Chemistry of naphthalene diimides

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Received 25th April 2007
First published as an Advance Article on the web 17th August 2007
DOI: 10.1039/b615857a

This *tutorial review* surveys recent developments in the chemistry of naphthalene diimides (NDIs) and explores their application in the fields of material and supramolecular science. It begins with a discussion of their general uses, methods of syntheses and their electronic and spectroscopic properties. Of interest to their application in the fields of conducting thin films and molecular sensors is the structure–function relationships that exist either as co-components of supramolecular ensembles as in the case of "nanotubes", or as the sole components in molecular wires. Also discussed are advances in NDI research within the areas of energy and electron transfer (covalent and non-covalent systems) and in host–guest chemistry including foldamer, mechanically-interlocked and ligand-gated ion channel examples. Finally, we explore the developments in the recent field of core-substituted NDIs, their photophysical properties and applications in artificial photosynthesis. We conclude with our views on the prospects of NDIs for future research endeavours.

Introduction

During the mid 1990s when the popularity of supramolecular chemistry was rising in what seemed to be an exponential fashion, one of us remembers an elegant description of chemistry using a language analogy as a means of representing the importance of supramolecular chemistry to the wider scientific community. In essence the atoms of the periodic table represent the letters of the alphabet. Combining groups of letters in a logical way form words in the same way that grouping atoms in a logical way form molecules. The higher complexities of language, for instance sentences, paragraphs *etc*, were analogous to supermolecules and higher complexity ensembles such as organelles *etc.* Underlying this analogy, is of course grammar and the importance associated with nouns, verbs, adjectives *etc* which allow the sentences that make up the paragraphs to make sense. Of major interest to this tutorial review are the verbs or "doing words", that is molecules that "do" by adding function to a particular supermolecule, ensemble or array. The nature of function is varied and open to the imagination of the designing chemist, though much function is measured electronically or spectroscopically.[1] The molecules of choice in most instances are aromatic molecules, which have well defined redox and spectroscopic properties. This introduction continues with a look at one such class, the 1,4,5,8-naphthalenediimides, their chemistry and the resulting principles of their association in the field of materials and supramolecular chemistry with a view to offering a more subjective primer for new sources of inspiration for related fields. Interested readers requiring a more detailed description

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Sheshanath Bhosale was born in 1976 in Indral Dist. Latur, India. He received his MSc from SRTM, University Nanded, India in 1999 before moving to the Freie University Berlin where he received his doctoral degree in supramolecular chemistry under the supervision of Professor J. H. Fuhrhop in 2004. After post-doctoral work at the University of Geneva as a Roche Fellow under the mentorship of Prof. S. Matile he was appointed as an Assistant Lecturer at Monash University. He is co-author of 25 publications primarily in the design and synthesis of artificial photosystems.

Chintan H. Jani

Chintan Jani was born in 1980 in Mumbai, India. He received his bachelor's degree in Science in 2001 from Fergusson College, University of Pune, India. He then moved to the University of Leeds, UK, and received his MSc in Nanoscale Science and Technology in 2003. He is currently doing doctoral research under the supervision of Prof. Langford exploring the applications of naphthalene diimides as sensors and supramolecular building blocks.

of the principles and methods will find the references at the end of this review insightful.

Among aromatic molecules that have found utility, particularly in the design of conducting materials, the 1,4,5,8-naphthalenediimides (NDIs) (also known as naphthalene carbodiimides) have attracted much attention due to their tendency to form n-type over p-type semiconductor materials.[2] The naphthalenediimides are a compact, electron deficient class of aromatic compound capable of self-organisation[3] and being incorporated into larger multicomponent assemblies through intercalation.[4] Functionalisation through the diimide nitrogens or *via* core substitution (substitution on the naphthalene core) produces analogues whose absorption and emission properties are variable.[5] For example, aromatic functional groups placed on the diimide nitrogens produce non-fluorescent or weakly fluorescent compounds while alkyl groups at these same positions produce the typical white–blue fluorescence of this class of compound. Core substituted NDIs (cNDIs) are rapidly merging as a class of their own in an attractive strategy to create highly colourful, conducting, functional materials with much different photophysical properties than their core unsubstituted counterparts.[5] It is with this versatility in properties that naphthalene diimides (Chart 1) have found popularity in the latter half of the 20th century and due, in part, to the pioneering work of Vollmann *et al.* in the early 1930s.[6]

The consideration that naphthalene diimides can act as ideal components for the creation of supramolecular functional materials (*e.g.* catenanes, rotaxanes and barrels)[7,8] has transpired as a result of their desirable electronic and spectroscopic properties over pyromellitic diimides and better fabrication properties than the perylene diimide dyes, the latter being a result of their enhanced solubility properties. Interest in NDIs also extends to biological and medical application, highlighting their versatility.[9,10] Simple naphthalenediimides bearing substitution on the diimide nitrogen are often used as electron acceptors, which, under the general supramolecular building block paradigm of partial charge transfer stabilization,[11] leads to novel molecular assemblies and supramolecular arrays as discussed in Sections 3–5.

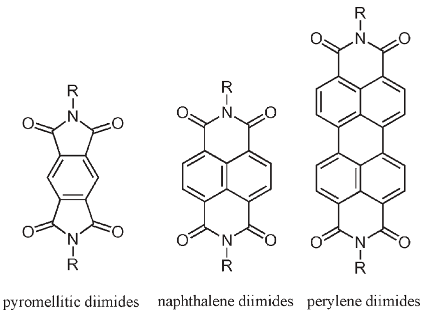


Chart 1 Aromatic diimides.

Steven J. Langford

Steven Langford was born in Sydney, Australia in 1967. He received his BSc with first class Honours from the University of Sydney in 1990 and PhD under the supervision of Prof. M. J. Crossley in 1993 at that same institution. After a successful two years work with Prof. J. F. Stoddart at Birmingham, UK as a Ramsay Memorial Fellow (1993–1995), he moved to UNSW to further his interest in electron and energy transfer processes under the mentorship of Prof. M. N. Paddon-Row (1996–1998). He was appointed as Lecturer within the School of Chemistry at Monash University, Australia in 1998 and he currently holds the Chair of Organic Chemistry at that same institution. In 2006 he was awarded a Young Investigator Award by the Society of Porphyrins and Phthalocyanines. His research interests are at the interface between synthetic organic chemistry and biology, applying supramolecular chemistry to mimic photosynthetic processes, molecular devices and studying motor neurone disease.

General chemical properties

Physical properties

1,4,5,8-Naphthalenediimides are neutral, planar, chemically robust, redox-active compounds usually with high melting points. The absorption and emission properties of *N*,*N*-dialkyl-substituted NDIs (in CH_2Cl_2), for example, comprise strong, structured absorptions below 400 nm, and a weak, mirror image emission with a 7 nm stokes shift (Fig. 1).[12] In toluene, excimer-like emissions have been observed suggesting ground-state aggregates are formed readily.

