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Review

Molecular Design and Synthetic Approaches to Electron-Transporting Organic Transistor Semiconductors[†]

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This review covers the various classes of molecular structures that may be used as the basis for the synthesis of organic semiconductors that favor electron transport in field-effect transistors and related electronic and optoelectronic devices. The types of compounds include tetracarboxylic diimides, heterocyclic oligomers, fullerenes, and metal complexes. Approaches to polymers are also mentioned. Although brief discussions of transistor operation and applications are included, the emphasis is on the rationale for choosing these structures, and synthetic routes to them. Performance of exemplary compounds in transistors is also discussed.

1. Organic Semiconductors

Organic semiconductors (OSCs), whether based on discrete molecules with molecular weights in the hundreds or on polymers with tens to hundreds of subunits, are solids into which charge can be reversibly introduced by the application of electromagnetic energy or chemical dopants. The charge carriers can be induced to migrate under the influence of electric fields, with the rate (or "mobility")-limiting step generally a thermally activated hopping process from one molecule or chain to another. In this respect, OSCs differ from inorganic network solids, in which charge carriers are delocalized over a large volume of the solid, and charge migration consists of a displacement of this "volume" spatially and also energetically within a band. Although some highly pure OSCs display some evidence of band transport, OSCs deposited under typical processing conditions show thermally activated mobility, which is defined as the speed of a charge carrier per unit electric field.

Field-effect transistors (FETs), including those based on OSCs, termed organic field-effect transistors (OFETs), operate via the reversible application of two electric fields. The schematic structure of a typical OFET is shown in Figure 1.

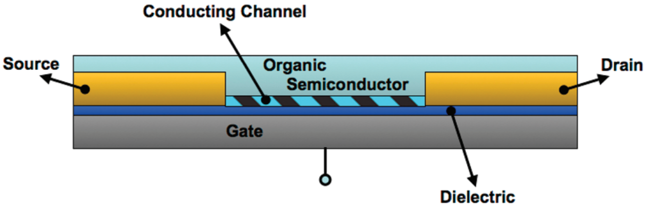

Figure 1. Layout of a typical OFET. The "bottom gate, bottom contact" configuration is shown. Other variations include "top contact", with the source and drain deposited on the upper surface of the OSC, and "top gate", with the gate dielectric deposited on top of the OSC followed by the gate itself, and the OSC originally deposited on a passive substrate.

The two fields are lateral, between the source and drain, and vertical, between the gate and semiconductor. The gate field induces a layer of charge at the OSC−dielectric interface, called the "channel", the magnitude of which depends on the capacitance of the dielectric and the gate field. The mobility within the OSC ideally reflects charge migration across a continuous material supporting the channel, induced by the drain field. In reality, the measured mobility incorporates various barriers and series resistances that are extrinsic to the OSC, some of which are gate-dependent. These include interface dipoles, morphological interruptions near contacts, charge traps on the dielectric surface, grain boundaries, chemical traps and dopants, and environmental influences. Mobility is enhanced by molecular shapes and process steps that decrease the number of morphological detriments, especially in the lateral direction. These include rigid and conjugated central cores with nonconjugated, flexible, sterically nonhindering, and high-aspect-ratio side chains (as shown in Figure 2), dielectric surfaces that promote the organization of such molecules into layers with the cores closely packed into sheets, and crystallization and annealing steps that allow these layered crystalline domains to extend across the entire device. In cases where intermolecular interaction is possible among the cores in all three directions, such as in fullerenes, crystallization that extends equally in all three dimensions is preferable.

A requirement for OFET operation is the ability of the OSC to stabilize the charge in the channel. The capacitance model assumes that charge may be equilibrated rapidly within the OSC. This is possible only if the OSC molecular orbitals are energetically accessible to practical applied voltages, and that charges, once injected, will not be quenched

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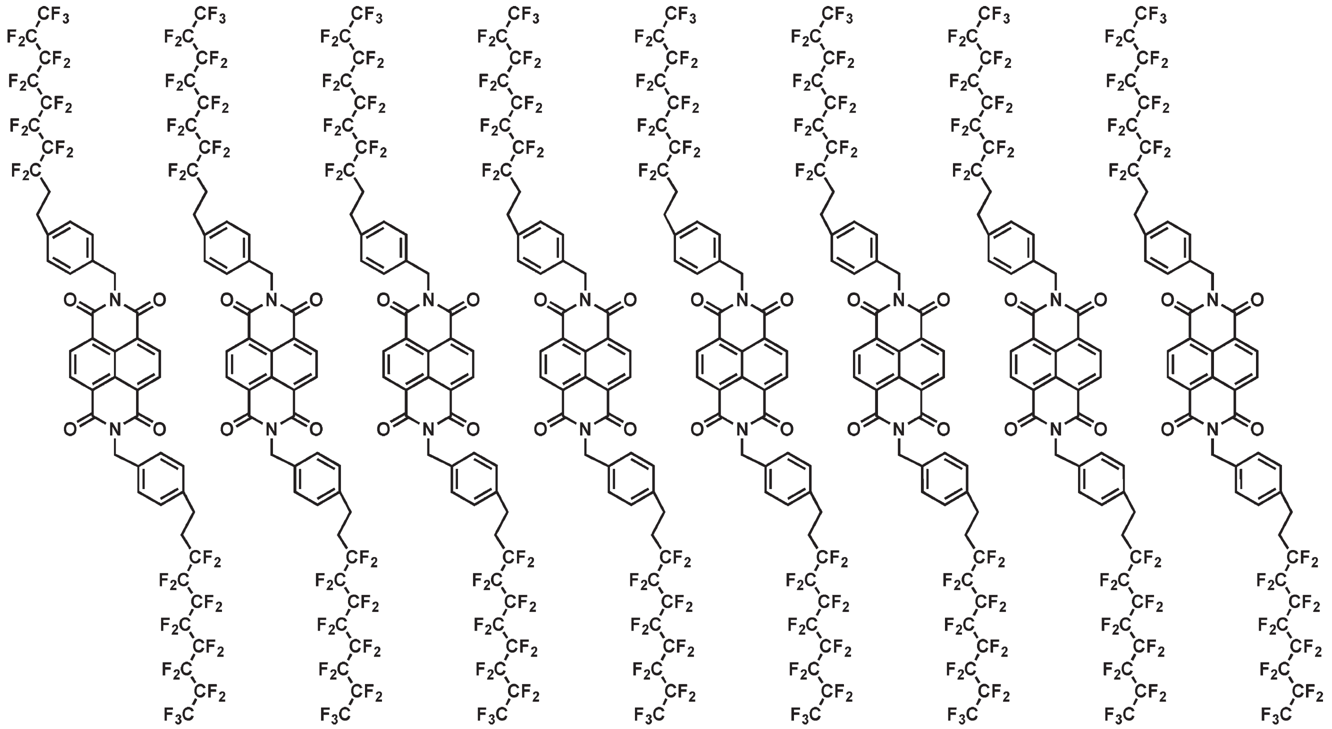


Figure 2. Layer of OSC molecules showing the core−side chain architecture and the arrangement in a charge-transporting layer.

by the environment. These chemical requirements are in addition to the requirement that the molecules within the OSC are in sufficiently close contact for facile charge transfer. These requirements are generally met by molecules with some extended π-conjugation, typically at least eight double bonds, and substituents that either increase the energy of the highest occupied molecular orbital (HOMO) so that oxidation is favorable or lower the energy of the lowest unoccupied molecular orbital (LUMO) so that reduction is favorable. A considerable amount of attention has been given to the tuning and consequences thereof HOMO and LUMO levels of semiconductors.[1] Generally, hydrophobic and densely packed side chains add kinetic stability of charge carriers against interaction with environmental chemical compounds, in addition to the thermodynamic stability conferred by the donating and accepting substituents.

The electron-transporting case for OFETs, utilizing "n-OSCs", is less common than hole transporting, though it is the focus of increasing research efforts. This interest stems from the need for both p- and n-channel materials for efficient logic circuits and organic solar cells. The design and synthesis of molecules for this purpose, electron transport ("n-channel behavior") within OFETs, is the subject of this review.

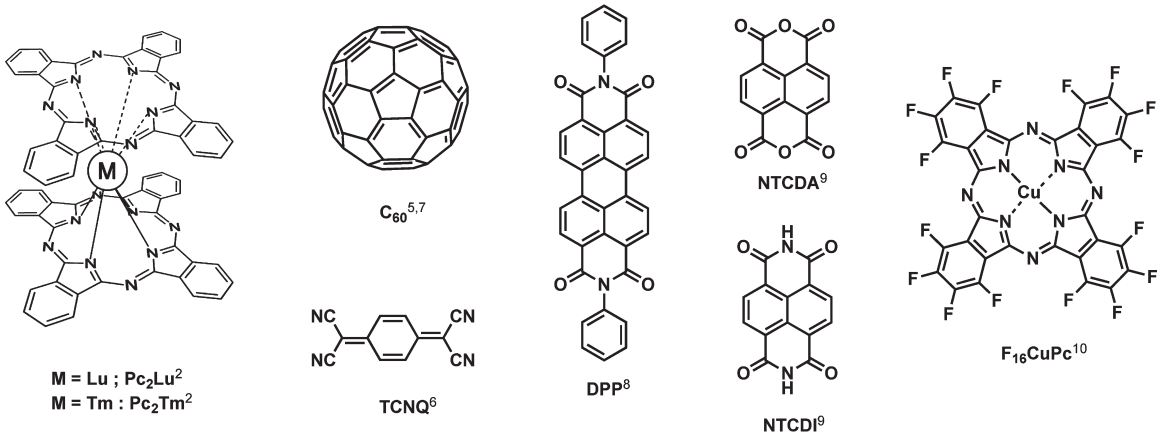
2. First Observation of n-Channel Organic Transistors

