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Dyes/Pigments

Strategies for the Synthesis of Functional Naphthalene Diimides

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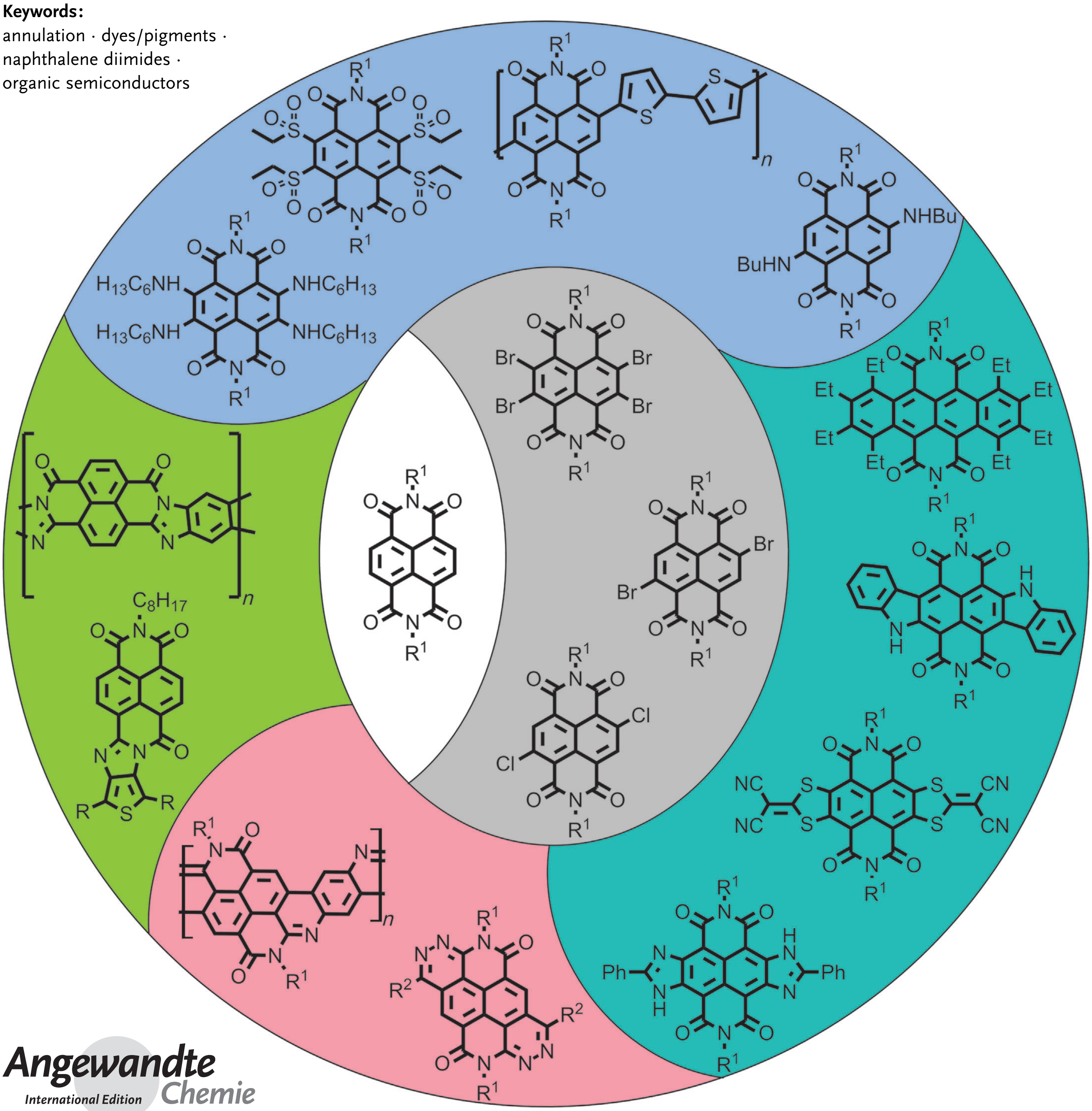

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Naphthalene diimides, which have for a long time been in the shadow of their higher homologues the perylene diimides, currently belong to the most investigated classes of organic compounds. This is primarily due to the initial synthetic studies on core functionalization that were carried out at the beginning of the last decade, which facilitated diverse structural modifications of the naphthalene scaffold. Compounds with greatly modified optical and electronic properties that can be easily and effectively modulated by appropriate functionalization were made accessible through relatively little synthetic effort. This resulted in diverse interesting applications. The electron-deficient character of these compounds makes them highly valuable, particularly in the field of organic electronics as air-stable n-type semiconductors, while absorption bands over the whole visible spectral range through the introduction of core substituents enabled interesting photosystems and photovoltaic applications. This Review provides an overview on different approaches towards core functionalization as well as on synthetic strategies for the core expansion of naphthalene diimides that have been developed mainly in the last five years.

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1. Introduction

The structure of the parent naphthalene diimide (NDI) compound is composed of a naphthalene core that bears at its four α-positions two electron-withdrawing imide groups, whose nitrogen atom can further be substituted with a variety of alkyl or aryl residues R^1. NDI is the smallest possible homologue of rylene diimides (RDI), among which perylene diimide[1] (PDI, $n=1$, Figure 1) is without doubt the most important one. Unlike perylene diimides, which display outstanding absorption properties and are, therefore, of high significance as industrial pigments, naphthalene diimides that lack substituents at the 2, 3, 6 and 7 core positions are, as a result of their smaller aromatic core, colorless solids—provided that they are of high purity—and in solution they absorb only UV irradiation with a wavelength smaller than 400 nm. Only the structurally related 1,4,5,8-naphthalenetetracarboxylic acid-1,8:4,5-dianhydride (NDA, Figure 1) was of industrial significance, being applied as a precursor for the production of industrially relevant perinone pigments.[2] NDA also serves as a precursor for the synthesis of many different kinds of NDI derivatives.

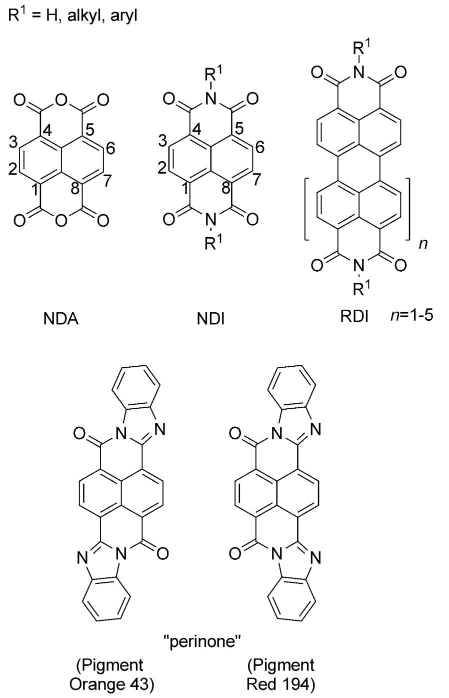

Figure 1. General structures of naphthalene dianhydride (NDA), naphthalene diimide (NDI), rylene diimides (RDI), and both isomeric perinones.

Although the field of perylene diimides[1] as well as of higher rylene diimides[3] has been fascinating a great number of scientists for decades because of their outstanding fluorescence properties,[4] naphthalene diimides had a "shadowy existence" until the turn of the last millennium. The redox properties of the NDIs alone could inspire a large group of researchers to explore different applications, with the employment as n-transporting materials in organic field effect transistors (OFET) being the most prominent one.[5] Simple NDI derivatives possess a planar aromatic scaffold and, as a consequence of the two annulated electron-withdrawing imide groups, they are easily and reversibly reducible. Solutions of NDI derivatives in dichloromethane show

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two reversible one-electron reductions (e.g. for $R^1 = n$-octyl: $E_{1/2}^{\mathrm{Red1}} = -1.10$ V and $E_{1/2}^{\mathrm{Red2}} = -1.51$ V versus ferrocene/ferrocenium (Fc/Fc$^+$); LUMO energy = −3.7 eV).[6] Moreover, the electron-withdrawing imide carbonyl groups effect a strong polarization of π-systems and thus the aromatic naphthalene core possesses a low π-electron density, which results in a positive quadrupole moment and a high π-acidity of the NDI core. Since imide substituents have little effect on the optical and electrochemical properties of NDI compounds, their solubility and aggregation behavior can be directed by functionalization in the imide position without significantly changing the electronic properties of the π-scaffold.

Functionalization of the NDI imide nitrogen atoms has led to various applications, for example, as radical anion salts with high conductivity[7] and as easily reducible electrochemical units in artificial photosystems[8] or in supramolecular architectures[9] (Figure 2). Initially, the Iverson research group utilized the, now well-established, charge-transfer (CT) complex motif composed of electron-poor NDI derivatives in combination with electron-rich 1,5-dialkoxynaphthalenes (DAN) to construct stabilized foldamers through CT interaction (Figure 2 a).[9c,10] Weak CT interactions result in these large molecules forming a defined structure with a flexible framework, similar to that in naturally occurring proteins. The anionic side groups attached to the backbone lead in aqueous solution to a folding with alternately stacked NDI acceptors and DAN donors, whose driving force can be attributed to the solvophobic effect as well as to the complimentary electrostatic interactions of electron-poor and -rich aromatic compounds.[11] The alternate stacking of NDI and DAN has also been employed as a template for the synthesis of the respective catenanes (Figure 2 b)[12] and rotaxanes,[9a,13] as well as for the structural stabilization of synthetic ion channels,[9d] while the aid of solvophobic effects enabled the construction of more complex molecular systems such as, for example, an NDI-based knot (Figure 2 c).[14]

The alternating stacking pattern could be perturbed by suitable functionalization of DAN and NDI derivatives with amide groups at the imide position, which led to self-sorting of both naphthalene derivatives through intermolecular hydrogen bonds.[15] Such CT interactions are accompanied by the emergence of a CT band in the UV/Vis spectrum, and thus evoke a color enhancement of otherwise colorless naphthalene derivatives. In this regard, NDI-containing organogels have been used as colorimetric sensors, thus allowing the recognition of regioisomeric dihydroxynaphthalenes.[16]

Moreover, the strong π-acidity of NDI derivatives has been discussed in conjunction with anion–π interactions.[17] The experimental evidence for anion–π interactions was obtained, on the one hand, in the gas phase by mass spectrometric detection of NDI–anion complexes with different anions. On the other hand, selective and efficient transmembrane anion transport across lipid bilayers in the presence of NDI derivatives has been confirmed, where anion–π interactions were involved. Rodlike, nitrogen-linked oligonaphthalene diimides serve as “slides”, along which anions at NDI units can hop from one binding site to the next to pass through the membrane.[17] Furthermore, Matile and co-workers have recently demonstrated the first example of the catalytic activity of an acidic π-surface based on an NDI scaffold, thereby opening up a further interesting research field.[18] In addition, Saha and co-workers have shown that during the interaction with strong basic anions, such as fluoride, an electron-transfer (ET) process between the anions and the electron-deficient NDI occurs, which can take place thermally or is just photoinduced (PET), depending on the position of the frontier molecular orbitals (FMOs) of the NDI and anion.[19]

Besides the donor–acceptor complexes, organic scaffolds[20] and supramolecularly organized systems have been created through appropriate functionalization of NDIs. Amino acid functionalized NDI derivatives were used to build-up helical nanorods that are held together through hydrogen bonding and can function, for example, as receptors for C_{60}.[21]

For the studies discussed thus far, no chemical modification of the four available positions of the NDI core was necessary and, indeed, studies on this subject were only reported sporadically in the literature until 2000. With that said, functionalization of the NDI core to modulate its optical and electronic properties initially appeared to be a peripheral research field.[22] However, this has changed fundamentally in the last few years, and NDI derivatives currently represent one of the most explored classes of organic compounds. The

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Frank Würthner, born in 1964, completed his PhD at the University of Stuttgart (Germany) under the supervision of F. Effenberger. After postdoctoral research at MIT in Cambridge/MA (USA) with J. Rebek, Jr., he worked for two years at BASF in Ludwigshafen (Germany), followed by Habilitation in Organic Chemistry at the University of Ulm (2001). In 2002, he became Chair of Organic Chemistry at the University of Würzburg, where he is also an executive director of the Wilhelm-Conrad Röntgen Research Center for Complex Material Systems (since 2006) and founder of the Center for Nanosystems Chemistry (2010).

