

67

to generate discrete zero-dimensional to polymeric two-dimensional coordination structures. These structures are further stabilized by hydrogen bonds and π···π interactions in the crystal lattice. Different coordination assemblies such as metallacycle, herrringbone network, grid network and 1D chain formed by different metal salts with **67** are shown in the Scheme **5**. Synergistic effects of metal ions and anions in self-assemblies formation were observed in these polymers, thus conformation of the assemblies could be tuned with the aid of ditopic ligands.[81]

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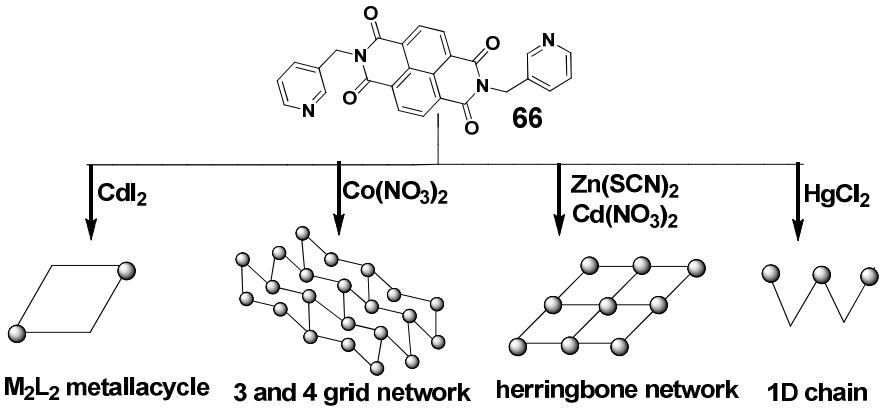
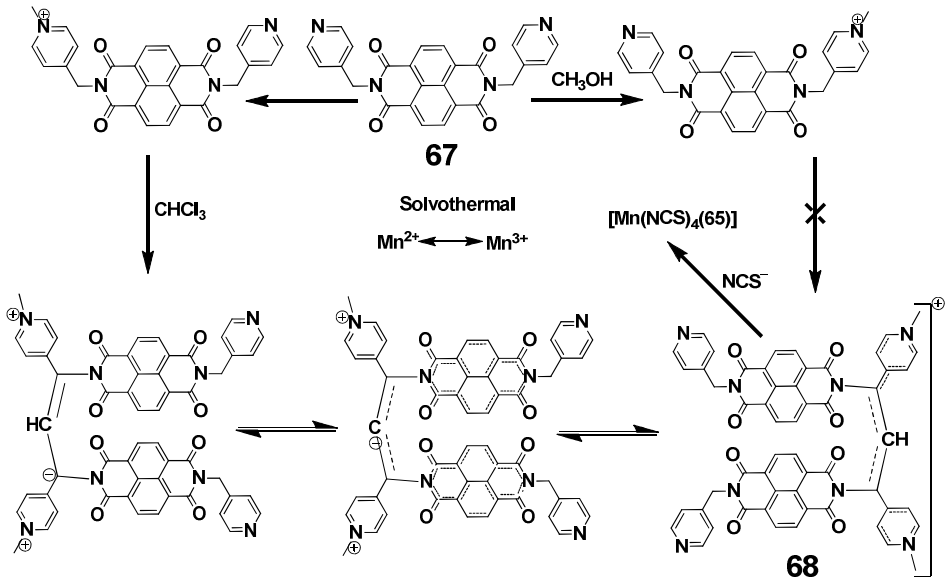


Scheme 5: Varieties of structures generated from a naphthlaimide derivative.

On the other hand, ligand **67** forms one dimensional coordination polymer through different reactions involving the C-H activation, C-Cl bond cleavage, C-C bond coupling, and pyridyl N-methylation of ligand occur.[82] Ligand, **67** react with manganese trifluoro-acetate dihydrate and sodium thiocyanate under solvothermal conditions results in formation of one-dimensional coordination polymer namely, $\{[Mn(NCS)_4(\mathbf{68})]\cdot 2.5H_2O\}_n$. This coordination polymer comprises of in situ generated new ligand (**68**) via a metal/ligand in situ reaction (Scheme 6).



Scheme 6: Formation of **67** from the reaction of **66** with manganese (II) ions.

