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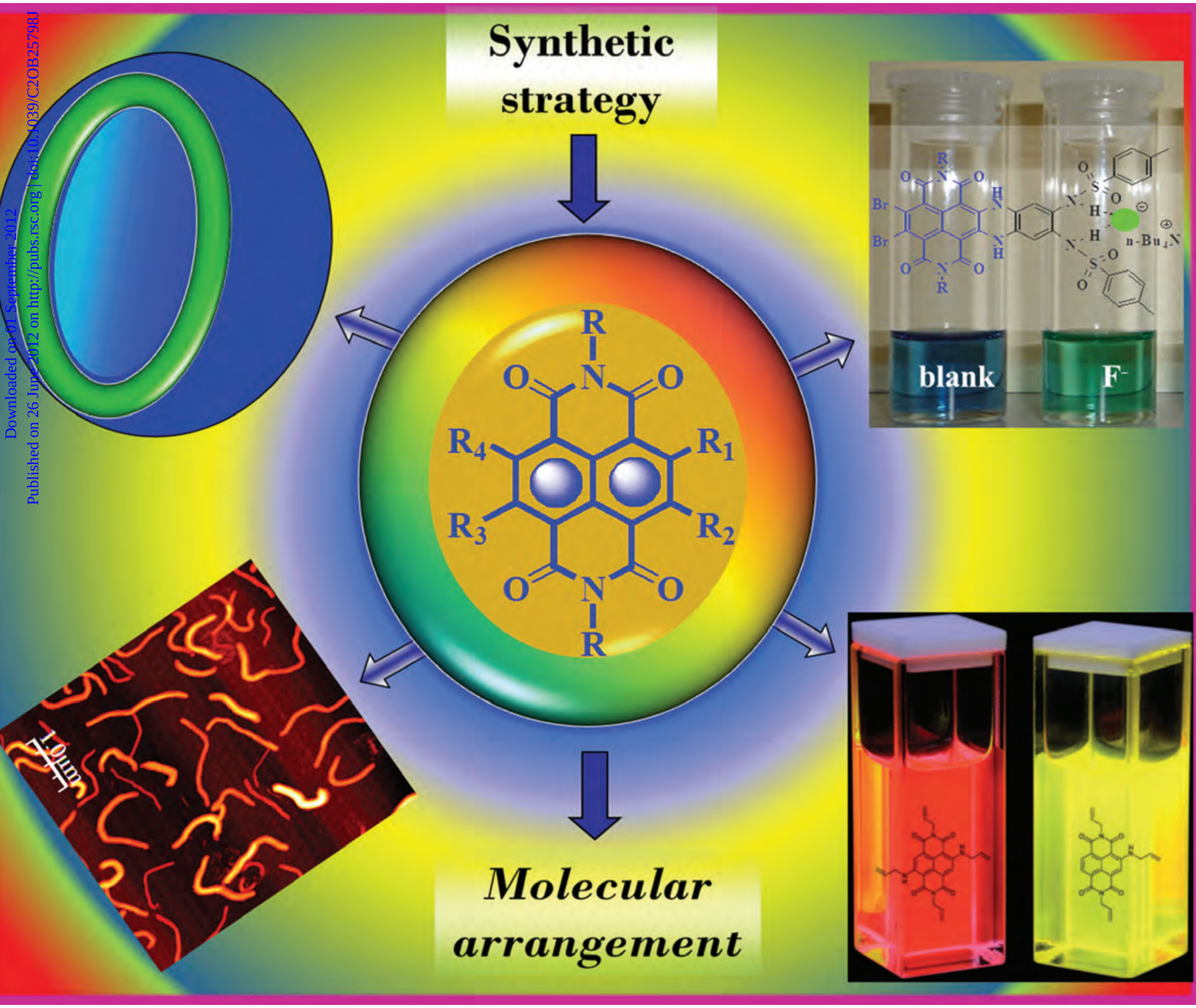

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EMERGING AREA

Recent progress of core-substituted naphthalenediimides: highlights from 2010

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Core-substituted naphthalenediimides (cNDIs) are rapidly emerging as a powerful strategy to create functional nanomaterials and their implications in biological and supramolecular chemistry are significant. Recent developments in the synthesis of cNDIs have allowed several groups to probe the function of this interesting class of dye molecules in a molecular and supramolecular sense. Core-substitution of the NDI can be seen as an opportunity to extend the planar, rigid core and could be used to prepare novel structures for applications in organic, biosupramolecular chemistry, biomedicine, materials science and organic solar cells. In this Emerging Area, we provide up-to-date recent progress in the field of cNDIs. We begin with a general discussion and the applications of cNDIs in the field of supramolecular chemistry *i.e.* generation of nanostructures such as vesicles and nanotubes *etc.*, and we also discuss advances in artificial photosynthesis. Following this is a section on their implications in the field of sensors, particularly DNA intercalation, anion sensing and NDI based pH sensors. Finally, we explore the recent development of cNDIs in organic solar cell applications. We conclude with our views on the prospects of cNDIs in future research.

Introduction

Core-substituted naphthalenediimides (cNDIs) are rapidly emerging as a class of their own in an attractive strategy to create

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Sheshanath V. Bhosale was born in 1976 at Indral-Dist. Latur, India. He received his MSc from the Swami Ramanand Teerth Marathwada University—Nanded, India in 1999. Dr Bhosale then worked as a project assistant at NCL, Pune before moving to the Freie Universität Berlin, Germany, where he received his doctoral degree in supramolecular chemistry under the supervision of Prof. J. H. Fuhrhop in 2004. He did his postdoc study with Prof. S. Matile at the University of Geneva, Switzerland, under the auspices of a Roche Fellowship. Then he worked at Monash University, Australia as an ARC-APD fellow. Currently he is working at RMIT as an ARC-Future Fellow. He is co-author of over 63 publications and his research interests are at the interface between organic and biomaterials, and supramolecular chemistry.

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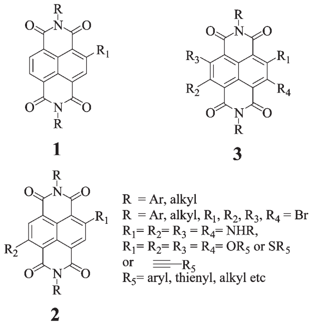


Scheme 1 General structures of cNDIs.

highly colourful, conducting, functional materials with much different photophysical properties than their core unsubstituted counterparts.[1–3] In the early 1990s cNDIs were known to the scientific community but primarily due to the pioneering work of Vollmann *et al*.[4] on NDIs bearing arylamino core substituents, which however lacked interesting optical properties. It may be for this reason that cNDIs were not studied intensely until recent developments by the Würthner group,[5] and later by many other groups who developed better synthetic protocols.[1–3] cNDIs are those containing functionality at positions 2, 3, 6, 7 on the naphthalene core, see models **1–3** as shown in Scheme 1.[6,7] At present, there are many ways to perform core-substitution of NDIs, especially cNDIs, with alkylamino- and alkoxy-core substitution (**2**) resulting in desirable optical properties such as bright colouring and high fluorescence, both of which can be tuned over a wide wavelength range by varying the electron-donating ability of the core substituents.[8–10] Those cNDI derivatives possess all of the characteristics needed for photosynthetic activity.[11,12]

In order to use cNDIs as dyes for organic solar cells, an increase in conjugation is required between the naphthyl core and the appended electroactive moieties. In this regard various groups have devoted their efforts towards core-substitution of NDIs with electron withdrawing and/or electron donating moieties such as aryl,[13–15] thiophene,[16] and cyano[13,17] utilising Suzuki coupling reactions.[18] These methods allow for the functionalisation of NDIs directly on the naphthyl core at the 2- or 2,6-positions *via* C–C linkages, and open up new strategies for solar cell applications.[3] Stille coupling has been used to make cNDIs more conjugated.[19] This approach was also used for the attachment of electron-rich bithiophenes for the preparation of conjugated copolymers of cNDI.[20] Tetrasubstituted cNDIs **3** have also been prepared *via* Br_4NDA with an excess of brominating agent, followed by diimide formation and nucleophilic substitution using several different strategies.[21–23] Using all of the above approaches, synthesised cNDIs derivatives have been used in a range of biomimetic and bio-inspired systems including electron and energy transfer,[24] to bridge the 'green gap,[12] n-type organic transistors[25] the formation of conjugated NDI-thiophene polymers,[23,26] potent G-quadruplex ligands for intercalation,[27] targeting cancer cells,[28] photoconducting materials,[29] in supramolecular antennae,[11,12] optically triggered transport investigations in metal–molecule hybrid setups[30] and air-stable, n-type transparent organic field-effect transistors.[31]

Professor Suresh K. Bhargava

Professor Suresh K. Bhargava is the leader of the Advanced Materials and Industrial Chemistry group at RMIT University. He received his PhD in Organometallic Chemistry from the University of Exeter in 1982. He held research fellowships at Australian National University and CSIRO before joining RMIT University's faculty as a lecturer in 1990. He has been awarded numerous awards and distinctions over the years, including the Ralph McIntosh medal, and was made a fellow of the RSC (London) in 2009 and a member of the Australian Academy of Technological Sciences and Engineering (AATSE) in 2010. He is the current Deputy Pro-Vice Chancellor International at RMIT in addition to his academic commitments.

Earlier research efforts have been the subject of three in-depth reviews focusing on synthesis and applications (supramolecular and solar cells) of NDIs and their derivatives.[1–3] Herein, we are highlighting recent (since 2010) progress in cNDIs in the field of supramolecular chemistry, sensors, photo-induced electron transport in artificial photosystems, and solar cell applications.