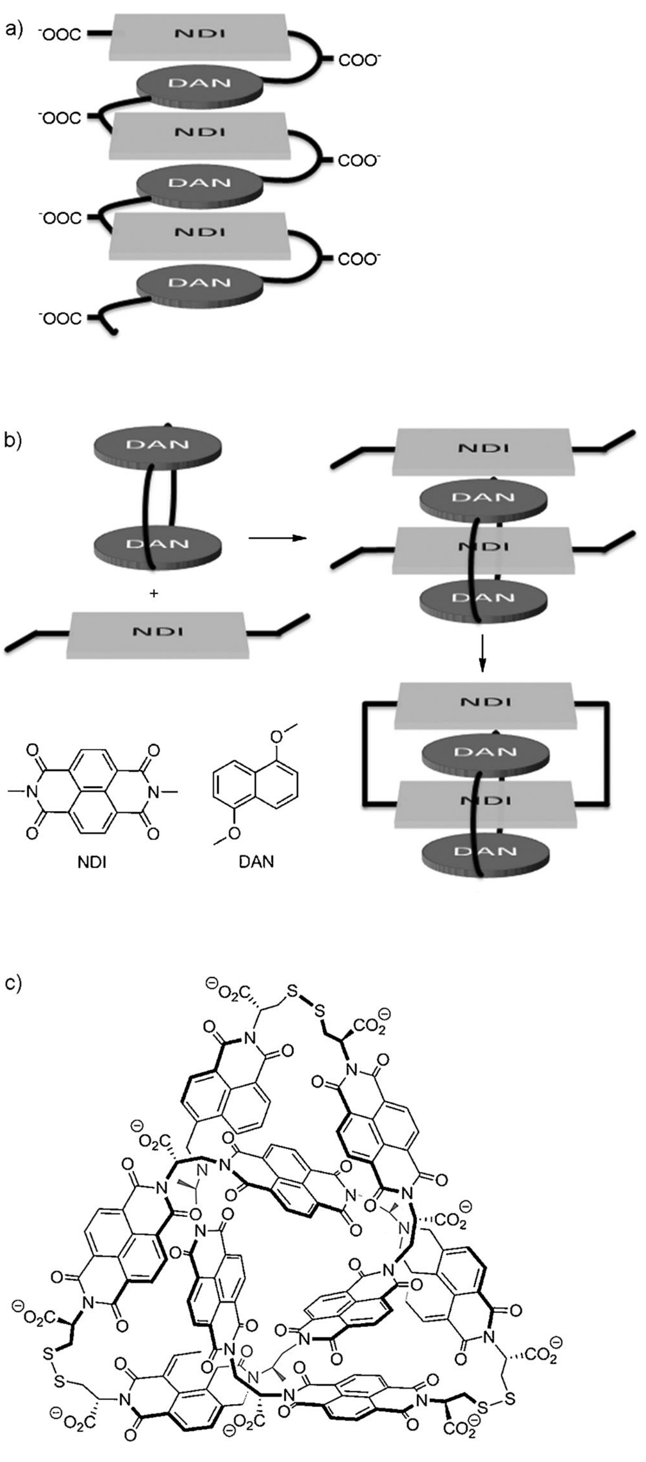


Figure 2. NDI derivatives as acceptor units in charge-transfer complexes for the construction of supramolecular structures: a) foldamer[9c] and b) [2]catenane.[12a] c) Structure of an NDI-based knot (modified from Ref. [14]).

optical and electrochemical properties of NDI derivatives can indeed be modified dramatically by relatively small structural changes at the NDI core, by substitution of hydrogen atoms at the NDI core with heteroatoms, for example. Incorporation of N, O, or S donor substituents at the core has led to NDI dyes of all possible colors and varied frontier molecular orbital levels,[23] which is of relevance for artificial photosynthesis.[24] The research group of Matile, moreover, made considerable efforts to construct supramolecular zipper assemblies with interlocked NDI π-surfaces as artificial photosystems on gold substrates.[25] They created n-/p-heterojunction cascades by suitable arrangement of core-substituted naphthalene diimides with different colors and redox potentials through generation of two antiparallel redox gradients between the NDI derivatives, on the one hand, and *p*-oligophenyl (POP) or *p*-oligophenylethinyl (OPE) backbone, on the other hand. Electrons and holes can be funneled separately in such cascades, so that an efficient photocurrent is generated upon photoexcitation of the NDI chromophore (Figure 3a).[25c]

A further application area of core-substituted NDI derivatives results in part from their outstanding emission properties, and interestingly their study started only about a decade ago.[22,26] In this regard, an attractive application was reported recently by Mayor, Krupke, and co-workers, who anchored an OPE-based rodlike molecule containing a central NDI fluorophore[27] as a molecular functional unit between two single-walled carbon nanotubes (CNTs).[28] Application of a voltage between the CNT electrodes led to electroluminescence being observed, impressively emphasizing the potential of this class of compounds as emitters (Figure 3b).

Besides these impressive new developments, which only became possible by core functionalization of NDI, the exploration of novel NDI derivatives in the last decade was motivated mainly by the fact that an already low-lying lowest unoccupied molecular orbital (LUMO) of the parent NDI can be further lowered by the incorporation of appropriate electron-withdrawing substituents (e.g halogen and cyano) to achieve air-stable electron transport in organic transistors.[5] Thus, followed by the first report of Katz et al. on an ambient-stable NDI-based OFET,[5a] the introduction of two cyano functional groups into the NDI core by Wasielewski and Marks marked an important progress in the field.[5b,c] To date, a core-dichlorinated NDI derivative with an electron mobility of 8.6 $cm^2\,V^{-1}\,s^{-1}$ in air is the record holder among n-channel transport materials (see Scheme 6 and Figure 5 in the next section).[29] Thus, the development of new NDI derivatives in the last few years was mainly aimed at optimizing materials for use in organic semiconductors. Since not only the molecular properties but also the packing features in the solid state are of great significance for this purpose, further variations, beyond the introduction of donor or acceptor substituents, of the main scaffold have to be accomplished, whereby core extension by annulation with further heteroaromatic units has attracted great interest.

The NDI derivatives made available by chemists in the last few years now cover a broad spectrum of structures and properties. In the following section we first give an overview on the basic strategies for substitution of the NDI core, followed by a comprehensive survey on the numerous synthetic concepts which lead to core-extended NDI derivatives. In regard to in-depth discussions on the properties and applications of core-substituted NDI derivatives, we refer to previously published review articles.[5d,e,23,30]

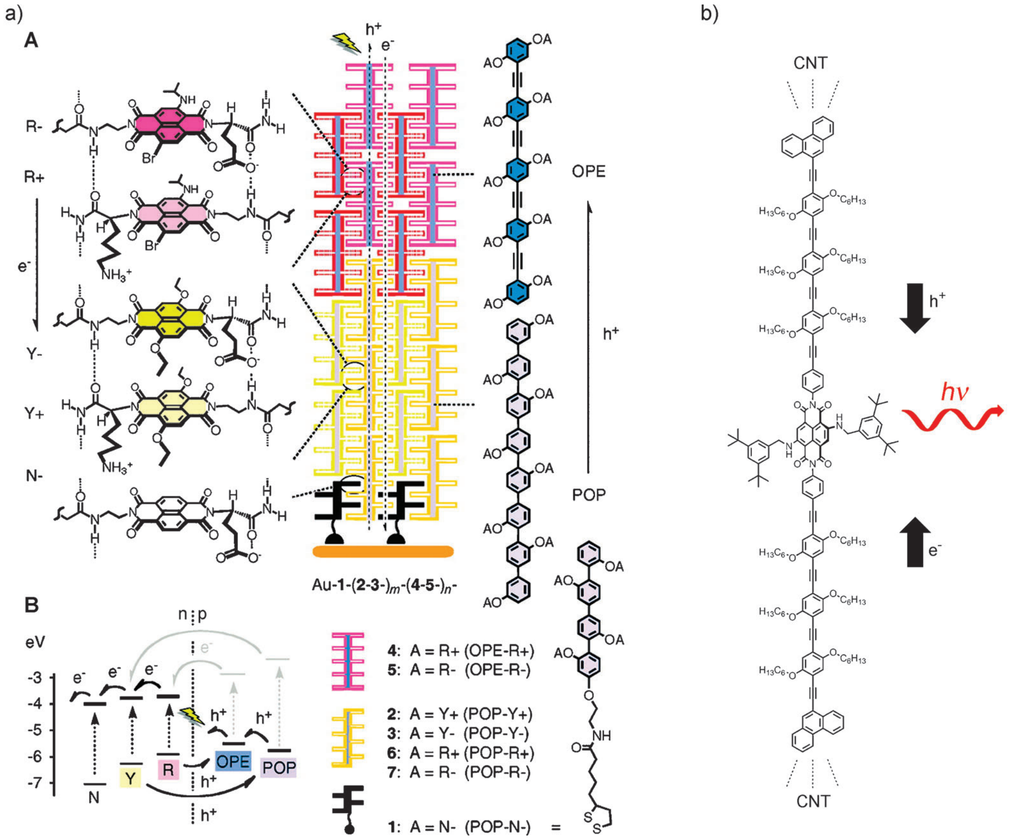


Figure 3. a) Zipper-type assembly as an n-/p-heterojunction photosystem. Reproduced from Ref. [25c] with permission. Copyright (2010) American Chemical Society. A) NDI stacking, B) redox gradient. b) NDI fluorophore as a functional unit in a molecular rod which is anchored between two single-walled carbon nanotubes and exhibits electroluminescence upon application of voltage.[28]

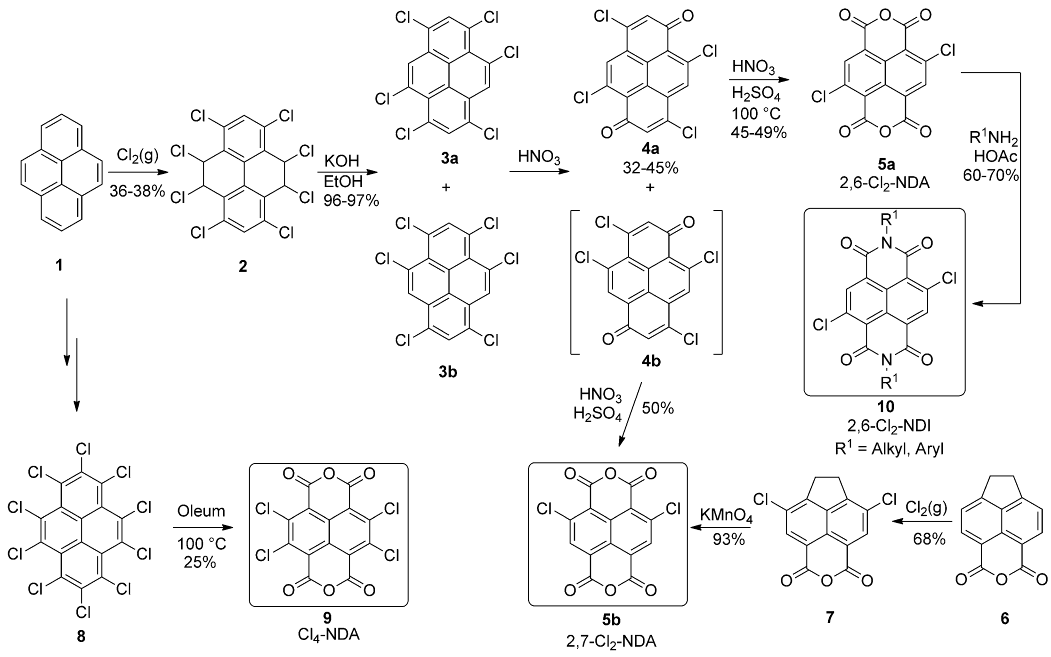
2. Core-Substituted Naphthalene Diimides

2.1. Synthesis of Core-Halogenated NDI Derivatives

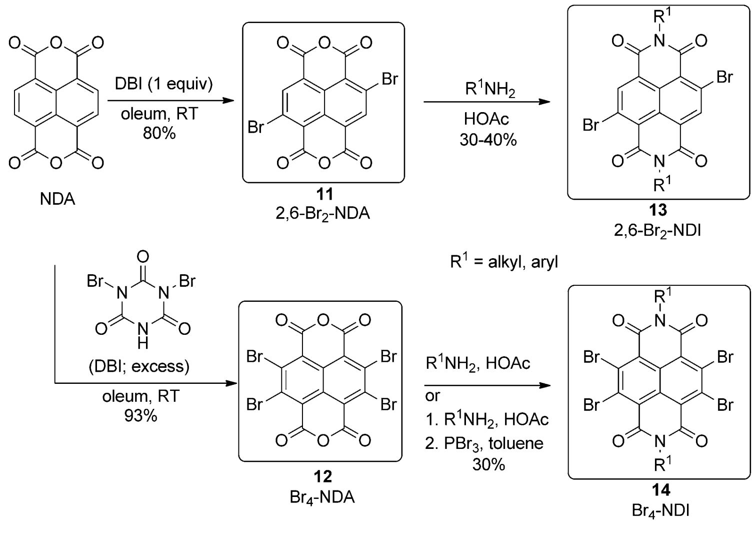
The synthesis of core-substituted naphthalene diimides usually starts from the respective halogenated naphthalene dianhydride (NDA), hence the substitution pattern at the NDI core is predetermined by the position of the halogen atoms on the precursor NDA core. Chlorinated NDI derivatives were already synthesized in the first half of the 20th century by Vollmann et al. in the laboratories of the chemical company Hoechst during the oxidative derivatization of pyrene **1** (Scheme 1).[31] A mixture of two regioisomeric hexachloropyrenes **3a** and **3b** was obtained after eightfold chlorination of pyrene, followed by a double base-induced elimination of HCl. Subsequent oxidation in hot oleum afforded a regioisomeric mixture of **5a** and **5b**, which could be separated by tedious recrystallization (Scheme 1).