Naphthalenediimides undergo single reversible one-electron reduction (chemically and electrochemically) at modest potentials (NDI: $E^1_{\mathrm{red}} = -1.10$ V *vs.* Fc/Fc$^+$ in CH_2Cl_2) to form stable radical anions in high yield. The radical anions are characterized by a set of intense and characteristic visible and near-infrared (NIR) absorption bands at >450 nm ($\lambda_{\max}$ = 476 nm) (Fig. 1) and by strong and highly structured EPR signals (Fig. 1(d)).[12,13] They are seen as attractive redox-active units because of their electronic complementarity to ubiquinones (E^1_{red} trimethylbenzoquinone = -1.20 V *vs.* Fc/Fc$^+$).[14] In this respect, they make excellent components for studying photoinduced electron transfer and in models of photosynthetic mimicry. Recent results in these areas have been set out in a review by us in 2006 and briefly discussed in Section 4.1.[15] Interestingly, EPR studies indicate that the electronic coupling is not confined to the diimide core, but also extends to the methane (CH_2) carbons of aliphatic substituents on nitrogen (Fig. 1(d)).[12] The overall structure of the EPR spectrum is substituent dependent which holds importance for the field of photoinduced electron transfer by yielding further insight into mechanisms of electronic coupling.

General syntheses and reactivity

The synthesis of symmetric NDI compounds is a simple and efficient one step procedure in which commercially-available 1,4,5,8-naphthalenetetracarboxylic dianhydride **1** (Sigma-Aldrich: 100 g = AUS$537) is condensed with the appropriate

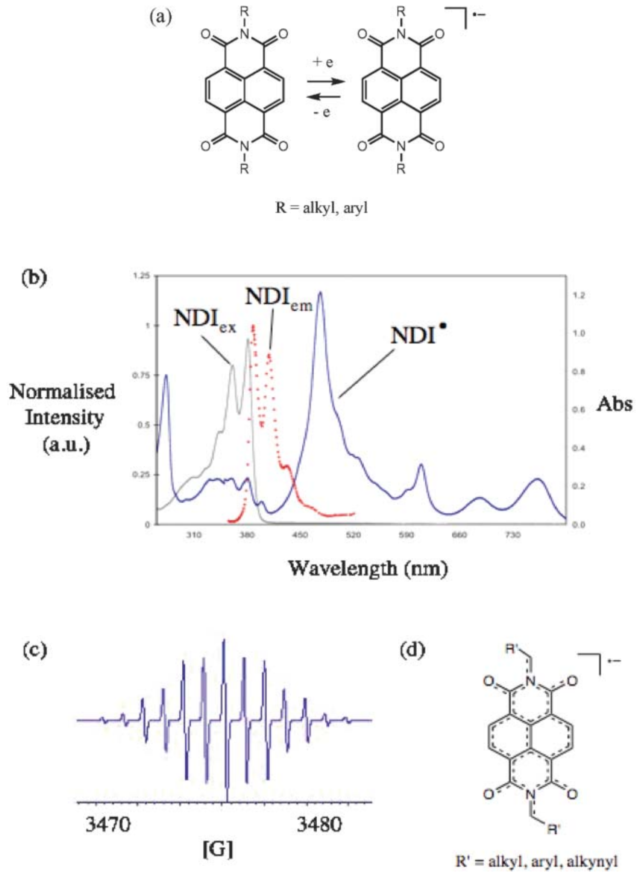
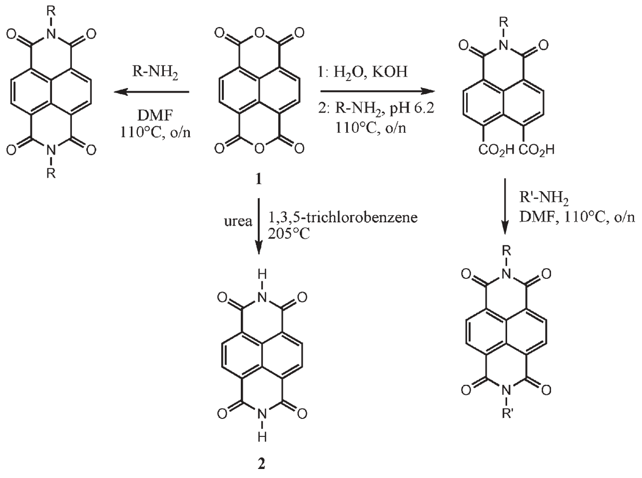


Fig. 1 (a) Bulk electron reduction of NDIs lead to high yields of the corresponding radical anion. (b) Characteristic absorption (grey) and emission spectra (red, normalised, λ_{ex} = 348 nm) for *N*,*N*′-dipentyl-NDI in DCM are obtained as well as the absorption spectrum for the radical anion of *N*,*N*′-dipentyl-NDI (blue) generated by electrochemical reduction. Near-infrared (NIR) absorption bands aid in the unambiguous identification of NDI radical anions. (c) The electron paramagnetic resonance spectrum of the radical anion of *N*,*N*′-dipentyl-NDI in DMF solution shows excellent structure consistent with coupling between the unpaired electron and the naphthalene diimide nitrogens and hydrogens and the NCH hydrogens of the appropriate side chains. (d) The radical anion is delocalised over the core naphthalene structure and also extends into hydrocarbon substituents on nitrogen.

primary amine in a high boiling solvent, usually DMF (Scheme 1). This method is clean and high yielding for a variety of amines and traditionally, this procedure is all that is required to synthesize the NDI. A variety of functional groups can be introduced at the imides using this procedure, and its simplistic nature makes it amenable to polymer chemistry.[16] In some instances, and especially when low boiling amines or heat-sensitive amines are used, a stoichiometric amount of K_2CO_3 can be added in order to drive the reaction to completion at lower temperature (<60 °C). The reaction time is commensurate with the temperature of the reaction mixture and the nucleophilic nature of the amine, ranging from 4–48 h. Recently, microwave-assisted conditions have been reported in which reaction proceeds quantitatively in 5 min.[17] The parent diimide **2** can be prepared by reaction of **1** with urea in refluxing 1,3,5-chlorobenzene (bp 205 °C) (Scheme 1),[18] by microwave assistance using formamide, or using aqueous ammonium hydroxide. Naphthalene diimides bearing two different substituents on the diimide nitrogens (*N*,*N*′-disubstituted NDIs) can be prepared by a method developed by Ghadiri which requires careful control of pH (Scheme 1). The difference in reactivity of anhydride and dicarboxylates is more satisfactory than application of a statistical approach.[19]

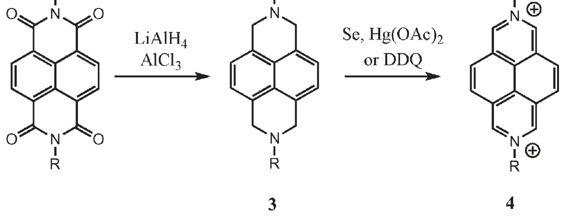


Scheme 1 General synthetic methods for preparing symmetric and *N*,*N*′-disubstituted NDIs.

The chemistry of the NDIs was pioneered back in the early 1970s by Hünig *et al.*[20] but came into fruition in the 1990s as researchers began to realize the potential of naphthalene diimides as useful precursors and the geometries associated with analogues in the field of supramolecular chemistry.[21,22] Reduction of naphthalene diimides ($LiAlH_4/AlCl_3$) leads to the tetrahydro-2,7-diazapyrene derivative **3** in typically good yield (>60% yield). Oxidation of the tetrahydro-2,7-diazapyrene **3** yields the quaternised 2,7-diazapyrenium salts **4** also in good yield (Scheme 2).

Solubility and aggregation

Naphthalene diimides contain a lipophilic naphthyl core and four polar carbonyl groups and hence are usually soluble in low polarity lipophilic solvents (toluene, DCM, chloroform) and polar aprotic solvents (*e.g.* acetonitrile, DMF, DMSO) depending on the imide substituents. Due to their planar aromatic nature, naphthalene diimides exhibit stacking in the solid-state with distances commensurate with π–π stabilisation. This phenomena can be utilized to form continuous stacks and in supramolecular applications (see Section 4), but can also provide a major hinderance with reduced solubility, especially



Scheme 2 Chemistry of 1,4,5,8-naphthalenediimides.