Several mononuclear and dinuclear copper complexes with ligands **69**-**72** have interesting packing features.[83] In these complexes weak interactions such as π···π, anion···π, solvent···π and C=O···π interactions give rise to extended structures.

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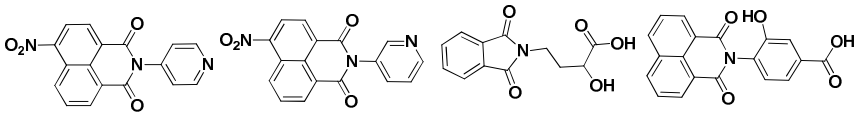

69 **70** **71** **72**

Trifunctional ligands **71** and **72** containing hydroxy group, carboxylic acid group show interesting supramolecular assemblies on formation of metal complexes. Flexible nature of ligand helps **71** to form coordination polymer by reacting with manganese (II) or zinc (II) salts. In case of the manganese coordination polymer competition between self assembling versus aquation at the metal ion sites while forming assemblies, results in inclusion of neutral metal complexes as guest in assemblies of chains of coordination polymer. On the hand, introducing the hydroxy group on a rigid aromatic unit attached to a naphthalimide unit such as in compound **72**, yields mononuclear metal complexes rather than coordination polymers.[84]

Biological probe as DNA binding and photo cleavage:

Imides are planar and have scope to either intercalate between helical coil of DNA or stacks between the folds of the DNA coil. 1,8-Naphthalimide derivatives thus have been used for DNA binding, anticancer and also used as cellular imaging agents. Generally being π···π deficient aromatic system[85] they bind to DNA[86] by insertion between the base pairs of double helix[87] and they exhibit good antitumor activity.[88] During intercalation the base pairs separate vertically thereby distorting sugar phosphate backbone and controls the degree of rotation between successive base pairs.[89] Introducing nitro or amine group at 3 or 4 position of a naphthalimide ring, not only makes the molecule to act as a targeting agent for biomolecules,[90] but also significantly affects the electronic properties. Due to such interactions the chemical, photochemical and spectroscopic properties of the DNA bound to a naphthalimide changes. On the other hand, bromo derivative of 1,8-naphthalimides having bromine atom at 3 and 4 positions are good candidates for photo-chemotherapeutic inhibition of enveloped viruses in blood and in blood products.[91] 1,8-Naphthalimides are powerful photo-reagents which can induce lesions in DNA molecules and as such possess the ability to kill cells when they are photoactivated.[92] Thus binding mode of naphthalimide may depend on the DNA sequences.

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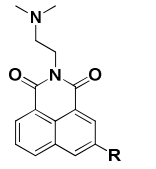
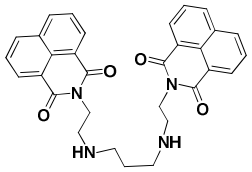


73a R = NH_2
73b R = NO_2



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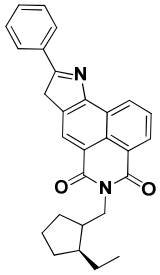
1,8-Naphthalimide derivatives such as amonafide, **73a** and mitonafide, **73b** as a DNA binding agent were tested for clinical trials.[93] Compound **73a** was found to stabilize double stranded DNA against heat denaturation.[94] Bis-naphthimides such as **74** have been developed for enhancement of DNA binding and antitumour activity.[95] These compounds act as a bis-intercalator and bind to DNA along the major groves and found to minimize the toxic side effect to healthy cells.[96] Gunnlaugsson *et al*. developed a series of bis-naphthalimides linked by the Troger's base moiety for DNA targeting.[97] These molecules are soluble in water that favour electrostatic interactions with the negatively charged phosphate backbone of DNA. Photophysical measurements showed that they bind to DNA with similar affinity and display dual mode of binding with one naphthalimide ring intercalated between DNA base pairs while the second one is groove-bound. Introduction of chiral amino acids into naphthalimide moieties (**75-77**) enable to overcome conventional low aqueous solubility and achieve enhanced cellular uptake. Naphthalimide derivatives having derived chiral side chain at the imide position such as leucine,[98] L-lysine,[99] and α-amino acid derived naphthalimide[100] have been reported to show DNA intercalating and photocleaving properties.