The first observation of an n-channel OFET was reported by Guillaud et al.[2] They studied lutetium and thulium bisphthalocyanines (Pc_2Lu and Pc_2Tm) as OSCs without any dopant. They initially tried a bilayer semiconductor in the structure $Pc_2Lu/PcZn/SiO_2$,[3] but this revealed p-channel behavior.[4] Eventually, they achieved the n-channel transistor after replacing PcZn, which they had expected to be an insulating layer, with an alkylsilane layer from octadecyltrichlorosilane (OTS), which is a rigorously insulating layer and is now very widely used at interfaces between oxide dielectrics and OSCs.[2] Without OTS treatment, the devices showed no FET behavior at all. In 1993, Hoshimono et al. reported a metal-doped C_{60} transistor[5] and Brown et al. reported a tetracyanoquinodimethane (TCNQ) transistor in 1994.[6] These original n-channel transistors could not be turned off under the condition of 0 V of gate voltage. In 1995, Haddon et al. demonstrated a C_{60} transistor with the high on/off ratio of 1×10^6 and electron mobility of $0.08\ cm^2\ V^{-1}\ s^{-1}$.[7]

n-Channel field effects for the tetracarboxylic dianhydride and unsubstituted diimides were observed in 1996. One was from perylenetetracarboxylic diimide (PTCDI)[8] and the other was from naphthalenetetracarboxylic dianhydride (NTCDA) and diimide (NTCDI).[9] The FET mobility of the PTCDI transistor was $1.5 \times 10^{-5}\ cm^2\ V^{-1}\ s^{-1}$, but that of the NTCDA transistor reached $3 \times 10^{-3}\ cm^2\ V^{-1}\ s^{-1}$. In 1998, Bao et al. finally demonstrated the air-stable n-channel transistors with copper hexadecafluorophthalcyanine ($F_{16}CuPc$), contradicting the assumption that an n-channel OFET would inevitably be unstable in air.[10] Structures of these prototypical n-OSCs are shown in Chart 1.

On the basis of these early observations of n-OFETs, researchers began to pay further attention to n-OFETs and tried to develop the n-OSCs for this particular aim. Furthermore, C_{60} and $F_{16}CuPc$ are established commercial products at high purity, so they have been widely studied by many researchers as an entrée into n-OFETs.

Chart 1. Structures of Some Early n-OSCs



3. Functionalizing n-Channel Organic Transistors from Substituted Tetracarboxylic Diimides

A. Core-Unsubstituted NTCDIs, PTCDIs, and Pyromellitic Diimides. Polycyclic aromatic compounds are promising n-channel materials. Naphthalenetetracarboxylic dimide (NTCDI), perylenetetracarboxylic diimide (PTCDI), and pyromellitic diimide (PyDI) derivatives containing different side chains can be synthesized by reacting corresponding tetracarboxylic dianhydrides with various amines. The diimide cores are shown in Figure 3. The structures of side chains used with tetracarboxylic diimides are shown in Chart 2. By varying side-chain length, degree of fluorination, and incorporation of phenyl or oxygenated groups, one could alter solubility or volatility of the molecules and packing and morphology of the deposited film. These properties help determine electrical performance attributes such as mobility and stability in air.

Molecules that contain extended π-systems and alkyl chains often form predictable biphasic assemblies. PTCDIs with long alkyl chain substituents (**2a**, n = 7, 12, 18) can persist in several crystalline and liquid crystalline phases,[11] and the one with the octyl side chain (**2a**, n = 8) exhibited mobility of 0.6 $cm^2\ V^{-1}\ s^{-1}$ under nitrogen.[12] With optimized deposition condiditions[13] (for **2a**, n = 5, 8, 12) or additional thermal treatment[14] (for **2a**, n = 13), two research groups also showed improved electrical performances on alkyl-substituted PTCDIs. Fluorinated alkyl side chain (**2b**, n = 3) allows dense and face-to-face packing, enabling mobility of 0.72 $cm^2\ V^{-1}\ s^{-1}$, which only slightly decreased upon air exposure.[15]

Branched alkyl substituents force a more specific assembly, but typically at at the expense of close intermolecular π−π stacking. Although these molecules can be used as solution processable matetials,[16] the undesired longer distance between conjugated cores may be

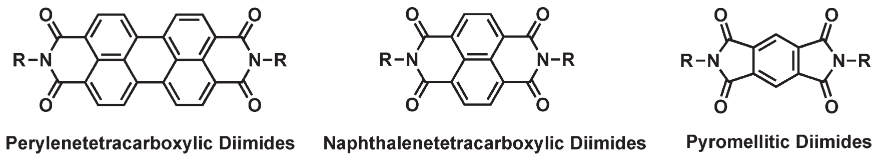
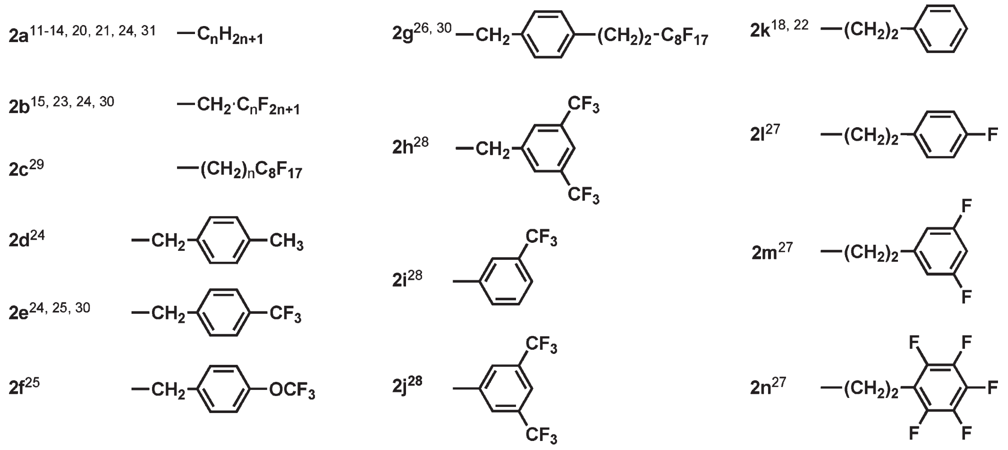


Figure 3. N-Substituted aromatic diimides.

Chart 2. N-Substituents on Tetracarboxylic Diimide OSC Molecules



responsible for the diffusion of oxygen to the deposited film and the associated formation of additional charege carrier traps.[17] Despite the lack of electron withdrawing groups, N-phenylethyl PTCDI (**2k**) still showed good air stability, probably owing to the favorable grain size.[18] LUMO energy levels of aniline-derived diimides can be lowered by increasing the number of fluorine substitutions on the aniline, which also betters stability in air.[19]

It is worth noting that the electrical performance depends strongly on the fabrication process and device scheme. N-tridecyl (**2a**, $n = 13$) PTCDI thin films grown by organic vapor phase deposition (OVPD), in which hot inert gas is used to carry the organic molecules, showed mobility of 0.3 $cm^2\ V^{-1}\ s^{-1}$.[20] Self-assembled nanowire networks obtained from solution of similar alkyl (**2a**, $n = 5, 8, 13$) PTCDI derivatives have mobilities on the order of 10^{-2} $cm^2\ V^{-1}\ s^{-1}$.[21] A microwire network fabricated using phenylethyl (**2k**) substituted PTCDI solution has demostrated mobility of 0.24 $cm^2\ V^{-1}\ s^{-1}$, and mobility of single microwires can be as high as 1.4 $cm^2\ V^{-1}\ s^{-1}$.[22]

After the first realization of n-channel OFET in air using $F_{16}CuPc$,[10] Katz et al. reported 0.1 $cm^2\ V^{-1}\ s^{-1}$ electron mobility in air with fluorinated alkyl (**2b**, $n = 7$) NTCDI and demonstrated inverters composed of p-channel OFET and n-channel OFET fabricated using a solution process.[23] The air-operable n-channel OFET with core-unsubstituted PTCDI (**2b**, $n = 3$)[15] was reported somewhat later compared with the NTCDI (**2b**, $n = 7$) OFET in 2000. It was more challenging to increase the material purity sufficiently in PTCDI derivatives. Generally, PTCDI derivatives have higher melting temperatures than NTCDI derivatives with similar side chains. Replacing alkyl substituents (**2a**, $n = 8, 12, 18$; and **2d**) with their fluorinated counterparts (**2b**, $n = 3$, 7 and **2e**) on NTCDI greatly improves the operability of NTCDI derivatives in air likely because of protection of the core from oxygen and moisture.[24] Trifluoromethoxy-benzyl (**2f**)-substituted NTCDI shows higher mobility than trifluoromethyl-benzyl (**2e**)-substituted NTCDI in case of bottom contact OFET although it shows slightly lower mobility than **2e** in the top contact OFET.[25] Long fluoroalkyl-terminated benzyl (**2g**) NTCDI further exhibits extraordinary mobility (0.57 $cm^2\ V^{-1}\ s^{-1}$) and on/off ratio (1×10^8).[26] NTCDI with a pentafluorophenylethyl substituent (**2n**) demonstrates good mobility in air even though it is deposited without heating the substrate and further allows transparent and flexible OFETs on plastic substrates that demand low-temperature processing.[27] The difference between **2l** and **2m** is only the number of F atoms and the substitution position, but NTCDI with **2m** is inactive as an n-channel OSC because of the less-effective $\pi-\pi$ stacking. Increasing the number of electron-withdrawing trifluoromethyl groups on aryl NTCDI from one (**2i**) to two (**2j**)[28] enables high mobility (up to 0.24 $cm^2\ V^{-1}\ s^{-1}$) and better stability against thermal stress than NTCDI with **2h**. 3-(Perfluooctyl)propyl substituted NTCDI (**2c**, $n = 3$) shows significantly higher electron mobility (0.7 $cm^2\ V^{-1}\ s^{-1}$) in air among NTCDIs with the same perfluorooctyl group attached to different alkylene chains ranging from 1 to 4 carbons (**2c**, $n = 1, 2, 4$).[29] The difference in mobility may be related to an odd−even effect of the CH_2 fragment, and a trade-off between side-chain rigidity and flexibility. The electrical stability of 3-(perfluooctyl)propyl -substituted NTCDI OFET against gate bias stress is comparable to that of a-Si TFTs, a promising for the transparent display backplane application.