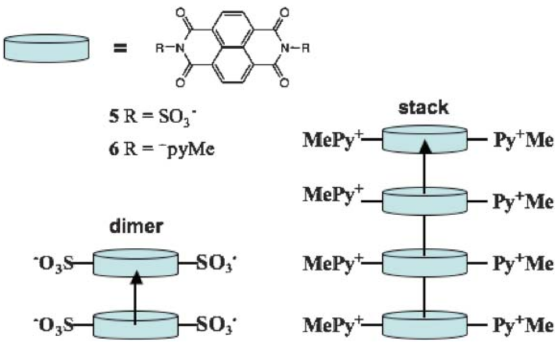


Fig. 2 Self-assembly of NDI units in aqueous NaCl solution after reduction. The difference in the type of assembly was rationalized to be a result of favourable hydrophobic and coulombic forces.

when substituted with aryl side groups. Since the solubility of NDIs essentially depends on the substituents on the imide nitrogens, long and bulky aliphatic substituents generally have higher solubilities.[23] On the other hand, in applications where aggregation is useful, the nature of the imide substituents can exploited to assemble NDI in solution and the solid phase.[24] For example, reduction of the diimides **5** or **6** with dithionite in aqueous solution lead to mainly dimers (in the case of **5**) and extended and highly ordered π-stacks in the case of the cationic structures generated through peripheral pyridinium groups (Fig. 2). Delocalization of the π-electrons along such stacks, as evinced by exciton bands at wavelengths >2000 nm, is an important characteristic with implication for use of this material as a so-called molecular wire. Interestingly enough, solvent characteristics play a large part in the stacking motif. In DMF solution, **5** acts as a monomer, while in the solid-state it forms extended π-stacks.

Self-assembly of naphthalene diimides bearing carboxylic acid groups have also been shown to form cylindrical microstructures on the surface of solid substrates.[25] The hydrogen bonding between carboxylic acid termini combined with the hydrophobic contacts between the NDI cores is mainly responsible for the formation of these supramolecular arrays. This approach has been recently evolved at a molecular level into hydrogen-bonded helical organic nanotubes by utilising the chirality inherent in a series of NDIs containing chiral α-amino acid derivatives (Fig. 3).[26]

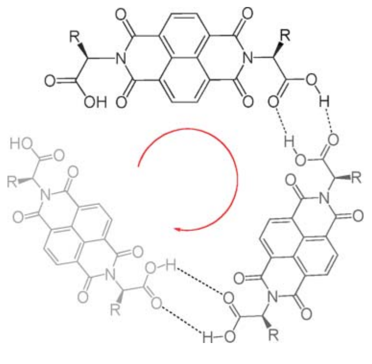


Fig. 3 The helical nature of a chiral NDI dicarboxylic acid assembly forms hydrogen-bonded organic nanotubes in solution and the solid state.

NDIs in materials chemistry

In order to fully exploit the potential of the aromatic imides as new functional materials, it is essential to incorporate them into organised supramolecular ensembles beyond the pseudo-1-D structures discussed to date. It has been argued that the incorporation of NDIs into thin films and other organized structures, *e.g.* nanotubes could pave the way for the preparation of pragmatic molecular based electronic devices such as field-effect transistors (FETs) which also require high stability under demanding processing conditions.

Thin films

Politi and co-workers constructed photoactive thin films of zirconium phosphonate with 1,4,5,8-naphthalenediimides upon silica or quartz substrates using phosphonate chemistry (Fig. 4).[27] Absorption spectroscopy indicates that the NDIs stack efficiently within the layers, which is supported by the large excimer-like emission seen by fluorescence measurements (λ_{ex} = 355 nm). When 16-layer films are irradiated under steady-state or flash photolysis (λ_{ex} = 355 nm) the initially colourless film turned a persistent pink indicating the formation the NDI radical anion. This result was further supported by the appearance of transient absorptions at higher wavelength which did not decay over the lifetime of the experiment (100 ms). Recently, this work was extended by incorporating amino acids and peptides between the silica and zirconium/NDI phosphonate layers to form novel bioactive materials.[2] Excitation of the NDI layer produces both triplet states (due to a high yielding intersystem crossing) as well as radical species in the presence of appropriate electron donors. Their study revealed that the lifetime of radical ion formation within the peptide was up to 100 times longer on the particle surface than in solution as a result of electron exchange process.

Naphthalene diimides applied as thin films on thiol-enhanced gold contacts as well as air-stable organic semiconductors

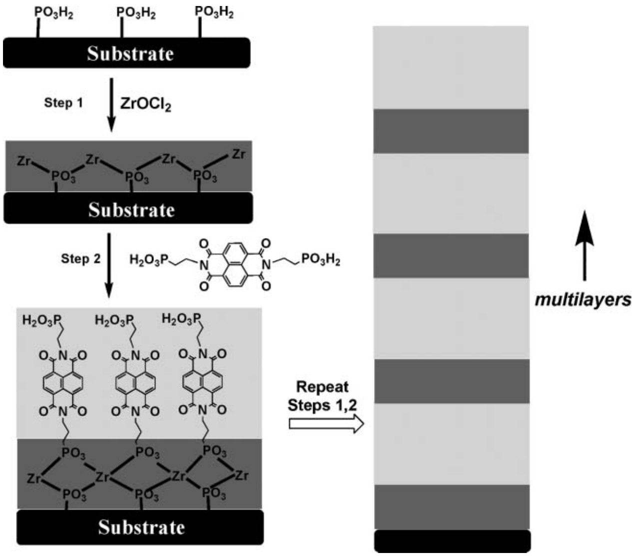


Fig. 4 Controlled growth of NDI/Zr thin films on silica electrodes lead to multilayers.

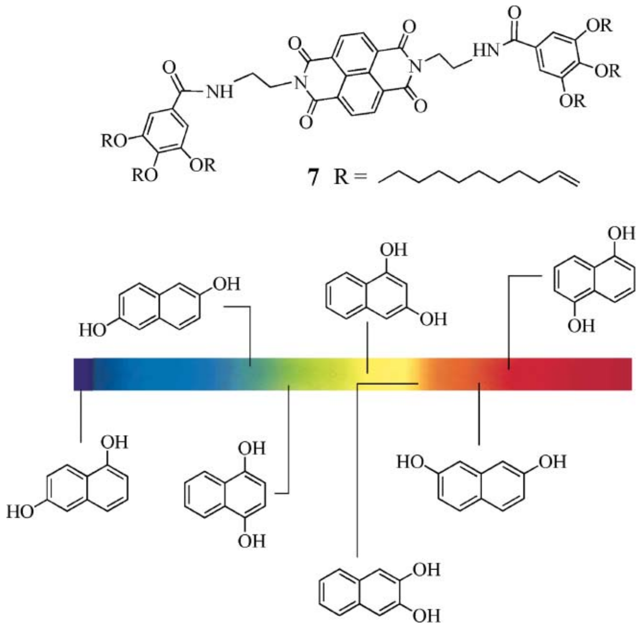


Fig. 5 The gelator **7** senses the individual isomers of dihydroxynaphthalene specifically through colorimetric changes upon mixing.

with high electron mobility have been used in the fabrication of solution-cast n-channel field effect transistors (FET). Integrating n-channel FETs with solution deposited p-channel FETs produces a complementary inverter circuit whose active layers are deposited entirely from the liquid phase.[27] Cyano cNDI semiconductors for air-stable, flexible and optically-transparent n-channel organic field-effect transistors have also been recently prepared with excellent results, comparable to that available using perylene dyes.[28]

Sensors

Recently, Shinkai and co-workers have described the features of a naphthalene diimide low molecular weight gelator **7** with utility in sensing the seven different positional isomers of dihydroxynaphthalene (Fig. 5) at millimolar concentrations by visible colour changes.[3] Temperature-dependent spectral changes upon the addition of the dihydroxynaphthalenes indicate a mixture of π–π stacking and partial charge transfer interactions stabilize the complex. The NDI gelator forms stable gels in 19 of 26 common organic solvents and shows a reversible sol–gel transition. It is important to note that solvophobic effects alone cannot explain the binding of the dihydroxynaphthalenes in the organogel matrix and hence this reorganisation process.