However, a two-step oxidation of hexachloropyrenes **3a**,**b** with nitric acid was more advantageous, as the oxidation at lower temperature could be stopped at the stage of tetrachloropyrene diones **4a** and **4b**, and their different solubility in nitric acid enabled their separation by filtration. In particular, isomer **4a** precipitated from the reaction solution and could be obtained in a pure form. Further oxidation of **4a** at higher temperature then affords the regioisomerically pure 2,6-Cl_2-NDA **5a**. The overall yield of this four-step synthesis under optimized conditions amounted to about 8%.[6] Tetrachloropyrenedione **4b** was purified by multiple recrystallizations, and subsequent oxidation then afforded 2,7-Cl_2-NDA **5b**. Vollmann et al. also introduced an alternative route to 2,7-Cl_2-NDA **5b** that was based on acenaphthalenedicarboxylic acid anhydride **6**, which was regioselectively dichlorinated to give **7**. The oxidation of **7** with potassium permanganate ensured the purity of the 2,7-Cl_2 regioisomer **5b.** The studies by Vollmann et al. also led to the synthesis of tetrachloro derivative Cl_4-NDA **9**, which was obtained in a similar way by the oxidation of decachloropyrene **8**.

Even though halogenated NDI derivatives have been accessible for 75 years by Vollmann's route, the intense research activity in the field of core-substituted naphthalene diimides has without doubt been initiated by the development of direct halogenation methods, such as the bromination of commercially available core-unsubstituted NDA (Scheme 2). Thus, Thalacker and Würthner reported for the first time the transformation of NDA with one equivalent of dibromoisocyanuric acid (DBI) to afford 2,6-Br_2-NDA **11**, which was obtained in a regioisomerically pure form.[6,32] Shortly thereafter, 2,3,6,7-tetrabromo-NDA (Br_4-NDA) **12** was made available simultaneously by the research groups of Würthner and Zhu through the reaction of NDA with DBI or elemental bromine.[33] Moreover, the treatment of NDA with sodium



Scheme 1. Synthesis of dichloro- and tetrachloro-NDA derivatives **5a**, **5b**, and **9** according to Vollmann et al.,[31] and synthesis of 2,6-Cl_2-NDI derivative **10**.



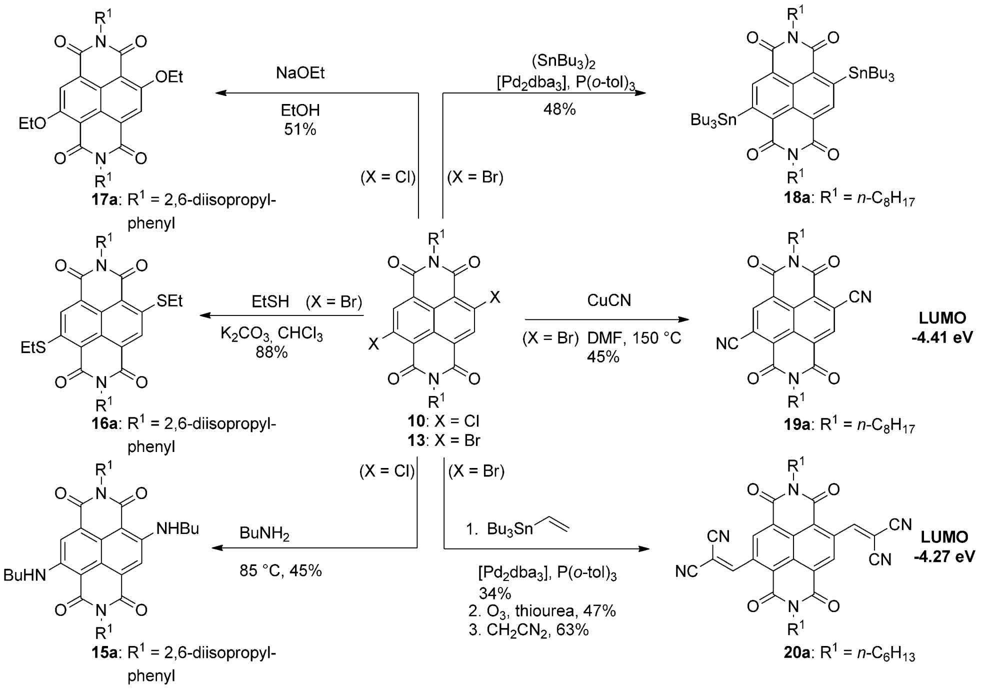
Scheme 2. Di- and tetrabromination of NDA with DBI to NDA derivatives **11** and **12**, and imidization of these anhydrides to the corresponding halogenated NDI derivatives **13** and **14**.

bromide/oleum[34] or 5,5-dimethyl-1,3-dibromohydantoin[35] in concentrated sulfuric acid led to the brominated NDA derivatives in similarly good yields as obtained with DBI. Of course, the mono- and tribrominated NDA derivatives are also accessible by bromination of the core; however, these compounds are of less significance because of their lack of symmetry.

Core-halogenated NDA derivatives, including **5a**, **11**, and **12**, which are of particular practical importance, are normally converted with primary alkyl or aryl amines (R^1NH_2) into the respective NDI derivatives **10** (2,6-Cl_2-NDI), **13** (2,6-Br_2-NDI), and **14** (Br_4-NDI; Schemes 1 and 2). These reactions were usually carried out in acidic media, on the one hand, to activate the carbonyl group and, on the other hand, to decrease the reactivity of the amines and thereby to suppress the core substitution, which competes with the imidization.[22] As a result of the increased reactivity of the fourfold-brominated naphthalene core, a two-step reaction procedure has become the most favored for the synthesis of Br_4-NDI derivative **14**. In this case, the reaction of NDA with the respective amine in acetic acid is terminated in time to obtain an intermediate with neighboring amide and carboxylic acid groups at the 1,4- and 5,8-positions.[33b] After work-up to remove excess amine, the crude product can be cyclized to Br_4-NDI **14** in the presence of phosphorous tribromide. A convenient variation of this method was introduced very recently by Zhu and co-workers that enables both steps to be conducted in a one-pot reaction in dichloromethane, and this variation led to the yield of the reaction being more than doubled.[36]

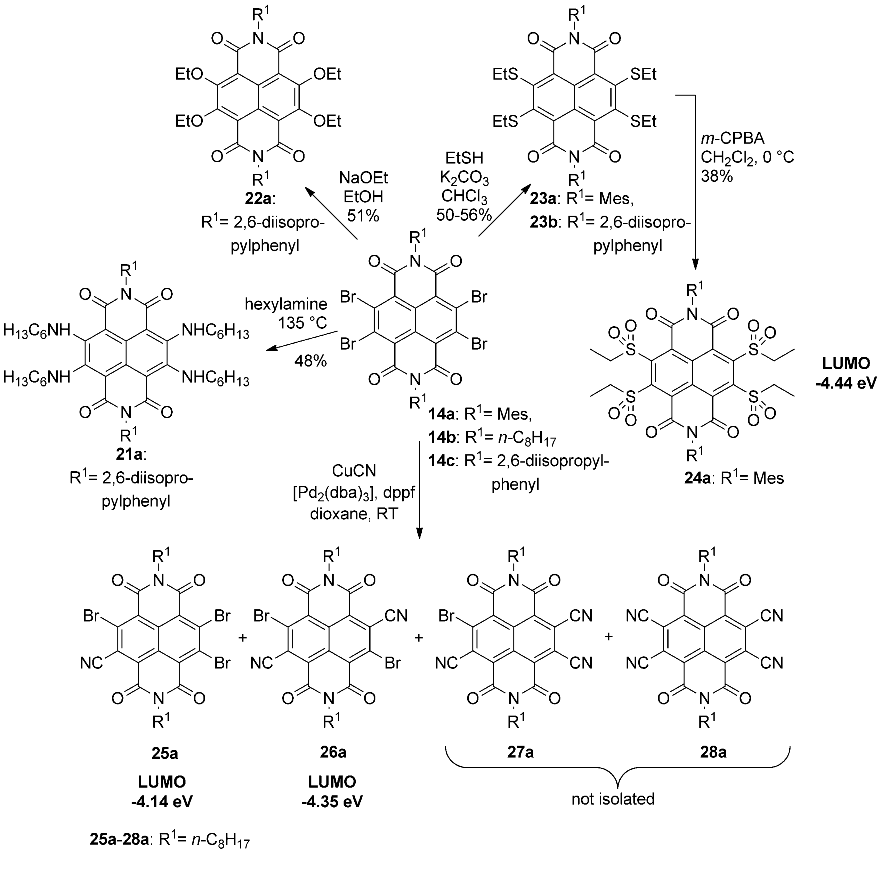
2.2. Core Functionalization with Nucleophiles

Core-halogenated naphthalene diimides are valuable precursors for the synthesis of a broad range of further core-substituted NDI derivatives (Schemes 3 and 4). The nucleophilic substitution of the halogen atoms of the 2,6-di- and 2,3,6,7-tetrahalogen NDI derivatives by heteroatom nucleophiles (derivatives **15**–**17**[22] and **21**–**23**)[6] takes place in good yields, and opens access to compounds with broadly



Scheme 3. Synthesis of core-disubstituted NDI derivatives. LUMO values are indicated for electron-deficient derivatives that are interesting for organic thin-film transistors (OTFTs).

adjustable optical and electrochemical properties (Figure 4).[22,23] In particular, good donor substituents, such as thiol or amino groups, alter the properties of NDI fundamentally, as the lone pairs of electrons in such donor groups undergo cross-conjugation with the electron-poor carbonyl groups.[22] Thus, chromophores with outstanding absorption and fluorescence properties over a broad spectral range became available.[6,22,33a,37] The reaction scopes can be further extended since the halogen exchange can be performed in a stepwise fashion, and the progressive exchange of halogen atoms by donor atoms results in a decrease of the reactivity towards nucleophiles.[22] While the lowest unoccupied molecular orbital (LUMO) levels of compounds are relatively less influenced by the variation of donors at the core, the highest occupied molecular orbital (HOMO) levels can be appreciably raised by electron-donating substituents. This results in a decrease in the band gap and a bathochromic shift of the absorption maxima. As a consequence of the favorable absorption and charge-transport properties of such NDI chromophores, 2,6-disubstituted NDI derivatives were applied, for example, for the construction of supramolecular light-harvesting systems in combination with zinc chlorins,[38] and as light-absorbing and charge-transporting units in self-organized artificial photosynthesis membranes, in which a proton gradient could be created by photoinduced electron transfer.[24] Moreover, such systems were applied in zipper-type aggregates for solar cells with inherent transport gradients.[25,39] In addition, core-substituted NDI chromophores found applications as pH or metal-ion sensors,[40] for the sensitization of singlet oxygen,[41] and for interaction with G-quadruplex DNA.[42]



Scheme 4. Syntheses of core-tetrasubstituted NDI derivatives and stepwise cyanation of Br$_4$-NDI **14**. LUMO values are indicated for electron-deficient derivatives that are interesting for OTFTs.

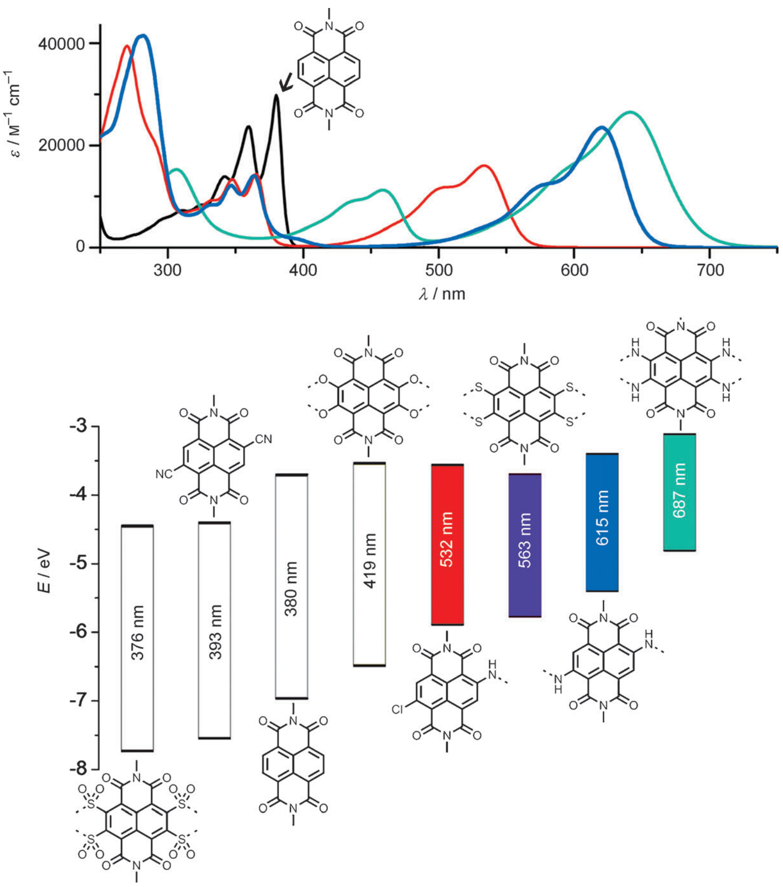
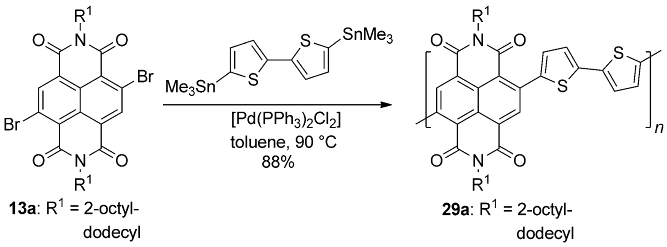