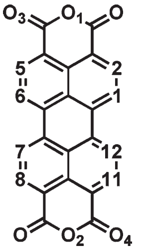


Figure 4. PTCDA substitution position labels.

Pyromellitic diimides, the N-substituted diimides with the smallest core, have been synthesized with side chains of **2b** with $n = 4$, **2e**, and **2g**, and show mobilities between 0.030 to 0.079 $cm^2\ V^{-1}\ s^{-1}$.[30] Terrylenetetracarboxylic diimide (TTCDI) is introduced as the more extended π-electronic system than PTCDI. TTCDI derivatized with pentyl side chains (**2a**, $n = 5$) shows electron mobilities as high as 0.072 $cm^2\ V^{-1}\ s^{-1}$ when measured under vacuum.[31]

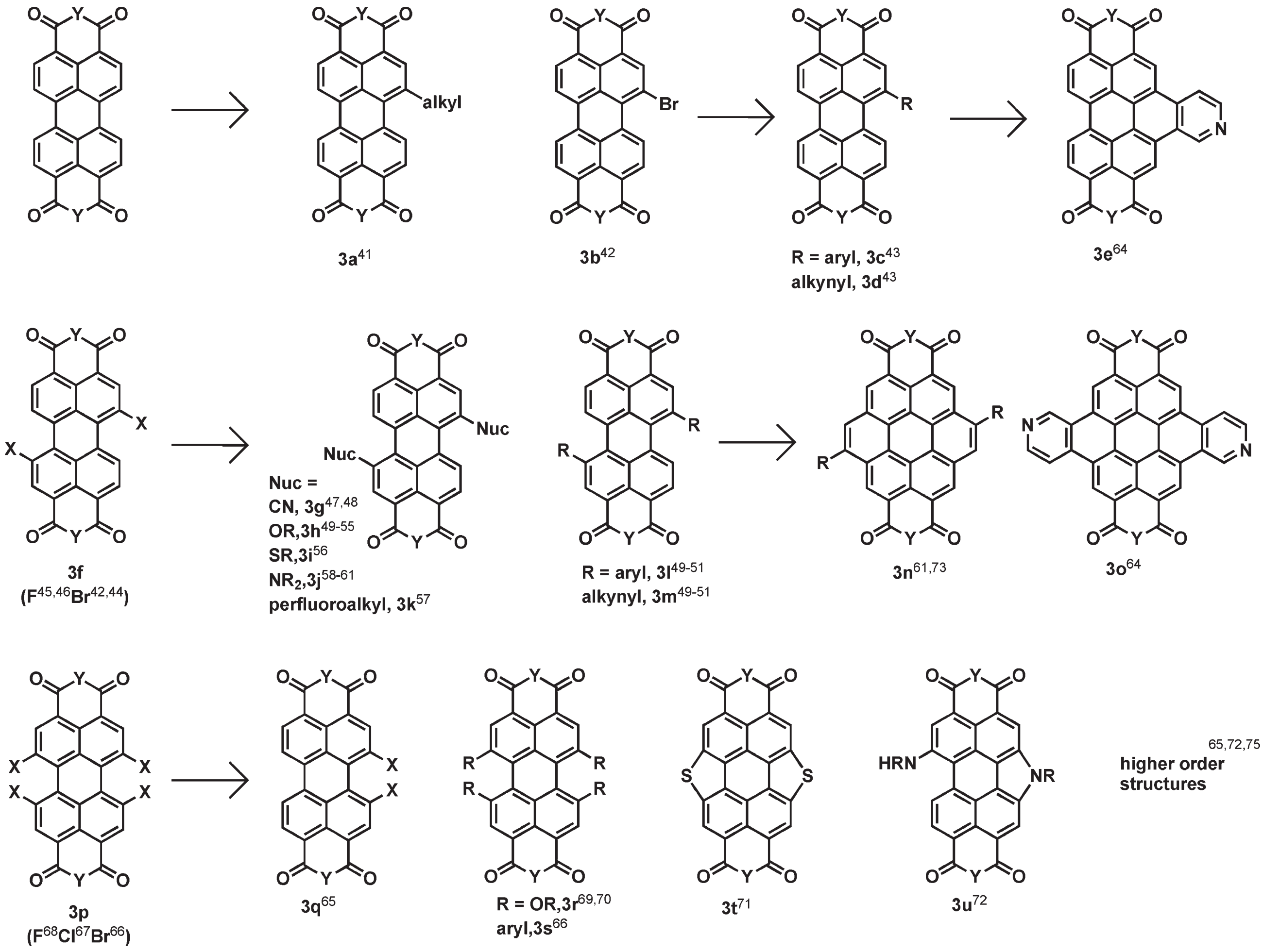
Although some general concepts, such as the effect of electron withdrawing groups, have been established, it remains difficult to "predict" the electrical performance of a molecule simply based on its chemical structure, because of the possible change in molecular packing and grain size. Synthetic effort toward materials with diverse series of substituents is needed to obtain a more insightful understanding.

B. Synthesis of PTCDI Derivatives. Perylene 3,4,9,10-tetracarboxylic acid diimides (PTCDIs) have rapidly become one of the most widely investigated n-type materials.[32] This is in part due to the ease with which the relatively inexpensive starting material, perylene 3,4,9,10-tetracarboxylic acid dianhydride (PTCDA), can be chemically modified to suit particular solubility, photophysical, or electron-bearing demands. The aim in this section is to provide a complete overview of the types of chemical transformations that have been developed to create new electron-transporting PTCDIs. The goal is to inspire the investigation of new synthetic methods and the synthesis of novel PTCDIs given the following subset of published methods.

For the functionalization of PTCDI, every peripheral atom (14 in total) is accessible for substitution, some more so than others. Substitution at the diimides (O1 and O2, Figure 4) has been the predominant focus of many research groups because of their widespread synthetic availability.

Anhydride Substitution. Symmetric Substitution (*O1, O2*). Most primary amines can be used to form diimides. Assuming that the PTCDA that is being functionalized contains no other reactive groups, heating PTCDA and zinc acetate in an appropriate solvent with the corresponding primary amine is the highest yielding method for exhaustive diimide formation.[33] Appropriate solvents should be polar, and the starting material should be appreciably soluble at the reaction temperature. Quinoline and dimethylformamide are commonly

Chart 3. Possible Core Substitutions of PTCDA(I); Y = O and/or NR and X = F, Cl, or Br



used solvents but also dimethylacetamide, isoqunoline, acetic acid, N-methylpyrrolidone, and pyridine have been used.

Asymmetric Substitution (*O1, O2*). There are two synthetic routes to asymmetric PTCDIs.[34] The first is to produce the asymmetric starting material where O1 is converted to NH while conserving O2. This is accomplished via treatment of PTCDA with KOH, and then AcOH (this breaks one anhydride open for reaction), and finally, reaction with ammonium hydroxide under high pH conditions. This material is then subjected to diimide formation under normal conditions to form the desired diimide on one side. The remaining NH-diimide can be deprotonated and used as a nucleophile in a substitution reaction to accomplish the second substitution. The reaction conditions for this last reaction usually involve a strong base to create the diimidium anion, a polar aprotic solvent such as dimethylformamide, and an appropriate alkyl halide. The second route involves formation of a symmetrical diimide and then a selective monoanhydride regeneration using potassium hydroxide in *tert*-butanol. The last step is to form the second diimide under normal reaction conditions.[35,36] The advantage of one over the other is not clear but probably relies on the synthetic difficulty of the amine to be substituted. A recent example of utilizing the second asymmetric synthesis to produce interesting materials is selective reaction of O1, O2, and O3.[37,38]

Anhydride Substitution (*O1, O2, O3, O4*). Reaction of PTCDA with diamines with the 1,2-diaminobenzene substructure result in substitution at O1 and O2 as well as the adjacent carbonyl (O3, O4). The resulting structure has an increased conjugation length, two fewer electron-stabilizing carbonyls, and a possibility for a mixture of isomers: one containing an inversion center and one containing an additional non-normal mirror plane. This synthetic strategy has also given rise to polymeric materials.[39,40]

Core Substitution: Bay Position. Monofunctionalization (*1*). Monoalkylation of the 1 position can be accomplished using palladium acetate and an appropriate alkyl halide (**3a**, Chart 3).[41] Though the yields are low (22−55%, isolated), this method stands alone as the only direct alkylation reaction for PTCDIs. Controlled bromination of PTCDIs can afford a monobrominated product (**3b**).[42] The monobromo PTCDIs are then ideal candidates for oligomer syntheses. Several dimers and trimers have been synthesized from monobrominated PTCDIs via Suzuki and Sonogoshira methods (**3c**−**d**).[43]

Difunctionalization (*1,7/6*). The most useful functionalization technique available for the discovery and production of polymeric materials is probably the dihalogenation of positions 1 and 7/6. Bromination[42,44] and fluorination[45] conditions have been reported (**3f**). In some cases, the halogenation is performed on PTCDA followed by subsequent diimide formation. In other cases, the halogenation is performed on PTCDI. Fluorination is accomplished via the Halex reaction.[46] Both the 1,7- and the 1,6-isomer are obtained from these halogenation reactions and oftentimes, the purification of the preferred 1,7-isomer is very difficult.