Supramolecular nanostructures of cNDIs

Non-covalent interactions play an important role in the construction of self-assembled and self-organised thermodynamically-stable structures at both the cellular and sub-cellular levels, within nano- to millimetre dimensions. These nanostructures are the result of a "bottom-up" strategy. One of the key goals of nanostructures is to assemble structural building blocks into regular arrays with new properties and emergent phenomena. Core-substituted NDIs can be seen as an opportunity to extend the planar, rigid naphthalene core of NDIs and prepare novel structures which promote spontaneous self-assembly. Earlier work by the Würthner group has shown that cNDI co-assembled with a melamine bearing two oligo(*p*-phenylene vinylene) chromophores results in the formation of heterocomplexes at the liquid–solid interface by using bias dependent imaging scanning tunnelling spectroscopy (STM). STM-images of the 1 : 1 mixture of the above two components show a highly disordered organization of the molecules.[32] Although there are many examples of optically active dyes which spontaneously self-assemble into nanostructures,[33,34] only a few examples use cNDI as a core-component. In these self-assemblies a balance of hydrophobic, hydrophilic, electrostatic, π–π stacking and hydrogen bonding interactions plays the major role in determining the aggregation phenomena.

In analogy to some natural systems, we have recently synthesized a novel derivative of cNDI bearing long alkyl chains on the core self-assembled into worm-like nanostructures through solvophobic control, which allowed for the establishment of

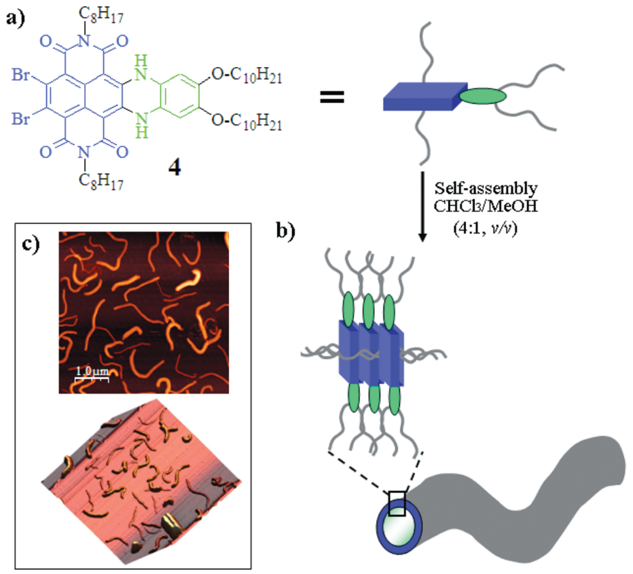


Fig. 1 (a) Structure of 2,3-alkyl chain-annulated cNDI, (b) a model illustrating the self-assembly mechanism and (c) AFM confirming the formation of worm-like nanostructures on the silicon substrate.

well-defined nanostructured aggregates for the first time using cNDIs (Fig. 1).[35] Typically, a cNDI derivative (**4**) consists of three important characteristics consistent with other specific methodologies used for studying supramolecular assembly representing a simplification in design:[32–34] (i) first is the aromatic core of the cNDI which is designed to optimize dispersive interactions (π–π stacking and van der Waals interactions) between the cores within a construct, (ii) the annulated aromatic core which extends the rigidity of the cNDIs, stiffening the surface of the construct in a cooperative fashion, and (iii) hydrophobic long alkyl chains which are capable of being influenced by solvophobic effects, and such molecular arrangements prevent crystallization and favour the directional growth of nanostructures in a 1-D fashion (Fig. 1).

The results demonstrate that introduction of 2,3-annulation to the NDI core affects the electron structure of cNDI in a similar fashion to 2,6- or 2,3,6,7-core substitution.[6,7] A particular example is the self-assembly behaviour of a 2,3-annulated, core-substituted naphthalene diimide **4**, which forms regular worm-like nanostructures in MeOH–CHCl$_3$. UV/vis and fluorescence spectroscopy of **4** in MeOH–CHCl$_3$ solvent mixes show J-type aggregation *i.e.* face-to-face π-stacks of cNDI chromophores, which is typical of other optically active dyes.[33,34] The aggregation of **4** was studied using atomic force microscopy (AFM) and transmission electron microscopy (TEM) in 10–40% v/v methanol in CHCl$_3$, and mostly irregular aggregates were seen by AFM at 10–30% v/v MeOH; however well-defined aggregated nanostructures formed at 40% v/v MeOH that extended to micrometres in length. The core design is unique in that total aromaticity of the core is a tolerant feature that could be exploited for an array of novel systems.

On the other hand, NDI bearing hydrophilic moieties on their cores, such as methoxytriethylene glycol-annulated core-substituted NDIs **5** (mTEG-cNDI) self-assemble into vesicular aggregates in DMSO and CHCl$_3$–MeOH (40%, v/v) as shown in Fig. 2.[36] The formation of vesicles in solution was confirmed by DLS (dynamic light scattering) studies and the average diameter of the vesicles was observed to be 90 nm in DMSO. Furthermore, vesicular nanostructures were visualised by means of AFM and TEM analysis. The diameter of the vesicles formed in CHCl$_3$–MeOH (6 : 4, v/v) falls into the range 17–20 nm and in DMSO in the range of 50–80 nm with uniformly sized layers (Fig. 2c).

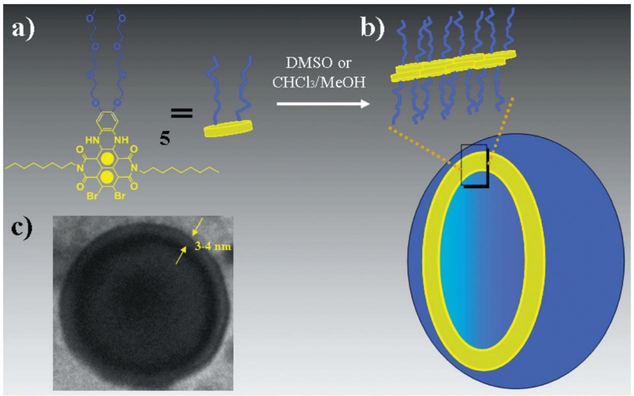


Fig. 2 Structure of 2,3-mTEG-annulated cNDI (a), a model illustrating the self-assembly mechanism (b) and TEM analysis of the self-assembled structure on a carbon grid.

We postulate, based on the evidence shown, that **5** self-assembles in a bilayer fashion with the hydrophilic ethoxy chains exposed both internally and externally to the polar solvent with the hydrophobic alkyl groups interacting in the middle of the bilayer and the balance of π–π-interactions between NDI cores directing the vesicular morphology. The regular morphological features of the present vesicles of cNDI may make them attractive in nanomaterial and biomaterial research.

The use of cNDIs in the construction of supramolecular functional multicomponent architectures on solid surfaces by employing self-organizing, surface-initiated copolymerization (co-SOSIP) in both well-oriented and -ordered multicomponent architectures on indium tin oxide (ITO) was recently studied by Matile and co-workers.[37,38] Typically, self-organization of cNDI monomers and ring-opening disulfide exchange polymerization are combined for controlled growth of the polymer on the ITO (Fig. 3). The supramolecular architectures designed using SOSIP with initiator **A** and propagator **B** using the following strategy: (a) deposition of initiator A on ITO followed by (b) activation with (*S*,*S*)-dithiothreitol (DTT), (c) self-organizing recognition of propagator B and ring-opening disulfide exchange and (d) continuation of co-SOSIP. cNDI π-stacks seem to be significant in building self-organisation in an ordered manner and their electron rich properties, color and redox properties transport electrons efficiently. The finding reveals that the activity of SOSIP architectures is clearly better than that of disordered controls, and the self-sorting strategy employed to build complex surface architectures is very promising with respect to practical applications in n- and p-type solar cells. This approach may provide rapid access to thick films with smooth, oriented surfaces, and long-range order and high precision surface architecture.