Figure 4. Schematic representation of the influence of core substituents on the energy levels of the frontier orbitals of selected NDI derivatives and a selection of the corresponding UV/Vis spectra. The wavelengths indicated represent the long wavelength absorption maximum of the corresponding compound in dichloromethane. The frontier orbital energies are calculated from cyclic voltammetry (CV) data (a potential of −4.8 eV for Fc/Fc$^+$ against a vacuum level was used). In the cases where no oxidation was observed, the HOMO level results from the difference between the LUMO energy and optical band gap; the values are taken from the literature.[6,17c,26a,33a]

In addition to heteroatom nucleophiles, numerous carbon nucleophiles were introduced in the form of organometallic compounds in transition-metal-catalyzed C−C cross-coupling reactions with NDI derivatives. Thus, appropriately coupled di-[26a,43] and tetrasubstituted[44] NDI derivatives could be obtained by Suzuki, Stille, or Sonogashira coupling. This approach found wide application, particularly for the synthesis of conjugated oligomers[45] and polymers,[46] which enabled donor–acceptor polymers to be created for organic electronics applications. The conjugative interactions of electron-poor NDI with appropriate electron-rich donor units can result in low band gap polymers. The synthesis of NDI-bithiophene copolymer **29a** by Facchetti and co-workers is shown in Scheme 5 as an example which has drawn a lot of attention because of its outstanding n-type semiconducting properties in solution-processed thin-film transistors.[47] Recently, the Marder research group demonstrated an alternative approach which enabled the conversion of 2,6-Br$_2$-NDI-C$_8$H$_{17}$ (**13**; R^1 = n-C$_8$H$_{17}$) into the respective 2,6-stannyl derivative **18a** in the presence of (SnBu$_3$)$_2$ (Scheme 3).[48] This functionality at the NDI core opens the possibility for an inverse coupling chemistry, whereby stannylated NDI can be reacted as a nucleophile with other aryl halides. In this way the NDI core was acylated,[49] and bi- and ter-NDI systems were obtained through direct coupling between stannylated and brominated NDI cores.[48]

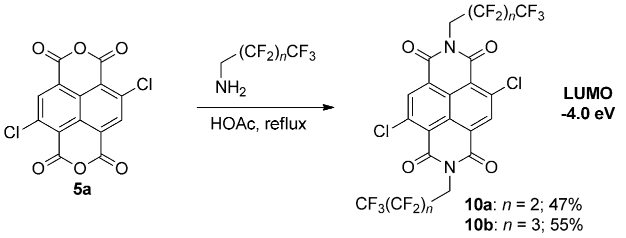
Although donor substituents on the NDI core raise the LUMO level only slightly, it can be significantly lowered by electron-withdrawing substituents (Figure 4). Quite a few approaches have been reported in the literature for this purpose, with the objective to increase the electron-deficient character of the NDI derivatives. The reason for this research activity is, on the one hand, that the stabilization of the LUMO is of great significance for the air stability of n-type semiconductors[5d,e] and, on the other hand, the opportunity provided by the increased π-acidity for improved anion-binding properties.[17,50] Halogenation of the core of NDI derivatives has turned out to be sufficient to enhance their electron-poor character for the realization of air-stable n-channel transistors.[51] The effect of halogen substituents on the LUMO of NDI derivatives is quite evident from comparison of the redox potentials of core-substituted NDI-C$_8$H$_{17}$ (−1.10 V versus Fc/Fc$^+$) with those of core-dichlorinated derivative 2,6-Cl$_2$-NDI-C$_8$H$_{17}$ (**10**; R^1 = n-C$_8$H$_{17}$), which exhibits its first redox potential at −0.95 V.[6] Thus, both chlorine atoms effect an increase in the redox potential by 0.15 V to a higher (less negative) value. The combined effect of electron-withdrawing halogen substituents at the core and fluorinated alkyl chains in the imide position results in a further decrease of the redox potentials, hence the first reduction of dichlorinated derivatives **10a** (R^1 = CH$_2$C$_3$F$_7$) and **10b** (R^1 = CH$_2$C$_4$F$_9$) appears at −0.79 V, which corresponds to a LUMO energy of about −4 eV relative to the vacuum level (Scheme 6). The outstanding electron mobilities of greater than 1 cm^{2}V^{-1}s^{-1} in vacuum-[51] and in solution-processed[52] thin-film transistors, as well as up to 8.6 cm^{2}V^{-1}s^{-1} in single-crystal transistors (Figure 5),[29] combined with their very high air-stability, make the NDI derivaties **10a**,**b** exceptional



Scheme 5. Synthesis of a conjugated donor–acceptor polymer by Stille coupling.

candidates for application as n-type semiconductors in organic electronics.

Furthermore, a wide range of electron-poor NDI derivatives, also with a very high potential for application as n-type semiconductors, were obtained by the exchange of halogen atoms. Besides individual examples, in which electron-withdrawing aryl,[26a,43b,44] perfluoroalkyl,[53] or highly effective sulfonyl residues (see NDI **24a**, Scheme 4; $E_{1/2}^{\text{Red1}} = -0.36$ V versus Fc/Fc$^+$, LUMO energy = −4.44 eV)[17c] were attached at the NDI core, cyano groups in particular appear to be of special interest because of their low reorganization energies[54] and smaller steric demand.[26a,55] A Rosemund-von-Braun reaction of 2-monobromo- and 2,6-dibromo-NDI led to the synthesis of the corresponding monocyano- and dicyano-NDI **19a**, respectively (Scheme 3).[55] A palladium-catalyzed approach[26a] is also known. The 2,6-(CN)$_2$-NDI derivative is characterized by a particularly low-lying LUMO (NDI **19a**: LUMO energy = −4.41 eV, Figure 4). However, despite intensive efforts, the substitution of the four bromine atoms of Br$_4$-NDI by cyano groups to afford (CN)$_4$-NDI has so far remained unsuccessful.[17a,b,56] Although one- or twofold exchange of bromine atoms by cyano groups proceeds successfully and the respective products **25a** and **26a** were precisely characterized, neither Br-(CN)$_3$-NDI **27a** nor the tetracyano derivative (CN)$_4$-NDI **28a** could be unequivocally proven or even successfully isolated (Scheme 4).[56] Clearly, naphthalene compounds substituted with four electron-withdrawing residues are destabilized by their strong propensity for oxidation, which hinders their isolation. The half-wave potentials determined by cyclic voltammetry lead to LUMO values of −4.14 and −4.35 eV for Br$_3$-CN-NDI **25a** and Br$_2$-(CN)$_2$-NDI **26a**, respectively. A highly electron-poor derivative with dicyanovinyl groups (**20a**, Scheme 3) was further reported by Marder and co-workers.[57]



Scheme 6. Synthesis of core-chlorinated NDI derivatives bearing fluorinated alkyl chains in the imide position.

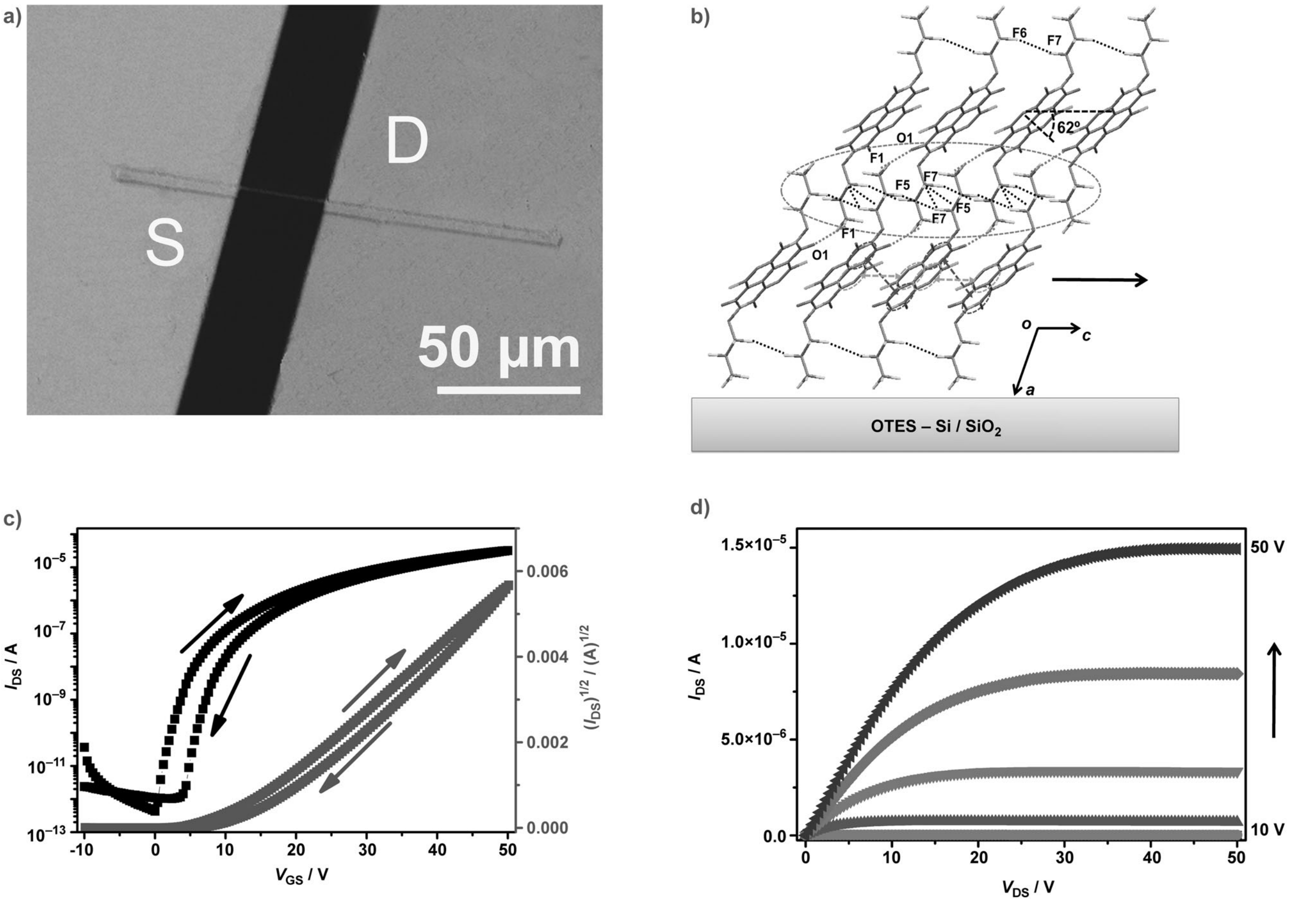
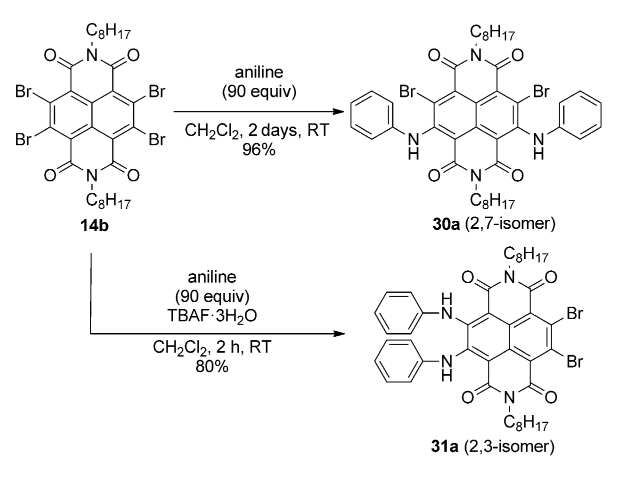


Figure 5. Single-crystal transistor with NDI **10a** as an organic semiconductor: a) SEM image of a single crystal with a deposited source (S) and drain (D) gold contacts; b) packing of **10a** in the single crystal and direction of charge transport; c) plot of drain current (I_{DS}; transfer curves, black) and square root of I_{DS} (gray) against gate voltage (V_{GS}) in the saturation regime; and d) dependence of I_{DS} on the drain voltage (V_{DS}) at different V_{GS} values (output curves) of the transistor (modified from Ref. [29]).