The 1,7-dibromo PTCDI is widely used as a starting material for many interesting functional PTCDIs. Copper-mediated and uncatalyzed nucleophilic substitution reactions occur very easily on the brominated PTCDIs due to the electron-poor nature of the molecule. A widely investigated material is the result of conversion of the bromines into nitriles via copper-mediated substitution (**3g**).[47,48] The dicyano-PTCDIs are commercially available from Polyera Corporation under the "Activ Ink" trademark. In addition to cyano groups, bromo substituents can be transformed into alkoxy-,[49−52] phenoxy-,[53−55] tetrathiafulvalene (TTF)-sulfide-,[56] perfluoroalkyl,[57] and amino-[58−61] groups (**3h−k**). The dibromo functionality is useful for constructing asymmetric PTCDIs. Utilizing stepwise sets of Suzuki and/or Sonogashira couplings, the end functionality on position 1 and 7 can be different aryl (**3l**) and/or substituted acetylenes (**3m**).[49−51] Asymmetric PTCDIs were synthesized to direct assembly either through amphiphilicity[51] or single-metal coordination sites.[49,50] Dibromo-PTCDIs are also the ideal candidates for the synthesis of polymeric materials. Polymers have been synthesized from 1,7-dibromo PTCDIs via Stille couplings.[62] Some have been made commercially available. The Sonogashira coupling has been applied to dibromo-PTCDI to make trimers[43] and higher-order oligomers.[63]

Difunctionalization (*1,12*). There is a unique reaction sequence that leads to a 1,12-difunctionalized PTCDI. This scheme involves a Suzuki reaction of a 1-monobrominated PTCDI with an electron-poor aromatic boronic acid. Subsequent heating allows for a regioselective nucleophilic addition of PTCDI at position 12 to the electron-poor aromatic to form a new six-membered ring (**3e**).[64] The latter part of the reaction probably follows a Chichibabin-type mechanism. This type of functionalization is particularly attractive for the exploratory synthesis of larger π-systems, drastically changing the molecular packing, the shape of the orbitals, and the solubility. One other way to functionalize just the 1,12-positions is to take a 1,6,7,12-tetrachloro PTCDI derivative and isolate the 6,7-dehalogenated product from reaction with copper iodide (**3q**).[65]

Tetrafunctionalization (*1, 6, 7, 12*). Exhaustive halogenation of PTCDA halts at the 1,6,7,12-tetrahalogenated product (**3p**) and does not proceed to halogenate any other positions. Tetrabrominated,[66] tetrachlorinated,[67] and tetrafluorinated[68] PTCDIs have been reported. Tetrabrominated PTCDIs can be converted to tetraaryl PTCDIs (**3s**) using Suzuki conditions.[66] Tetrachlorinated PTCDIs can be converted to the tetra-phenyl ether (**3r**) via a nucleophilic aromatic substitution reaction of the phenolate in NMP at medium temperatures (120 °C) for long reaction times (69 h).[69,70] Facile modification of the phenolated PTCDIs lead to J-aggregate materials. Tetrachloro PTCDIs are even more susceptible to nucleophilic displacement of halogens than mono- or dihalogenated analogs. Reaction with *tert*-butyl disulfide in the presence of palladium catalyst results in a thio-bridged compound (sulfur bridges positions 6−7 and 1−12), which has intermolecular hydrogen-bonding (**3t**).[71] Under similar conditions, primary amines form a 1,12-bridged 7-amino 6-dehalogenated product (**3u**).[72]

Operating under the same principles as the 1,12-difunctionalization scheme, tetra-functional PTCDIs can be attained via a 1,7/6-dibrominated PTCDI. Suzuki reaction of the 1,7/6 position with 4-pyridyl boronic acid and subsequent intramolecular cyclization proceeds to form a dipyridylated coronene core (**3o**).[64] An alternative reaction scheme for converting PTCDI into a coronene-type core is through a Sonogashira coupling of a terminal alkyne with a 1,7/6-dibrominated PTCDI. That product then undergoes a DBU-catalyzed nucleophilic aromatic substitution cyclization to the coronene core (**3n**).[61,73]

Dimerizing and trimerizing PTCDI units leads to still further extension of the conjugated systems, dependent upon the steric ability of monomers to have significant $\pi-\pi$ overlap. From tetrahalogenated PTCDI, an Ullman reaction with copper iodide and L-proline will result in a statistical mixture of condensation products and dehalogenation products.[65] Dehalogenation can be minimized by a lower reaction temperature. From simple Ullman couplings, the targets that have been synthesized are: 1,12,6′,7′-tetrachloro-PTCDI dimer,[72] 1,12-dichloro PTCDI dimer,[65] 1,12,6′,7′-tetraiodo-PTCDI dimer,[74] the completely dehalogenated PTCDI dimer,[75] and trimers.[75] Chlorinated dimers have then been further reacted to form the aforementioned, sulfur- and nitrogen-bridged derivatives.[65,72]

Core Substitution: Ortho Position (*2, 5, 8, 11*). C−H activation at the 2,5,8, and 11 positions of PTCDIs using the ruthenium catalyst $RuH_2(CO)(PPh_3)_3$, affords the addition of arylboronic esters.[76] Yields in the range of 69−83% were obtained for most boronic acids tested. The tetra-aryl PTCDIs were easily purified because of high conversion (low percentage of partial reaction) and the degree of molecular change between the starting material and the product.

C. Synthetic Approaches to NTCDI-Substituted Derivatives. Like PTCDA, naphthalene-1,4,5,8-tetra-carboxylic acid dianhydride (NTCDA) is a very common starting material for producing n-type naphthalene-1,4,5,8-tetracarboxylic acid diimides (NTCDIs). The chemistry is very similar but more limiting because of fewer available aromatic positions. Figure 5 shows a summary of the recent synthetic tools for developing new NTCDIs.

Anhydride Substitution. Symmetric and Asymmetric Substitution (*O1, O2*). Substituting the anhydride in NTCDA follows the same conditions as PTCDA. The only notable difference is that lower boiling solvents can often be used because of the higher solubility of NTCDIs in general.

Anhydride Substitution (*O1, O2, O3, O4*). Reaction of NTCDA with 2,3-diamines also forms the five-membered heterocycles, as they do with PTCDAs. A recent example uses the prototypical 1,2-diaminoethane.[77]

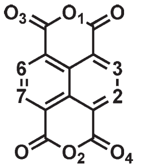


Figure 5. NTCDI substitution position labels.

Core Substitution. Mono- and Difunctionalization (*2, 6*). Mono- and 1,3-dibromination of NTCDA are possible via control of standard bromination conditions. 2,6-Dibromination of NTCDA can be performed with dibromoisocyanuric acid in hot sulfuric acid solution with good yield.[78] Conversion of bromides into cyano is accomplished using copper-mediated substitution.[79] It is also possible to convert the monobromo NTCDI into a 2,3-disubstituted NTCDI or the 2,6-dibromo NTCDI into a trisubstituted derivative using nucleophilic substitution with ethylene diamine. The product of the reaction with ethylene diamine can be oxidized to make compounds that have interesting redox chemistry and narrower bandgaps.[80] Dichlorination of NTCDA[81] is facile and allows for similar chemistry to dibromo NTCDIs. Transition metal coupling reactions work on these halogenated NTCDIs. A recent example is the Suzuki reaction on both dibromo and dichloro NTCDIs.[82]

Tetrafunctionalization (*2, 3, 6, 7*). Tetrachlorination[81] and tetrabromination[80] are possible. The same chemistry that is available to mono- and difunctionalized NTCDIs is also available to the tetrahalogenated. For example, reaction of tetrabromo NTCDI with ethylene diamine yields the expected tetra amino-functionalized NTCDI.[80]

Approach toward N-Type Materials Synthesis. There should be a call-to-action for synthetic chemists to take these published methods and use them to create new series of possible n-type materials. The use of the word "series" is important. As mentioned above, in order to gain a deep scientific understanding of the differences between n-type materials, subtle and organized structural changes are key. The difference between a methyl and an ethyl could (and in most cases does) vastly change final purity, crystal packing motif, sublimation temperature, solubility, as well as other properties that can affect final device performance. The field is filled with a hodgepodge of materials: some are structurally simple, but most are very elaborate. This field commands more thorough investigations into series of structurally similar n-type materials to add to our understanding of the requirements for maximizing performance. When reporting new materials, crystal structures, thin film X-ray diffraction, cyclic voltammetry, and elemental analysis should be standard data to be reported alongside electronic characterization. The formulation of new ideas to contribute to the field of organic semiconductors is made difficult by incomplete data sets, making it nearly impossible to compare materials from different research groups.

