Lewis Acids and Bases as Molecular Dopants for Organic Semiconductors

Colin R. Bridges *,[a] , Thomas Baumgartner *,[a]

[a] Department of Chemistry, York University, 4700 Keele Street, Toronto, ON, M3J 1P3, Canada

email: cbridges@yorku.ca, tbaumgar@yorku.ca

KEYWORDS

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ABSTRACT

Controlling the concentration of charge carriers (mobile electrons and holes) in organic semiconductors is vital to precisely controlling their electronic properties. Significant efforts have gone into understanding how molecular dopants induce charge carriers in organic semiconductors. The most widely used doping mechanisms occur *via* electron transfer (i.e., oxidation or reduction of the semiconductor) or *via* reaction with a strong Brønsted acid. Recently, strong Lewis acids have been observed to induce p-type charge carriers in organic semiconductors with greater efficiency than classical dopants. The mechanism of Lewis-acid doping could not easily be unified with either classical doping methods and has been under intense scrutiny over the past 5 years. Very recently the Lewis-acid doping effects have been shown to be due to water impurities in commercial Lewis acids forming strong Brønsted acids. This means that many studies on doping using Lewis acids may be occurring *via* a Brønsted-acid doping mechanism. This recent revelation explains some observations in literature, but not all, and there are still unanswered questions. The nature of the Lewis acid and organic semiconductor can significantly impact the doping mechanism and the doping efficiency. Additionally, strong evidence for alternative doping mechanisms using Lewis acids not involving water have been shown. Lewis-acid doping has mostly been studied as a p-type dopant method on Lewis-basic polymers. There is growing literature showing Lewis bases can also act as n-type dopants, excluding Brønsted-acid doping as a possible mechanism. In this tutorial review, we will present a brief overview on molecular doping of organic semiconductors, survey the literature on p-type and n-type Lewis doping, outline several proposed mechanisms, and speculate on some possible mechanisms using literature observations.

1 INTRODUCTION

1.1 Doping inorganic and organic semiconductors

The doping of group 14 semiconductors like silicon is accomplished by introducing electron rich (group 15) or electron deficient (group 13) elements as lattice impurities. Herein, n-type doping serves to raise the Fermi energy, allowing for facile injection of mobile electrons into the conduction band. p-Type doping lowers the Fermi energy, bringing vacancies close to the valence band allowing for easy promotion of electrons from the valence band, forming mobile holes therein. [1-3] These mobile electrons and holes are n-type and p-type carriers, respectively. This method of adjusting the Fermi level allows precise control over the semiconductors' electronic properties, including charge carrier mobility, charge carrier concentration, polarity (p-type or n-type), and conductivity. The ability to precisely control the electronic characteristics of silicon semiconductors has made this technology incredibly versatile, and they have become ubiquitous in our lives over the past several decades. Semiconductors comprised of organic small molecules and polymers have been under investigation as alternatives to silicon, or as semiconductors for applications where silicon is not suitable (i.e., flexible, stretchable, or transparent applications). Analogous doping by introducing lattice impurities does not apply to organic semiconducting materials, leaving their carrier concentrations mostly intrinsic (~10^{16} cm^{-3}) and difficult to control. [4] This reality has severely hampered the function and versatility of organic semiconductors, thus far excluding them from applications where high carrier mobility or fine control over the charge carrier properties of circuit elements are vital. In an organic field-effect transistor it is relatively uncommon for a material to have a hole or electron mobility of over 1 $cm^2V^{-1}s^{-1}$, [5, 6] whereas silicon-based field-effect transistors can have mobilities in excess of 1000 $cm^2V^{-1}s^{-1}$. [7] This demonstrates the limitations of field-effect doping in controlling the charge carrier concentration of intrinsic organic semiconductors. Introducing dopants that increase the charge carrier concentration of organic semiconductors is critical to achieving higher mobility and conductivity. In addition, nearly all high-performance organic semiconductors show significant ambipolar character (i.e., hole and electron mobility of similar magnitude), and adding dopants as a method to suppress hole or electron mobility is crucial for achieving reliable on-off behavior in complementary-type devices and logic circuits. This combination of field-effect doping with molecular doping allowed for the fabrication of a high performance all-organic inverters, [8, 9] and indicates that combining doping methods may allow for organic semiconductors to be deployed in new applications. There has been incredible progress in understanding how the molecular structure of organic semiconductors impacts Fermi energy, [10] crystal structure, paracrystallinity, [11, 12] energetic disorder, [13, 14] intermolecular interactions, [15-17] transfer integrals, [18] and intrinsic traps/defects, [19, 20] and how all these factors in turn impact their charge carrier properties. Still, the doping of organic semiconductors has only a modest impact on the electronic properties compared to what is achievable in inorganic semiconductors. [21]

Molecular dopants for organic semiconductors have been studied for several decades, however their development has not matched pace with the development of intrinsic organic semiconductors. Doping organic semiconductors was first accomplished using small molecule oxidants such as AsF_5, Br_2 and I_2 vapors, which drastically improved conductivity of polyacetylene from $\sigma \sim 10^{-6}\ \Omega^{-1}\ cm^{-1}$ to $\sigma > 10\ \Omega^{-1}\ cm^{-1}$. [22] Such dopants suffer from being volatile and highly reactive, making it difficult to control their concentration and side reactions over time. As such they are unsuitable for the precision carrier concentration control required for modern semiconductors. Metal-based dopants like SbF_5 and $FeCl_3$ gained popularity as they were not volatile, allowing for constant doping levels over time. These dopants have largely orthogonal solubility to organic materials, so as organic semiconductors advanced from insoluble to soluble materials, it became difficult to find processing or doping methods where the doped polymer-inorganic metal complex would remain soluble, flexible, processable, and stretchable. [23]