We mentioned in the introduction that naphthalene diimides are capable of intercalation as a result of their planar aromatic structure. These properties have been used by Takenaka *et al.* to extensively study DNA sensing. In this work, a NDI bearing two redox-active ferrocenyl moieties is used to electrochemically sense and discriminate double-strand DNA (dsDNA) from single stranded DNA (ssDNA). The complex dsDNA/NDI is thermodynamically and kinetically more stable than the ssDNA/NDI complex because of the ability for intercalation with the former DNA form.[29]

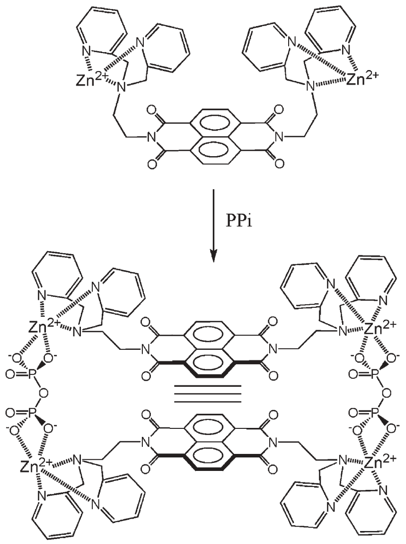


Fig. 6 Binding pyrophosphate (PPi) in a 2 : 2 ratio with the NDI yields a selective sensor at physiological pH.

A unique example of pyrophosphate (PPi) sensing at physiological pH uses the unique excimer output of an NDI dimer (Fig. 6) to differentiate between itself and other phosphate containing biomolecules such as ATP, ADP and AMP in aqueous solution.[30]

Nanotubes and rods

Bolaamphiphilic naphthalene diimides such as **8** are able to self-organize into supramolecular arrays in aqueous solution and, ultimately, produce cylindrical microstructures on the surface of solid substrates (Fig. 7(a)).[25] In a different strategy, Ghadiri and co-workers investigated the use of designer cyclic peptides bearing NDI side chains in forming nanotubes as a facile method for the preparation of a new class of synthetic biomaterials (Fig. 7(b)). These nanotubes, which use a hydrogen bond-directed assembly approach of the cyclic peptides to bring the NDIs on adjacent cycles within close proximity (3.6 Å), act as a useful model system for studying NDI–NDI charge transfer reactions after reduction with dithionite by emission spectroscopy.[19] Atomic force microscopy (AFM) on mica, graphite or silica was used to characterize the nanotubes. Interestingly, evidence suggests that stable nanotubes are formed in solution only in the presence of sodium dithionite as the absence of the reducing agent gave only amorphous structures. The described self-assembling cyclic-D,L-α-peptide nanotubes demonstrate high stability on surfaces even after two months exposure to ambient temperature.

NDIs in supramolecular chemistry

Energy and electron transfer

There is considerable interest in the development of chemical systems capable of forming long-lived charge-separated states for advances in solar energy conversion, molecular-based optoelectronics, and a variety of other applications. In the last two decades, the construction of artificial porphyrinic arrays for solar energy conversion using covalent and non-covalent

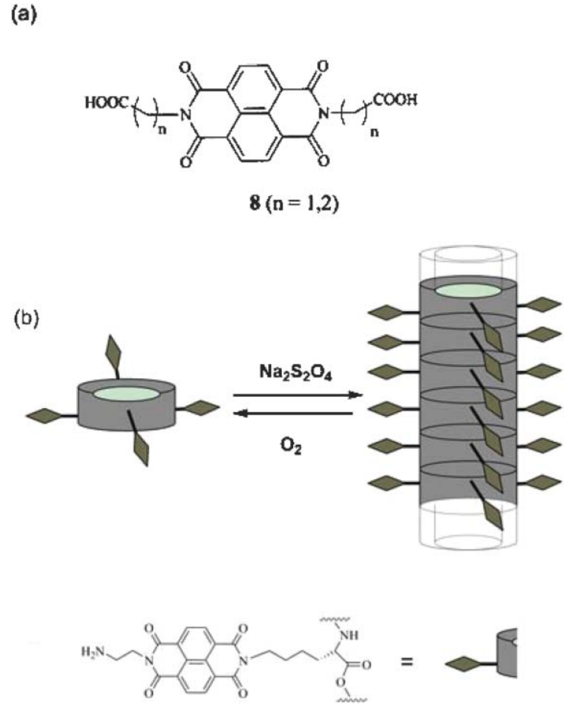


Fig. 7 (a) Bolamphiphilic NDIs such as **8** lead to rod-like structures in the solid state. (b) Schematic illustration of a redox-promoted NDI-peptide self-assembled nanotube.

strategies have been developed.[31] In rigid, covalently linked systems, long-lived charge-separated states are produced by a sequence of vectorial electron transfers that take the electron to an acceptor separated from the donor *via* a bridge, though many factors are involved in gaining efficient photoinduced electron transfer. Naphthalene diimides have made useful contributions to the evaluation of design principles because of their ease of synthesis and electron accepting properties (Section 2.1) and the similarity of these properties to the naturally-occurring acceptors of plant and bacterial photosynthetic reaction centres. This area has been the recent subject of a review by us,[15] so only a few examples to illustrate the usefulness of naphthalene diimides are made.

Covalent systems

In 1993 Osuka *et al.* synthesized a series of fixed-distance triads **9** consisting of zinc porphyrin (ZnP), free-base porphyrin (H_2P) and naphthalene diimide moieties which are bridged by aromatic spacers which modulate the center-to-center distance between ZnP and H_2P from 13 and 17.2 Å (Fig. 8(a)).[32] Upon photoexcitation (λ_{ex} = 532 nm), long-lived charge-separated states in the order of 0.14–80 μs in THF solvent were obtained by a relay approach. The steady-state fluorescence and transient absorption techniques indicate the occurrence of very efficient ($\phi_1 \approx 0.8$) intramolecular singlet–singlet energy transfer from the zinc porphyrin to metal free porphyrin and subsequently charge separation between H_2P and NDI resulting in the formation of $(ZnP)^{\bullet +}$–H_2P–$(NDI)^{\bullet -}$. The lifetimes and efficiency of the charge-separated states across **9** series exhibited distance dependant behaviour, as defined by the rigid bridges **9a–d**.