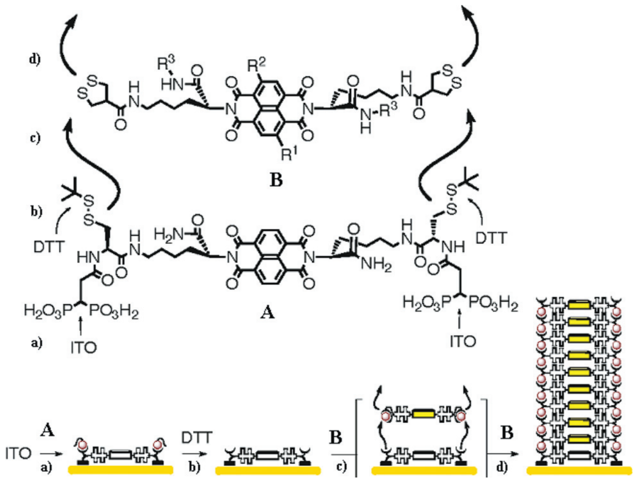


Fig. 3 Systematic design of SOSIP architecture with initiator **A** and propagator **B** on an ITO surface employing four steps (a–d). Reproduced from ref. 37, with permission from ACS.

cNDI based sensor

The development of a fluorescent sensor for *in vivo* and *in vitro* analysis has been the focus of many chemists and biologists. Fluorescent sensors have the general advantages of high sensitivity and real-time screening. While the literature reveals that there are many available fluorophores, new fluorophoric systems with more challenging properties are still in high demand. Core-substitution of NDIs with electron-donor groups are creating highly colored, fluorescent, and conducting functional materials, well suited to sensing applications.[5]

(i) cNDIs based ligand for G-quadruplexes and cancer cell activity

It is well known that NDIs are capable of intercalation due to their planar aromatic structure. As a result, cNDI bearing two redox-active ferrocenyl moieties has been used to electrochemically sense and discriminate double strand DNA (dsDNA) from single stranded DNA (ssDNA).[39] More recently, using a similar strategy the group of Neidle has synthesised a series of tetra-substituted cNDIs with *N*-methylpiperazine end groups on the core of the NDIs and evaluated the G-quadruplex ligand binding (Fig. 4).[40] These derivatives have been shown to have very high affinity and selectivity for telomeric G-quadruplex DNA over duplex DNA, together with selective toxicity in a panel of cancer cell lines. To confirm this, various techniques has been used and in particular circular dichroism (CD) studies show that cNDI bearing *N*-methylpiperazine end groups induce the formation of a parallel G-quadruplex topology. These cNDI derivatives revealed complexation between a 22-mer intramolecular human telomeric quadruplex *via* its crystal structure, and molecular recognition, including face-to-face π–π-interactions on all available G-quartet surfaces but no intercalation into the potassium-templated G-quartet stacks.

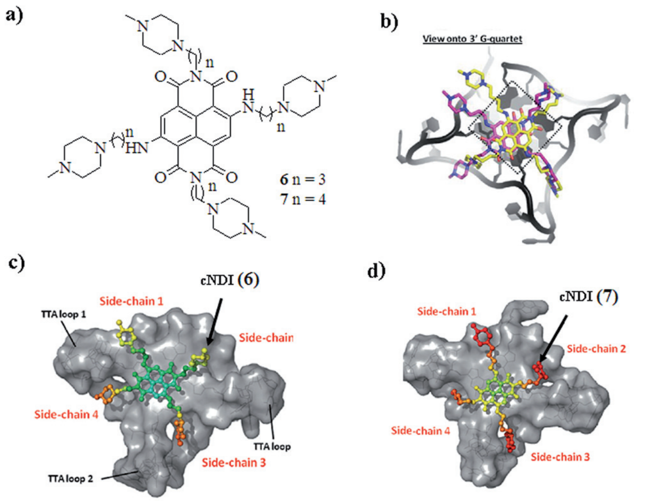


Fig. 4 (a) Structures of cNDI (**6** and **7**) used in this study, (b) rmsd overlap of **6** (purple) and **7** (yellow) onto a G-quartet plane highlighting the asymmetric positioning of the ligands over the G-quartet, and (c, d) representation projected onto the plane of the terminal G-quartets, of the Gtel22 quadruplex solvent-accessible binding surfaces with the bound ligands 4 and 5 shown colored by crystallographic temperature factors (in Å^2). Reproduced from ref. 40, with permission from ACS.

(ii) Anion sensor

Anions play an important role in many biological processes and in many industrial applications and products. Among various anions, fluoride has attracted the interest of chemists as it has been used in dental care and as a dietary supplement. A large intake of fluoride ions can lead to human pathologies, such as osteoporosis and the fluorosis type of diseases. Thus, it is very important to develop new and sensitive methods for fluoride ion detection. Existing fluoride ion sensors are mainly based on the approach of binding site-signalling. Our current research activities based on molecular recognition and sensing are focused on the development of cNDI-based artificial receptors for the selective sensing of fluoride. In this regard, we have reported two different approaches (1) an optical chemosensor for fluoride ions based on cNDIs bearing a bis-sulfonamide moiety which exhibits high selectivity for fluoride ions and (2) cNDI bearing acetylene–trimethylsilane moieties as a fluorogenic probe for the selective detection of fluoride ions; both approaches are shown in Fig. 5.[41,42] In the first approach, we have used 2,3-annulated cNDI bearing tosyl moieties, which serve as colorimetric fluoride sensors (Fig. 5a). In the presence of TBAF, the absorption of cNDI **8** at 615 nm shifts to 715 nm.[41] This bathochromic effect has been explained by deprotonation of the tosylamide by the more basic fluoride to give an H-bonded complex of NH and F$^-$. The cNDI **8** shows unique selectivity and reactivity for fluoride over other anions in CHCl$_3$ by a two-stage deprotonation process leading to a colorimetric response, and in DMSO solution the cNDI **8** is shown to be highly selective for fluoride over other anions with more pronounced changes in absorption characteristics. In the second approach, we have demonstrated the use of a cNDI bearing trimethylsilylacetylene (**9**) moieties as a colorimetric and fluorescent chemodosimeter for fluoride (Fig. 5b).[42] The detection of anions was carried out by

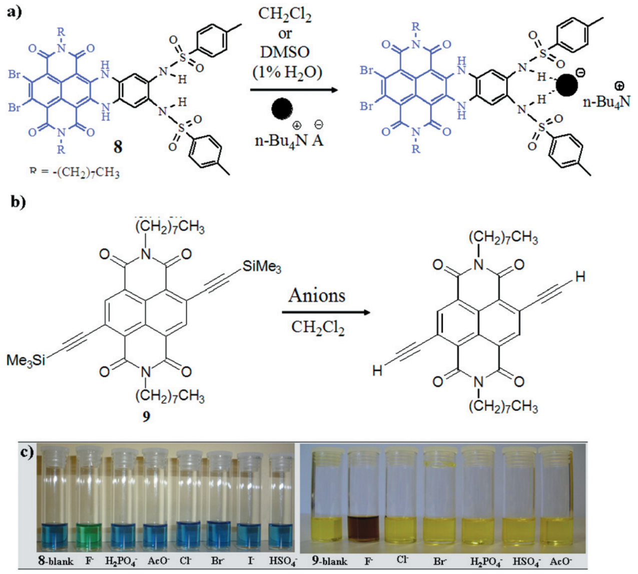
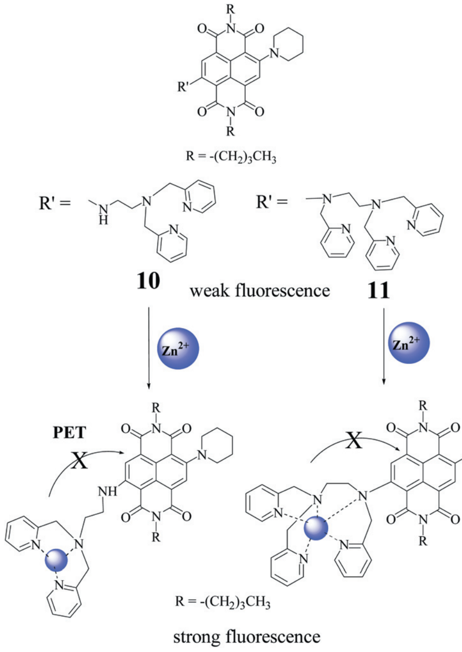


Fig. 5 (a) Structures of cNDI bearing tosyl receptors (**8**) and the anion binding event, (b) the detection of anions by desilylation of the detector cNDI-di-ATMS **9** and (c) tubes displaying color changes of sensors **8** and **9** in CH_2Cl_2 upon addition of 5 and 10 equiv of different anions (as their TBA salts) respectively.



Scheme 2 Schematic illustration of a binding event of Zn^{2+} with cNDIs (**10**, **11**).

desilylation of the detector using NMR and changes visible to the naked eye as well as changes in the electronic properties of cNDIs by UV/vis absorption and fluorescence spectroscopy. The results demonstrate that the cNDI based chemodosimeter is selective for fluoride over other anions used in this study, such as Cl^-, Br^-, HSO_4^-, AcO^- and $H_2PO_4^-$. The sensing process is rapid and takes only tens of seconds to minutes.

Interestingly, sensing responses of color changes upon addition of 3 equiv. of anions to cNDI in chloroform of: no anion, F^-, $H_2PO_4^-$, AcO^-, Cl^-, Br^-, I^-, HSO_4^- as their tetrabutylammonium salts were observed in both sensors (**8** and **9**). Typically: cNDI **8** is blue and changes color to green. In the case of **9**, a yellow to dark brown change occurs upon addition of fluoride anion, and no effect from other anions was observable to the naked eye. The cNDI molecule has a number of advantages over other existing chromophores used in sensing applications as it absorbs in the visible region, and has unique fluorescence properties, and its color changes are also visible to the naked eye, an advantage for sensing purposes.