4. Perfluoroaryl or Perfluoroalkylaryl Oligomers

After the early reports of n-channel materials containing fluorine substitutions, such as perfluoro copper phthalocyanine (F_{16}CuPc)[10] and fluorinated alkyl NTCDI,[23] the fluorine atom has been a most useful substituent for the n-channel organic materials. The unsubstituted p-channel material, CuPc, was transformed into the n-channel material, F_{16}CuPc, when the periphery was perfluorinated.

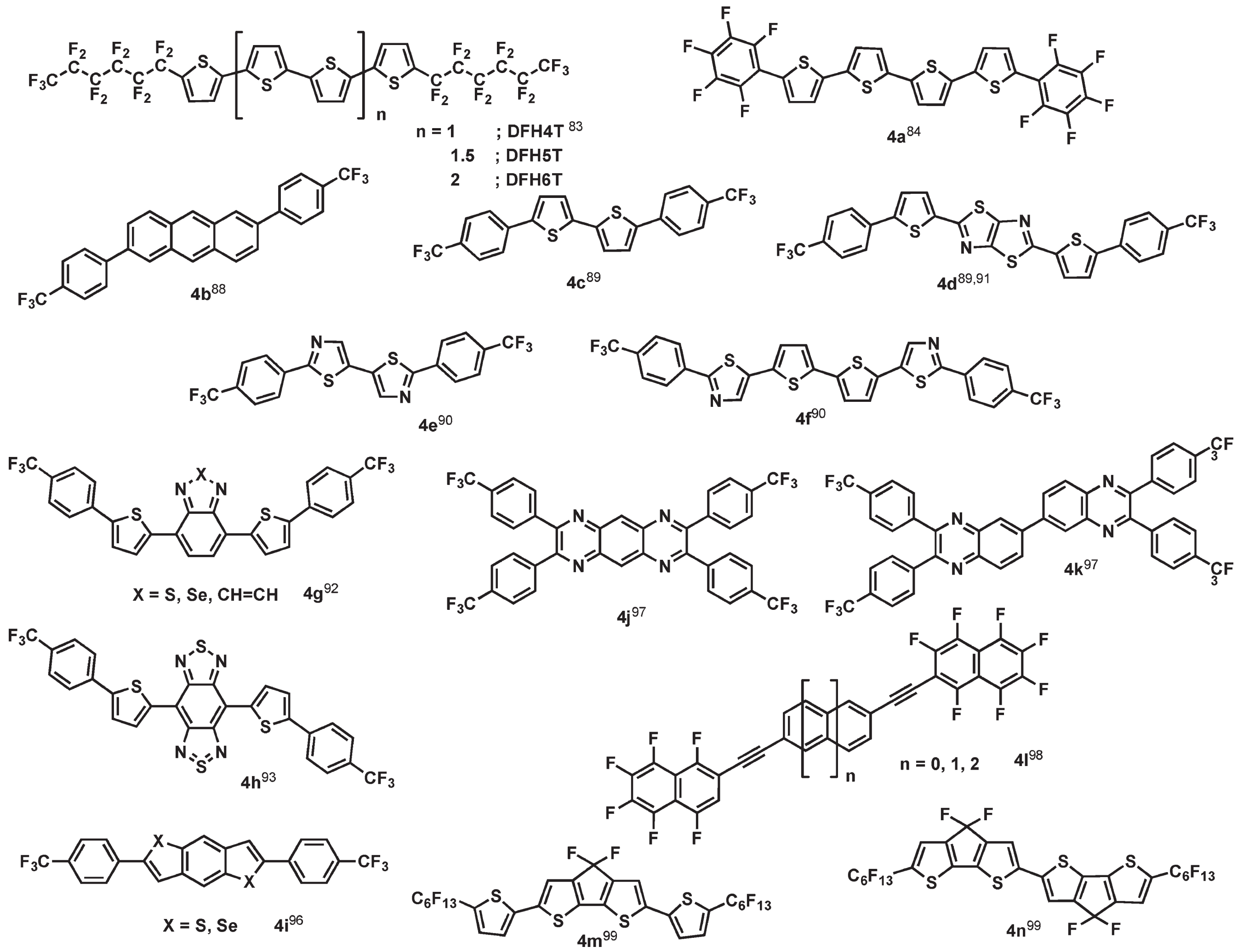
The initial trials on oligomeric systems were performed on derivatives of the well-known p-channel thiophene oligomers.[83,84] These oligothiophene derivatives (DFH4T-6T, **4a**) showed electron mobility comparable to that of the hole mobility of the parent p-channel thiophene oligomers. Extensive studies about them were reported later and the high mobility of 0.43 cm^2 V^{-1} s^{-1} was achieved through the optimization of the substrate annealing temperature.[85−87] In 2005, the Yamashita group reported several oligomers with trifluoromethylphenyl end groups (**4b**−**f**).[88−90] One (**4e**) of them, containing thiazole, showed the high electron mobility up to 1.83 cm^2 V^{-1} s^{-1} in vacuum but the threshold voltage was quite high.[90] The electron mobility of the thiazolothiazole derivatives (**4d**) was improved from 0.3 to 1.2 cm^2 V^{-1} s^{-1} by employing long alkyl self-assembled monolayers.[89,91] The same group has developed other trifluoromethylphenyl derivatives.[92,93] In particular, a transistor with benzothiadiazole (**4g**) derivative showed n-type light-emitting FET characteristics.[92] Benzothiadiazole is also a widely used building block for polymer light-emitting diodes[94] and polymer solar cells.[95] Using benzobis(thiadiazole) (**4h**), Yamashita eventually achieved high-performance n-channel organic transistors in air with low threshold voltage.[93] Similarly, other compounds with trifluoromethylphenyl groups (**4i**−**k**) showed n-channel characteristics,[96,97] as did compounds with the perfluorophenyl group.[84] In some cases, the core was an electron-rich fused ring.[96] The perfluoronaphthalene group (**4l**) was also used for n-channel oligomers,[98] resulting in inferior performance. They also included acetylenic triple bonds, which are rare in organic semiconductors. Ie et al. reported oligothiophenes with a difluoromethylene bridge (**4m,n**).[99] In the single-crystal X-ray data, the linked thiophenes kept their planarity but the electron mobilites (0.018 and 0.0013 cm^2 V^{-1} s^{-1}) were somewhat smaller than that (0.059 cm^2 V^{-1} s^{-1})[85] of DFH4T. Representative oligomers are shown in Chart 4.

n-Channel OFETs based on most these class materials were unstable in air or suffered from high threshold voltage. Perfluoroaryl and perfluoroalkylaryl groups increased the capability of assemblies of the constituent molecules for electron transport, without interrupting the crystallinity of the molecules. However, they generally did not lower the LUMO levels enough for n-OFETs to operate in air. The additional combination of electron deficient heteroaromatic rings aids in the attainment of more air stable n-OSCs like in the case of **4h**.

5. Carbonyl-Functionalized Oligomers

As discussed above, aromatic tetracarboxylic anhydride and diimide derivatives were reported among the first n-channel materials. These compounds have four carbonyl groups, which are the electron-withdrawing groups in their structures allowing the LUMO levels to be at low enough

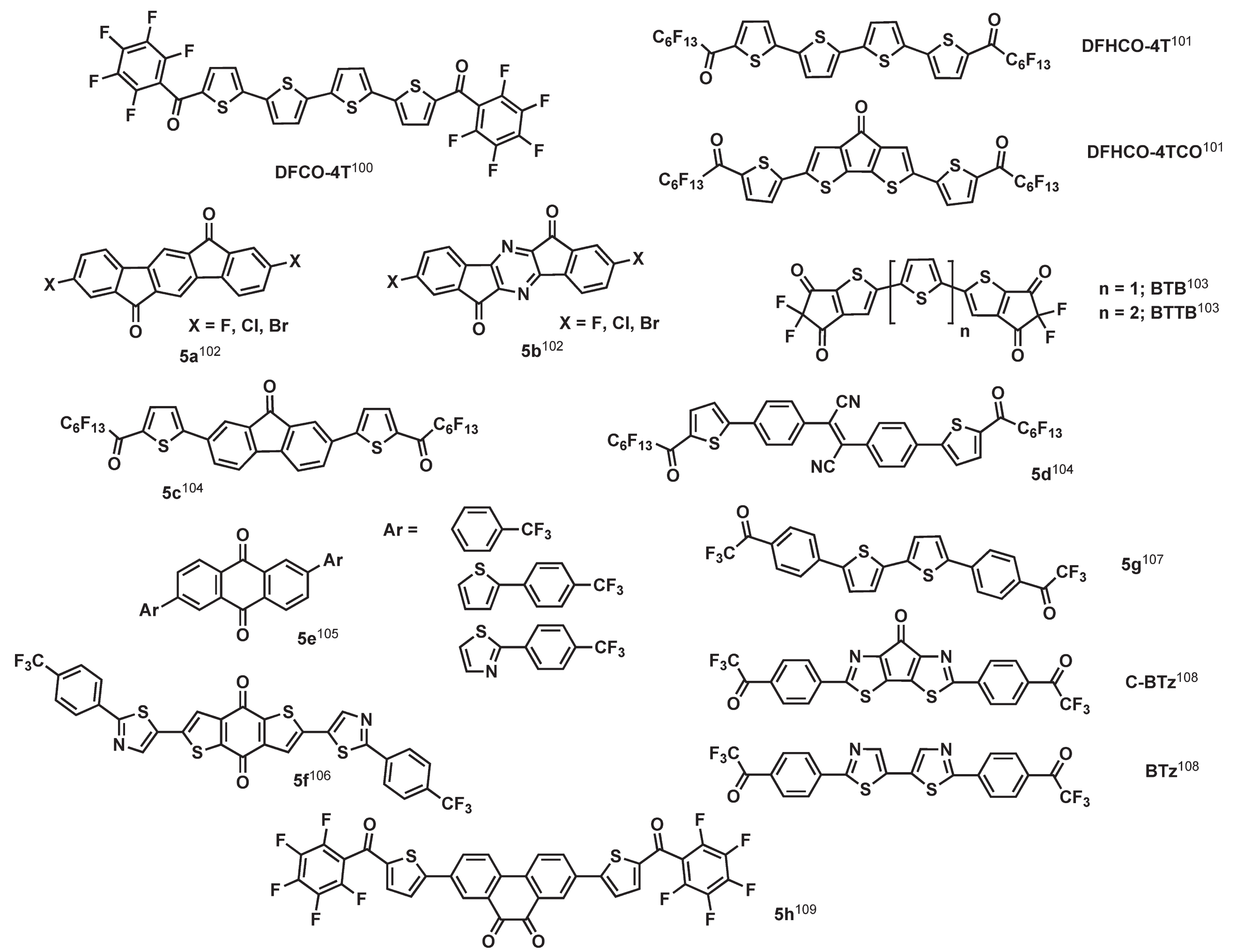
Chart 4. Representative n-Channel Fluoroaryl or Fluoroalkylaryl Oligomers