2.3. Substitution Pattern at the NDI Core

Although the constitution of 2,6-core-substituted NDI derivatives is deduced from the respective 2,6-dihalogen NDI precursors and hence is unambiguous, the substitution reactions of two bromine atoms at Br_4-NDI by nucleophiles can, in principle, lead to three different isomers. Such reactions were initially not investigated, as the transformation of Br_4-NDI with nucleophiles was basically aimed at completely replacing all the halogen atoms on the core.[33a] However, only exchange of two of the core halogen atoms of Br_4-NDI opens up interesting opportunities to also achieve those substitution patterns which are not accessible from core-dihalogenated precursors. Reactions in which only two bromine atoms are exchanged were initially reported with 1,2-phenylenediamine, where the regioselectivity of the substitution reaction results essentially from the annulation of the bidentate diamino nucleophile through replacement of two neighboring bromine atoms.[58] In fact, very few examples are known where the substitution pattern of the nucleophilic disubstitution at Br_4-NDI was investigated with monodentate nucleophiles. One example of this is the previously mentioned derivative 2,6-Br_2-3,7-$(CN)_2$-NDI **26a**, which was obtained by cyanation of the respective Br_4-NDI.[56] The single-crystal analysis of the corresponding fourfold-substituted derivative, which was obtained by subsequent reaction with *p-tert*-butylthiophenol, confirmed the 3,7-positions of the two cyano groups. Moreover, we have recently reported that the three possible regioisomers resulting from nucleophilic disubstitution of Br_4-NDI with amine nucleophiles can indeed be prepared and the regioselectivity can be decisively influenced by the applied reaction conditions, such as solvents or by using additives.[59] Nearly exclusive formation of 2,7-diamino-3,6-dibromo-NDI **30a** was observed in the reaction of Br_4-NDI-C_8H_{17} **14b** with aniline in a variety of solvents and in the absence of additives (Scheme 7). However, the addition of tetrabutylammonium fluoride (TBAF) has a drastic effect on the regioselectivity of this reaction, with 2,3-diamino-6,7-dibromo-NDI **31a** being formed selectively in the presence of this additive, but otherwise under identical reaction conditions. The third possible isomer 2,6-diamino-3,7-dibromo-NDI was formed in trace amounts, at best. The change in the regioselectivity of this reaction effected by fluoride ions was attributed to the deprotonation of the monoamino-NDI intermediate, which could be identified by UV/Vis and NMR spectroscopy. Moreover, this study allowed the structure of a previously published 2,6-diamino-3,7-dibromo-NDI to be disproved,[60] as it concerns the 2,3-diamino-6,7-dibromo isomer.

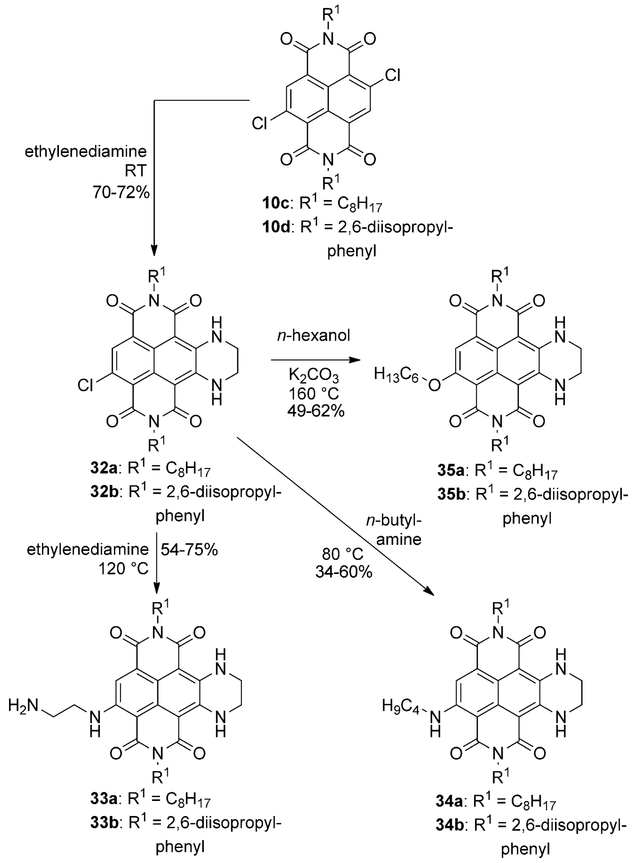


Scheme 7. Regioselectivity in the disubstitution of Br_4-NDI **14b** with aniline in the absence and presence of TBAF.

2.4. Substitution at Core-Unsubstituted NDI

In fact, only a few examples are known where core-unsubstituted NDI derivatives were applied as starting compounds for core substitution. Examples of this are the 1,3-dipolar cycloaddition at the NDI core reported by Gryko et al.[61] and the synthesis of a 2,7-core-dialkylated derivative by Marks, Wasielewski, and co-workers. A 1:1 mixture of 2,6- and 2,7-core-dialkylated NDI derivatives was obtained without any regiocontrol in this ruthenium-catalyzed reaction of a core-unsubstituted NDI derivative with styrene; however, this mixture could subsequently be separated by HPLC.[62]

Interestingly, triple core-substituted NDI derivatives are also accessible from twofold halogenated precursors; in this case a C–H bond is thus also functionalized (Scheme 8).[63] Indeed, the reaction of Cl_2-NDI derivatives in ethylenedi-



Scheme 8. Threefold core substitution of Cl_2-NDI.

amine at room temperature does not proceed through successive exchange of the two chlorine atoms. Interestingly, it instead leads first to a ring closure to form the triple core-substituted derivative **32**, whose remaining chlorine atom can then be replaced by further heteroatom nucleophiles (derivatives **33**–**35**). These compounds have attracted considerable attention because of their high fluorescence quantum yields, which at up to 70% are the highest values so far for NDI derivatives. It is noteworthy that the longitudinal ring expansion of core-unsubstituted NDI derivatives to **36** (Figure 7 in next section) led also to a core annulation, but to a less extent.[64]

3. Core-Annulated Naphthalene Diimides

The longitudinal expansion of conjugated systems by additional naphthalene units within the series of rylene diimides was explored systematically by Müllen and co-workers. Thus, in addition to the already known perylene diimide (PDI, $n=1$; Figure 1), the higher homologues terrylene ($n=2$),[3a,b] quaterrylene ($n=3$),[3c,d] pentaarylene ($n=4$), and hexarylene diimides ($n=5$)[3e,f] became accessible, whose absorption bands shift by about 100 nm to longer wavelengths with each additional naphthalene unit. Likewise, the expansion of π-systems in the orthogonal direction could be realized by annulation of carbocyclic units at the bay position of PDI.[65] The outstanding importance of PDIs has resulted in the higher homologues of NDI within the rylene series being introduced in the literature as an independent class of compounds, and hence are not considered as core-expanded naphthalene diimides. Here, annulated systems, which are derived from the NDI scaffold by ring condensation, need to be mentioned in particular. In principle, three strategies are conceivable for the expansion of the conjugated system of naphthalene diimides: annulation along the N-N axis (longitudinal, strategy A in Figure 6) and skewed (diagonal, strategy B), as well as perpendicular to the N-N axis (lateral, strategy C). The functionalization can formally be performed at the imide nitrogen atom, at the carbonyl group of the imide unit, as well as at core positions in different combinations. The synthetic methods for strategy C were made available in the numerous reports of the core substitution of NDI mentioned before, and these methods are mainly based on the substitution of bromine atoms at NDI by heteroatom nucleophiles or metal-catalyzed C–C coupling reactions. Interestingly, this whole area of chemistry has been developed only within the last five years, which, particularly in view of the extensive exploration of PDI core expansion at the end of the last century, might be a surprise.

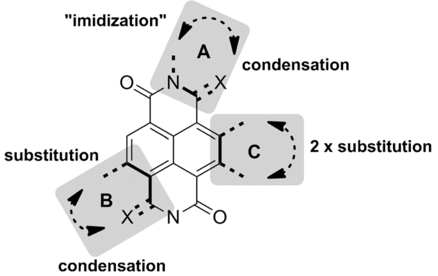


Figure 6. Schematic representation of strategies for the expansion of the NDI core: longitudinal (strategy A), diagonal (strategy B), and lateral (strategy C). Depending on the strategy, the functionalization can take place at the imide nitrogen atom, imide carbonyl group, or at the naphthalene core.

3.1. Longitudinal Core Expansion

The longitudinal expansion according to strategy A can be achieved by imidization and concurrent condensation of the carbonyl group at an anhydride function with a bidentate nucleophile. In this regard, industrially relevant are the already mentioned perinones (Figure 1), which were synthesized in the first half of the 20th century at the I. G. Farbenindustrie A.G. initially as vat dyes and later they gained importance as pigments.[2,66] These dyes were obtained from the NDA-related monoanhydride of naphthalenetetracarboxylic acid and phenylenediamine. The conversion of NDA with ethylenediamine also affords bisamidines **37**, which are apparently formed by the oxidation of the primary condensation product, while the corresponding iminoimide **36** is formed either by the reaction of ethylenediamine with the respective *N*-aryl-NDI (R^1 = aryl) or by co-condensation with an alkyl amine (R^1 = alkyl).[64] Moreover, mono- or bilaterally annulated compounds can be formed, whose conjugated systems are extended with annulated five- (**38a**,**b**,[67] *trans*- and *cis*-**40**)[68] or six-membered rings (**39a**,**b**)[69] (Figure 7). This strategy was also applied to construct a disk-shaped molecule **41**, in which three NDI molecules are condensed at a central triphenylene core.[70] In 1966 a similar strategy was already reported for the construction of the ladder polymer BBL **42**, which was formed from naphthalenetetracarboxylic acid and 1,2,4,5-tetraaminobenzene and, with an appreciable electron mobility of 0.1 $cm^2 V^{-1} s^{-1}$ in air, represents one of the first examples of an n-type semiconducting polymer.[71]

A mixture of two constitutional isomers was always obtained in the synthesis of twofold annulated molecules, and these needed to be separated from each other. In the case of perinones, both isomers *Pigment Orange 43* and *Pigment Red 194* (Figure 1) could be separated by precipitation, and this is of high significance for their practical application as industrial pigments because of their distinct optical properties.[2] Although the isomers *trans*-**37** and *cis*-**37** could also be separated by chromatography,[64] no separation was reported for the compounds *trans*-**40** and *cis*-**40**.[68] The expansion of the conjugated system of NDI goes along with a bathochromic shift of the absorption, thus these compounds are usually colored, even if no additional heteroatom substituents are involved at the core. NDI shows a structured band with an absorption maximum at 381 nm in chloroform, while derivative **36**, which is extended by only one five-membered ring, shows a bathochromic shift of the broadened absorption band to 436 nm. The condensation with a second five-membered ring resulted in a further red-shift, and accordingly the absorption maxima for *trans*-**37** and *cis*-**37** appear at 448 and 511 nm, respectively.[64] The absorption maxima of monobenzannulated derivatives **39a** and **39b** appear at 425 and 423 nm, respectively,[69a] while significantly red-shifted maxima slightly above 750 nm were found for the isomeric mixtures of *trans*- and *cis*-**40**. In this case, the influence of electron-rich (oligo)thiophene units is noticeable.[68]