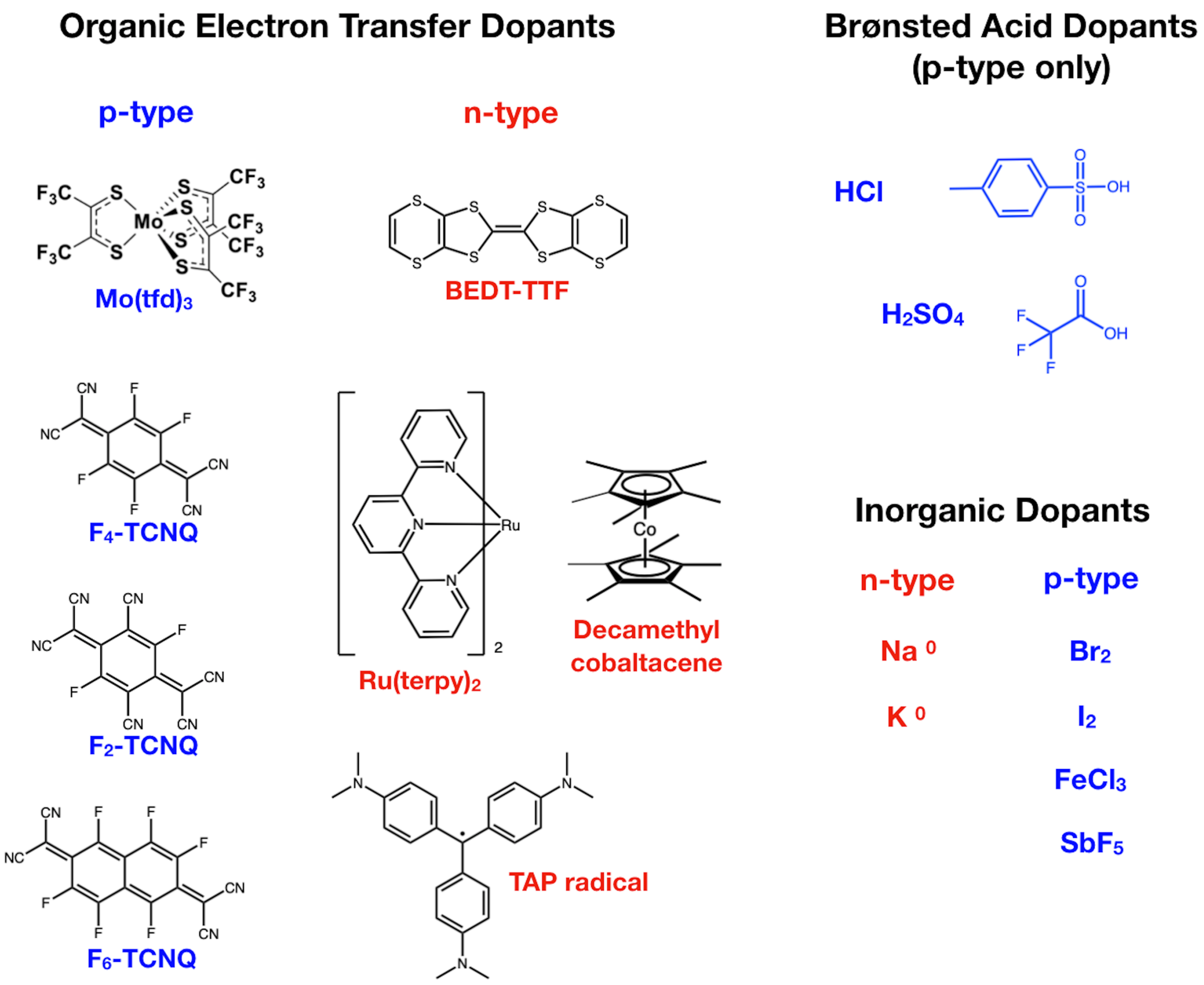


FIGURE 1 Examples of common dopants used for organic semiconductors. Adapted with permission from ref. 23. Copyright 2016 American Chemical Society.

1.2 Overview of doping mechanisms

Doping using Brønsted acids has been shown to significantly increase the conductivity of polymer films. In the case of Poly(ethylenedioxythiophene):Poly(stryrenesulfonate) (PEDOT:PSS), conductivity has been measured in the range of 100-1000 S/cm. [24] Its high conductivity and processability have made it perhaps the most widely used conjugated polymer in thin-film electronics. The mechanism for Brønsted-acid doping is not exactly known, making it difficult to maximize dopant efficiency using materials design. It is suggested that Brønsted-acid doping occurs via protonation, followed by hole transfer from the protonated species to a neutral species, thereby introducing a mobile radical cation (polaron) as a p-type dopant on the organic semiconductor (Figure 2C). [23] Due to this, Brønsted acids are exclusively p-type dopants, and the lack of an n-type equivalent limits its practical application. Fully organic dopants were developed in an attempt to achieve materials having better dopant integration into the organic matrix, as well as softer, more processable doped organic semiconductors. These dopants operate by donating or removing an electron from the material (oxidizing or reducing), inducing an n-type electron or p-type hole in the organic semiconductor. These charges delocalize and can act as mobile charge carriers, thereby acting as a method of controlling the concentration of p- and n-type carriers, along with all other electronic properties. A basic overview of doping mechanism is presented in this review for reference (Figure 2).

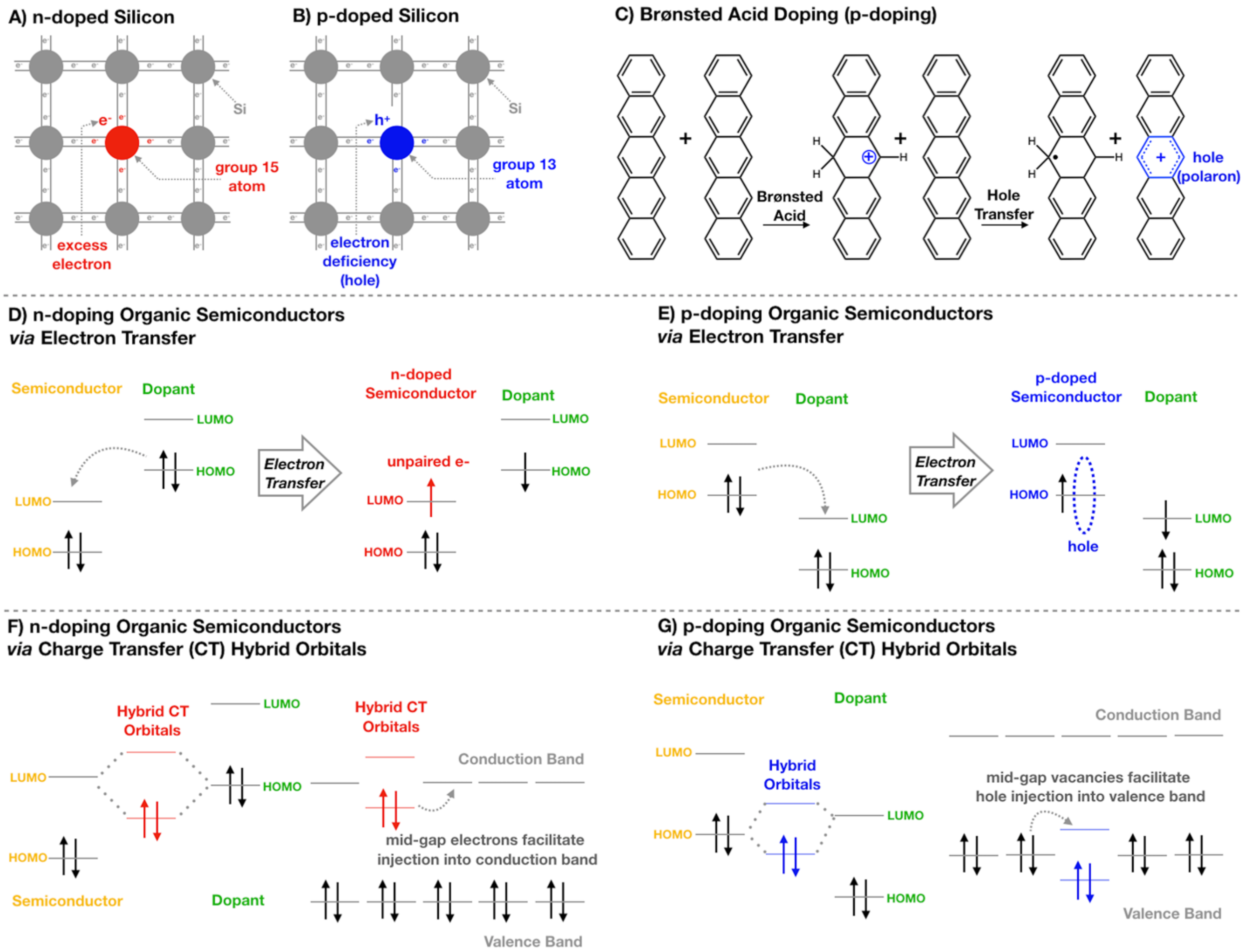


FIGURE 2 A simplified look at different doping mechanisms and their relation to doping in inorganic semiconductors (A, B). Brønsted-acid doping involves protonation and hole transfer between molecules (C). Adapted with permission from ref. 23. Copyright 2016 American Chemical Society. Electron-transfer doping involves oxidation or reduction of the organic semiconductor, and relies on offset HOMO and LUMO values for the dopant and semiconductor. This induces free holes or electrons in the material that contribute to the mobile carrier concentration (D, E). Charge-transfer doping involves hybridization of the HOMO and LUMO of the dopant and semiconductor, but does not necessitate that the HOMO be offset from the LUMO as in electron transfer doping. This hybrid orbital introduces mid gap states that are either filled (n-type) or empty (p-type), allowing facile promotion of an electron into the conduction band or induction of a hole into the valence band (F, G). Adapted with permission from ref. 28. Copyright 2017 John Wiley and Sons.