energy to accept and transport electrons. The Marks group introduced carbonyl groups to the oligothiophenes[100] along with fluorinated side groups,[83,84] utilizing the good crystal packing tendencies of the oligothiophenes. DFCO-4T with perfluoracyl groups showed n-channel characteristics, but DHCO-4T without the fluorines showed p-channel characteristics. The performance of DFCO-4T was quite high with 0.45 cm^2 V^{-1} s^{-1} of electron mobility in the vacuum, comparable to that of diperfluorophenylquaterthiophene[86] in which the perfluorophenyl is directly connected to 4T without the carbonyl group. But DFCO-4T was somewhat soluble in organic solvents, in contrast to the diperfluorophenylquaterthiophene. It was possible to fabricate the transistor using drop-casting and the device also showed high electron mobility of 0.21 cm^2 V^{-1} s^{-1}. DFHCO-4T and DFHCO-4TCO with the perfluorohexylcarbonyl group instead of the perfluorophenylcarbonyl group showed n-channel characteristics with the electron mobility of 0.34 and 0.08 cm^2 V^{-1} s^{-1}, respectively.[101]

The Yamashita group reported indenofluorenedione (**5a**) and diindenopyrazinedione (**5b**) derivatives having two carbonyl groups in the middle of the compounds.[102] The OFETs of the diindenopyrazinedione derivatives (**5a**) had smaller threshold voltage than those of the indenofluorenedione derivatives. Among them, the diindenopyrazinedione derivative with F showed the highest performance with 0.17 cm^2 V^{-1} s^{-1} of mobility and 17 V of threshold voltage (V_{th}). Ie et al. introduced the difluorodioxocyclopenta[*b*]thiophene to the end of oligomers.[103] As a result, BTTB and BTB showed n-channel FET behavior. Lee et al. reported the oligomers with electron-deficient cores, fluorenone (**5c**) and fumaronitrile (**5d**), and the perfluorohexylcarbonyl group as n-channel materials with 0.06 and 0.03 cm^2 V^{-1} s^{-1} of mobility.[104] The Yamashita group has also developed quinone derivatives (**5e,f**), on which two carbonyl groups are located at the center of the compound, and which also have trifluoromethylphenyl groups attached.[105,106] The benzo[1,2-*b*:4,5-*b*′]-dithiophene-4,8-dione derivative (**5f**) has a low LUMO so that its OFET showed similar mobility in air (0.12 cm^2 V^{-1} s^{-1}) compared to under vacuum (0.15 cm^2 V^{-1} s^{-1}).[106] The Aso group combined the trifluoroacetylphenyl group with the bithiophene (**5g**) or bithiazole unit (C-BTz, BTz).[107,108] The carbonyl-bridged oligomer, C-BTz showed 0.06 cm^2 V^{-1} s^{-1} of mobility in the vacuum, which is slightly less than that of DFHCO-4TCO, but its OFET showed a fair stability in air having mobility of 0.014 cm^2 V^{-1} s^{-1} . The Marks group has developed air-stable n-channel materials by changing the bithiophene on the

Chart 5. n-Channel Carbonyl-Functionalized Oligomers



center in DFCO-4T to the phenanthrenequinone (**5h**), which has two carbonyl groups.[109] The OFET from this quinone oligomer was very stable in air, showing negligible change in V_{th} and a slight decrease in mobility (from $0.018\,cm^2\,V^{-1}\,s^{-1}$ to $0.015\,cm^2\,V^{-1}\,s^{-1}$) compared the device under vacuum. Moreover, the OFET was stable over one year, maintaining the high on/off ratio of 1×10^6. Oligomer carbonyl OSC molecular structures are shown in Chart 5.

The highest mobility of this class of compounds is lower than that from the previous class, but overall stability is better because carbonyl group lowers LUMO levels of the n-OSCs. It is noticeable that most of this class of n-OSCs have several fluorines.

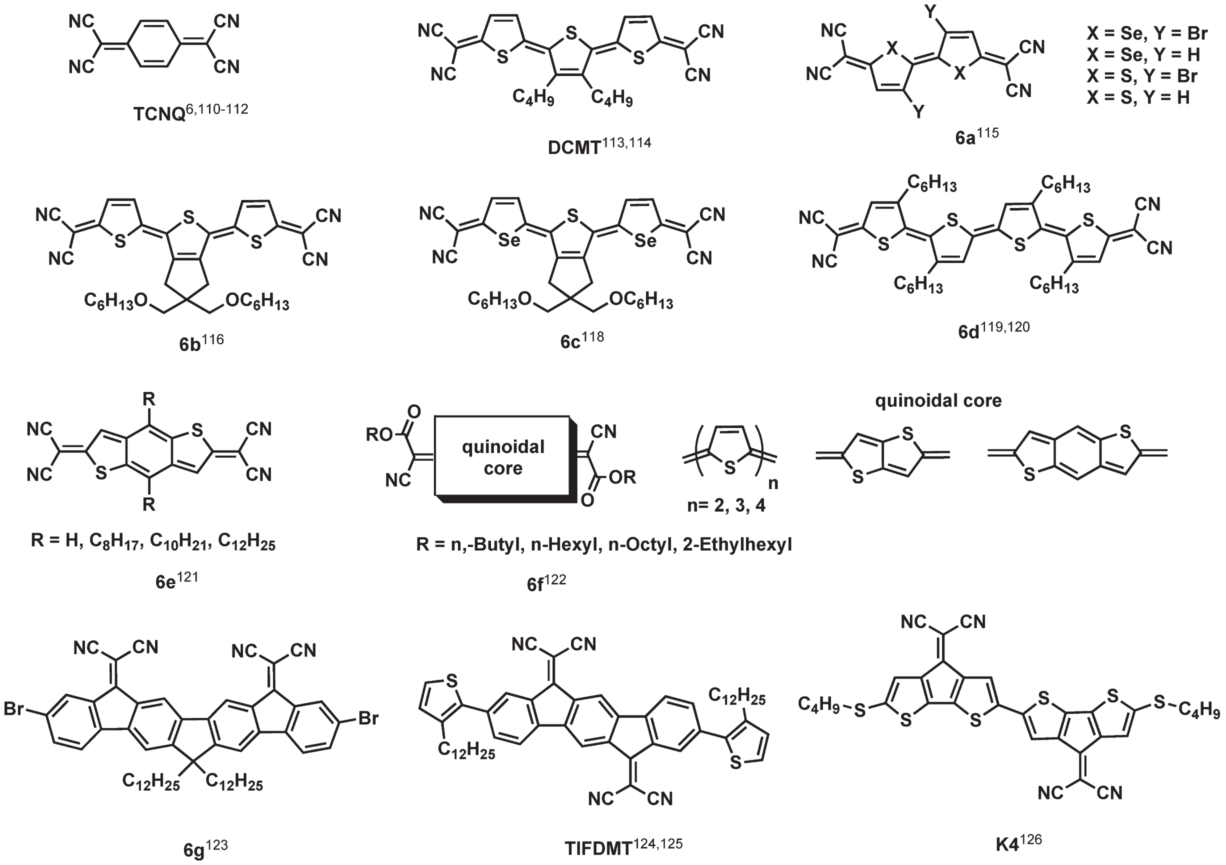
6. Cyanovinyl Oligomers

7,7,8,8-Tetracyanoquinodimethane (TCNQ)-based compounds have long been known as excellent electron conductors, TCNQ itself being a very strong electron acceptor. Thus, it was expected to be a promising candidate for an n-channel organic semiconductor. The TCNQ OFET using conventional vacuum deposition showed very low electron mobility.[6] However, the intrinsic electronic properties of pure crystalline TCNQ are apparently suitable for OFET operation. The Rogers group demonstrated the TCNQ n-OFET with using a single-crystal semiconductor and vacuum gap dielectric layer using the lamination technique.[110] Later, Yamagishi and Uemura et al. reported an n-OFET of a TCNQ single crystal on the SiO_2 or ionic-liquid electrolyte dielectric layers.[111,112]

Before these TCNQ single crystal n-OFETs, the quinoidal terthiophene with the cyanovinyl group (DCMT) was reported as n-channel material in OFETs using vacuum deposition or casting methods by the collaboration of the Frisbie and Mann groups.[113] The terthiophene formed polycrystalline films with grains as large as 10 μm. In the single-crystal structure, the closest intermolecular distance was 3.47 Å. Moreover, this compound showed ambipolar behavior through the optimization of the device.[114] This was the first report of an ambipolar transistor with one OSC.