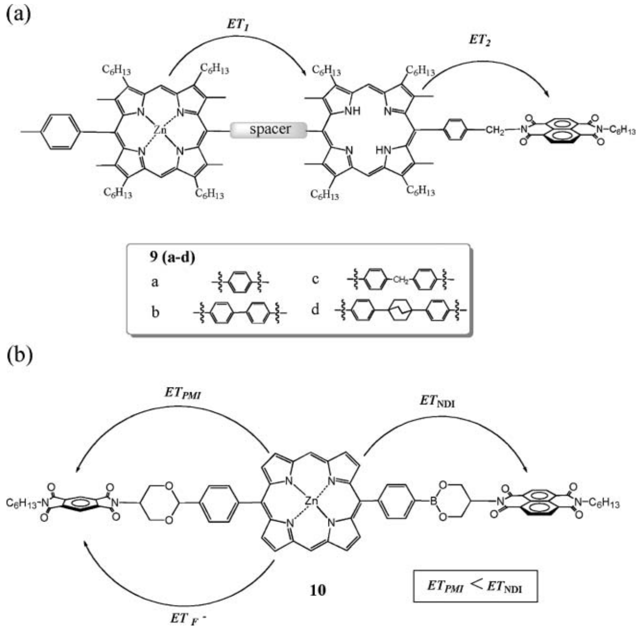


Fig. 8 Examples of covalently-linked multichromophoric systems capable of photoinduced electron transfer. (a) Osuka's system **9**, (b) The triad **10**, bearing two acceptors, was used to demonstrate ET switching between NDI and PMI groups.

The triad **10** (Fig. 8(b)) bearing a Zn(II) porphyrin donor and pyromellitimide and NDI groups antipodally placed on the porphyrin periphery has been examined as a means of modulating the electronic coupling between donor and acceptor and hence controlling the direction of intramolecular electron transfer between NDI and pyromellitimide acceptors.[33] Photoexcitation of the Zn(II) porphyrin led preferentially to a CS state involving the NDI radical anion as a result of its better accepting properties and greater ET efficiency. Upon addition of fluoride, which complexes to the boron centre, the electronic coupling in this pathway is switched OFF causing ET to occur completely occur in the direction of the pyromellitimide. The ON/OFF switching of ET was possible through conversion of the trigonal planar boron centre to a tetrahedral geometry, which was further shown to have implications for the energetics, geometry and coupling between donor and acceptor. Such systems, in which manipulation of the electronic properties of the bridge are possible, give insight into the subtle changes affiliated with the specific directionality of ET within the photosynthetic reaction centre. Other triad systems bearing NDIs have also contributed strongly to the field of photoinduced electron transfer.[34,35]

Non-covalent systems

In last decade, the construction of artificial photosystems for solar energy conversion by using a non-covalent approach has paralleled that based on covalent bonding. An advantage of using non-covalently assembled structures is the simple and fast interchange of components within the systems and does not require the lengthy synthetic routes that covalent systems do. Multichromophoric assemblies in which a supramolecular event is needed to promote electron transfer are also of particular interest due to their biological relevance. Naphthalene diimides offer two interesting advantages above and beyond their complementary photophysical and electronic properties. The imide structure of the parent diimide **2** is isostructural with the nucleic acid thymine, hence it should be available for complementary hydrogen bonding. The versatility in synthesis suggests that a range of functional groups capable of non-covalent interactions (*e.g.* metal ligation) should be possible. This sub-section introduces these two non-covalent approaches as a theme to preparing dyads for application.

Sessler proposed the first rigid, coplanar hydrogen bonded dyad **11** (Fig. 9(a)), bearing a porphyrin donor and NDI acceptor, in which the hydrogen bond complementarity between the diimide and a 2,6-diaminopyridine lead to a triple point hydrogen bonding motif.[18] Steady state fluorescence of **11** is quenched with respect to that of TPP and the NDI acceptor, suggesting charge transfer quenching of the porphyrin singlet excited state in the supramolecular complex. The emission decay profile of the solution containing the two components and hence a proportion of **11** shows biexponential decay (λ_{ex} = 573 nm, λ_{em} = 640 nm) with the faster component (τ_1 = 1.2 ns) being assigned to the complex **11**. Intra-ensemble ET was deduced to be rapid ($k_{ET} = 7.6 \times 10^8$ s^{-1}) and efficient (ϕ = 0.91), using time-resolved techniques.

A second generation supramolecular ensemble is shown as **12** (Fig. 9(b)).[36] Having the NDI acceptor motif directly attached to the *meso* position of a Zn(II) porphyrin reduces both the conformational freedom of the ensemble as well as provide a more suitable "through-bond" pathway for ET. ^{1}H NMR spectroscopic studies determined a 1 : 1 stoichiometry and binding constant (K_a) of 3×10^2 M^{-1} in C_6D_6 for the complex. Steady state fluorescence studies in C_6H_6 using a substantial excess of the NDI showed significant fluorescence quenching (70%) compared to the porphyrin alone. Time-resolved picoseconds transient absorption studies (λ_{ex} = 532 nm, C_6H_6) provided some evidence for the formation of a NDI radical anion ($k_{CS} = 4.1 \times 10^{10}$ s^{-1}) and decayed over 270 ps. A deuterium effect (k_H/k_D) of *ca.* 1.5 for the rates of CS and charge recombination also provides evidence for complexation.

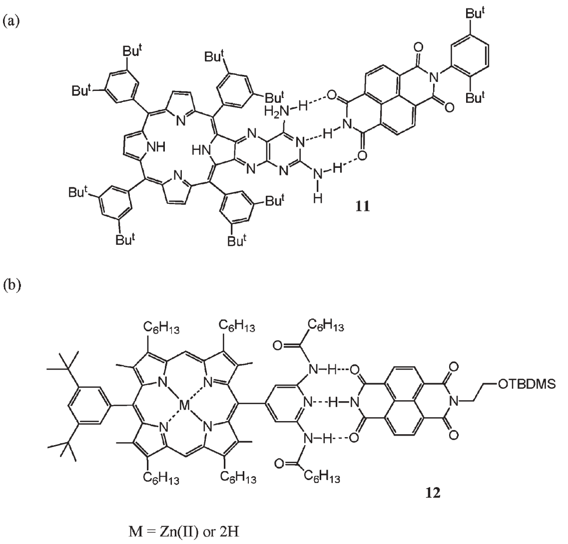


Fig. 9 (a) The rigid coplanar dyad, assembled by three-point hydrogen bonding, undergoes ET with a rate $k_{ET} = 7.6 \times 10^8$ s^{-1} (λ_{ex} = 575 nm). (b) A novel non-covalent bonded example employing hydrogen bonding to mediate ET processes.

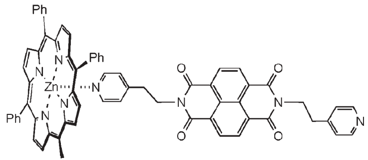
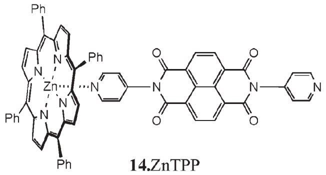
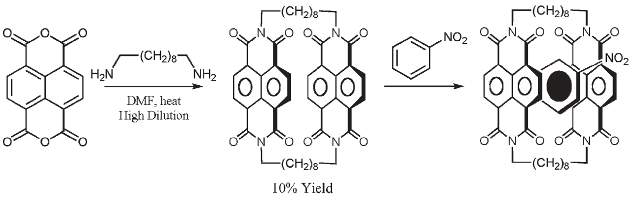
	In CH_2Cl_2	
	k_{CS} (x10^9 s^{-1})	τ
 **13**.ZnTPP	2.8	1.2 µs
 **14**.ZnTPP	>20	<0.01 µs

Fig. 10 Simple dyad ensembles utilising Zn(II)···N coordination bonds facilitate ET with µs lifetimes.