Briefly, for electron-transfer doping to occur, the HOMO-LUMO levels of the dopant and organic semiconductor need to be offset. For n-type doping, the HOMO of the dopant must be higher than the LUMO of the organic semiconductor for an electron to transfer to the conduction band of the organic semiconductor and become mobile. For p-type doping, the LUMO of the dopant must be lower than the HOMO of the organic semiconductor. This allows electron transfer from the valence band of the organic semiconductor to the dopant, inducing mobile holes therein (Figure 2D,E). Typically, these charge carriers will have distinct optical signatures, making absorption spectroscopy one of the simplest ways to observe doping in organic semiconductors. Since these charge carriers represent an unpaired electron, electron paramagnetic resonance (EPR) spectroscopy is a useful tool to quantify doping, with the resonance frequency and splitting allowing for structural assignment of the doped organic semiconductors. A similar mechanism to electron transfer requires frontier orbital hybridization between the dopant and organic semiconductor, creating mid-gap states in the organic semiconductor. This allows for promotion of electrons out of the valence band, or into the conduction band, inducing mobile holes in the valence band and mobile electrons in the conduction band (Figure 2F,G). A more advanced overview of these doping mechanisms is beyond the scope of this review; for in-depth reviews on the methods of quantification, analysis and mechanisms of doping for organic semiconductors, the readers are referred to the excellent reviews by Leo, Koch, and Moulé. [23, 25-28] It is important to note that while the presented data focus on measuring polarons using EPR and optical spectroscopy, these measurements do not capture all carriers. For instance, bipolarons are spin-less and would not show up using EPR measurements. For an in-depth discussion on the structure and detection of the various charge carriers in organic semiconductors we direct the reader towards an excellent review by Brédas et al. [29] Furthermore, not all carriers are necessarily mobile, and some induced carriers detected by EPR and optical spectroscopy will be bound due to limits in morphology, ion interactions, and dopant diffusion. In spite of these complications, studies discussed herein generally show that the mobile carrier concentration, mobility, and doping level strongly correlate with polaron concentration and dopant amount. Because of this, and due to limits in currently available data, the doping efficiency will be discussed in the context of the optical and EPR signatures of polarons.

There are many electron-transfer p-dopants in the literature, whereas designing electron-transfer n-type dopants has remained difficult due to the high reactivity of materials having such high HOMO levels. This remains a key roadblock in doping organic semiconductors. Organic dopants still cause organic semiconductors to aggregate in solution and often increase the melting point, preventing them from being easily processed into high-quality films. [26, 30, 31] Dopants are used to limited effect in organic transistors and organic light-emitting diodes (OLEDs), and advancing the materials, methods, and understanding of doping organic semiconductors is critical for improving their efficacy and advancing organic electronics as a whole.

2 DISCUSSION

2.1 Initial reports of Lewis acids as dopants

As doping moves beyond Brønsted-acid doping and oxidation/reductions, the effect of non-oxidative Lewis acid adducts on the electronic properties of organic semiconductors had been sporadically investigated. This is distinct from oxidizing Lewis acids like $FeCl_3$ or SbF_5 in that the impact on the electronic properties results from Lewis acids forming polarized π-adducts rather than integer electron transfer, and the Lewis-acid dopants do not have required HOMO-LUMO offsets to act as electron-transfer dopants. The first reports showed how vapor-doping with boron trifluoride could increase the conductivity of poly(p-phenylene vinylene) (PPV) in a similar magnitude to iodine vapors (Figure 3). [32] This study did not investigate the mechanism but speculated that BF_3 coordination to the vinylene group on PPV could induce a positive charge on the backbone, acting as a mobile hole. These results suggested Lewis-acid interactions could induce charge carriers in organic semiconductors *via* π-base:Lewis-acid interactions, making them potentially promising dopants.

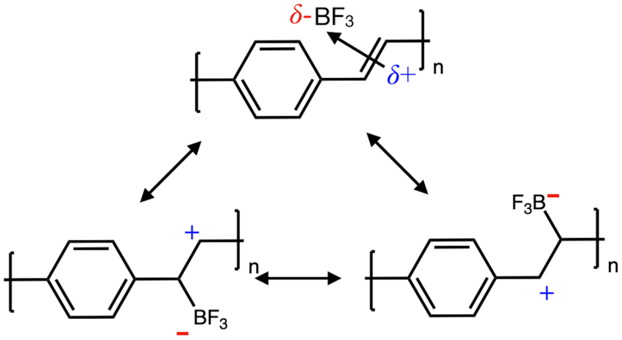


FIGURE 3 Proposed interactions between PPV and boron trifluoride inducing mobile holes in PPV. Adapted with permission from ref. 32 from The Royal Society of Chemistry.

2.2 Optical properties of Lewis acid complexes

Lewis acid complexes with organic semiconductors had not been investigated systematically until 2009, when Welch *et al.* introduced Lewis acids of varying strengths to conjugated oligomers consisting of alternating benzo-2,1,3-thiadiazole (BTZ) electron acceptors and dithienosilole electron donor units. [33] The authors found that a low-energy optical absorption increased monotonically with the addition of Lewis acids and the intrinsic oligomer absorbance decreased. This behavior indicates that a new chromophore is being generated with the addition of Lewis acids, and the low-energy absorbances suggest charge transfer or electron transfer in organic semiconductors. In this case, crystallography data revealed the Lewis acid coordinated to a single nitrogen on each BTZ unit with stoichiometric equivalence, and absorbance spectroscopy showed that stronger Lewis acids triggered the emergence of lower energy absorptions (Figure 4). Welch *et al.* extended this study to analogous alternating copolymers having cyclopentadithiophene donors with BTZ and pyridal[2,1,3]thiadiazole (pBTZ) acceptors. [34] Generally identical optical responses were observed upon Lewis-acid coordination, with the authors using ^{1}H-NMR and ^{19}F-NMR spectroscopy to show preferential binding to stronger Lewis-basic moieties (pyridyl nitrogens over thiazole nitrogens).