Imperiali *et al.* have given an explicit elucidation of biomolecular interactions of 4-*N,N′*-dimethylamino-1,8-naphthalimide.[101] Solvatochromic chiral amino acid based fluorophore **78** can detect dynamic protein-protein interactions through fluorescence resonance electron transfer process in water as medium.[102a]



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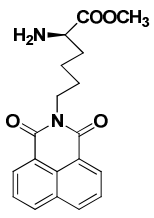

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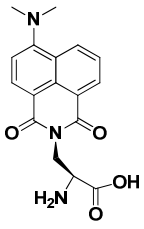

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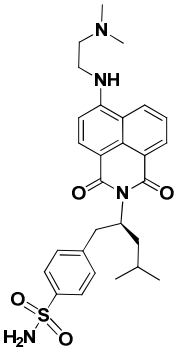

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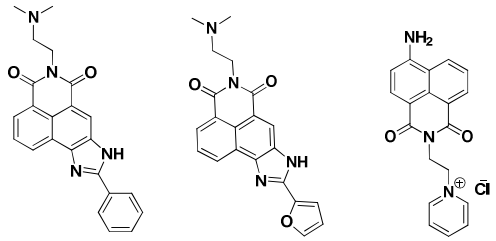
Imidazole based naphthalimides **79-80** show cyctotoxic activity against human colon carcinoma cell and they have higher affinity towards DNA due to additional heterocyclic ring attached to the naphthalimide unit. Such heterocyles have better stacking interactions as compared to parent naphthalimide derivative.[103a] Anchoring pyridine through flexible connector at imide site of 1,8-naphthalimide such as in molecule **81** makes such molecule conducive for binding with DNA.[103b-c]



79 **80** **81**

Cationic side chain interacts with phosphate backbone of DNA or with guanine.[104] Spectroscopic titrations show that side chain binds to DNA and remains in the major groove. In all these cases non-covalent interactions play the key role in the stabilisation of different assemblies.

Naphthalimide based transition metal complexes are found to be chemotherapeutic agents for cancer.[105a] In an recent study the molecular recognitions of bovine serum albumin with various naphthalimide derivatives and their potential cancer activity has been illustrated.[105b] Platinum complexes such as **82-83** overcome cellular resistance to cis-platin, which is a common problem encountered in cis-platin based chemotherapeutic complexes.[105e] These complexes also show enhanced DNA binding affinity and cytotoxicity.[105f]

Cobalt (II) complexes based on naphthalimide derivatives **84** are found to induce DNA cleavage. They exhibit high cytotoxicity against HeLa cervical cancer cells upon UV-irradiation.[106a] Several ruthenium (II)-naphthalimide complexes were identified as

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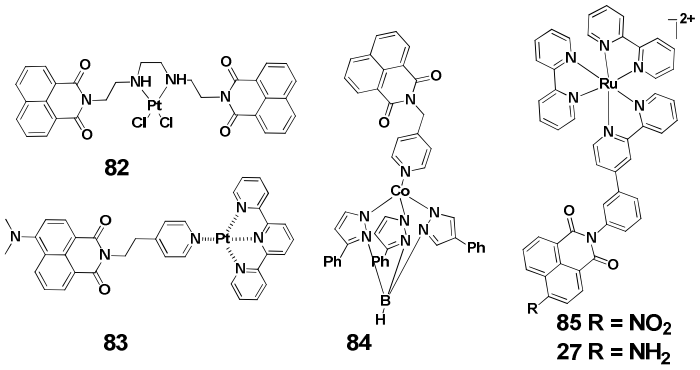
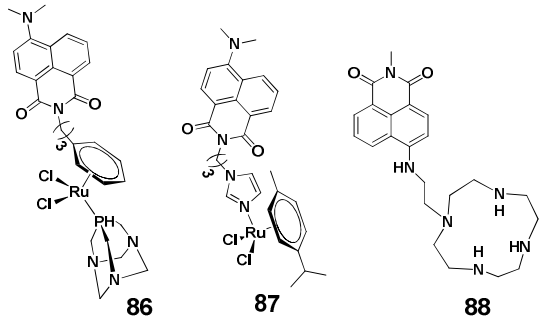


potential DNA binders as well as photocleaving agents. Complexes **85** and **27** show hypochromism and a red shift in absorption spectra in the presence of DNA.[106b]



Ruthenium (II) arene complexes **86-87** which have naphthalimide derivative as additional part of ligand get intercalated by DNA.[107] Intercalation of naphthalimide unit within DNA and binding of ruthenium (II) arene unit with proteins enhance anticancer selectivity. Metal complexes of naphthalimide-cyclam conjugates show in-vitro antitumor activities.[108] Zinc (II) complex **88** is a potential antiproliferative agent found to be active in cancer cell lines.