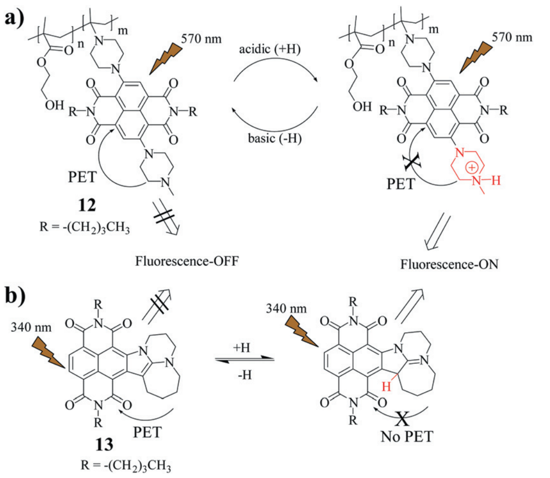
(iii) Fluorescent chemosensors for zinc ions based on cNDIs

Recently, the Tian and Zhu group designed and synthesized two novel and highly sensitive fluorescent probes based on cNDI *i.e.* *N*,*N*′-di-*n*-butyl-2-(*N*-{2-[bis-(pyridin-2-ylmethyl)amino]ethyl})-6-(*N*-piperidinyl)-NDI (**10**) and *N*,*N*′-di-*n*-butyl-2-[*N*,*N*,*N*′-tri-(pyridin-2-ylmethyl)amino]ethyl-6-(*N*-piperidinyl) (**11**) bearing *N*,*N*-di(pyridin-2-ylmethyl)ethane-1,2-diamine and *N*,*N*,*N*′-tri-(pyridin-2-ylmethyl)ethane-1,2-diamine as the receptor moieties on to the core for Zn^{2+} respectively.[43] Ultimately, upon binding of Zn^{2+} with both (**10** and **11**) the ionophores demonstrate completely different ligand effects on photoinduced electron-transfer (PET) and intramolecular charge transfer (ICT) under physiological conditions (Scheme 2), while other metals have no such effect. Upon binding of Zn^{2+} with cNDI **10**, fluorescence enhancement was observed, which is a typical characteristic of PET.

In contrast, **11**, upon the coordination of Zn^{2+}, exhibits diminishing electron delocalization of the NDI moiety, which results in interruption of the ICT. Receptor **10** shows several advantages as a probe for sensing Zn^{2+}, such as the response wavelength falling in the desired NIR region beneficial for high light penetration in biological tissues. A PET-based turn-on fluorescent type exhibits a maximum response and may be useful for discriminating Zn^{2+} over other cations *via* the difference in fluorescence intensities. The authors also performed imaging using chromophores **10** and **11** for intracellular Zn^{2+} ions in living human nasopharyngeal epidermal carcinoma cells, and showed it to be a highly selective sensor.

(iv) pH Sensor based on cNDIs

The detection and control of pH and ions play an important role in chemistry, biochemistry, cellular biology, and drug delivery. pH sensors which have the capability to tune their properties as a function of pH are very useful in the areas of biology and environmental science, and are also very important in medicine for determining the state of diseases. To achieve these aims, two broad methods are already established for studying pH sensing capability. The first is to use ion-sensitive microelectrodes and the second utilizes fluorescent dyes. In both the cases, the chemosensors are mostly based on ICT and PET. As we have discussed earlier cNDIs are particularly desirable sensor candidates because they are small and easy to prepare, functionalise and give relatively broad solubility in a range of solvents, as well as the capability to tune fluorescence (ON/OFF).[43] Using this



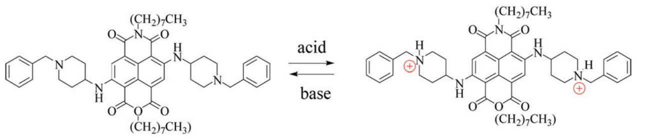
Scheme 3 Fluorescence OFF–ON sensor based on cNDI through pH control by manipulating PET.

strategy, Matile and co-workers developed a protocol for synthesis of cNDI bearing sulfoxides and sulfones in the core, and to use those derivatives for enantioselective self-sorting on planar, *p*-acidic surfaces of chiral anion-p transporters into lipid bilayer membranes.[44]

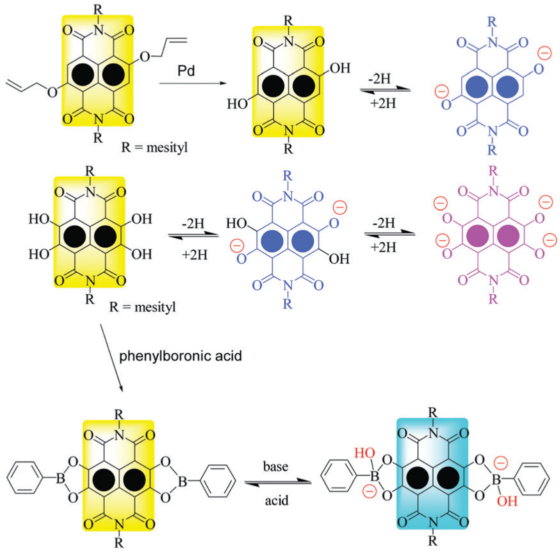
On the other hand, introducing chemosensors into polymeric backbones *via* covalent or non-covalently linkages can be easily employed to fabricate devices and chips fixed onto microbioreactors, and may be capable of avoiding the phase separation and concentration quenching of chromophores.[45] With this in mind, Zhu and co-workers synthesised a long wavelength fluorescent hydrophilic copolymer based on poly(2-hydroxyethyl methacrylate) (PHEMA) containing the pendant group consisting of a cNDI chromophore which serves as a pH-sensitive unit (Scheme 3a).

The target polymeric chemosensor system, PHEMA was chosen as the main polymeric matrix due to its high hydrophilicity, and its ability to form good films which avoids the fluorescence self-quenching induced by aggregation. The system developed has significant advantages over other sensors, as front-face excitation and emission collection can greatly minimize the fluorescence and scattering contribution from the cell mass. The film shows high sensitivity to environmental acidity, with excellent linear response to pH values in the range of pH 4.6–8.0. The fluorescence enhancement (Fluorescence-ON) in acidic environments is due to PET blocking occurring from the protonation of the methyl-substituted piperidine nitrogen NDI fluorophore **12** under neutral conditions, resulting in Fluorescence-OFF (Scheme 3). Of significance is the fact that the isosbestic point in the near-IR region can be used as an excitation wavelength to minimise overlapping interference from biological samples. In terms of the convenience in synthesis and response to pH, the chemosensor film developed here based on cNDIs-PHEMA (**12**) could potentially be applied as a low-cost microbioreactor pH indicator for high-throughput bioprocessing.

Using a similar strategy Li and co-workers described the use of novel cNDIs bearing 1,8-diazabicyclo[5.4.0]undec-7-ene pendant (**13**) units as pH controlled fluorescence switches (Scheme 3b).[46] The protocol is very simple: unsubstituted NDI reacts with DBU in the presence of CuI in THF/toluene at 75 °C. After column chromatography, NDI-DBU was obtained in a 20% yield as a green product. Its absorption and emission spectra dramatically changed upon the addition of trifluoroacetic acid (TFA) in MeCN solution, and recovered on further addition of triethylamine (TEA), thus the system shows significant utility due to the reversible nature of the pH sensor.



Scheme 4 A cNDI bearing two piperidine rings on the core exhibits a reversible protic response by addition of TFA and by TEA.



Scheme 5 pH-responsive cNDIs bearing catechols and boronic esters on the core, and their deprotonation by acid–base titration.

The Langford group has shown that cNDI bearing two piperidine rings on the core exhibits a reversible protic response through both colour and emission by addition of TFA and by TEA (Scheme 4).[47] In particular upon addition of TFA, an increase in the fluorescence quantum yield from 0.5 to 0.67 and a blue shift from 618 nm to 598 nm in absorption was observed, and interestingly the system can be fully reversed upon addition of TEA and the cycle is repeatable many times.

Matile and co-workers also developed a novel protocol for the synthesis of cNDI bearing hydroquinone, catechol, boronic esters and imines in the core and used them for pH-responsive sensors (Scheme 5).[48]

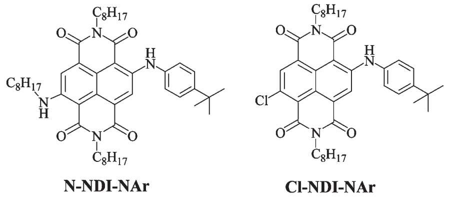
Typically: Pd-catalyzed deallylation gives hydroquinone on the core of the NDIs under mild conditions, followed by deprotonation of hydroquinone by weak base in a water-containing medium, followed by excited-state intramolecular proton transfer which yields a second bathochromic emission. In particular upon addition of acid, a large shift in absorption is observed *i.e.* deprotonated cNDI absorbs in the NIR region (~640 nm). Interestingly, in neutral pH cNDI bearing four –OH groups (catechol) absorbs at ~490 nm, which is an approximate 20 nm red shift from cNDI with only two –OH groups. The shift and increasing intensity of this bathochromic emission with four hydrogen-bond donors in the core of cNDI compared to two donors was observed in four steps due to intramolecular proton transfer and hydrogen bonding. Deprotonation of hydroquinone, catechol and boronic ester cores provides access to an impressive panchromism up to the NIR absorption. Furthermore, cNDIs with oxidative imination on the core exhibit red shifts up to 638 nm upon protonation. Similarly cNDI bearing boronic esters, imines, and hydroquinones were found to be reversibly pH sensitive.

All of the above methods can also be further utilized for the establishment of novel energy transfer systems as covalent building blocks by manipulating the pH of the systems.