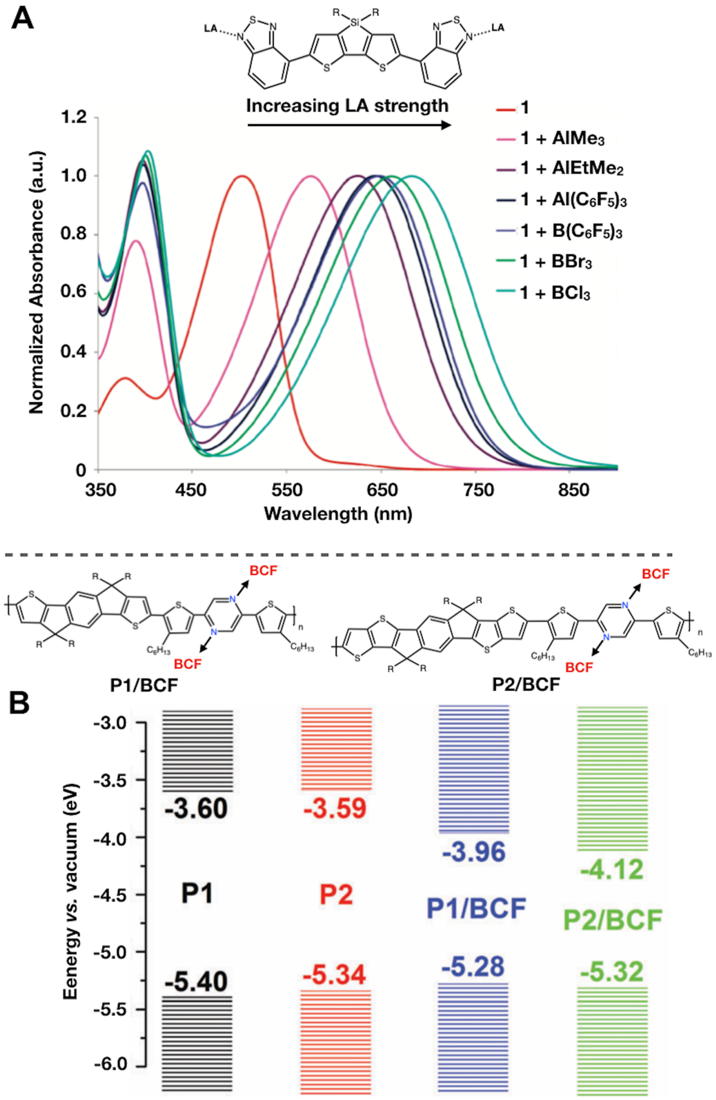


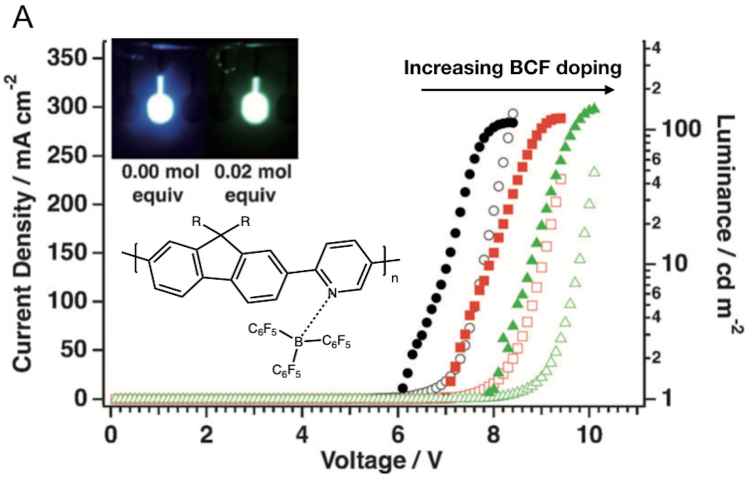
FIGURE 4 (A) Effect of Lewis-acid coordination on the optical properties of a conjugated oligomer. The magnitude of the red shift depends on the strength of the Lewis acid, R= 2-ethylhexyl. Adapted with permission from ref. 33. Copyright 2009 American Chemical Society. (B) Effect of Lewis-acid coordination on the HOMO and LUMO energies of Lewis-basic organic semiconducting polymers. Lewis-acid coordination lowers the LUMO energy but leaves the HOMO energy relatively untouched R = *p*-hexylphenyl. Reproduced with permission from ref. 36 from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry.

Further studies investigated how Lewis-acid coordination changed the energy levels of various Lewis-basic organic semiconductors using cycling voltammetry. In this case, $B(C_6F_5)_3$ (BCF) coordination lowered the LUMO, but mostly left the HOMO unchanged, thereby lowering the optical gap overall by almost 1 eV (Figure 4). [35, 36]

These results were shown to be fairly general, with quinoxaline [37] and azaisoindigo [38] showing substantial narrowing of their optical gap and lowering of the LUMO upon complexation. Polymers/oligomers based on diketopyrrolopyrroles, [39] fluorenes, [40] and thiophenes, [41] also show this effect when co-polymerized with Lewis-basic moieties like pyridine, BTZ, and pBTZ. Detailed computational studies showed that after Lewis-acid coordination, there was fractional charge transfer from the Lewis-basic organic semiconductor to the Lewis acid. This electron-withdrawing effect increased the strength of the electron accepting monomer (BTZ) via induction. This results in the slight raising of the HOMO but a much more significant lowering of the LUMO and was responsible for the low energy optical absorbance observed in previous studies. [42, 43] If the electron-withdrawing effect is strong enough, the computations indicated that positive charges could be induced within the material to act as mobile holes accounting for the observed doping. Whether or not this is the case is still unclear to date, as the impact of Lewis-acid coordination on the charge-carrier properties of organic semiconductors had not yet been investigated in depth.

2.3 Electronic properties of Lewis acid complexes

The first indication that Lewis-acid complexation could impact the carrier properties occurred in a 2011 paper by Zalar *et al.* Upon complexation with BCF, a new red-shifted emission peak emerged, along with an increase in turn-on voltage resulting from the BCF adduct having a lower HOMO, thus increasing the hole injection barrier (Figure 5). [44] Later, Huang *et al.* fabricated transistors using a mixture of copper phthalocyanine and BCF as thin-film transistors. [45] Upon exposure to ammonia vapors, BCF was transferred from the Lewis-basic transistor material (copper phthalocyanine) to the stronger Lewis base, ammonia. This significantly increased the mobility and current observed for these transistors, and these sensors were able to detect levels of ammonia as low as 0.35 ppm. These qualitative studies show a shift in electronic properties upon Lewis-acid complexation, suggesting that it directly impacts mobile carrier concentration and there may be a doping effect. In general, the mechanism of action for doping using Lewis acids is discussed as adding charge carriers (doping), but also filling low lying traps with low HOMO level materials. This reversible trap filling in the presence of stronger Lewis acids is what Huang *et al.* leveraged to use these blended materials as electronic ammonia sensors, and similar sensors have used blends of Lewis acids and organic semiconductors. [46] In this review we will focus on the doping effects of Lewis acids on organic semiconductors rather than trap filling.



B

Mol. Equiv. BCF	Mobility [cm^2 V^{-1} s^{-1}]	Activation Energy [meV]	Carrier Density [cm^{-3}]
0	3.2×10^{-5}	280	3×10^{15}
0.01	1.5×10^{-3}	210	5×10^{17}
0.02	2.5×10^{-3}	190	1×10^{18}
0.05	1.5×10^{-3}	200	4×10^{18}
0.10	8.2×10^{-4}	200	4×10^{18}
0.25	3.1×10^{-5}	270	3×10^{18}

FIGURE 5 Effect of increasing Lewis-acid coordination on the color, electroluminescence, and turn on voltage of a Lewis-basic polymer, R = n-octyl (A). Figure A adapted with permission from ref. 44. Copyright 2012 John Wiley and Sons. Impact of Lewis-acid coordination on the hole mobility and carrier concentration of Py-DTS (B). The Lewis acid-base interaction in Py-DTS induces holes, causing an increase in hole mobility. Figure B adapted with permission from ref. 47. Copyright 2013 John Wiley and Sons.

Zalar *et al.* later quantified this effect by showing that BCF could increase the mobile carrier concentration in an organic semiconducting polymer having alternating monomers of Lewis-basic pyridine and dithienosilole (DTS-Py). The authors fabricated thin-film transistors of DTS-Py with varying degrees of BCF added (0.01 to 0.25 monomer equivalents), which increased the hole mobility by two orders of magnitude and decreased the activation barrier to charge transport (Figure 5). [47] At higher than 0.1 molar equivalents of BCF, the mobility was observed to decrease, as the morphology of the semiconductor was disrupted. The carrier concentration increases to a concentration of 4 x 10^{18} cm^{-3} with increasing BCF incorporation, close to 2 orders of magnitude higher than the carrier concentration of intrinsic (undoped) organic semiconductors. These results are hallmarks effects of p-doping on charge transport, and firmly show that Lewis acids can be used as p-dopants in conjugated polymers. Perhaps the most interesting result is that BCF-doped polymers are EPR silent, meaning there are no unpaired electrons. The currently understood mechanisms of doping for organic semiconductors using Brønsted acids and single electron transfer to generate unpaired electrons are present in the form of polarons, giving these materials strong EPR signals and broad, low-energy absorbances in the infrared region. The BCF-doped Lewis-basic organic semiconductor displays neither of these optical indications of classical p-doping despite the electronic properties indicating these materials are strongly p-doped. This suggests that Lewis acids may be used as effective dopants for organic semiconductors, and that they operate *via* a different mechanism than electron transfer.

Poverenov *et al.* compared Lewis-acid doping with electrochemical doping using alternating copolymers of 3,4-ethylenedioxythiophene (EDOT) and BTZ. The polymers were first p-doped by electrochemical oxidation, giving them the expected broad infrared (IR) absorptions that signify polarons (Figure 6). [48] The exact same behavior was seen when doping with BF_3, and to a lesser extent, when using the weaker Lewis acid triphenylborane. While no EPR data were obtained, the conductivity increased in these materials by a similar magnitude for electrochemical and Lewis-acid p-doping. Importantly, strong Brønsted acids did not impact the optical or electronic properties of these polymers, indicating that Lewis-acid coordination is critical for achieving this p-doping effect. The authors termed this approach “non-oxidative doping” since they did not expect any formal electron transfer to BF_3 from the polymer.