The formation of stable coordination complexes of Zn(II) porphyrins by axial ligation using pyridine ligands ($K_a \approx 10^3$–10^4 M^{-1}) provides a synthetically easy method of assembling simple dyads in which the NDI acceptor occupies a position distal (time averaged) to the metal centre. The most recent example synthesized by us is shown in Fig. 10.[37] This simple supramolecular dyad **13** forms in solution through axial coordination of Zn(II)TPP and a *N*,*N'*-diethylpyridyl terminated NDI. Photoexcitation of **13** in non-polar solvents at 604 nm, which corresponds to an absorption unique to this complex, results in charge separation with lifetimes of 1 to 100 µs depending on the solvent used as evinced by transient absorption spectroscopy. The longevity of the CS state is rationalised on the basis of intersystem crossing, which is allowable provided ET from the singlet state is impeded by poor electronic coupling between the donor and acceptor. This last point was confirmed using the NDI system **14** devoid of the alkyl spacer group. In this case, both CS and CR were much faster (τ_{CS} < 0.01 µs) and comparable to that observed in other systems. The electron recombination from the triplet charge-transfer state (CT^T) is formally forbidden as it involves an inversion of electron spin and a longer-lived CT state would result. Fukuzumi and co-workers, later that same year, demonstrated the charge-separated state of a similar Zn(II) porphyrin–NDI complex, produced by photoinduced electron transfer, has the longest lifetime (450 µs at 288 K), ever reported for donor–acceptor systems linked covalently or non-covalently in solution.[38]

NDIs in host–guest chemistry

One of the key goals of supramolecular chemistry is to assemble structural building blocks into regular arrays with new properties and emergent phenomena. Host–guest chemistry has tremendous potential to provide us with strategies with which to design and build these structures. These new properties may improve our understanding of



15

Scheme 3 Formation and inclusion properties of Lehn's NDI macrocycle.

non-covalent interactions, or they may endow useful functionality. Catalysts, sensors, molecular machines and computers are all possible applications. The structural and chemical properties make NDIs ideal candidates for host–guest interactions (*vide infra*), in particular donor–acceptor charge transfer type complexes. Their electron deficient and aromatic nature is important for face-to-face aromatic interactions with electron donors and their rigid, planar structure along with the ability to be functionalized with a wide variety of side groups to tune their properties means that their assemblies have strong, well defined directionality in space. NDIs have been widely studied with respect to host–guest systems such as intercalation, foldamers, ion channels, catenanes and rotaxanes. Their ability in this area was highlighted in 1987 by the Nobel Laureate Jean-Marie Lehn. In an unassuming paper, Lehn and co-workers discussed the formation of the cyclophane **15** comprising two NDI units linked by two alkyl chains, and its molecular recognition properties with nitrobenzene (Scheme 3).[39]

NDI–DAN foldamers

Non-covalent interactions such as aromatic–aromatic, hydrogen bonding and complementary electrostatics are also responsible for the array of amazing characteristics and functions of natural polymers. Foldamers are an interesting class of polymers in which the electronic complementarity between units contained within the polymer cause the polymer to fold in an organized and predictable manner. Non-natural foldamers emulate the structures of natural polymers such as proteins and DNA and help investigate non-covalent interactions of these natural foldamers. Naphthalenediimides and DANs (DiAlkoxyNaphthalenes) have been utilized to form a series of foldamers (and in other work, aedemers) whose structure is a result of the strong donor–acceptor interactions and solvophobic driving force of π–π interactions in aqueous environment.[40] DAN–NDI–DAN trimers have been shown to fold into pleated structures in solution while DAN–DAN–NDI trimers adopt an intercalative folding (Fig. 11). Variable temperature studies in larger foldamer systems also show a colour based temperature dependence.[41]

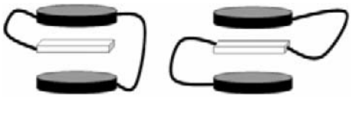


Fig. 11 DAN–DAN–NDI trimers (left) adopt an intercalative folding *via* π–π interactions while DAN–NDI–DAN trimers (right) have been shown to fold into pleated structures in solution while.

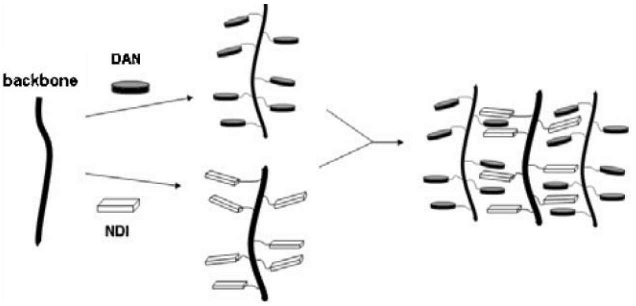


Fig. 12 A representation of the polymers polyDAN and polyNDI and their combination to form supramolecular structures.

The synthesis of independent DAN and NDI polymers, achieved by functionalisation of polyethylene-*alt*-maleic anhydride with the respective monomers, and their mixing in water (1 : 1 ratio) leads to the formation of discrete heteroduplexes through an aedemer (intercalative) arrangement, whose solid-state properties are different from the sum of the two oligomers.[41] The supramolecular polymer structure is maintained due to the electrostatic repulsion experienced on each chain due to the terminal carboxylate groups. These groups not only enhance aqueous solubility but also keep the chains "elongated" in solution thereby increasing interaction between complimentary NDI ad DAN polymer chains (Fig. 12).[42]

Catenanes and rotaxanes

Catenanes and rotaxanes have attracted much attention in nanoscience and material science due to their ability to undergo translational isomerism upon external stimulus (*e.g.* electronic, photonic or protic).[11] An obvious extension, though quite independent, from the previous section is the use of electron rich aromatics, such as DAN, found in many designer crown ethers in complement with NDIs through one of the catenation or rotaxane forming strategies, *e.g.* clipping or threading, to form novel redox-active mechanically interlocked structures (Fig. 13(a)). Catenanes based on NDIs have been synthesized by a number of groups including ours, usually using a threading and clipping protocol through a preformed ring component (Fig. 13(b)).[7,8] In some instances, the rotational isomerism associated with a dissymmetric ring component *e.g.* **16** has been observed. Solid tethered [2]rotaxanes have also been reported wherein the NDI are immobilized on OH-functionalized polymer beads.[43]

Neutral, bistable [2]rotaxanes that show redox-controllable switching have also been reported.[44] Here, NDI and pyromellitic diimide units are chosen to form the π-electron poor recognition sites (the so-called "stations") and the crown ether DN35C10 acts as a π-electron-rich shuttle (Fig. 13(c)). Redox controlled switching of the crown occurs between the stations of the [2]rotaxanes upon reversible, single electron reduction of the NDI.