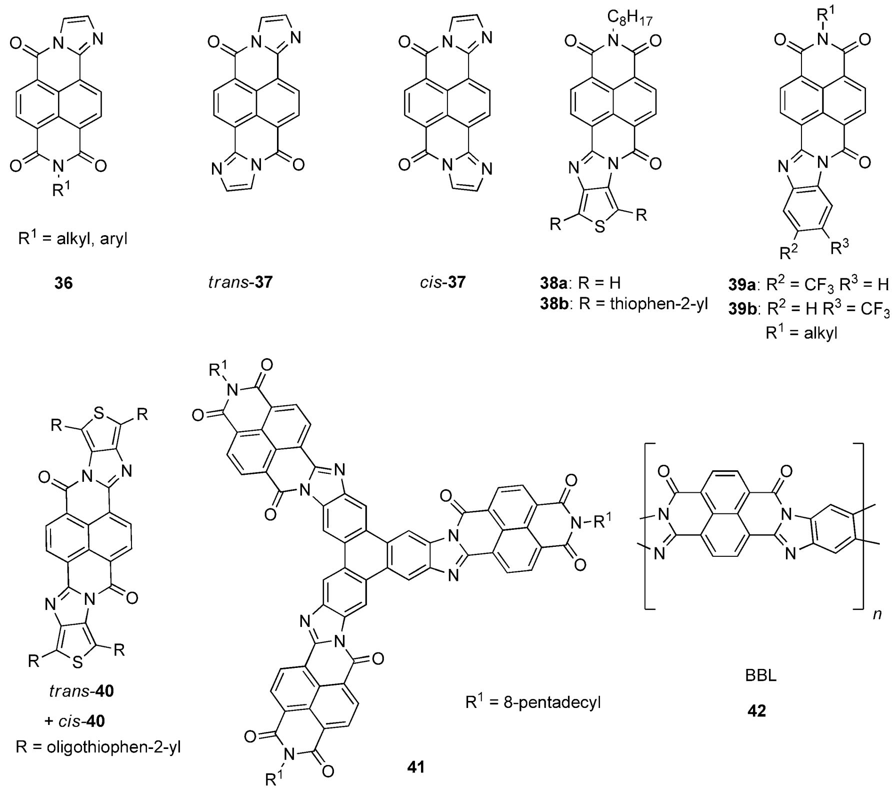
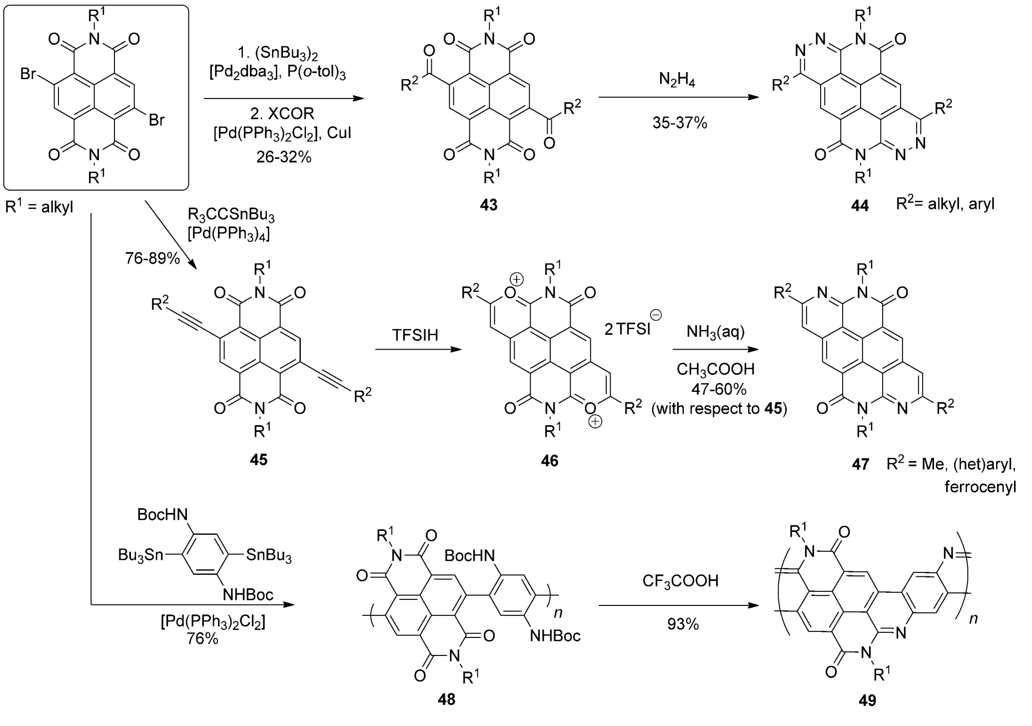


Figure 7. Structures of longitudinally extended naphthalene diimides.

3.2. Diagonal Ring Expansion

In contrast to the previously discussed longitudinal core expansion, annulation to diagonally expanded NDI derivatives (strategy B) was developed quite recently, whereby the imide carbonyl group is derivatized by condensation and concomitant substitution at the naphthalene core. Three such systems are currently known in the literature and their synthesis starts from 2,6-Br_2-NDI (Scheme 9). In all these routes, the functionalization of the naphthalene core by a Stille cross-coupling was first performed, followed by a condensation reaction at a carbonyl group. In the first example reported by Marder and co-workers, 2,6-diacyl-NDI derivative **43** was synthesized from the respective distannyl derivative and acyl halide.[49] The conversion of acyl derivative **43** with hydrazine results in a double condensation to finally afford the desired NDI derivative **44** with two annulated pyridazine units. The NDI derivative **47** with annulated pyridine rings could be obtained from dialkinyl-NDI **45** (accessible by Stille coupling with alkinylstannanes) in two steps according to a procedure of Zhang and co-workers.[72] The conversion of **45** with strongly acidic bis(trifluoromethanesulfonyl)imide (TFSIH) leads through cyclization to the pyrylium cation **46**, and its structure (R^2 = ferrocenyl) was confirmed by single-crystal analysis. Condensation with aqueous ammonia finally affords the NDI derivative **47**. Strategy B was also applied to construct diagonally condensed, NDI-based ladder polymers, as shown by Luscombe and co-workers.[73] After a Stille coupling of 2,6-Br_2-NDI with di-*tert*-butyl-(2,5-bis(tributyl-



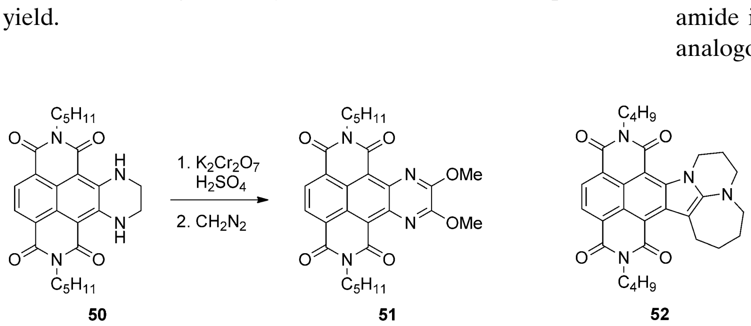
Scheme 9. Synthesis of diagonally expanded NDI derivatives **44** and **47**, and that of the NDI-based ladder polymer **49**. Boc = *tert*-butoxycarbonyl.

stannyl)-1,4-phenylene)dicarbamate, the Boc-protected amino groups of polymeric compound **48** were cleaved under acidic conditions and condensed with the neighboring carbonyl groups of the NDI-imide units to form the ladder polymer **49**, whose framework is based on a diagonally extended NDI.

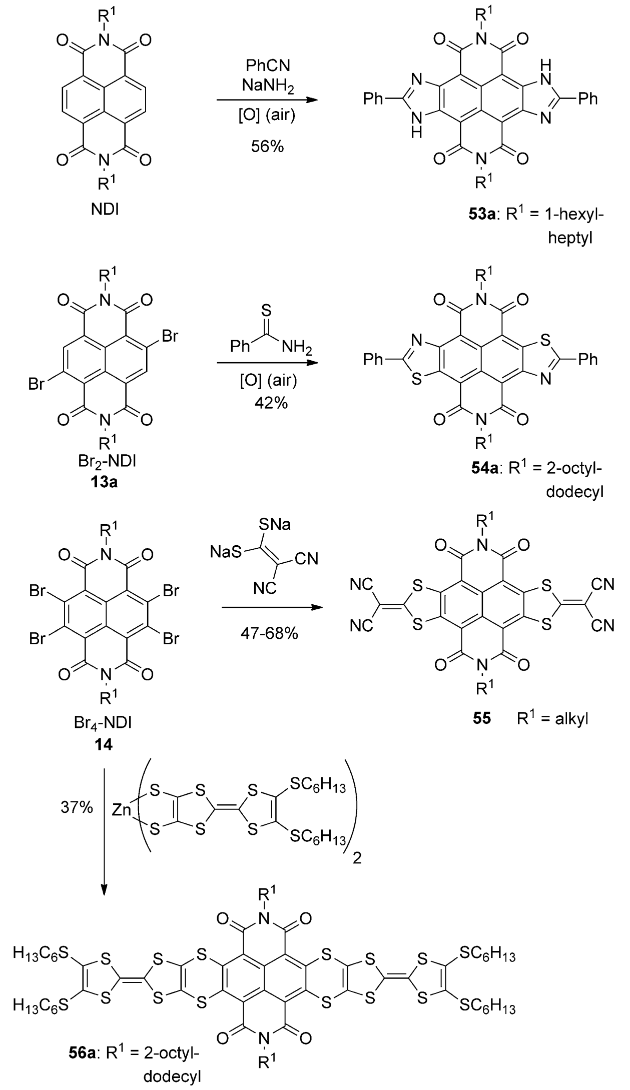
The diagonal expansion also results in a red-shift of the UV/Vis absorption. A bathochromic shift of the absorption maxima by about 50 to 60 nm, relative to that of core-unsubstituted NDI, was observed for **44** (422 nm, $R^2 = n$-pentyl; 433 nm, R^2 = phenyl).[49] Quantum chemical calculations show that the expansion of the conjugated systems goes along with an increase in the frontier molecular orbital energies, especially for the HOMO, and hence results in a decrease in the optical band gap. The optical transition for compound **44** exhibits a high HOMO–LUMO transition character. The absorption maxima of **47** is further red-shifted to 466 nm (R^2 = methyl) or 480 nm (R^2 = phenyl).

3.3. Lateral Ring Expansion

The lateral expansion of the NDI scaffold (strategy C), which has also only been explored within the last five years, is achieved by the exclusive functionalization of core positions of naphthalene. The first example of a laterally extended and fully conjugated NDI is the benzo[*g*]chinoxaline-type compound **51**, which is extended by a pyrazine ring. It is accessible from ethylenediamine-substituted NDI derivatives[33a,63] and composed of three condensed rings (Scheme 10).[74] For this purpose, Freccero and co-workers used 2,6-Br_2-NDI, which was converted into the 2,3-disubstituted NDI **50** by dehalogenation with ethylenediamine. The oxidation of the ethylene group to dione and further reaction with diazomethane finally provided **51**. The study by Freccero and co-workers, however, deals mainly with synthetic access to the aforementioned dione and its properties as a pH senor and G-quadruplex-binding ligand,[75] while the electronic properties of compound **51** were not further explored. Moreover, Li and co-workers presented a copper-catalyzed reaction of core-unsubstituted NDI-C_4H_9 with 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) to afford the core-extended NDI derivative **52** with three conjugated condensed rings.[76] The main focus of this work was on the optical properties of **52** and its cation $[\mathbf{52}+H]^+$, generated through protonation, which stands out because of its significantly increased fluorescence quantum yield.

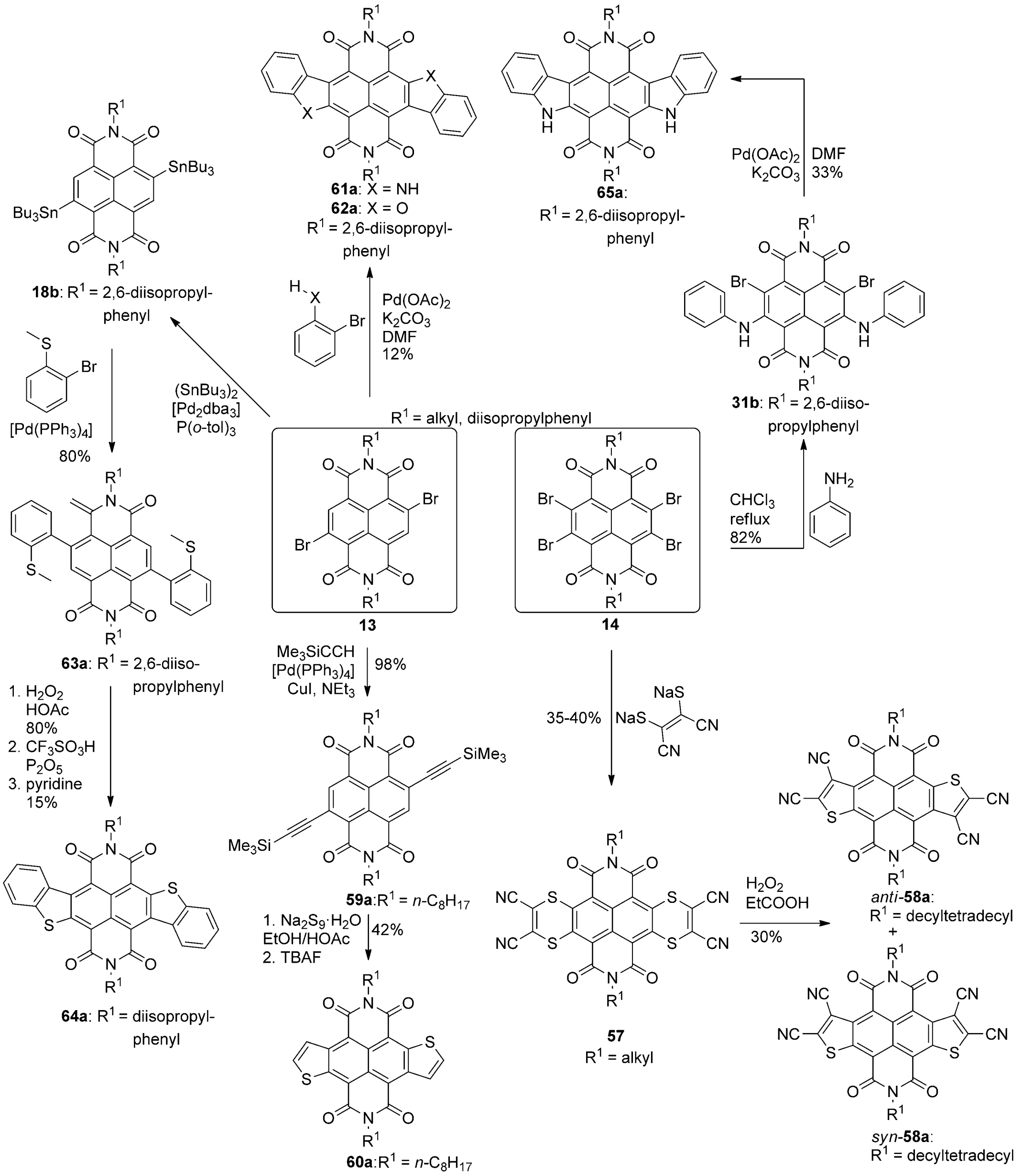


Scheme 10. Two examples of NDI derivatives with lateral unsymmetrically extended cores.