Photoinduced electron transport

There is significant interest in the development of macromolecular chemical systems which form long-lived charge-separated states for scientific and industrial advances in solar energy conversion, molecular-based optoelectronics, and other applications. NDIs have made useful contributions to the evaluation of design principles because of their ease of synthesis and electron donating and/or accepting properties, and the similarity of these properties to naturally-occurring photosynthetic reaction centres in plant and bacterial systems.[5] In early work, Odobel and coworkers described the use of cNDIs as a core unit in the synthesis of a Ru(bpy)$_3$-cNDI-Ru(bpy)$_3$ system and as also having a significant effect on the electronic coupling between electron donor and acceptor.[49] To understand the role of NDIs in photosynthesis, the group of Würthner synthesised rainbow zinc chlorin rod antennas based on cNDIs utilizing the coupling of zinc chlorins with NDIs to harvest light and transfer the photonic energy to the chlorophyll centers.[50] Earlier work by Bhosale *et al.* described a breakthrough in cNDI chemistry *via* the creation of an artificial photosynthetic system: tetrameric M-helix based on cNDIs that is long enough to span a lipid bilayer membrane and undergo symmetry-breaking ultrafast and quantitative photoinduced charge separation.[12] Further development in this area was made by the Matile group by creating zipper assemblies to build artificial photosystems with multicolor cNDIs on solid substrates successively.[51] cNDI derivatives have been also used previously for distance dependent Förster resonance energy transfer (FRET)[5] and single molecules studied.[52] This area of research has been revived by us recently,[1–3] thus we will illustrate herein the progress of cNDIs in recent years.

Recently, joint work by Riedle and co-workers described the influence of core-substitution on the ultrafast charge separation and recombination in arylamino cNDIs.[53] In this work the authors have investigated the effects due to variation of the core-substituent on photoinduced charge transfer (PCT) using femtosecond absorption spectroscopy on the two arylamino cNDIs (Cl-NDI-NAr and N-NDI-NAr) as shown in Scheme 6. Furthermore, *ab initio* calculations were used to support the quenching mechanism and in particular the differences in the excited state lifetimes. Both molecules have the same carbon scaffold and an arylamino core-substituent, however, they differ by the second core-substituent. Their finding reveals that the two compounds: N-NDI-NAr and Cl-NDI-NAr exhibit an ultrafast charge separation within ~3 ps after optical excitation into the S1 partial CT state. However, the second substituent was found to be rather insensitive in contrast to the donor moiety. This is in contrast to the charge recombination step leading back into the electronic ground state which takes approximately 70 ps in the case of N-NDI-NAr and 11 ps in the case of Cl-NDI-NAr. The *ab initio* calculated energy gap between the fully charge separated and the electronic ground state of N-NDI-NAr is 0.2 eV larger than in the case of Cl-NDI-NAr, and the energy gap rule can account for the variation of the dynamics. Thus, the larger energy gap leading to a six-fold increase in the lifetime of the fully charge separated state (from 11 to 70 ps) is realistic. These findings should be helpful for the application of NDI derivatives in artificial solar energy conversion.



Scheme 6 Chemical structure of the two arylamino cNDIs (N-NDI-NAr and Cl-NDI-NAr).

Synthesis and photophysical study of cNDI-porphyrin arrays

On the other hand, nature uses porphyrins and chlorophyll derivatives in its photosynthetic reaction centre, and porphyrins are probably the most used building blocks in multichromophoric systems.[1] These chromophores are widely used due to their similarity to natural pigment systems as well as the possibility of tuning their optical and redox properties by varying the nature of the substituents and/or of the central metal atom. There has been great work done by many scientists through synthesizing dyads and triads for long-lived charge separation. For example, free-base and Zn-porphyrins can be combined to form arrays for light harvesting, whereas the association of free-base or zinc with gold porphyrins results in charge separation (CS).[11] However, in most systems the porphyrin is the electron donor and quinone is an electron-accepting group with a high reduction potential that usually does not absorb in the visible. cNDIs have recently emerged as powerful elements in the design of multichromophoric systems.[1–3] Substitution by one, two or up to four electron-donating groups on the naphthalene core introduces a new optical transition with charge transfer character located in the visible region, and with an energy that can be fine-tuned by varying the nature of the core substituents.[2] Recently, we reported femtosecond-resolved spectroscopy of the excited-state of two dyads consisting of either a free-base or zinc–porphyrin attached to a tetra-core-substituted NDI unit *via* a 2,3-annulated linkage (Fig. 6).[54]

The excited-state dynamics of both FbTPPNDI and ZnTPPNDI are strongly solvent dependent with a lifetime of the emissive state that shortens by a factor of 500–1000 when going from a non-polar to a medium polarity solvent. In

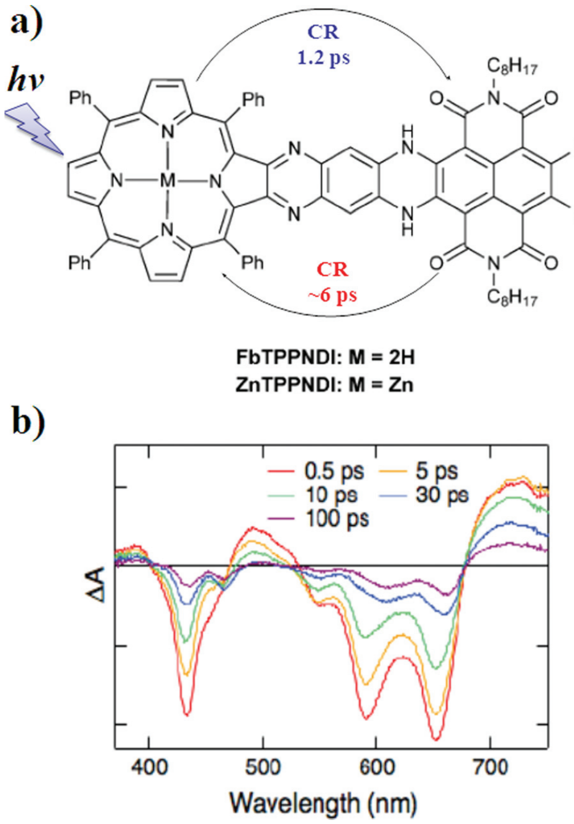


Fig. 6 (a) Structures and schematic illustration in photoinduced electron transfer in novel dyad system (cNDI-porphyrin) and (b) ultrafast photoinduced e$^-$ transfer in the cNDI-porphyrin dyad. Reproduced from ref. 54 with permission from the PCCP Owner Societies.

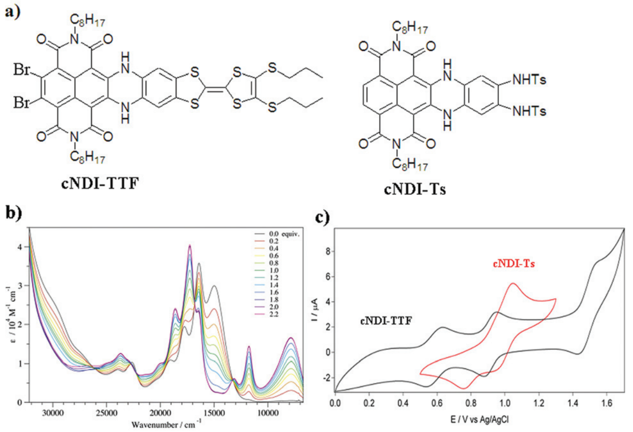


Fig. 7 (a) Chemical structures used for this study, (b) UV/vis-NIR absorption spectra of the oxidation of cNDI-TTF (2.25×10^{-5} M) in CH_2Cl_2 upon addition of aliquots of $FeCl_3$ and (c) cyclic voltammograms of cNDI-TTF (4.45×10^{-4} M, black line) and the reference compound cNDI-Ts (3.74×10^{-4} M, red line) in CH_2Cl_2; $TBAPF_6$ (0.1 M) on platinum electrode at 200 mV s^{-1}. Reproduced from ref. 55, with permission from Elsevier.

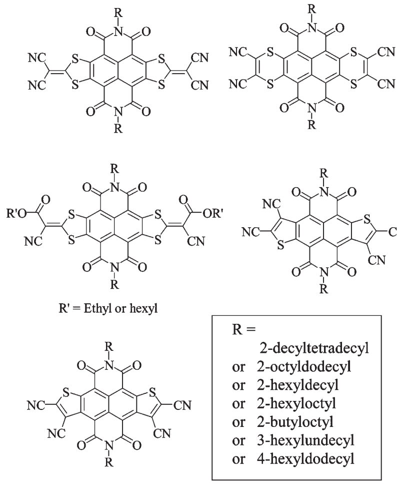
dichloromethane, the charge separation from the porphyrin to the cNDI unit was observed within 1–3 ps, however charge recombination was observed within 10–20 ps. This impressive effect may be due to both the strong electronic coupling between the two chromophores (porphyrin and cNDI) and due to this coupling the driving force of charge separation is largely positive in non-polar solvents and slightly favourable in polar solvents.