The bithophene and biselenophene (**6a**) were introduced instead of terthiophene in n-channel quinoidal compounds by Kunugi et al.[115] These compounds also showed n-channel behavior but the electron mobilities were much lower than that of DCMT. In 2007, Handa et al.[116] reported the solution-processable n-channel material based on quinoidal terthiophene (**6b**) incorporating a bis(hexyloxymethyl)cyclopentane unit rather than the butyl group of DCMT. DCMT showed the excellent electron mobility of $0.2\,cm^2\,V^{-1}\,s^{-1}$ in a vacuum-prepared OFET

Chart 6. n-Channel Cyanovinyl Oligomers



TCNQ[6,110-112]

DCMT[113,114]

X = Se, Y = Br
X = Se, Y = H
X = S, Y = Br
X = S, Y = H

6a[115]

6b[116]

6c[118]

6d[119,120]

R = H, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$

6e[121]

n= 2, 3, 4

quinoidal core

R = n,-Butyl, n-Hexyl, n-Octyl, 2-Ethylhexyl

6f[122]

6g[123]

TIFDMT[124,125]

K4[126]

but 2 orders of magnitude less mobility in solution cast devices. Their group already had reported the oligothiophenes with bis(butyloxymethyl)cyclopentane group.[117] However, these molecules were not suitable as OFET materials because of the excessive number of side groups, which reduced intermolecular interaction in the solid film. After changing the butyl group to hexyl and attaching this solubilizing group only to the center thiophene in the terthiophene, they achieved 0.16 $cm^2\ V^{-1}\ s^{-1}$ of electron mobility through the solution process.[116] Recently, they also reported a quinoidal trimer based on a selenophene-thiophene co-oligomer (**6c**) as a solution-processable ambipolar material.[118] Although its electron mobility was one order lower than that of the terthiophene derivative, its hole mobility was as high as 0.007 $cm^2\ V^{-1}\ s^{-1}$, similar to the electron mobility. Therefore, they demonstrated the air-operable inverter with this ambipolar material using spin-coating methods.

Ribierre and Aoyama et al.[119] fabricated the very interesting complementary logic gates and lateral p−n diodes from the dicyanomethylene-substituted quinoidal quaterthiophene (**6d**). Although the synthesis of this compound had been reported 15 years ago,[120] its OFET mobility had not been reported. Moreover, they observed the conversion form the ambipolar material to n-channel-only material by the thermal annealing or direct laser writing. Using this unique property, they were able to laser-pattern p- and n-regions in solution-processed thin films.

After the Takimiya group reported soluble quinoidal benzodithiophenes with the cyanovinyl group (**6e**) as n-channel materials,[121] they additionally developed ((alkyloxy)carbonyl)cyanomethylene-substituted quinoidal compounds (**6f**) as a new class of n-channel OSCs.[122] These compounds had slightly higher LUMO levels than dicyanomethylene-substituted compounds but their LUMOs were low enough to allow the n-channel OFET in air. When the quinoidal core was as long as 4T, the compound showed ambipolar behavior.

There are other nonquinoidal oligomers[123−126] with dicyanomethylene groups as n-channel materials. The dicyanomethylene group was condensed to the carbonyl group to provide stronger electron accepting capability, just as the low band gap sensitizer, (2,4,7-trinitro-9-fluorenylidene)malononitrile (TNFDM), was developed from 2,4,7-trinitrofluorenone (TNF) for the organic photorefractive materials.[127,128] Initially, these oligomers (**6g**, TIFDMT) were designed to be building blocks for n-channel polymers.[123,124] Eventually, the 2,8-di-3-dodecylthiophene-indeno[1,2-*b*]fluorene-6,12-dimalononitrile (TIFDMT) had the sufficiently low LUMO level (< -4.1 eV) to show good n-channel OFET behavior with 0.16 $cm^2\ V^{-1}\ s^{-1}$ of electron mobility in air.[125,126] However, one of them, 6,6′-dibutylsulfanyl-[2,2′-bis[4-dicyanovinylene-4H-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene] (**K4**) with −3.7 eV of LUMO showed the high electron mobility up to 0.34 $cm^2\ V^{-1}\ s^{-1}$ only in vacuum.[126] Oligomers with cyanovinyl conjugation are shown in Chart 6.

This class is very attractive as soluble processable n-OSCs or ambipolar OSC. Even though there is no fluoro substitution, the cyanovinyl groups enable oligomers to have significant electron transporting capabilities, while also reducing the band gaps of the molecules.

7. Fullerenes

C_{60} and other higher fullerenes (C_{70}, C_{84}, etc.) are extraordinary n-channel materials because of their symmetrical shapes, substantial electron affinity, and superior charge transport ability.[129] Fullerene thin films are most commonly obtained by thermal evaporation. By chemical modification, solubility of fullerenes can be further increased, providing additional process flexibility. Because of their significant electron-acceptor capability, radical,[130] nucleophilic, and cycloaddition reactions are typical approaches for fullerene functionalization.[131]

Among these methodologies, the 1,3-dipolar cycloaddition reaction is the most effective and versatile process, and a wide variety of 1,3-dipolar reagents including diazo compounds,[132] azide,[133] nitrile oxides,[134] nitrile imine,[135] azomethine ylides,[136] nitrile ylides,[137,138] and pyrazolidinium ylides[139] have been reported to react with the carbon−carbon double bonds of fullerenes. Microwave irradiation can promote 1,3-dipolar cycloaddition and achieve shorter reaction time and higher yield.[140]

Because of the ease preparation of various diazo and azide precursors, 1,3-dipolar cycloaddition adducts methanofullerenes and iminofulleres have been the most investigated n-channel fullerene derivatives.[141] While [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is widely used as the electron accepting part in bulk-heterojunction organic solar cells, much effort has been put on the synthesis of PCBM-like derivatives for higher mobility, better ambient stability, and desired morphology in transistors and solar cells. The self-assembling ability provided by long alkyl chains enables the fabrication of highly ordered crystalline films,[142] thus achieving higher electron mobility. Long perfluoroalkyl chains can further improve the air stability.[143] By substituting the phenyl ring of PCBM with electron-donating or electron-withdrawing substituents, the LUMO levels of the fullerene derivatives can be varied to change the open circuit voltage of bulk-heterojunction solar cells.[144] The alkyl chain length in a series of PCBM-like derivatives has been shown to significantly influence the mobility of the film blended with P3HT.[145] The presence of long (20 carbons) alkyl chain and a semiperfluoro alkyl tail would also dramatically change the morphology and hydrophobicity.[146] A [5,6]-open iminofullerene,[147] which holds the intact C_{60} π-electron system, has been reported to show higher mobility than PCBM.

Endohedral fullerenes, fullerenes with enclosed atomic or molecular species, can also act as 1,3-dipolarophiles to form similar cycloaddition products. Endohedral metallofullerene FETs fabricated with $Dy@C_{82}$,[148] $La_2@C_{80}$,[149] and $Pr@C_{82}$[150] showed n-channel normally-on properties.

Compared with other n-channel materials, fullerene derivatives have not been as widely directed toward transistor applications. Much effort on the study of fullerene materials is instead focused on phase separation of polymer/fullerene blends in solar cells.