Scheme 11. Synthesis of five-membered-ring-annulated heteroatom-containing NDI derivatives.

The first example of a symmetric, laterally core-extended NDI **53a** was presented in 2010 by Langhals and Kinzel (Scheme 11).[77] In contrast to the core expansions described below, these authors did not start with a core-substituted NDI precursor. Instead, they converted a core-unsubstituted naphthalene diimide through oxidative cyclization to the core-extended NDI **53a** by using benzonitrile and sodium amide in the presence of atmospheric oxygen. Interestingly, analogous transformations with 2-naphthonitrile and 4-dimethylaminobenzonitrile were also successful. The mechanism of this reaction was not discussed by these authors. A Chichibabin-type reaction of electron-poor NDI with the amide anion or in situ generated amidinate anion in a first step is conceivable in this case, as discussed before for the reaction of NDI with ethylenediamine (Scheme 8).[63,64] An oxidative ring closure takes place in the second step. A similar concept was later used by Zhang and co-workers for the synthesis of thiazole analogue **54a**.[78] In contrast to the Langh-



Scheme 12. Syntheses of heteroatom-containing core-extended NDI derivatives.

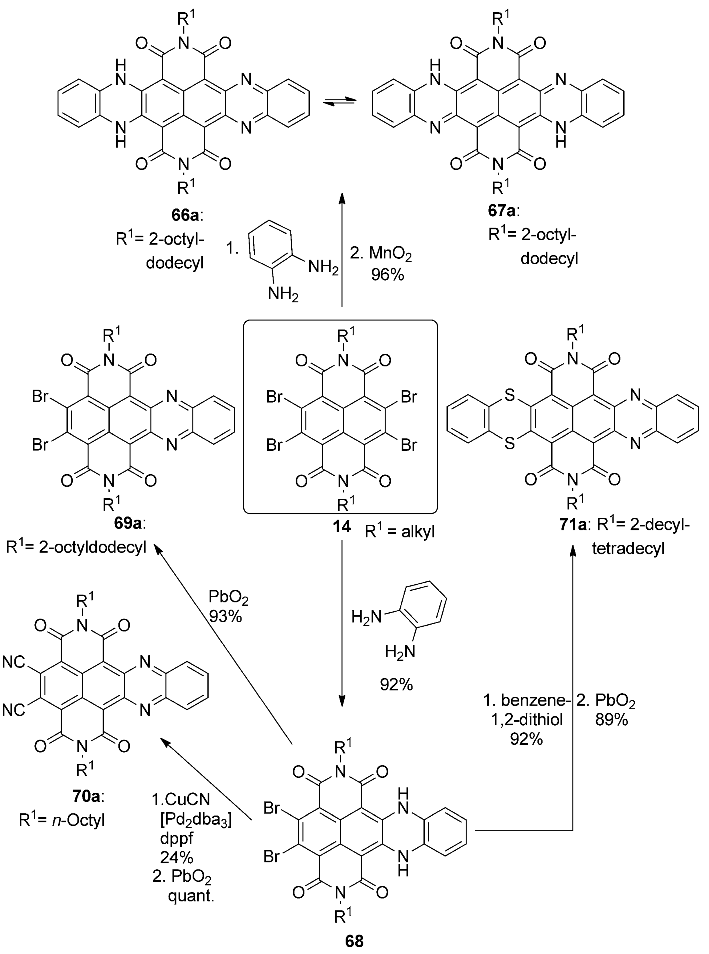
als method, a core-substituted 2,6-Br_2-NDI was used as the starting compound and converted with benzothioamide in air, thus affording **54a** after nucleophilic substitution and subsequent oxidative ring closure. The reaction of the respective Br_4-NDI with benzothioamide as an unsymmetrical bidentate nucleophile leads, however, to a mixture of two constitutional isomers: the depicted *anti*-derivative **54a** and its *syn* congener.

The NDI ring expansion with five-membered-ring heterocycles containing two heteroatoms developed by Zhu and coworkers leads to the class of compounds **55** (Scheme 11), where a fourfold brominated naphthalene core is laterally extended by nucleophilic substitution with 1,1-dicyanoethene-2,2-bis(thiolate).[79] The conjugated character of the extended NDI core was revealed by quantum chemical calculations, thus confirming a regular delocalization of the HOMO over the whole extended core. On the other hand, the electron-withdrawing cyano groups ensure these compounds have a particularly low-lying LUMO. Derivatives with long, branched alkyl chains in the imide position have received great attention, in particular as solution-processable, air-stable n-type semiconductors, and their electron mobilities of above 3.0 $cm^2 V^{-1} s^{-1}$ in air rank amongst the highest for such systems.[80] These important results for a new class of organic semiconductors resulted in much further work in the last few years, in which the synthesis of laterally extended NDI derivatives by substitution with dithioles or dithiolates was varied according to the same synthetic concept. Examples in this regard are the compound with peripheral cyanoacetate groups which is an analogue of **55**, the derivative **57** that was obtained by six-membered-ring annulation with 1,4-dithiine-2,3-dicarbonitrile (Scheme 12),[79b] and Zhang developed sulfur-rich (for example **56a**, Scheme 11)[81] as well as laterally extended unsymmetric derivatives.[82] Depending on the position of their frontier molecular orbitals, these derivatives function as p-type, n-type, or ambipolar organic semiconductors.

The reaction of **57** with hydrogen peroxide is quite interesting. This reaction led to a mixture of isomeric derivatives *syn*-**58a** and *anti*-**58a**, which are laterally extended by two thiophene rings and have a naphthodithiophene core (Scheme 12).[79b] A selective synthesis of *anti*-naphthodithiophene diimides has recently been introduced by the Takimiya research group.[83] Starting from 2,6-bis(trimethylsilylethinyl)-NDI **59a**, the ring closure was accomplished with sodium sulfide nonahydrate. The TMS group could be cleaved with TBAF to give the core-extended derivative **60a**. Moreover, core-extended NDI derivatives with annulated indole, benzofuran, or benzothiophene units were introduced by us and by the Wang research group (Scheme 12). As one of the first examples of core-extended NDI derivatives with heterocycles, *anti*-carbazolocarbazole diimide (CbDI) **61a** was synthesized from isomerically pure 2,6-Br_2-NDI by a palladium-catalyzed one-pot reaction with 2-bromoaniline.[84] The synthesis of the corresponding oxygen compound **62a** occurred in an analogous manner with 2-bromophenol.[85] A selective route to the *anti*-benzothiophene analogue **64a** in isomerically pure form was presented recently by Wang and co-workers.[86] Starting from 2,6-distannyl-NDI **18b**, the NDI core was substituted through Stille coupling with 2-bromothioanisol to obtain **63a**. After oxidation of the thioether function in **63a** to form sulfoxide, ring closure to **64a** takes place in trifluoromethanesulfonic acid in the presence of phosphous pentoxide, which is followed by demethylation in pyridine.

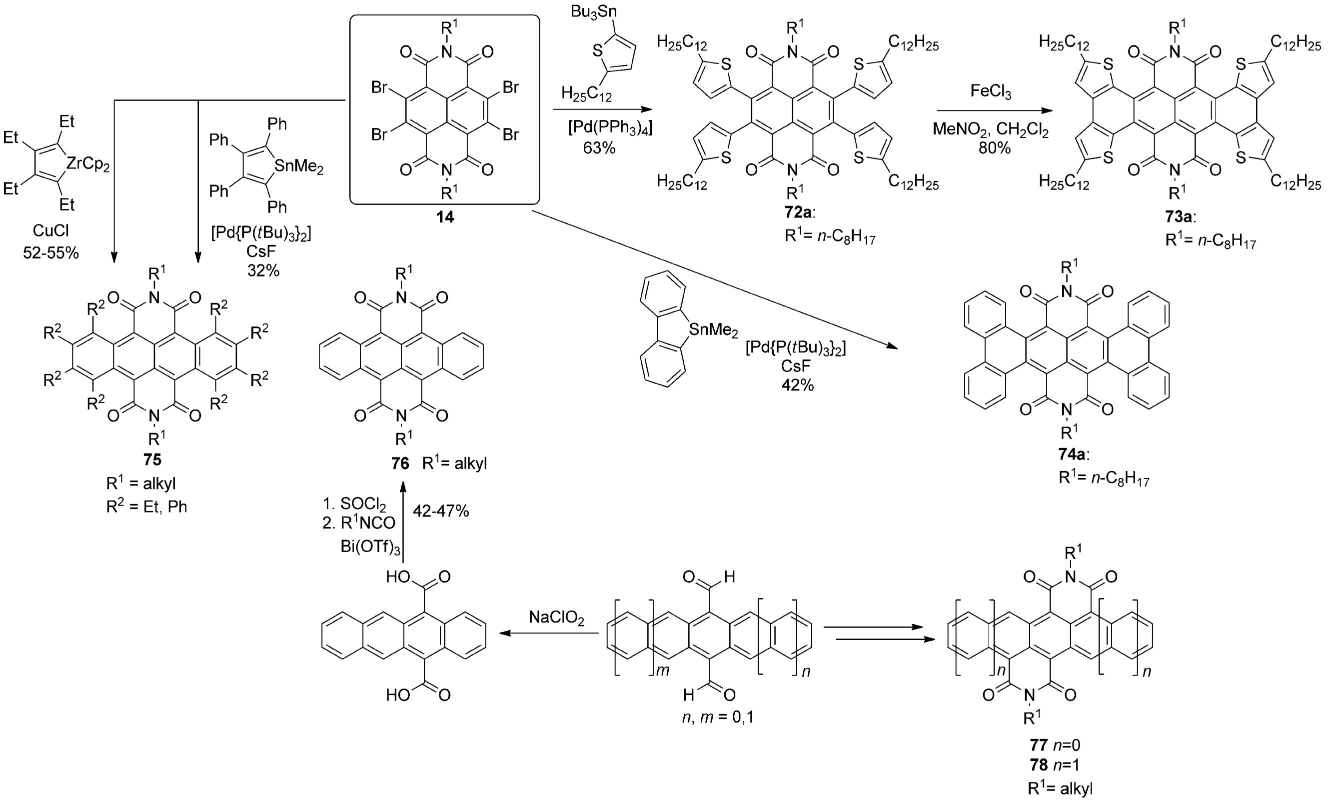
The strategies for core expansion illustrated so far afford either inversion symmetric compounds selectively when starting from isomerically pure 2,6-Br_2-NDI, or isomeric mixtures if starting with Br_4-NDI, provided that no regular exchange with bidentate nucleophiles takes place, as is the case in the synthesis of **55**. On the other hand, the selective synthesis of carbazolocarbazoles such as **65a** occurs with *syn*-connectivity.[85] For this we have made use of the 2,7-regioselectivity of the nucleophilic substitution of Br_4-NDI with aniline (see Schemes 7 and 12). This can be followed by a palladium-catalyzed ring closure. Moreover, the synthesis of core-substituted derivatives of **65a** has been accomplished either by applying the corresponding phenyl-substituted NDI precursor or by subsequent chlorination.[85]

In addition to the above-mentioned NDI-based heteroatom-containing polycycles, Zhao and co-workers have targeted the synthesis of derivatives with an azaacene core (Scheme 13).[87] Indeed, tetrahydrotetraazaacene was obtained by substitution of the four bromine atoms of Br_4-NDI with two equivalents of phenylenediamine. The subsequent oxidation with manganese dioxide furnished dihydrotetraazaacene in its two tautomeric forms **66a** and **67a** with benzoid and quinoid structures, which are in equilibrium with each other. This equilibrium is strongly influenced by the solvent polarity, with the dipolar benzoid structure prevailing in polar solvents. Attempts to isolate the respective tetraazaacene failed. Although its formation was observed during the course of further oxidation of the dihydro derivative with lead(IV)oxide, it could not be isolated because of its low stability. Similar strategies were also applied to synthesize further unsymmetrical NDI derivatives possessing a diazatetracene core. The two bromine atoms of dihydro precursor **68** could be substituted by mono- or bidentate nucleophiles, so that after oxidation, in addition to dibromo derivative **69a**, compounds with cyano groups (**70a**)[88] or annulated derivatives (e.g. **71a**)[89] became accessible.



Scheme 13. Expansion of the NDI core to derivatives with an azaacene core.