Ligand-gated ion channels

The term "ligand gating" is normally used in regard to functioning cellular transporters and channels. The term implies a

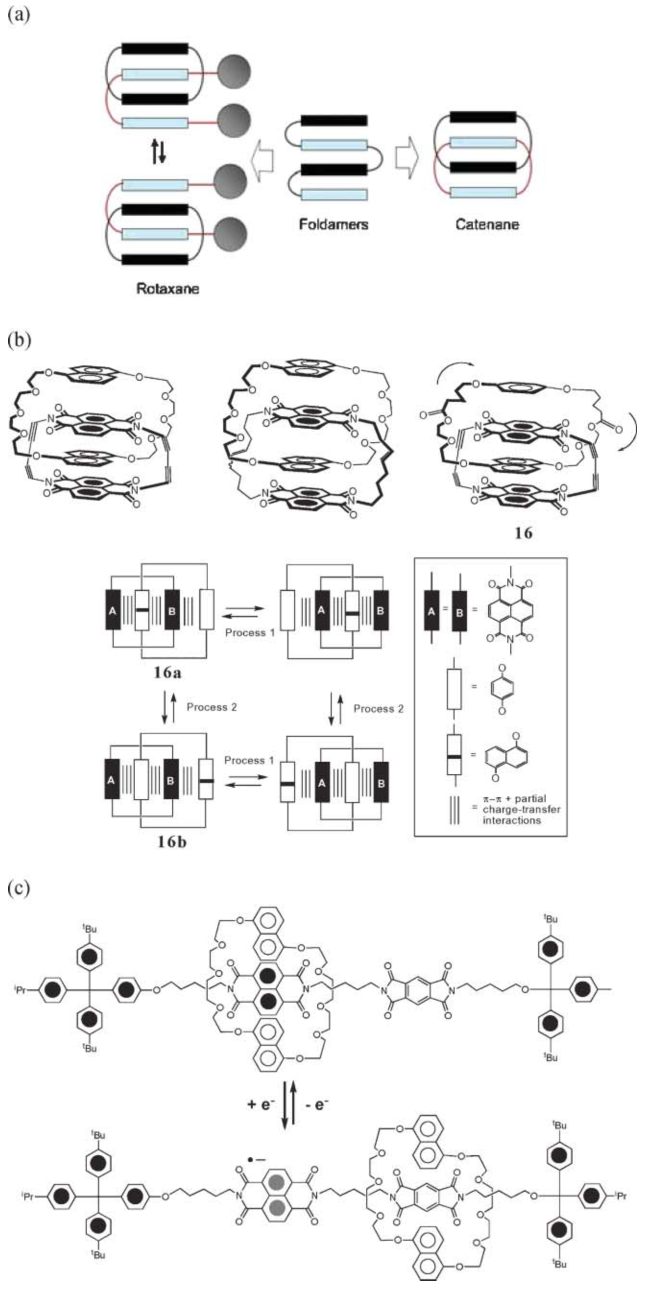


Fig. 13 (a) A conceptual transfer from foldamers to rotaxanes and catenanes bearing NDIs. (b) Examples of [2]catenanes formed by threading and clipping. (c) A [2]rotaxane using pyromellitimide and NDI "stations" acts as a prototype of an nanoelectromechanical switch.

ligand-mediated increase in "activity" as a result of structural implications (ligand-mediated changes in channel conformations). Self-organised rigid-rod π-helices containing naphthalene diimides have been reported to undergo dramatic channel conformational changes upon intercalation with aromatic compounds (Fig. 14).[45] The rigid-rod helices comprising *p*-octiphenyls with eight NDI units form a closed channel conformation lacking internal space which, upon intercalation with aromatic ligands *e.g.* DAN, untwist to give open barrel-stave ion channels. Conductance experiments on the channels in lipid bilayers show a highly co-operative and selective ligand gating that produces small, long-lived, weakly anion selective and ohmic ion channels. Structural studies conducted under conditions relevant for function provide experimental support for helix-barrel transition as the origin of ligand gating.

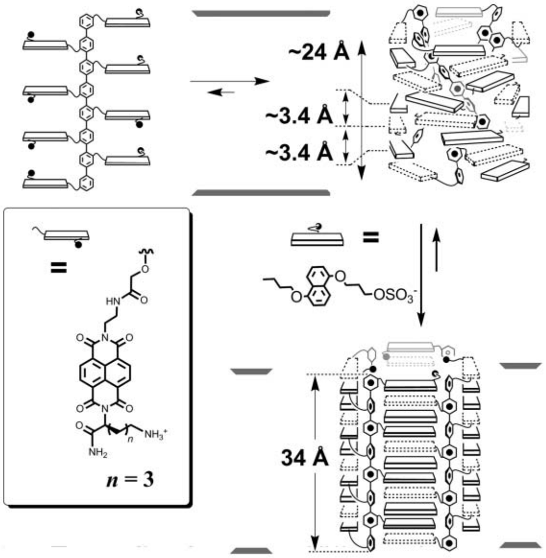
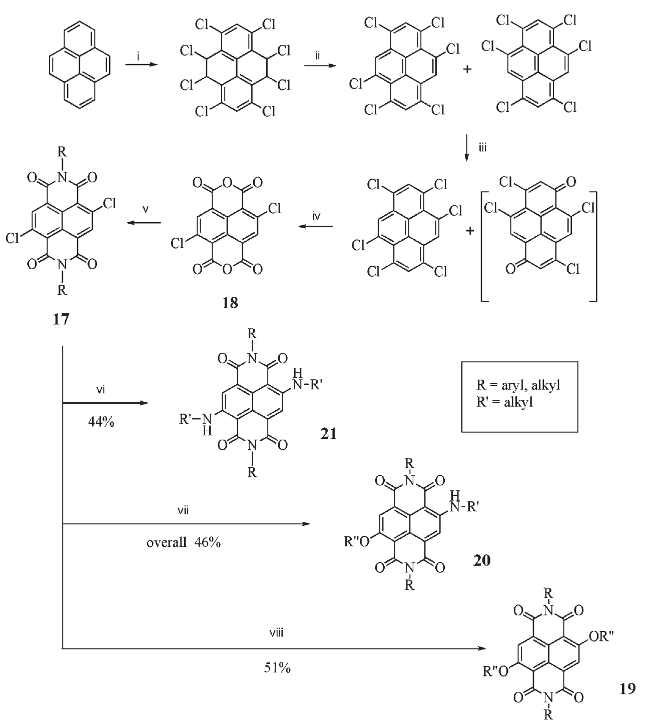


Fig. 14 Ligand-gated opening of rigid-rod π-helix ion channel by intercalation of DAN ligands into closed scaffolds containing naphthalenediimides.

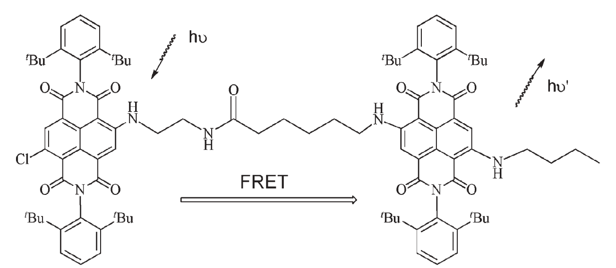
Core-substituted NDIs

Synthesis, absorption and emission properties

Core substituted NDIs (c-NDIs) are those containing functionality at positions 2, 3, 6, 7 on the naphthalene core, *e.g.* **17** (Scheme 4). The disappointing optical properties of Vollmann's early NDIs containing an arylamino core substituent may be the reason why core-substituted NDIs had never been really studied in great depth.[6] The ready introduction of alkylamino- and alkoxy- core substitution accomplished by Würthner *et al.* in 2002 with newly realized properties have changed this view.[5] These brightly coloured and highly fluorescent NDIs can be synthesised in two steps in moderate yield from the anhydride **18** which is available in four steps from commercially-available pyrene (Scheme 4). Of interest is the differing reactivity of the anhydride and chloronaphthalene groups in **18** to substitution. Reaction of two equivalents of amine yields the antipodally substituted dichloro-cNDIs in moderate yield. Further reaction with excess amine or alkoxide yields the diamino- or dialkoxy-cNDIs in moderate yield. Careful control in terms of stoichiometry and conditions can yield a better than statistical mix of the monoalkoxy-monochloro-cNDI which can undergo further reaction with alkylamines to yield the monoalkoxy-monoamino-cNDI in moderate yield (Scheme 4).[46] Redox properties of NDIs are also influenced by core substituents. As the dichloro-substituted NDI **17** possesses a low reduction potential, it is a promising candidate for n-type organic semiconducting materials which are still very rare.[28] In contrast, substituents at the imide positions do not have any significant effect on the chromophoric properties.