Conclusions and outlook:

Supramolecular assemblies of naphthalimides are guided not only by substituent present, but also on solvent and ions interacting with naphthalimides. More importantly л-stacking interactions help the self-assembling properties to make definite impact on molecular and ion recognition. Stacking interactions make different types of assemblies contributing to their properties. It may be noted that π-interactions in a simple arene substituent may occur in different ways and two major structural features are identified as end···face and edge···face C-H···π (arene) interactions; and lateral off-set and face···face as shown in Figure 13.[109]

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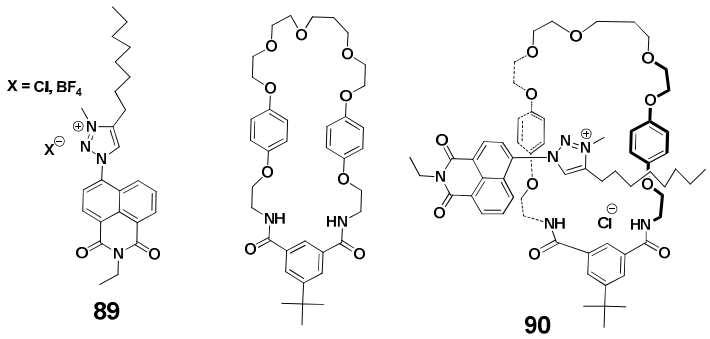
Figure 13: Different ways of placing a benzene ring over another benzene ring leading to weak interactions

Such π-stacking interactions are of the magnitude of interaction energy in the range of 0.5 kcal/mol to 2.46 kcal/mol and valid at a distance 3.3-4.8Å.[110] Thus, it would be interesting to develop selective synthetic methods to form multinuclear metal complexes guided by π-stacking interactions. Presence of optical or electrochemical signalling units make avenues for development of naphthalimide based molecular devices such as molecular switch and molecular machines.



Scheme 7: Few scaffolds suitable for anion binding

For example anion-templated rotaxane structure **90**, incorporating naphthalimide triazolium motif, **89** (Scheme 7) exhibit selective, uni-directional, anion-induced shuttling. Ability of a naphthalimide triazolium threading component are shown to form interpenetrated assemblies with counter-anion-dependent co-conformations.[111] In an naphthalimide containing molecular machine shown in Scheme 8 has been developed based on time-resolved vibrational spectroscopy in which departure and arrival of a macrocycles were independently observed through formation of radical anion on naphthalimide moiety.[112]

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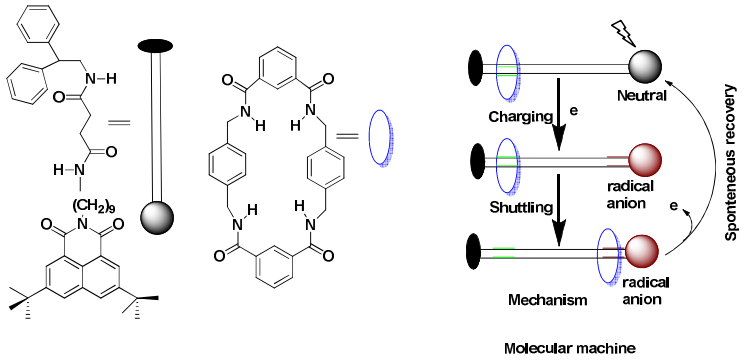

Scheme 8: A molecular machine based on naphthalimide derivatives

Self-assemblies of the phthaloylglycinato transition metal complexes provide interesting examples in which lattice water molecules are tightly held by hydrogen bond interactions.[113a] Structure of phthaloylglycinato and its complex with zinc(II) is shown in