In the development of molecular electronics, molecular systems having two or more redox-active centres with cooperative interactions are of prime interest. To create such systems recently, we have synthesised tetrathiafulvalene (TTF)-functionalized cNDI dyads (Fig. 7) and explored their electrochemical and photophysical properties.[55] Typical, a tetrathiafulvalene donor was attached to the NDI core *via* a diaza rigid bridge affording a new planar dyad. It is very well known that TTF is one of the most intensively investigated redox-active organic molecules due to its intrinsic properties *i.e.* two easily accessible oxidized states ($TTF^{\cdot+}$ and TTF^{2+}) and it also displays distinctly different physical properties. A strong electronic absorption profile extends far into the visible spectral region, which originates from its inherent electronic donor–acceptor nature. Diverse electronic excited charge-transfer states were generated in different oxidation states, leading to almost full absorption in the visible to near-IR region, with high extinction coefficients. The oxidized radical species show a strong tendency to undergo aggregation in which the long-distance attractive interactions overcome the electrostatic repulsions. It was also observed that in this rigid and planar structural characteristic, significant π–π interactions were observed in the presence of a strong absorption in the near infra red (NIR) at 1270 nm upon chemical oxidation by $FeCl_3$. Upon oxidation of cNDI-TTF with $FeCl_3$, a bleaching of the ICT band at 15 000 cm^{-1} (667 nm) and an associated gradual growth of new lower-energy absorption bands at 13 070 cm^{-1} (765 nm) and 11 740 cm^{-1} (852 nm) is observed which are characteristic of the cation radical species $(\text{cNDI-TTF})^{\cdot+}$ and another ICT transition at 7870 cm^{-1} (1270 nm) was observed which is attributed to the aggregation of this radical cation species $(\text{cNDI-TTF})^{\cdot+}$ (Fig. 7b). The electrochemical properties of the cNDI-TTF dyad and the reference compound cNDI-Ts in CH_2Cl_2 were probed by cyclic voltammetry. The cNDI-TTF dyad undergoes three reversible processes, which are related to oxidations of the TTF core to the radical and dication species (Fig. 7c, black line) as compared to cNDI-Ts (Fig. 7c, red line). This observation is not unexpected on the basis of simple electrostatic arguments; the TTF unit is oxidized first in the cNDI-TTF dyad. Electrochemical and photophysical properties demonstrate the combination of pronounced redox behaviour, and a strong photoinduced intramolecular charge-transfer (PICT) process within the NDI-TTF dyad.[55]

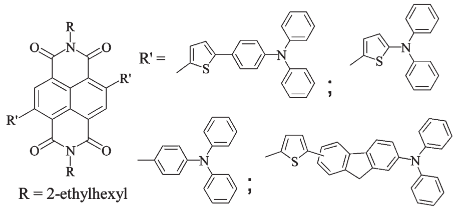
Recently, Zhao group synthesised cNDI derivatives with 2,6- or 2,3,6,7-amino substituents and studied photophysical properties using steady-state and time-resolved spectroscopy.[56] Nanosecond time-resolved transient difference spectroscopy confirmed that triplet–triplet annihilation based upconversion with quantum yield up to 18.5% was observed. Interestingly at room-temperature long-lived triplet excited states of NDIs are observed.

cNDIs in organic solar cells

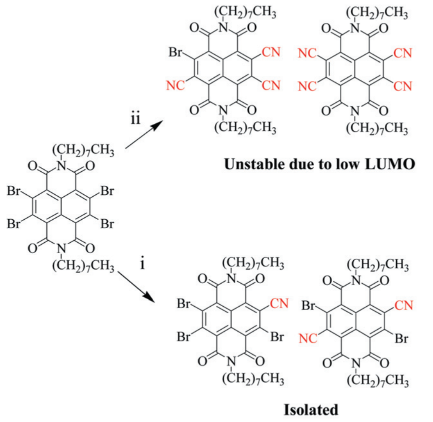
Organic thin-film transistors (OTFTs) are currently the subject of intensive research activity by many chemists due to their promise as components for emerging low-cost, large area, and



Scheme 7 Core-expanded NDI derivatives for OTFTs.



Scheme 8 cNDIs bearing *N*,*N*-aryl amino groups for OTFTs.



i) CuCN, $Pd_2(dba)_3$dppf, dioxane, rt, ii) CuCN, $Pd_2(dba)_3$dppf, dioxane, 50°C, 24 h

Scheme 9 Synthesis of cyanated naphthalene diimides.

flexible electronic devices. There is growing interest in the synthesis of n-channel semiconductors as a significant number of organic p-channel semiconductors are available already.[57] In last decade or so, many optically active compounds have been tested, among these cNDIs appear to be very promising for n-type transfer under ambient conditions in comparison to p-channel semiconductors.[3] In this development, cNDIs with annulated sulfur-containing heterocycles and tetracene diimide bearing terminal electron withdrawing groups exhibit n-type transport with high electron mobilities.[58–60] On the other hand spin-coated NDI-based polymers give ambient stable mobilities of 0.85 $cm^2\ V^{-1}\ s^{-1}$ and current On/Off ratios in the order of 10^6–10^7 in a top-gate bottom-contact configuration on glass as well as vacuum deposition for inkjet printing.[61]

For more detail on OTFTs please refer to Würthner and Stolte's recent review.[3] This review has been mostly focused on OTFTs, while herein we highlight the most recent progress in this field. Joint work of the Gao and Di groups has shown that cNDI bearing 2-(1,3-dithiol-2-ylidene)malonitrile groups exhibits high electron mobility (0.51 $cm^2\ V^{-1}\ s^{-1}$), and air-stability with current On/Off ratios of 10^5–10^7 under ambient conditions for n-channel OTFTs.[62] Continuing work by the same groups has described the synthesis of four novel core-extended NDIs fused with sulphur heterocycles and end capped with electron withdrawing groups for air-stable n-channel OTFTs (Scheme 7).[63] The synthesised core-substitutions of NDI were performed using 2-(1,3-dithiol-2-ylidene)malonitrile or 1,4-dithiine-2,3-dicarbonitrile (DTDCN) or alkyl 2-(1,3-dithiol-2-ylidene)-cyanoacetate or 2,3-dicyanothiophene moieties for air-stability and compounds bearing branched *N*-alkyl substituents at the diimide position with carbon atom numbers from 12 to 24 for good solubility of the material. Furthermore their findings revealed that increasing the chain lengths at the imide position decreases electron mobility. Solution-processed, bottom-gate organic thin film transistors based on a new series of compounds were synthesised and found to operate well in air with electron mobility ranging from $\sim 10^{-6}$ to 0.26 $cm^2\ V^{-1}\ s^{-1}$, depending on the nature of the branched *N*-alkyl substituent and the π-backbone structure.

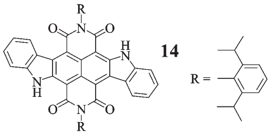
Chou and co-workers have synthesised a novel series of donor–acceptor–donor triad-type compounds with NDI as an acceptor and *N*,*N*-aryl amino groups on the core as donors (Scheme 8).[64] All synthesised derivatives show moderate to strong two photon absorption (2PA) as cross-sections measured with a Z-scan method (229–1092 GM), and all of these compounds with 2PA properties emit in the near-IR region (>740 nm).

Chi and co-workers developed a method for the core-substitution of tetra-bromonaphthalene diimide with stepwise cyanations giving a series of cyanated compounds *i.e.* from mono- to tetra-cyano-NDI (Scheme 9).[65] Among them monocyanated NDI and dicyanated NDI was isolated, however, tricyanated and tetracyanated NDI shows instability towards moisture. The partially cyanated intermediates show interesting properties towards air-stable n-channel semiconductors with moderate electron nobilities with organic field effect transistors (OFET) electron mobility up to 0.05 $cm^2\ V^{-1}\ s^{-1}$.

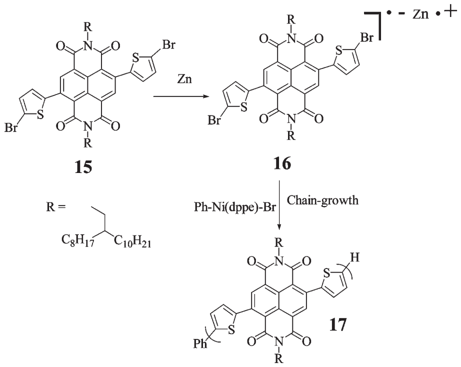
A literature survey reveals that cNDI has frequently been used in n-type transport OTFTs.[2,3,62–64] However, recently, the Würthner group has discovered that a novel flat extended, fully conjugated core of this NDI derivative bearing an annulated-carbazole with diisopropylphenyl groups at the diimide positions (Scheme 10) possessing an extended p-core enables charge-carrier transport in thin films, showing highly efficient p-channel transport. Typically, for compound **14** a large hole mobility (0.56 $cm^2\ V^{-1}\ s^{-1}$) and a current On/Off ratio of 10^6 in the bottom-gate was observed, which is unprecedented for cNDI-based semiconductors.[66]

cNDI based polymers

Interest in the use of polymers with cNDI for the preparation of materials for OFTS is also growing. Jenekhe and co-workers



Scheme 10 Structure of carbazolo[2,3-*b*]carbazole-6,7:13,14-tetracarboxylic acid diimide.

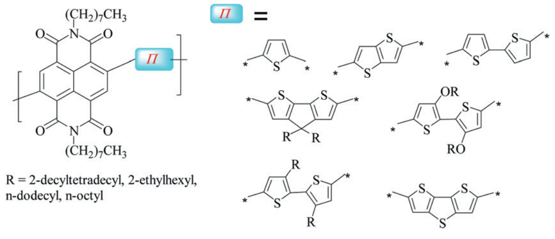


Scheme 11 Preparation of the dibromo-thiophene/Zn radical anion monomer and chain-growth polymerization of NDI-based anion-radical monomers with Ni-catalyst leading to conjugated controlled molecular weight polymers.