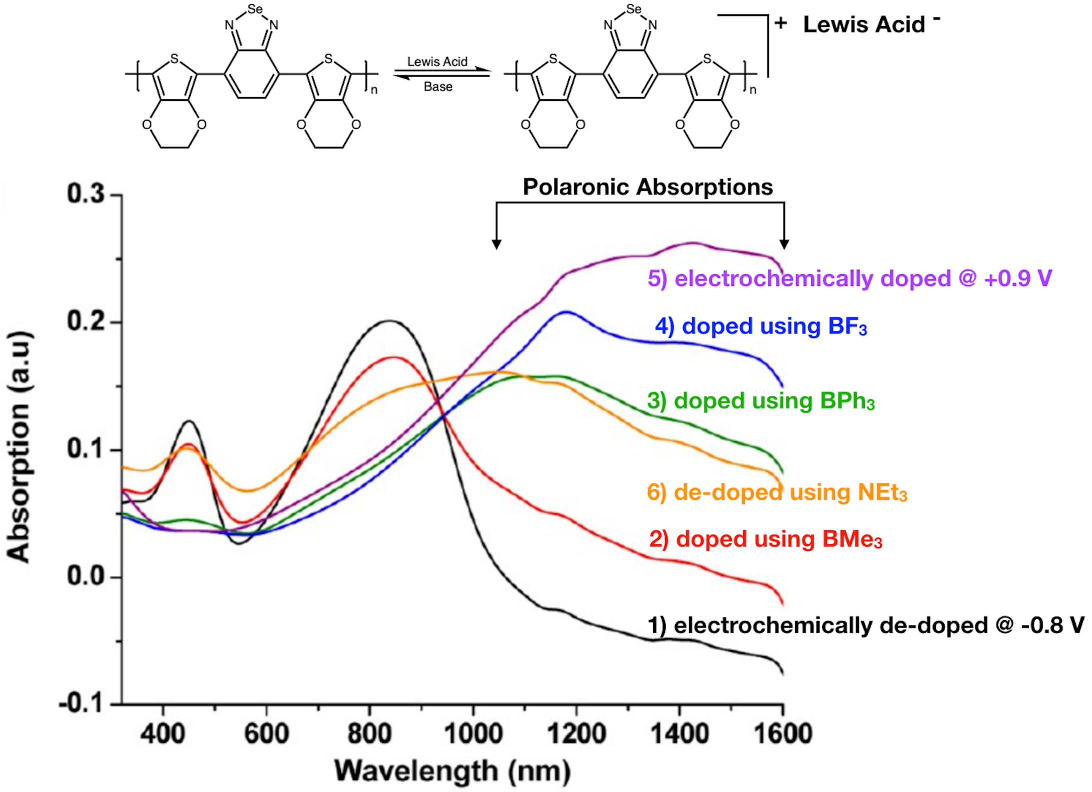


FIGURE 6 Optical properties of a donor-acceptor alternating polymer after electrochemical oxidation, Lewis-acid coordination, electrochemical de-doping, and Lewis-base de-doping. Strong polaronic absorptions indicate radical cations are induced by both electrochemical doping (oxidation) and Lewis-acid coordination, pointing to similarities in their mechanism. Adapted with permission from ref 48. Copyright 2014 American Chemical Society.

Later, Yan *et al.* showed how BCF-doped organic semiconductors displayed electronic p-doping and that the mechanism was not occurring *via* the traditional electron-transfer mechanism. The authors designed a Lewis-basic polymer using alternating indenopyrazine and thiophene repeat units (PIDT) designed to interact with Lewis acids, but also to lower the HOMO energy such that this polymer would not readily be doped using oxidative (electron-transfer) mechanisms.[49] Between 0 equivalents and 0.1 equivalents of BCF, the hole mobility increases by an order of magnitude, and the threshold voltage decreases significantly as more dopant is added (Figure 7). The Fermi energy (E_F) of PIDT was found to decrease from -4.34 eV to -5.14 eV, stabilizing close to the HOMO of PIDT. Lowering of the Fermi energy is an unambiguous sign of p-doping that had yet to be observed using Lewis acids. Collectively these results are typical of organic semiconductors doped *via* electron transfer. The key requirement for p-doping *via* electron transfer is that the HOMO of the organic semiconductor must be higher than the LUMO of the p-dopant (BCF). The low-lying HOMO of PIDT (-5.8 eV) means even some of the strongest organic p-dopants like F_4-TCNQ (LUMO = -5.2 eV) would not undergo electron transfer with it. The LUMO of BCF is significantly higher than any of the dopants used in electron-transfer doping (-3.2 eV), and in theory it should not participate as a p-dopant. [50] Since significant p-doping is definitely observed, the authors propose an alternate mechanism whereby Lewis-acid coordination to pyrazine causes strongly electrophilic "pyrazinium like" cation, though whether it is formally cationic is unknown. This complex significantly decreases the LUMO of the affected monomer to the extent that empty molecular orbitals now form within the band gap of the bulk semiconductor, leading to the facile promotion of electrons from the valence band, thereby inducing a hole resulting in the observed p-doping effect. This doping mechanism has been extensively described by Méndez *et al.*, who showed that complexes pulling electron density out of organic semiconductors could result in fully mobile charges at relatively low dopant incorporation by forming polarized π-complexes, termed charge transfer doping. [27, 51] Qualitatively these observations are similar to what Zalar *et al.* observed using BCF as a dopant for electroluminescent materials, [44, 47] both showing increased hole mobility and hole concentration without having any formal electron transfer.

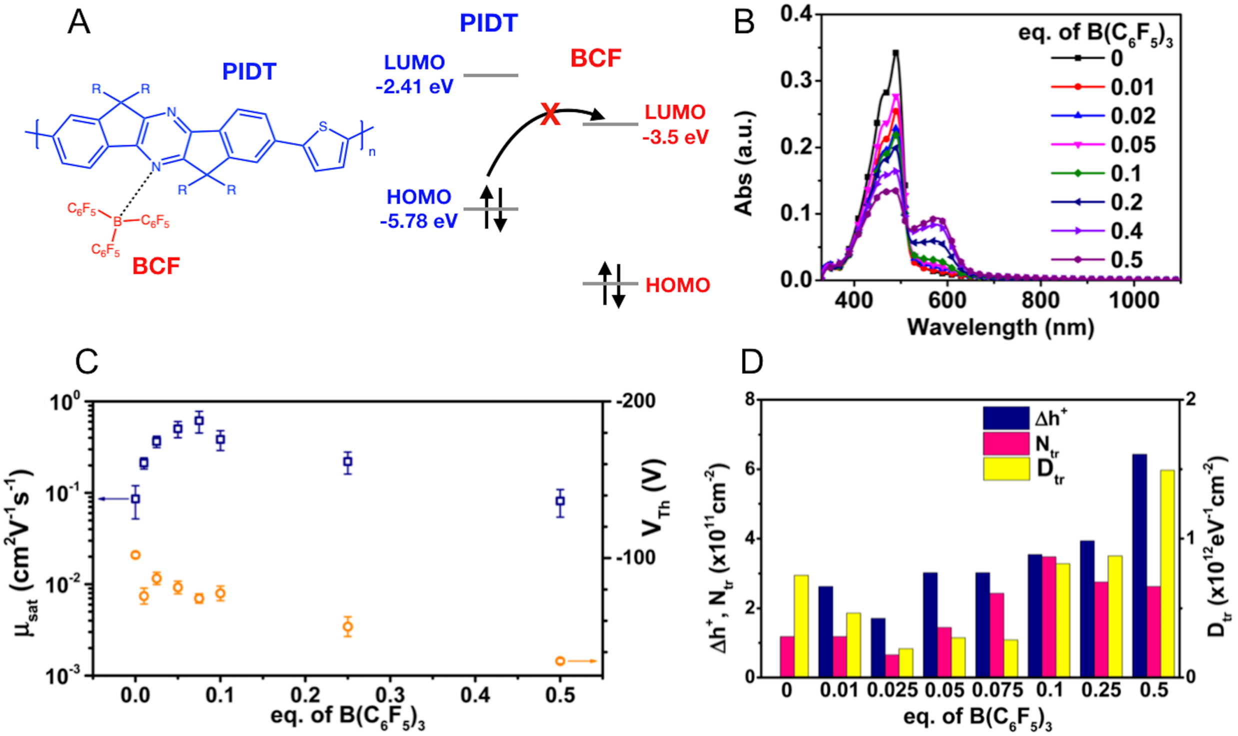


FIGURE 7 PIDT interactions with BCF showing how electron transfer is not favored (A). The impact of Lewis-acid coordination on the optical properties (B), hole mobility and electronic properties (C), and concentration of holes (h^+), interfacial traps (N_{tr}) and total traps (D_{tr}). BCF coordination does not induce free carriers as polarons *via* electron transfer, but clearly increases the measurable amounts of holes, and significantly increases the hole mobility of PIDT. R = n-$C_{16}H_{33}$. Adapted with permission from ref. 49. Copyright 2015 American Chemical Society.