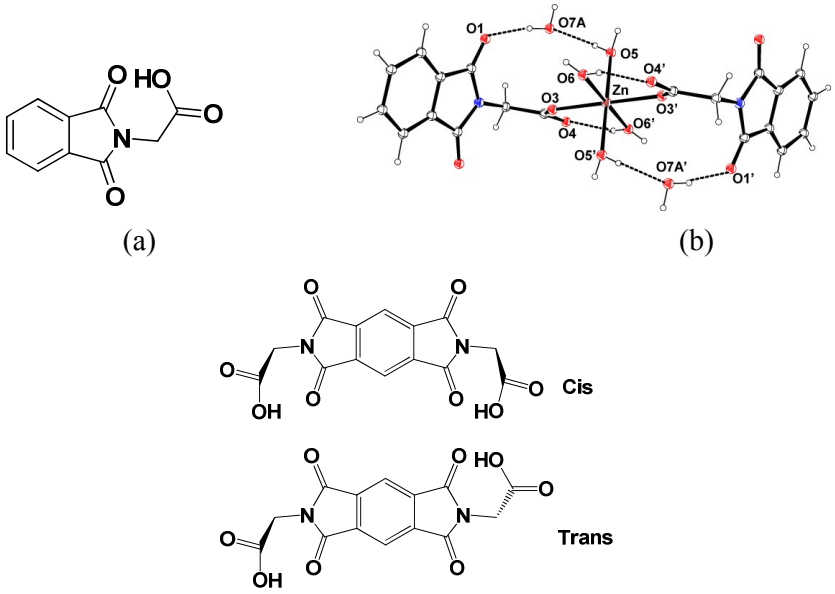

Figure 14: (a) Structure of N-phthaloylglycine, (b) Structure of tetra-aqua-bis-N-phthaloylglycinato zinc (II) dihydrate (c) Cis and trans rotamers of N,N'-bis(glycinyl)pyromellitic diimide.

Figure 14a and 14b. On the other hand β-pleated structures in phthaloylgycylglycinate complexes with nickel and copper were observed.[113b] N-phthaloylglycine forms series of host guest complexes with aromatic hydroxy and amines.[113c] N,N'-bis(glycinyl)pyromellitic diimide adopt cis or trans rotamer (Figure 14c) and these rotamers play important role in molecular recognitions[28,113d]. On the other hand, in N,N'-

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bis(phenylglycinyl)pyromellitic diimide, C-H···π interactions play a major role to stabilise different host-guest complexes with poly aromatic hydrocarbons.[27-28]

Structural studies on the positional isomers of the N-(pyridylmethyl)-1,8-naphthalimide shown in the Figure 15, suggested that the packing patterns except in the case of N-(2-pyridylmethyl)-1,8-naphthalimide were controlled by π–π and C-H···π interactions[113e-f]

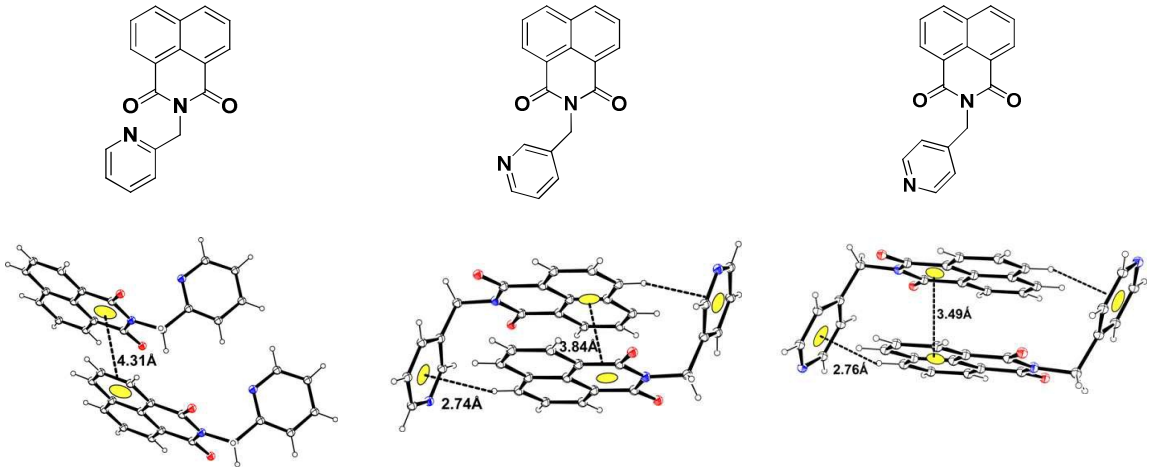

Figure 15: Three positional isomers of N-(pyridylmethyl)-1,8-naphthalimide and their respective self-assemblies.