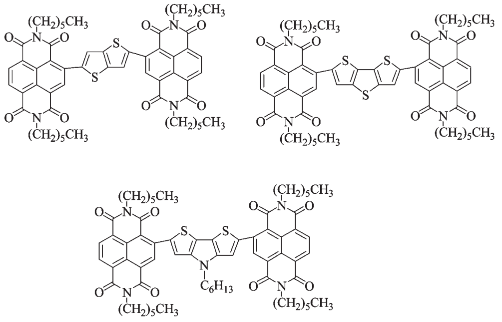
have synthesised a homologous series of six novel oligothiophene–naphthalene diimide-based oligomer semiconductors with donor–acceptor architecture, which respond well in bulk heterojunction solar cell applications. This is the first example with the highest photovoltaic efficiency of the preparation of non-fullerene BHJ polymer solar cells based on cNDIs.[67] Further development was performed by Luscombe and co-workers, who recently synthesised four new highly soluble cNDI-thiophene copolymers based on cNDI with thiophene as the polymer unit on the core, and obtained n-type electron mobilities of 0.076 $cm^2\ V^{-1}\ s^{-1}$ for all of the reported polymer compounds.[68] This group has also synthesised series of NDI based polymers with imine-bridged ladders and characterized the solution-processable n-type cNDI copolymers for OFET applications. Average electron mobilities are 0.0026 $cm^2\ V^{-1}\ s^{-1}$, which shows an electron-mobility improvement of 4 orders of magnitude, with On/Off current ratios on the order of 10^4 reported.[69] Most interestingly and more recently, Senkovskyy and co-workers have used a chain-growth polymerization strategy for synthesising cNDI polymers *via* an anion radical strategy (Scheme 11).[70]

Guo *et al.* synthesised a series of alternating donor–acceptor copolymer based on cNDIs with seven different thiophene moieties with varying electron-donating strength (Scheme 12).[71] Synthesised cNDI based on the thiophene moiety copolymer exhibited n-channel and ambipolar field-effect transistors with good electron transport with maximum electron mobility of 0.07 $cm^2\ V^{-1}\ s^{-1}$ in bottom-gate/top-contact device geometry.

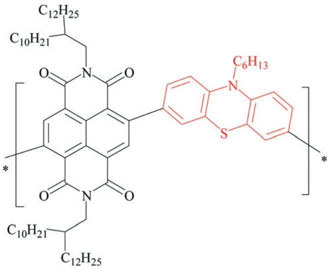
Polander *et al.* synthesised a series of bis(cNDI) derivatives with thiophene bridges utilising standard palladium-catalyzed Suzuki coupling of brominated NDI and distannyl fused-ring heterocycle derivatives in moderate yields (Scheme 13).[72] All derivatives show high electron mobility up to 9.8×10^{-3} $cm^2\ V^{-1}\ s^{-1}$ and a threshold voltage of −14.4 V was observed.



Scheme 12 Structures of donor–acceptor copolymer based on cNDIs with different thiophenes.



Scheme 13 General structures of thiophene bridged bis(cNDI).



Scheme 14 Chemical structures of copolymers.

Zhan and co-workers synthesised conjugated polymers of cNDI and phenothiazine for n-channel OFETs employing Pd-catalyzed Suzuki coupling polymerization with or without phase-transfer catalyst Aliquat 336 (Scheme 14).[73] The electron mobilities obtained from the cNDI-based copolymers are as high as 0.05 $cm^2\ V^{-1}\ s^{-1}$ and On/Off ratios as high as 10^5 in nitrogen, which are among the best reported so far.

Symmetric, highly electron-deficient building blocks 2,6-bis-(2-bromothien-5-yl)naphthalene-1,4,5,8-tetracarboxylic-*N*,*N*′-bis-(2-octyldodec-yl) diimide radicals (**16**) were prepared from bromo-thiophene-cNDI *via* zinc mediated synthesis and further polymerization of **16** in the presence of nickel catalyst was performed, leading to the corresponding bithiophene-NDI conjugated polymer (**17**) with low polydispersity, and specific end-functions. This polymer exhibits n-type transport with electron mobilities similar to other reported cNDIs.[74]

Novel derivatives of cNDIs

Nowadays core-substitution of NDI has become a fascinating area on one hand, and the other hand these derivatives have

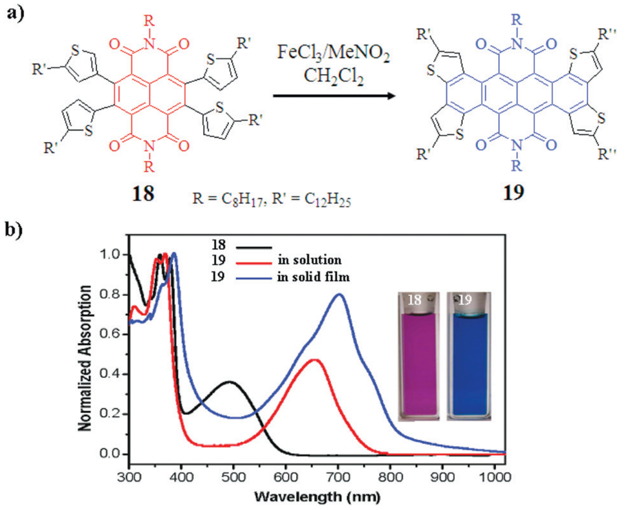
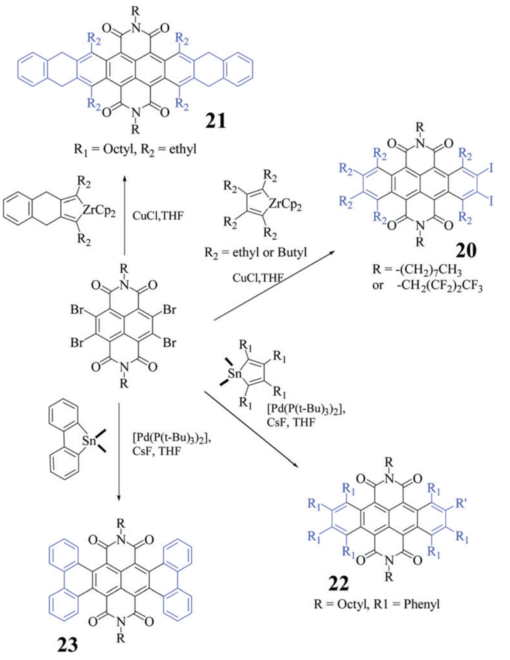


Fig. 8 (a) Structures of tetrathienyl-substituted NDI (18) and tetrathienyl-fused tetracene NDI (19), (b) UV/vis spectra of **18** and **19** in chloroform solution (1.0×10^{-5} M) and in thin film; photos for the dilute solution of **18** and **19** in chloroform. Reproduced from ref. 75, with permission from ACS.

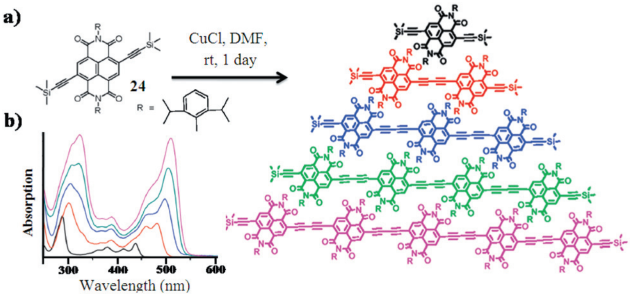
become very useful in the development of nanotechnology. Chi and co-workers have synthesised the first tetracene-cNDI derivative (**19**) with four electron-rich thiophene units fused to the core of NDI by oxidative cyclodehydrogenation using $FeCl_3$ (Fig. 8).[75] Interestingly, the color seen for this conjugated cNDI derivative (**19**) was blue as compared to the colour without fused NDI **18** (with four thiophenes) which is purple. An important difference between these two derivatives (**18** and **19**) is the absorption maximum of the charge transfer peak. Absorption of tetracene-cNDI was red-shifted by about 160 nm after ring closure, as compared to **18** (494 nm), indicating that tetracene-cNDI has a small band gap due to intramolecular donor–acceptor interaction, as well as extended π-conjugation. In the solid state, tetracene-cNDI showed a bathochromic shift of 47 nm due to aggregation. Furthermore, the electrochemical energy gap was calculated to be 1.52 eV. OFETs based on tetracene-cNDI mainly exhibit n-type behaviour, with an average saturation electron mobility $\mu_{sat}(e) = 4.83 \times 10^{-3}$ cm^2 V^{-1} s^{-1}, with On/Off ratio $= 5 \times 10^5$. Tetracene-cNDI also shows ambipolar charge transport in thin film field-effect transistors of $\mu_{sat}(h) = 9.0 \times 10^{-4}$ cm^2 V^{-1} s^{-1} and On/Off ratio $= 10^3$–10^4 for p-channel operation.

In another recent example, Li and co-workers have jointly synthesized novel tetracene-cNDI derivatives (**20–23**) based on direct double ring extension of electron deficient NDI bearing metallacyclopentadienes (Scheme 15).[76]

In particular, double aromatic annulations were carried out as follows: the coupling of Br_4cNDI with zirconacyclopentadiene was carried out in THF using copper chloride at 50 °C giving good yields of **20** and **21**. In conjunction, the authors also synthesised different substituents onto the extended aromatic cores. Interestingly, the introduction of semiperfluoroalkyl chains at the imide positions of the Br_4cNDIs also proceeded well, achieving triply annulated benzene derivatives by a double coupling reaction of cNDIs in the presence of $[Pd(P(t\text{-}Bu)_3)_2]$ and CsF in THF at 70 °C gives good yields (**22** and **23**). All obtained compounds absorb in the near infra-red (NIR) region due to this property, and this new molecule may be suitable for n-type semiconductors and solar cell materials in the future. Furthermore, this interesting route based on direct double ring extension involving organometallic reagents may offer a new way to access stable and higher acene cNDIs in the future.