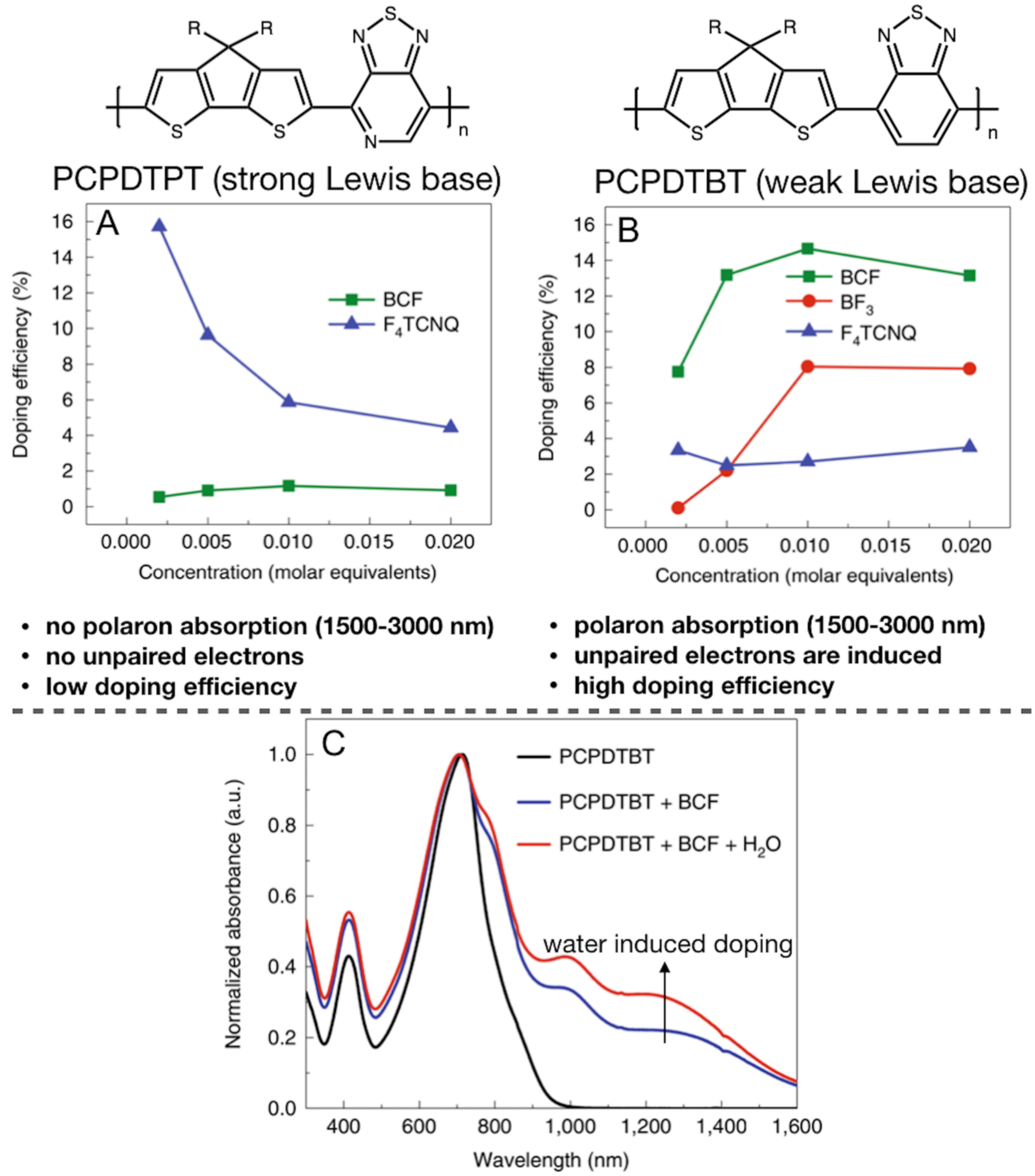
Until now, mechanistic studies have occurred on polymers having Lewis-basic sites (i.e., pyridyl or thiazole nitrogen atoms), and charge carriers were thought to have been formed *via* hybrid orbitals formed due to B-N coordination. Pingel *et al.* studied Lewis-acid doping on poly(3-hexylthiophene) (P3HT), where the sulfur can be considered only a weak Lewis base that does not bind strongly with BCF. [52] They found that F_4-TCNQ and BCF induce mobile holes with 18% efficiency, that polaron concentration correlated strongly with mobile holes concentration, and that BCF-doped materials have more mobile charge carriers. Despite similar p-doping effects, the presence of F_4-TCNQ anions show electron-transfer doping and BCF anions are not detected. In the absence of a Lewis-basic site, BCF may be acting as a Lewis acid and P3HT as a π-base with non-specific π-interactions facilitating the p-doping effect similar to what was observed with BF_3 and BCF (*vide supra*). [32]

Improved understanding of Lewis-acid doping has translated directly to the improved function of organic electronic devices like OLEDs, solar cells, and thin-film transistors. [44, 47] BCF and copper(II)hexafluoroacetylacetonate were used as soluble p-dopants in solution processable hole transporting layers, effectively increasing their p-type conductivity. This directly gave rise to an enhanced current, power output, and long-term stability in the OLEDs, [53] and improved the power conversion efficiency of solar cells from 6.25 % to 13.93 %. [54] Lewis-acid interactions have also been shown to suppress phase separation in blended materials, thus allowing for better mixing of the electron donors and electron acceptors in solar cells. [55, 56] This led to BCF and $Zn(C_6F_6)_2$ being used synergistically as dopants and morphology modifiers in transistor consisting of the Lewis-acid dopant, polymer, and small molecule organic semiconductors. [57, 58] These effects combined have allowed for transistors having hole mobilities in excess of 20 $cm^2V^{-1}s^{-1}$, among the highest values reported date.

The obvious functional improvements Lewis acids gave to organic electronic devices drove interest but attempts to understand the mechanism have been met with inconsistent results. P-doping is evidenced by an increase in conductivity/carrier mobility or an increase in carrier concentration, however the optical signatures of p-type carriers (polarons) are not always present. Zalar *et al.* [44, 47] and Han *et al.* [49] observed that their p-doped materials were EPR silent and did not show broad IR absorbances indicative of polarons, whereas Poverenov *et al.* [48] and Pingel *et* *al.* [52] showed distinct broad IR absorbances upon p-doping, and Pingel *et al.* showed EPR signals that increased with BCF content. The fact that the signatures of electron-transfer doping (i.e., polaronic optical absorptions and strong EPR signals) are present with mismatching HOMO-LUMO levels that do not allow for electron transfer further confuse the results. These differences in doping mechanisms using the same dopants are problematic. Lewis acids have proven to be some of the most effective dopants to date, but without understanding the underlying mechanism further optimization will be blind.

2.4 Overlap between Lewis-acid doping and Brønsted-acid doping mechanisms

Yurash *et al.* made significant steps toward understanding the Lewis-acid doping mechanism after systematically studying a variety of strong Lewis acids, Brønsted acids, and electron-transfer dopants with organic semiconducting polymers having strong (PCPDTPT) and weak (PCPDTBT) Lewis-basic sites (Figure 8). The authors measured the doping efficiency for each class of organic semiconductor by comparing the degree of polaronic absorption in the IR, change in EPR signal, increase in conductivity, and number of free carriers induced as a function of dopant concentration. [59] They found that Lewis acids can be more effective p-dopants than electron-transfer dopants and Brønsted-acid dopants, and that the performance of Lewis acids depended on the Lewis basicity of the organic semiconductor. BCF coordination with a strong Lewis-basic organic semiconductor-like PCPDTPT resulted in a new localized, red-shifted absorbance that did not appear to be polaronic. This was coupled with marginal increases in EPR signal, conductivity, and carrier concentrations that lagged far behind what was observed when using the electron-transfer dopant, F_4-TCNQ. These results indicate no p-doping, and BCF is impacting the optical properties but not the charge carrier concentrations. Organic semiconductors having a weak Lewis-basic site showed a broad absorbance in the IR indicating the presence of polarons. Free carriers were confirmed by an increasing EPR signal upon doping. The authors also observed that as more Lewis-acid dopant was added, the conductivity increased significantly, and the number of free carriers and doping efficiency were higher than what was induced *via* electron transfer doping using F_4-TCNQ. This shows BCF is acting as an effective p-dopant. Combined, these results indicate that strong Lewis acid-base interactions interrupt the doping mechanism, and effective doping was only present when a strong Lewis-basic site on the material was absent (Figure 8).