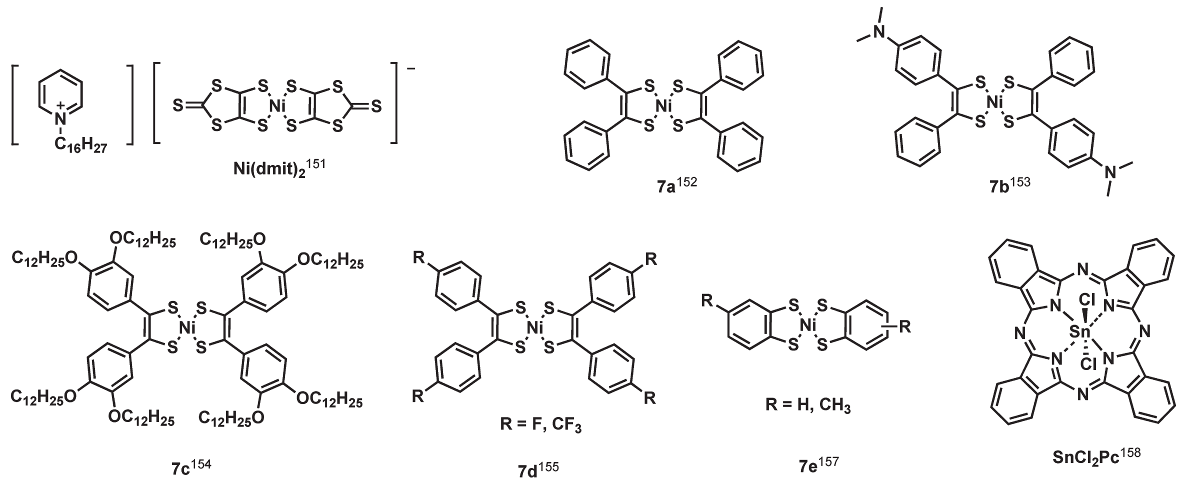
8. Metal Complexes

Over one decade after the observation of n-channel OFET behavior for the Langmuir−Blodgett film of Ni(dimt)$_2$,[151] another nickel complex was reported as the n-channel organic semiconductor by Taguchi and Mori et al.[152] The vacuum deposited film of bis(dithiobenzil) nickel (**7a**) showed 2×10^{-5} cm^2 V^{-1} s^{-1} in air and 3×10^{-6} cm^2 V^{-1} s^{-1} in the vacuum for bottom contact configuration of Al electrodes. Anthopoulos et al.[153] demonstrated complementary-like circuits in air using bis (4-dimethylaminodithiobenzyl) nickel (**7b**), which showed ambipolar OFET behavior with the mobility of the order of 10^{-4} cm^2 V^{-1} s^{-1} in air. Cho et al.[154] reported Ni bis (dithiolene) complexes with long alkyl chains (**7c**) and fabricated an OFET with mobility of 1.3×10^{-3} cm^2 V^{-1} s^{-1} under N_2 using solution deposition. They used Ag electrodes instead of Al. Wada and Mori et al.[155] synthesized a series of tetraphenyl Ni bis(dithiolene) complexes (**7d**). Electron mobilities were on the order of 1×10^{-4} to 1×10^{-6} cm^2 V^{-1} s^{-1} in the vacuum. Among them, the fluoro and trifluoromethyl derivatives had higher first reduction potentials, corresponding to 4.5−4.6 eV of LUMO level, than other alkyl derivatives. When the (TTF)(TCNQ) salt was used as S-D electrodes, 9×10^{-5} cm^2 V^{-1} s^{-1} of mobility was achieved in air. Ni bis(o-diminobenzosemiquinonate) complex (**7e**) was reported as p-channel material.[156] Because of the very narrow band gap of this material, Noro et al.[157] were able to fabricate an ambipolar transistor using Ca electrodes and a PMMA dielectric layer. The electron mobility of the device reached to 1.6×10^{-2} cm^2 V^{-1} s^{-1} with 4.3×10^{-3} cm^2 V^{-1} s^{-1} of hole mobility under N_2 atmosphere. These Ni complexes have square-planar cores which may have been favorable for charge-transport-capable crystal packing. Structures of these metal complexes are shown in Chart 7.

In light of the long history of $F_{16}CuPc$ as an n-channel material, there has been continued interest in metal phthalocyanines. However, most of these have been p-channel. In 2008, Song et al. reported the phthalocyanato tin(IV) dichloride ($SnCl_2Pc$) as the n-channel material.[158] They achieved the electron mobility of 0.30 cm^2 V^{-1} s^{-1} and the on/off ratio of 10^6 in air for an OFET with a para-sexiphenyl (p-6P)-modified SiO_2 dielectric layer. After storage in air for 45 days, the mobility was still as high as 0.12 cm^2 V^{-1} s^{-1}.

Metal complexes have been less reported as n-OSCs than other classes. Generally, they require more effort for purification using sublimation than small organic molecules because of their high melting points. However they are still promising as n-OSCs and the exploration of them including the synthesis of new metal complexes for n-OSCs is needed. Collaborative research between organometallic chemists and device physicists is necessary, as has been done for OLEDs and dye-sensitized solar cells (DSSCs).

Chart 7. n-Channel Metal Complexes



9. Molecular Subunits for n-Channel Polymers

n-Channel polymers are a relatively unexplored class of materials that are of great interest for printable inks and other low-cost processing techniques.[159] A key question is: would conjugated or nonconjugated (side chain) polymers be preferred? Does the electron hop from subunit to subunit or rather travel through an extended conjugated pathway? By increasing the conjugation length, the HOMO level increases as the LUMO level decreases, possibly resulting in the material being ambipolar (or p-type) because of the lowering the ionization potential of the π-system. The main mode of attack toward n-type behavior in polymers is to simply link together known n-type carbonyl-containing and fluorous subunits with as few linkage atoms as possible, hoping that the resultant material performs well.

Diimide-based polymers are the most investigated and have been obtained in three ways: (1) Suzuki or Stille couplings of dibromo PTCDI[160,161] and NTCDI[161,162] with (oligo)thiophene units; (2) condensation of NTCDA or PTCDA with a bis(1,2-diamino) subunit to form the O1$-$O4 substituted subunit;[39,40] or (3) radical polymerization of an asymmetric PTCDI acrylate.[163,164] A unique dithienylated 7-membered diimide monomer unit was developed by Letizia et al.[165] Izuhara et al. synthesized a water-soluble n-type polymer that relies on the formation of pyridinium subunits, postpolymerization, for both n-type behavior as well as a desired solubility profile.[166] The most promising polymers are the NTCDI-based ones from the Facchetti group with electron mobilities of $0.45-0.85$ cm^2 V^{-1} s^{-1}.[167]

10. Circuits and Functional Devices with n-Channel Organics

Properties of n-channel materials can be chemically tailored to meet specific need in numerous applications in various devices. Discussion on fabrication and characterization of the electronic components is beyond the scope of this article. Here we simply list some important examples applying n-channel organics.

A. Complementary Circuits. Organic circuits have mostly been made with unipolar circuits, where a constant cross-current results in extra power consumption. In complementary circuits, the electric current is blocked by one of the two transistors, and the switching current flows mostly internally, so complementary circuits can be operated with less energy, higher speed, and greater circuit stability. The realization of low-power complementary circuits requires suitable n-channel components with electrical properties that match with those of well-developed, high-performance p-channel materials.

Complementary circuits with larger-scale integration and operation speed of 1 kHz was achieved by incorporating p-type α-sexithiophene (α-6T) with n-type F_{16}CuPc.[168] The combination of p-channel pentacene and n-channel F_{16}CuPC yields low-voltage (between 1.5 and 3 V) OTFTs in complementary circuits with low power consumption (less than 1 nW per logic gate), enabling battery-powered devices.[169]

B. Sensors. Currently, most sensing applications are limited to the detection of small vapor analytes.[170] Small molecule organic semiconductors usually exhibit better stability in the detection of chemical vapors. A long fluoroalkyl substituted NTCDI has been used to build a sensor platform with a phenolic NTCDI receptor for the detection of nerve agent simulant dimethyl methylphosphonate (DMMP).[171] Other fluorinated aryl NTCDIs also demonstrated corresponding changes in saturation current, mobility, or threshold voltage upon exposure to dinitrotoluene (DNT), which serves as a simulant for the more hazardous trinitrotoluene (TNT).[172]

Most organic semiconductors, even for those with high stability in ambient environment, would experience a baseline drift due to gate bias stress. To avoid device recalibration, a ring oscillator sensor circuit, consisting of n-channel F_{16}CuPc and p-channel didodecyl α-sexithiophene (DDα6T), has been shown to operate with a frequency response independent of the current drift.[173] For biosensing using OTFTs, a substrate is usually exposed to an analyte solution and then dried.[174] This becomes a challenging goal for n-type materials because of their incompatibility with water.

C. Diodes. A diode is an important component in radio frequency identification (RFID) tags, solar cells, and light-emitting displays. Two organic diodes were fabricated by combining n-channel PTCDA with p-channel polypyrrole (PPy) or poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS).[175] Both NTCDA/PPy and NTCDA/(PEDOT:PSS) diodes showed breakdown voltages of about 9 V and rectification ratios exceeding 4×10^3. The incorporation of p-channel P3HT and n-channel 5FPE-NTCDI (NTCDI with substituent **2n**) provides sufficient lateral charge carrier mobilities, allowing the operation of diodes with lateral layouts.[176] The large uncovered surface of the heterojunction in lateral diodes and the tunable surface potential through the additional gate terminal enables the observation of the potential across organic p-n interface with the simultaneous measurement of charge transport.

D. Solar Cells. The state-of-the-art organic solar cells consist of a bulk-heterojunction active layer based on electron-donating poly(3-hexylthiophene) (P3HT) and the electron-accepting fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). Although numerous PCBM derivatives have been developed and applied with various fabrication methods and material combinations,[177,178] most of them show poorer photovoltaic performance, and only a few show comparable or slightly better properties. The commercially available PCBM remains one of the most popular electron-accepting components. It is essential to realize more comprehensive understanding of the relationships between fundamental material properties (e.g., molecular orbital, solubility, and crystallinity), and resulting electrical performance including open-circuit voltage and short-circuit current.[179]

11. Conclusion and Outlook

There are fewer distinct molecular structures that lead to n-OSC films as opposed to p-OSCs, and that the stabilization requirements are somewhat more stringent for n-OSCs. However, it is clear from the broad range of compounds covered in this manuscript that a menu of choices for n-OSCs is available with performance as amorphous films, molecular crystal films, and polymers that is nominally equivalent to that of the well-established p-OSCs. Analogous processing options are also available, which is important for the fabrication of individual devices (solar cells, diodes, light-emitting devices) and complementary logic circuits that require both n-OSCs and p-OSCs to be deposited on monolithic substrates via processes that are minimally intricate and mutually nondestructive. Design rules for n-OSCs are now well-established, though further research into the simultaneous optimization of printability, stability, and charge carrier mobility is needed. Finally, applications where an inorganic n-channel material, which would generally have higher mobility and greater stability, should be substituted for an organic, should be considered carefully. Such situations might include the need for deposition via molecular solutions, the need for polymerlike mechanical properties, the requirement to avoid overly high temperature annealing, and the desire for electronic reporting of specific chemical interactions. Focusing on these kinds of application opportunities, the chemistry described in this review could be beneficially utilized. For a more detailed overview of the performance of many of the materials mentioned in this article, readers can peruse recent review articles.[32,180,181]

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