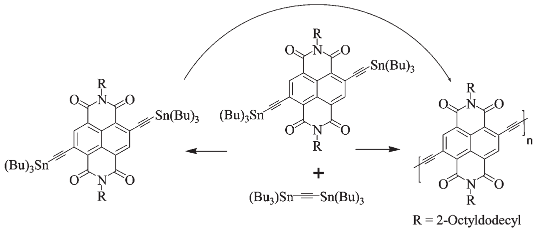


Scheme 15 Synthetic route for synthesis of tetracene-cNDI derivatives (**20–23**) from Br_4cNDI.

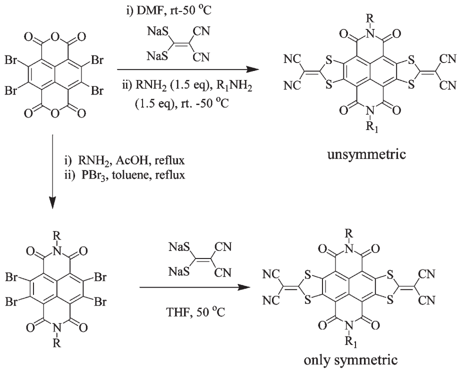


Scheme 16 (a) Synthetic route for the oligomers of cNDIs from 1,6-di-((trimethylsilyl)ethynyl)-cNDIs **24** and (b) UV/vis absorption spectra of the oligomers: colour of spectra related to oligomers shown in (a). Reproduced from ref. 73, with permission from ACS.

Recently, Wang and co-workers have developed one pot protocol for the preparation of well-defined oligo-butadiynylene-cNDIs containing up to five NDI moieties by oxidative homocoupling of 1,6-di((trimethylsilyl)ethynyl)-cNDIs **24** in the presence of a stoichiometric amount of CuCl in *N*,*N*-dimethylformamide (DMF) at room temperature (Scheme 16a).[77] The UV/vis absorption spectra of these homogeneous oligomers showed well-defined bathochromic shifts in the absorption band with the increasing number of NDI units within the oligomers, for example 438, 482, 498, 506 and 510 nm for one, two, three, four and five NDI units respectively (Scheme 16b).



Scheme 17 Synthesis of conjugated cNDI polymer.



Scheme 18 Synthesis of one-pot unsymmetrical tetra-core-substituted NDIs.

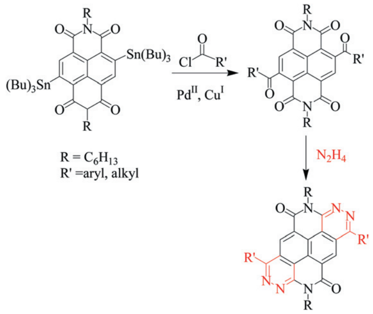
Very recently Iverson and Alvey developed a new synthetic strategy for the synthesis of cNDI conjugated polymers (Scheme 17).[78] Typically, brominated NDI is reacted with bis-(tributylstannyl)acetylene utilising Stille coupling procedures.

More recently, joint work by the Gao and Zhu groups developed a one-pot protocol for core-expansion of NDIs *via* first a nucleophilic aromatic substitution reaction and then an imidization reaction (Scheme 18).[79] This methodology allows utilization of an asymmetric functionalisation of the imide position of Br_4NDA, and furthermore the method is very useful for an easy and low-cost preparation of diverse n-type organic materials. The authors have also shown that a few of their derivatives synthesized with this method exhibited high electron mobilities of up to 0.70 $cm^2\ V^{-1}\ s^{-1}$ in ambient conditions.

Marder and co-workers have synthesised for the first time 2,6-diacyl derivatives of NDIS *via* Stille coupling reactions of the 2,6-distannyl derivatives with acyl halides. Interestingly the reaction of these diketones with hydrazine gave phthalazino[6,7,8,1-*lmna*]pyridazino[5,4,3-*gh*][3,8]phenanthroline-5,11(4*H*,10*H*)-dione fused-ring derivatives in moderate yields (Scheme 19).[80]

Very interesting developments were made by the Franco group on cNDI, demonstrating mechanically activated molecular switching through single molecule pulling based on a cNDI stacker and the behaviour of the thermal fluctuations, stress maxima, and dynamical bis-stability in terms of molecular transport properties (Fig. 9).[81]

The stacker **25** bearing two complementary aromatic rings, a NDI- and a pyrene tetrol joined together by a short chain, that π-stack strongly due to the four hydrogen bonds that can form between the hydroxy (–OH) and carbonyl (–C=O) groups within the aromatic moieties stabilizes the stacked conformation.



Scheme 19 Synthetic strategy of phthalazino[6,7,8,1-*lmna*]pyridazino-[5,4,3-*gh*][3,8]phenanthroline-5,11(4*H*,10*H*)-dione fused-ring derivatives.

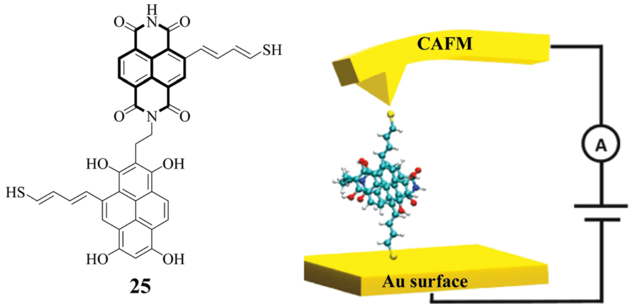


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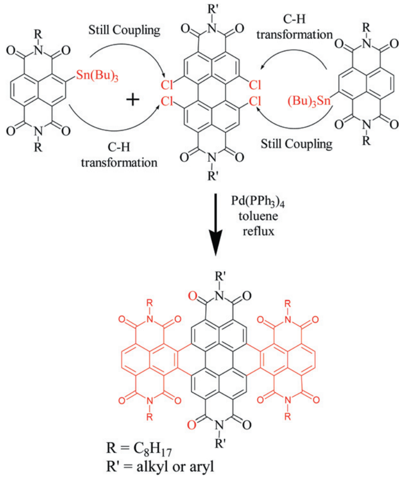
Fig. 9 The structure of a stacker consisting of cNDI joined with pyrenetetrol *via* a short aliphatic chain (**25**). Model represents schematic of a single-molecule pulling/molecular electronics setup. In it, a molecule is attached to a metallic surface and a CAFM tip and a voltage (A) is applied across the junction, and the resulting current can be measured. Reproduced from ref. 75, with permission from (ACS).

One end of the stacker is bonded to the Au surface and the other end is bonded to a conducting atomic force microscopy tip (CAFM) tip attached to a cantilever. A voltage is then applied across the junction and the resulting current measured. The resulting switch is reversible and both the "on" and "off" phases can be tuned. The results and insights presented might lead to the development of a series of novel mechanically controlled molecular devices.

The Marder group has synthesised a new family of hybrid rylene derivatives *via* a combination of Stille coupling and C–H transformation (Scheme 20).[82] The synthesised novel p-system extended derivatives not only broaden the absorption spectrum but also increase the electron affinities for the electron injection and transport with ambient stability. Among the synthesised derivatives one exhibits excellent OTFT characteristics under ambient conditions.

Furthermore, the group developed an efficient method for the synthesis of 2-stannyl and 2,6-distannyl NDIs.[83] They have also used the above derivatives in Pd-catalysed coupling reactions for the synthesis oligomer such as bi- and ter-NDI derivatives.

Li and co-workers described a novel cNDI based near-IR "turn-on" fluorescent chemosensor with high selectivity for Hg^{2+} ions through an intramolecular charge transfer (TICT) mechanism[84] and a cNDI-based sensor with long wavelength absorption and emission used to image intracellular Hg^{2+} ions in living HeLa cells.



Scheme 20 Hybrid rylene arrays have been prepared *via* a combination of Stille coupling and C–H transformation.

Very recently, Matile and co-workers synthesised a series of novel derivatives of amphiphilic cNDI and used them for imaging microdomains in giant unilamellar vesicles.[85]

Perspectives

Core-substituted NDI recognition systems are likely to contribute to a new generation of bio-inspired materials in biotechnology and nanotechnology, high throughput identification screening systems, and are also likely to provide new energy transduction systems. Furthermore, the ability to form informative nano-scale assemblies will be vital to advances in the development of novel sensors and techniques for medical, biochemical, industrial and environmental applications. Research on cNDIs has already provided an intellectual grounding in molecular recognition acid/base pH responses, anion sensing, DNA intercalation *etc.* for the assembly of complex arrays based on biological building blocks. The importance of NDI-porphyrin functionalised systems was gauged by the recent demand on solar energy conversion that requires application of multilayers and distance- and time-dependent study of electron transfer. Further developments of donors on the core of NDIs with the desired distances for charge separation will provide molecular systems and supramolecular arrays, which are capable of solar energy conversion and other photonic applications. Over a short period of time, several design strategies have been implicated for the creation of functional p-stack architectures in bilayer membranes and have also emerged in biosupramolecular self-assembly. This includes the formation of ion channels by stacked rosettes such as guanine or folate quartets and the formation of self-assembled nanostructures from solution to solid substrates (nanotubes, vesicles, layer-by-layer assemblies). We hope that these highlights will inspire young chemists and biologists to explore novel and easy chemical scaffolds synthesis and the application of cNDIs in biological systems as well as in materials chemistry. Research into the performance of devices such as organic photovoltaic (OPV) devices and alternative OFET device conditions and architectures is the subject of future investigation and development.

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