- **no polaron absorption (1500-3000 nm)**
- **no unpaired electrons**
- **low doping efficiency**

- **polaron absorption (1500-3000 nm)**
- **unpaired electrons are induced**
- **high doping efficiency**

FIGURE 8 Impact of Lewis-acid doping on the optical and electronic properties of organic semiconducting polymers having different Lewis basicity. The strong Lewis-basic polymer shows low doping efficiency for the Lewis acid compared to F_4-TCNQ (A), and no polarons are induced when BCF is added. The weakly Lewis-basic polymer shows higher doping efficiency with BCF than F_4-TCNQ (B), and strong polaronic absorptions in the IR. The addition of water to PCPDTBT doped with BCF induces more charge carriers, indicating Brønsted acid doping is occurring after complexation with BCF forms a strong acid (C). Adapted with permission from ref. 59. Copyright 2019 Springer Nature.

The doping effects observed in the weak Lewis-basic material were identical to those observed for electron-transfer doping. Given that the HOMO and LUMO levels were not matched for electron transfer to occur, the authors sought alternative mechanisms that could induce polarons in organic semiconductors. One clue was found when the addition of water to BCF-doped materials caused an increase in the optical and electronic properties expected for p-doped materials (Figure 8C). BCF can interact with water to form a strong acid. This BCF-H_2O complex can act as a Brønsted-acid dopant, which the authors suggest occurs *via* the following mechanism: First, BCF-H_2O protonates the organic semiconducting polymer backbone forming a BCF-OH anion and localized cation on the polymer backbone. Second, a neutral polymer transfers an electron to the positively charged monomer, giving two polymers: a neutral protonated radical and a delocalized cationic radical having a BCF-OH counterion (Figure 9A). It is this delocalized cationic radical polaron that is responsible for the observed p-doping effects (polaronic optical absorption, increase in conductivity and free carriers). This mechanism is corroborated using electron-nuclear double resonance spectroscopy (ENDOR), confirming the experimental spectra matches the predicted paramagnetic species produced by the Brønsted acid doping mechanism (Figures 9B and 9C). This indicates BCF alone is not the dopant, that water impurities are critical to forming the BCF-H_2O active dopant, and that this doping mechanism relies on electron transfer from a neutral semiconductor to a protonated semiconductor. Hydrated Lewis acids are highly effective at controlling the p-type conductivity of organic semiconductors, and this method is promising for future applications.

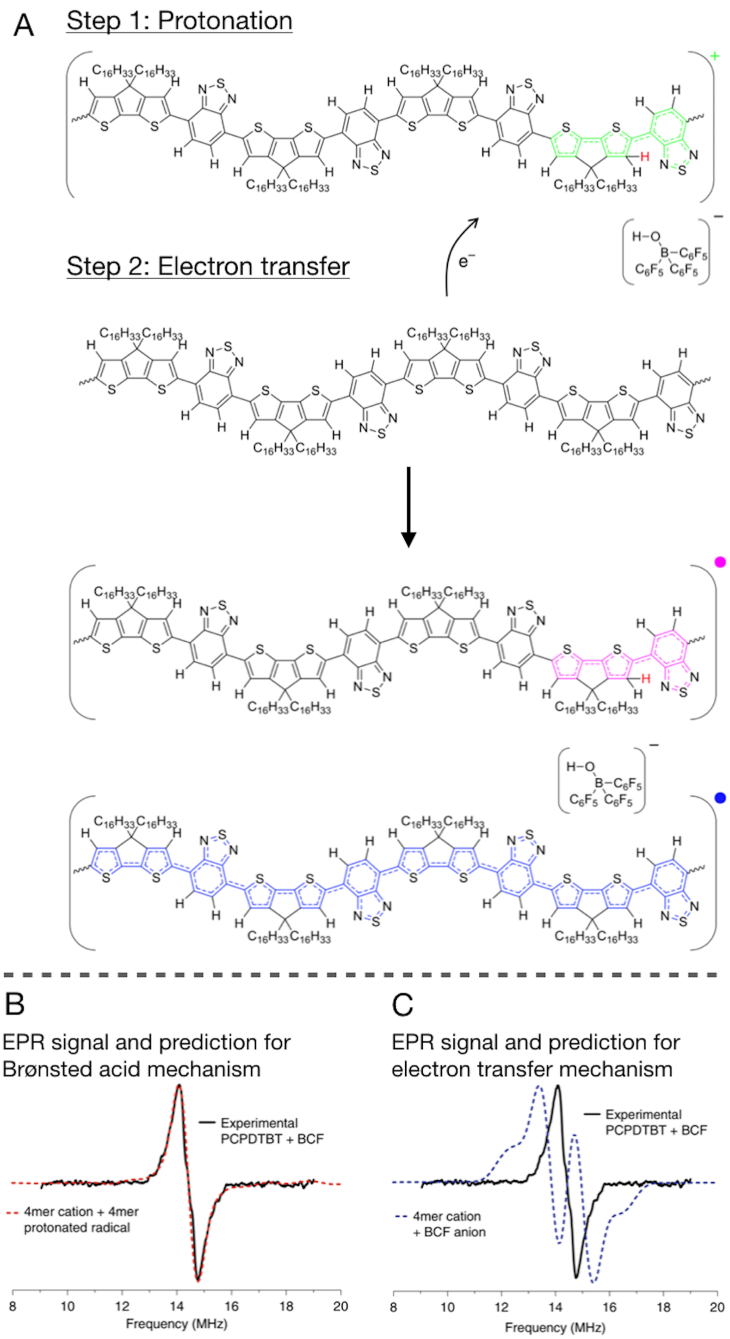


FIGURE 9 Proposed mechanism for the Brønsted-acid doping of PCPDTBT using BCF with water impurities (A). This mechanism is reminiscent of proton doping and is supported using calculated and experimental ENDOR spectra. Calculated polarons being consisting of a PCPDTBT radical cation, a BCF anion, and a PCPDTBT protonated radical match experimental results closely (B), whereas calculated polaron structures with a BCF anion and PCPDTBT cation do not match experimental spectra (C). Adapted with permission from ref 59. Copyright 2019 Springer Nature.

2.5 Possible alternative mechanisms for Lewis-acid doping

The result mentioned above is surprising. It indicates that the Lewis-acid doping effect is due largely to water impurities, and the mechanism of action is identical to that of Brønsted-acid doping. It is also somewhat discouraging since Brønsted-acid doping is limited to p-type doping, indicating there may not be an analogous n-type doping mechanism using Lewis bases. The fact that water increases the doping levels of polymers having excess Lewis acids is definite proof that this water complex is responsible for the observed p-doping effect, and that Lewis acids are promising as Brønsted acid dopants warranting further study. Other studies are not as definitive, and there still may be a case for Lewis acids being p-dopants *via* alternative mechanisms. BCF is a more effective dopant than strong Brønsted acids (HCl and trifluoroacetic acid) and F_4-TCNQ, which induces polarons with nearly 100% efficiency. [52, 60] This would require BCF to contain close to 100 mol % water impurities to form the necessary amount of the active BCF-H_2O dopant. [61] BCF and other strong Lewis acids are commonly used as catalysts wherein water would deactivate or decompose the Lewis acid, thus BCF and other Lewis acids are readily purchased in their anhydrous form and are compatible with Schlenk techniques or glove boxes. Because of this, water impurities may not be attributable to all the p-doping for all previous studies using different Lewis acids.