Different solid state structures of mononuclear transition metal complexes formed from a flexible imidazole based naphthalimide ligand show anion recognition and solid state fluorescence of such complexes are governed by packing patterns.[113g] Antiferromagnetic properties of one 1D coordination polymer of copper(II) with isophthalic acid containing naphthalimide with spiral duplex structures have been reported[113h] Coordination polymer of dicarboxylic acid with 1,8-naphthalimide containing ancillary ligands of manganese(II) ions have shown single chain magnet properties.[113i] The imide derived from phenolic and carboxylic acids and metal carboxylate complexes are important to accommodate different amounts of nitrogen containing aromatic heterocycles.[113j-m] In such studies multiple numbers of pseudo-polymorphs from same guest are characterised. Several naphthalimide derivatives forms also form gels.[113n]

Absorption spectra of a monomer differs from the assemblies of same type of molecules in solution and from the spectral shifts, aggregation causing a shift towards short wavelength from monomer is referred to as J-bands, and towards longer wavelength is called as H-bands. Accordingly, the types of aggregates associated with the respective assemblies is

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called as J-aggregates and H-aggregates.[114] In solid state the relevance of J and H-aggregates contributing to fluorescence requires much attention. The naphthlimides being planar units, the self-assembling[113f] may lead to parallel, or partially parallel, opposite dipolar end facing opposite or same direction may contribute to fluorescence such studies are yet to make headway and requires definite attention. Supramolecular interactions such as π-stacking interactions and some other weak interactions also influence the fluorescence behaviour of naphthalimide based compounds. Naphthalimide based ligand generally shows a dual fluorescence behaviour in different solvent via different mechanism such as excited state intramolecular proton transfer and excited state with extended conjugation.[115] Solvatoemissive dual fluorescence emission in the three positional isomers of N-(4-pyridylmethyl)- 3-nitro-1,8-naphthalimide were observed.[113o] This N-(4-methylpyridinium)-3-nitro-1,8-naphthalimide chloride salt posses chloride-water cyclic tetrameric clusters in its self-assemblies which are formed by interactions of two chloride (Figure 16) and two water molecules having some relevance structural features of anion channels.

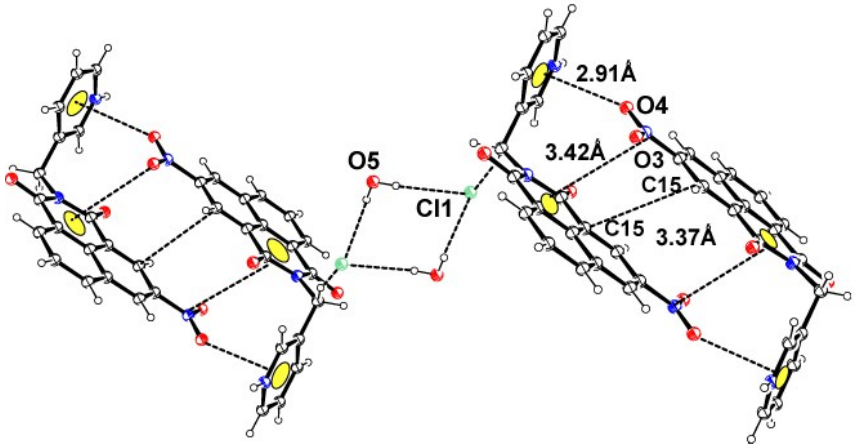

Figure 16: Tetrameric chloride-water cluster stabilised by self assemblies of N-(4-methylpyridinium)- 3-nitro-1,8-naphthalimide cations

Among all interactions stacking interactions are dominant interactions in aromatic imides, which guide the overall supramolecular structure and makes impact in material properties such as molecular recognitions, fluorescence emissions, optical and magnetic properties. Many of the higher analogues have shown potential in non-conventional energy sources, such as in water splitting, solar energy harnessing and some have been identified for their interesting binding substrates to biological molecules and medicines, hence there is definite scope to design suitable to stack in different manners influencing physical

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properties. Thus, focus of the future crystal engineering work with imide derivatives could be on (a) Design and synthesize stable solid state supramolecular assemblies for signal transduction, (b) Assemblies with transition metal complexes for interesting material properties (d) Design assemblies of imide based compounds for medicinal and biological applications and (e) Uses of soft assemblies of imides for supramolecular assemblies through bottom up approach. These materials will continue to pay role in biological sciences; environment and material chemistry where crystal engineering approach would find a key role disseminate the inherent properties associated to make generalised understanding at molecular level.

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