Scheme 4 Synthesis of core substituted naphthalene diimides (c-NDIs) from pyrene: *Reagents and conditions*: i. Cl_2, I_2 (catalytic), 1,2,4-trichlorobenzene, 25–110 °C, 38%; ii. KOH, EtOH, 80 °C, yield isomers 96–97%; iii. fuming HNO_3, 0–5 °C, yield 32–45% (isomer in bracket can be separated); iv. fuming nitric acid, conc. H_2SO_4, 100 °C, 5 min, yield 45–49%; v. $R–NH_2$, HOAc, 120 °C; v. $R–NH_2$, 85 °C; vii. NaOR″, rt, then $R'–NH_2$, 0 °C; viii. NaOR″, rt.



22

Fig. 15 The bichromophoric compound **22** undergoes highly efficient fluorescence resonance energy transfer (FRET) upon excitation.

In striking contrast to arylamino core substitution, brilliant colors and intense fluorescence (ϕ ≈0.5–0.8) are found with alkylamino and alkoxy core substituents. Introduction of the weaker π-donor alkoxy group *e.g.* **19** yields compounds with a yellow/green fluorescent (λ_{max} = 469 nm; λ_{em} = 484 nm). Introduction of the stronger alkylamino π-donors *e.g.* **20** result in a bathochromic shift for both the monoalkoxy-monoamino-cNDI (λ_{max} = 534 nm; λ_{em} = 564 nm) and for the diamino-cNDI **21** (λ_{max} = 620 nm; λ_{em} = 650 nm). The reduction potentials of the cNDIs decrease correspondingly across this series.

Applications

Core substituted naphthalene diimides are finding use in a range of biomimetic and bioinspired artificial systems including electron and energy transfer systems, in synthetic multifunctional pores and as transmembrane channels.[47–49] The overlap of absorption and emission bands in **19–21** correspond to favourable photophysical properties and such bichromophoric models *e.g* **22** have been synthesized for studying highly efficient fluorescence resonance energy transfer (FRET) (Fig. 15). Such photophysical processes are highly desirable for unraveling binding and folding events in biomaterials amongst others.[5]

The use of cNDIs for more elaborate artificial photosynthetic reaction center mimics has been demonstrated through incorporation of the rigid-rod π-*M*-helices **23** in lipid bilayer membranes (Fig. 16). The artificial photosystem was prepared by self-assembly of four *p*-octiphenyl moieties each bearing eight amino-cNDIs along the rigid-rod scaffold (Fig. 14).[47] The photosystem was characterized in vesicles equipped with EDTA as a sacrificial reductant, 1,4-naphthoquinone-2-sulfonate as an internal electron acceptor (Q), and HPTS as an internal fluorescent pH meter (Fig. 14). In this

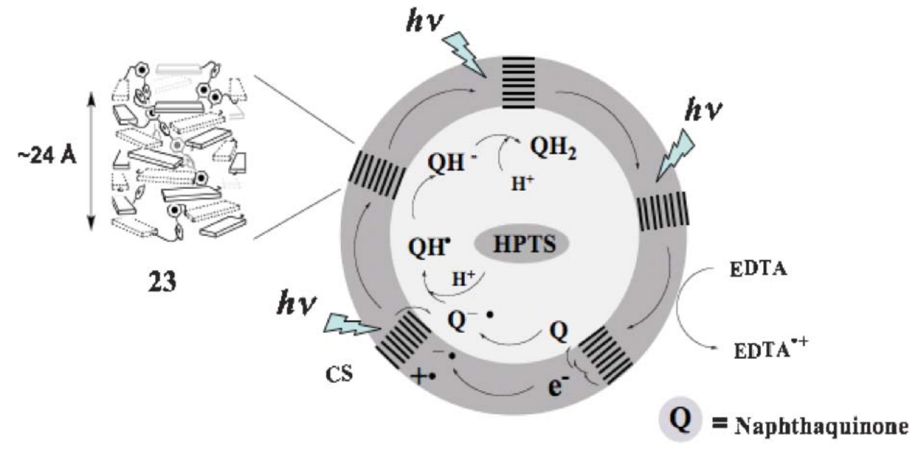
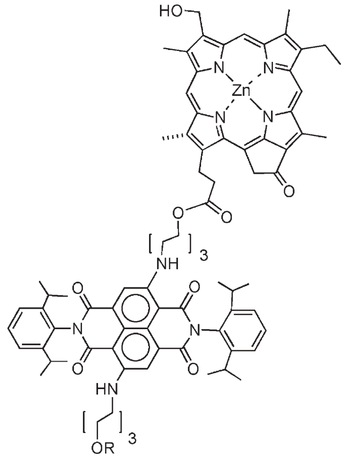


Fig. 16 Rigid-rod π-*M*-helix **23** as a supramolecular photosystem that can open up into an ion channel after intercalation. Transmembrane photoinduced electron transfer from EDTA donors to quinone acceptors Q is measured as formal proton pumping with light across lipid bilayers. HPTS is used to measure intra-vesicle deacidification. The formation of **23** is shown in Fig. 14.

system, transmembrane charge separation in response to photoirradiation of the self-assembled helix is translated into an external EDTA oxidation [$E_{1/2}$ (NHE) $\approx$430 mV] and internal quinone reduction [$E_{1/2}$ (NHE) ≈ -60 mV]. The fluorometric detection of photoactivity by intravesicular deacidification is detected by the HPTS dye. The addition of a DAN ligand causes an immediate collapse of the proton gradient leading to little HPTS fluorescence. The activity of the photosystem was reflected in near quantitative and ultrafast formation (<2 ps, >97%) of the charge-separated state (τ = 61 ps) as evinced by transient absorption spectroscopy.

Conclusions

Over a short period of time, several design strategies for the creation of functional NDI architectures have emerged. This includes the formation of covalent and noncovalent functional supramolecular materials such as thin films, ion channels that function by ligand gating, gelators for sensing aromatic systems and as prototypes of molecular switching devices such as catenanes and rotaxanes. The optical nature of these materials and modulation of other physical properties (*e.g.* redox properties) has been a result of aromatic electron donor–acceptor interactions. Despite their success to date, it is clear that core-substituted NDIs add significantly to their perceived use as a result of their colorful properties and charge mobilities within precise supramolecular organisations. The usefulness of these characteristics to create function in lipid bilayer membranes was confirmed with the synthesis of smart photosystems and to fulfill green gaps in light harvesting systems (Fig. 17) thereby adding to the area of artificial photosynthesis.[50] Research on functional NDI architectures will in any case contribute to the major effort in basic research on smart optoelectric nanomaterials, according to pertinent reports,[51] that are needed today to meet tomorrow's energy demands in a sustainable way. From a fundamental viewpoint, molecularly well-defined π-conjugated oligomers remain ideal model systems for the investigation of the relationships between structural parameters, photon–electron conversion and long-lived charge separation. Naphthalenediimides will continue to provide researchers with an ideal basic building block with which to build novel molecular architectures that bridge the gap between the molecular and macroscopic worlds.



R = 3,5-bis(dodecyloxy)benzoyl

Fig. 17 Molecules such as this porphyrin-appended cNDI may be applicable as full spectrum absorbers.

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