Examples of NDI derivatives with heteroatom-free, acene-type core skeletons are to date still rare (Scheme 14). Chi and co-workers succeeded, after quadruple Stille coupling of a thiophene-2-yl-stannane to Br_4-NDI, in the oxidative coupling of the thiophene substituents at the respective NDI **72a**.[90] Product **73a** formally has a heteroatom-free tetracene core, which is condensed with four thiophene rings angularly and thus comprised of eight annulated core rings in total. The analogous tetrabenzotetracene derivative **74a** was prepared by Wang and co-workers through a double Stille cross-coupling reaction.[91] The syn-



Scheme 14. Syntheses of tetracene diimides **73**–**76**, and those of anthracene and pentacene diimides **77** and **78**.

thesis of tetracene diimide **75** was accomplished by the reaction of Br_4-NDI precursor with zirconium cyclopentadiene in the presence of copper(I)chloride or by a double Stille cross-coupling with 1,1-dimethyl-2,3,4,5-tetraphenylstannol.[91]

Thus, the core-expanded NDIs with structure **75** obtained in this way bear substituents at the tetracene core that are predefined by the substituent pattern of the employed metallacycles. The spatial proximity of these substituents to the imide oxygen atoms evokes a twisting of the tetracyclic scaffold, as evident from a single-crystal structure. This might be the reason why, in contrast to the previously discussed planar heterocyclic core-extended NDI derivatives shown in Schemes 11 and 12, no particularly powerful organic transistors based on the accessible acene diimides has so far been achieved. An approach to unsubstituted tetracene diimides, which is, however, not based on naphthalene diimide but the imide groups are instead introduced to the tetracene scaffold by this approach, was presented by Yamada and co-workers.[92] The synthesis starts with tetracene-5,12-dicarboxylic acid, which is accessible by oxidation of the respective dialdehyde. After activation of the acid groups to acid chlorides, the resulting intermediate could be cyclized with an alkylisocyanate in the presence of a Lewis acid to give the tetracene diimide **76**. The analogous reaction sequence with anthracene-9,10-dicarboxylic acid or pentacene-6,13-dicarboxylic acid affords the inversion-symmetric acene diimides **77**[93] and **78**.[92] Moderate electron mobilities of $10^{-3}\,cm^2V^{-1}s^{-1}$ were reported for a derivative of **76** ($R^1 = C_6H_{13}$). The condensation of NDI and PDI derivatives across their core positions was developed by Marder, Wang, and co-workers.[94] Thereby, two monostannyl-NDI derivatives were coupled to the bay position of a tetrachlorinated PDI.

The electronic properties of all laterally core-extended NDI derivatives are strongly changed by structural modification, which affects both the optical properties and the position of the frontier molecular orbitals and hence the semiconducting properties as well. Quantum chemical calculations have shown that the HOMO is normally delocalized over the whole conjugated core, while the LUMO remains localized at the initial NDI core. Figure 8 illustrates this for CbDI **61a**, core-unsubstituted NDI, and the carbazolocarbazole scaffold as examples. The extension by indole annulation leads to a strong increase in the HOMO level, relative to that of core-unsubstituted NDI. In addition, the shape of the HOMO of CbDI resembles that of the carbazolocarbazole scaffold. In contrast, the LUMO of CbDI closely resembles that of NDI in terms of its shape and energy level. Therefore, these compounds can be considered as hybrids of archetype rylene diimide n-type semiconductors, whose transport properties are determined by the LUMO, and archetype (hetero)acene p-type semiconductors, whose transport properties are determined by the HOMO.

The combination of electron-withdrawing imide groups and the electron-rich carbazole scaffold indeed results in ambipolar transport behavior of **61a** and **65a** in organic thin-film transistors, whereby the hole-transport properties are up to four orders of magnitude better than the electron-transport properties. This was attributed to the molecular packing induced by the steric demand of the 2,6-diisopropylphenyl

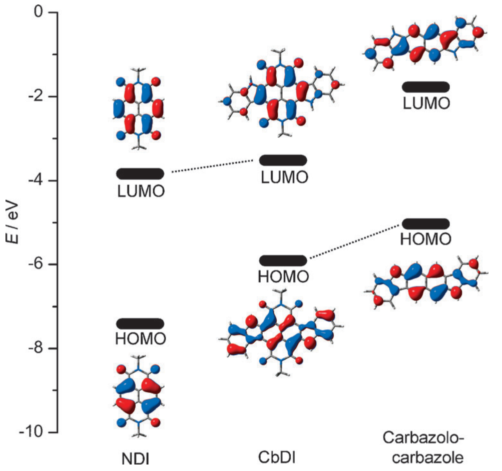


Figure 8. Calculated energy levels and shapes of the frontier molecular orbitals of naphthalene diimide (left), CbDI **61 a** (middle), and carbazolocarbazole scaffold (right) by a DFT method (basic set: 6-311++G**, functional: B3LYP). For simplicity, the NDI and **61 a** contain methyl groups at the imide positions.

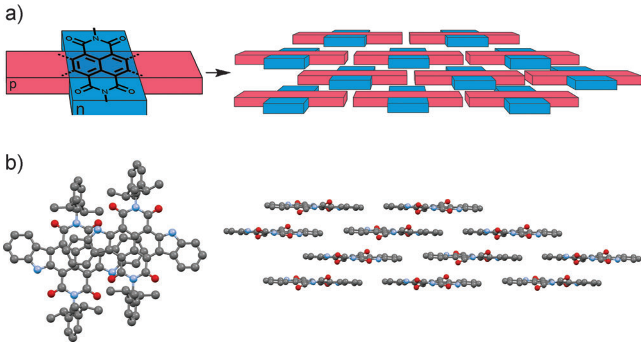


Figure 9. a) Schematic illustration of the molecular segments (the HOMO is delocalized along the red segment and the LUMO along the blue segment) responsible for the p- and n-channel transport characteristics in core-extended NDI-(hetero)acene (left) and in an ideal packing (right) for hole transport, as a result of pronounced HOMO–HOMO overlap.[84] b) Displaced stacking of carbazolocarbazole cores (left) caused by sterically demanding imide substituents and the resulting brick-type packing motif of the π-surfaces (right) of CbDI **65 a** in the single crystal (H atoms are omitted).[85]

group in the imide position, which allows a better π-π contact between the HOMOs (red) than the LUMOs (blue) of the neighboring molecules (Figure 9). Thus, by localizing the frontier molecular orbitals along different molecular axes, the transport characteristic become adjustable between the acene-type (p-channel) and rylene diimide-type (n-channel) through the packing directed by the substituents.[84,85]

Symmetrical core-expanded naphthalene diimides with annulated five-membered-ring heterocycles (Scheme 11) in most cases show intense absorption bands ($\varepsilon = 2\times10^4$–$5\times10^4\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$). Laterally extended derivatives with electron-withdrawing 1,1-dicyanoethene-2,2-bis(thiolate) units (**55**) are characterized by a substantial decrease in the band gap and markedly lowered LUMO levels (LUMO energy ca. −4.4 eV). Lower LUMO values were also found for the cyano-substituted isomeric naphthodithiophene derivatives *syn-* and *anti-***58 a** (LUMO energy −4.5 eV).[79b] Compounds **61 a**, **62 a**, and **64 a**, which differ from each other only in the respective heteroatom, show clear differences in their UV/Vis spectra. While the oxygen-containing compound **62 a** (R^1 = 2,6-diisopropylphenyl) exhibits an absorption maximum at 474 nm in dichloromethane, benzothiophene derivative **64 a** as well as carbazole derivative **61 a** show two broad absorption bands in the visible range (**64 a**: 586 and 494 nm in $CHCl_3$, **61 a**: 622 and 491 nm in CH_2Cl_2). The stronger electron-donating +M effect of the nitrogen atom, relative to that of sulfur, is reflected in the bathochromic shift of the absorption band to a longer wavelength (**64 a**: 586 nm in $CHCl_3$, **61 a**: 622 nm in CH_2Cl_2). However, the second absorption band of both compounds is nearly unchanged (**64 a**: 494 nm, **61 a**: 491 nm). Interestingly, the electrochemically determined LUMO level of the sulfur derivative **64 a** is located at −3.96 eV ($E_{1/2}^{\mathrm{Red1}} = 0.85$ V versus $\mathrm{Fc/Fc^+}$)[86] and thus lower than those of the oxygen (−3.86 eV)[85] and nitrogen (−3.73 eV)[84] analogues. It is worth mentioning that, although both isomeric carbazolocarbazole derivatives **61 a** and **65 a** have the same redox properties, their absorption spectra differ and accordingly so does their color (**61 a** is green, **65 a** is red), thus emphasizing the significance of the selective synthetic access to these two compounds.

The properties of the acene diimides shown in Scheme 14 can be interpreted analogously to those of heteroacene diimides. Thus, the lowering of the LUMO level of the corresponding diimides with respect to that of the parent acene scaffold effects a decrease in the band gap. Accordingly, the UV/Vis absorption spectra of tetracene diimides **73–76** display a considerable red-shift of the absorption maxima compared to those of parent NDI ($\lambda_{\mathrm{max}} = 380$ nm, CH_2Cl_2) and tetracene ($\lambda_{\mathrm{max}} = 475$ nm, CH_2Cl_2).[95] The tetracene diimides **75** and **76** all show two less-intense absorption bands ($1\times10^4\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$) in the visible and one intense maximum in the near-UV region of the electromagnetic spectrum. The maximum of the long-wavelength band for the planar molecule **76** (R^1 = isopropyl) appears at 624 nm in chloroform and that of persubstituted derivatives of structure **75** at 737 ($R^1 = n\text{-}C_8H_{17}$, R^2 = Et) or 756 nm ($R^1 = n\text{-}C_8H_{17}$, R^2 = Ph) in dichloromethane. The significant decrease in the band gap of these derivatives compared to that of parent tetracene or NDI was implied by quantum chemical calculations. Also here, as in the case of the previously discussed *anti*-carbazolocarbazole derivative **61 a**, the HOMO of the tetracene diimide is similar to that of tetracene, both in its shape and energy level, while the LUMO is nearly identical to that of NDI. This newly attained electronic feature results in a decrease in the band gap and consequently in a bathochromic shift of the long-wavelength absorption maximum, which can basically be described as a HOMO→LUMO excitation.

A hypsochromic shift of the absorption maximum relative to that of **75** and **76** was found for tetrabenzotetracene diimide **74 a** ($\lambda = 584$ nm in CH_2Cl_2). This effect is in agreement with Clar's rule and already known for polycyclic aromatic hydrocarbons. It can be explained in terms of the high benzoid character order of four angularly annulated benzene rings, through which the effective conjugation in the molecule is reduced.[91,96] The exchange of angularly condensed benzene rings by thiophene rings in derivative **73a** again evokes a bathochromic shift of the absorption maximum ($\lambda = 655$ nm in chloroform).[90] The oxidized heteroacene diimides **69a** and **70a** display absorptions with band edges at about 600 nm. Moreover, the electrochemical reduction of heteroacene diimides **69a** and **70a** is much more facile than that of the respective dihydro compound; thus with cyano groups, electron-poor compounds such as **70a** with a LUMO energy significantly lower than −4.0 eV were obtained.[88]

4. Conclusion and Outlook

In this Review we have highlighted the enormous increase in the number of chemical structures derived from the parent naphthalene diimide, which has only been explored over a few years, fueled by great interest in organic n-channel semiconductors. Since in the past, NDI derivatives substituted only in the imide position were particularly the focus, the range in the electronic properties of these colorless compounds was initially rather narrow. The “renaissance” of core-chlorinated NDI and the subsequently developed synthesis of core-brominated NDI derivatives became the basis for the subsequent enormous increase in research activities, which have addressed the structural modifications of NDI. The electron-deficient character of NDI derivatives also facilitated the efficient stepwise nucleophilic substitution of halogen substituents, and allowed incorporation of electron-donating oxygen, sulfur, and amino nucleophiles. The ensuing increase in the HOMO energy resulted in a decrease in the optical band gap and enabled a shift in the absorption spectra of the derivatives over the entire visible range. Thus, a broad series of NDI dyes with very good absorption and emission properties became accessible. On the other hand, different methods have been shown to be successful for the introduction of electron-withdrawing substituents to enhance the electron-deficient character of the compounds, thereby affording NDI derivatives with particularly low-lying LUMO levels and outstanding π-acidity.

Motivated by excellent n-channel transistors based on simple NDI derivatives, the study of ring annulation at the NDI core has played an increasing role in the last few years. The lateral expansion to acene and heteroacene diimides has the particular charm of combining two valuable classes of organic semiconductors—p-type semiconducting (hetero)acene and n-type semiconducting rylene diimides—in one molecule. A relatively small range of synthetic methods, such as nucleophilic substitution and metal-catalyzed coupling, enable core-extended NDI derivatives to be obtained, which can, depending on the structure, markedly differ in their electronic properties from those of the initial NDI as well as from each other. Core-extended NDI derivatives have inspired great interest, particularly for application in organic electronics as the electron-poor counterpart to mostly p-type semiconducting acenes and heteroacenes as n-type or ambipolar materials. The future challenge in this field is to ultimately select, from a multitude of now available basic structures, those molecules which are most appropriate for further optimization in regard to synthetic accessibility, solubility, processability, and stability in devices. Finally, many of the presented core-annulated NDI derivatives appear to be interesting as lead structures for organic solar cells, in which they can replace fullerene as a result of their low-lying LUMOs. In addition to their ability to absorb solar light, the possibility to vary the LUMO levels appears to be a great advantage. Furthermore, with their interesting absorption and emission properties, core-substituted naphthalene diimides may enable additional functionalities to be incorporated into supramolecular architectures (e.g. catenanes, rotaxanes), which might be utilized for the creation of molecular sensors or light-induced switches or machines.

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