Alternative mechanisms for Lewis-acid doping not using water are supported by surveying literature results. Yurash *et al.* showed strong coordination of BCF to Lewis-basic polymers prevented the BCF-H_2O Brønsted-acid dopant from forming, thereby preventing p-doping. In contrast, Zalar *et al.* [44, 47] and Han *et al.* [49] showed that strongly Lewis-basic polymers doped with BCF definitively displayed p-doping effects on their electronic properties without the optical signatures for a protonated or delocalized cation intermediate. Poverenov *et al.* [48] showed that

Lewis acids could act as p-dopants for a non-Lewis basic organic semiconductor using triphenylborane and boron trifluoride. These Lewis acids decompose in water without forming strong Brønsted acids, making it unlikely that a highly acidic Borane-H_2O complex is doping the material *via* Brønsted acid doping.

Taken together, these results indicate Lewis acids may have separate impacts on the electronic structure of organic semiconductors depending on the presence of water. Some studies have shed light on anhydrous mechanisms by which Lewis acids can p-dope organic semiconductors. As shown in a previous section, Han *et al.* [49] used Lewis-acid coordination to pyrazine to create an electrophilic “pyrazinium like” cation. This complex was hypothesized to induce empty molecular orbitals within the band gap of the bulk semiconductor, allowing for easier injection of mobile holes into the valence band (Figure 10A). [51]

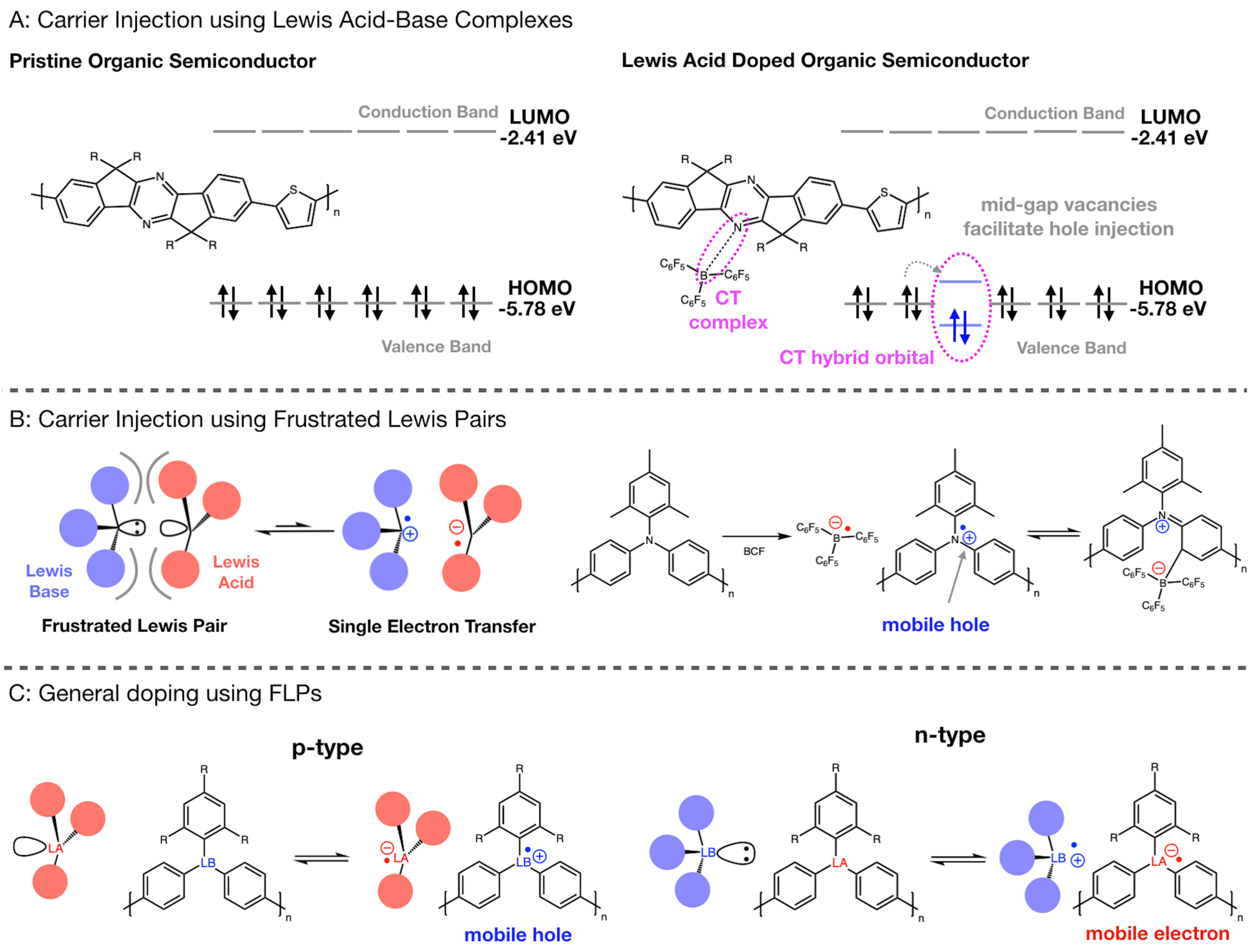


FIGURE 10 Proposed mechanism for p-type doping using BCF interactions with a Lewis-basic organic semiconductor using hybrid CT orbitals. Electrons can be promoted from the valence band of the material to the vacant mid-gap orbitals, facilitating hole injection into the valence band (A). Proposed mechanism for doping using FLPs, which exist as an equilibrium between sterically hindered Lewis pairs, and an ion pair resulting from single electron transfer (B). Adapted with permission from ref. 65. Copyright 2017 Elsevier. FLP doping is observed using a pair of sterically hindered Lewis pair: PTAA and BCF (B). Adapted with permission from ref 62. Copyright 2019 American Chemical Society. A general scheme showing how FLP doping using an organic semiconductor and a bulky Lewis acid (LA) or base (LB) could result in mobile electrons or holes being injected into the organic semiconductor (C).

Later, Ye *et al.* showed that BCF coordination to poly(triarylamine) (PTAA) increased the number of mobile holes in the material, and studied the complex using ^{11}B and ^{1}H NMR. [62] They observe PTAA proton signals become shifted downfield, indicating BCF is withdrawing electron density from the hydrogen atoms. Due to steric bulk on BCF and PTAA, a direct B-N adduct cannot form, rather a frustrated Lewis pair (FLP) having a BCF radical anion and a triphenylamine radical cation is first formed. [63-65] This FLP with stronger ionic character is postulated to be the mechanism of injection of positive carriers into PTAA (Figure 10B). The BCF anion was confirmed using ^{11}B NMR spectroscopy, and this FLP ion pair is supported by previous studies looking at FLPs. [63-65] A radical cation induced by an FLP on PTAA is certainly expected to contribute to the mobile hole concentration in an organic semiconductor. This mechanism does not seem to suggest a protonated BCF-H_2O intermediate, but rather only requires Lewis acid-base interactions. While this mechanism does formally suggest electron transfer, the HOMO of PTAA is significantly lower in energy than the LUMO of BCF indicating electron transfer is not energetically favorable. [50, 66] FLP interactions have been shown to catalyze many reactions so it may be possible that the FLP interaction allows for this type of electron transfer to occur, since single electron transfer between FLPs with mismatched energy levels has been shown. [65, 67] Using FLPs to induce mobile charge carriers in organic semiconductors has not garnered further study, but this phenomena may have been observed in previous studies on PTAA interactions with Lewis acids. [58] Thinking of FLPs as dopants offers new and potentially valuable insight into molecular design principles that could govern this type of doping (Figure 10C).

2.6 N-type doping using Lewis bases

If Lewis acids coordinating to organic semiconductors can act as p-dopants through mechanisms related to FLPs, orbital hybridization, or highly polarized π-complexes, then an analogous n-type mechanism should exist for strong Lewis bases. N-type Lewis-basic doping could be incredibly important for controlling the carrier properties of organic semiconductors, since designing stable n-type dopants using the electron-transfer mechanism has been challenging. Herein, a strongly electron-donating moiety such as a lone pair or anion should be able to interact with conjugated systems and impact the carrier properties and designing such molecules may be easier than designing stable n-type electron transfer dopants.

Indeed n-type doping using Lewis bases has been observed, though there has been little systematic work in understanding how to improve this doping mechanism. Guha *et al.* first studied this in depth with perylene diimide (PDI) derivatives interacting with anions of varying Lewis basicity (*e.g.*, fluoride, iodide, and hydroxide). [68] Normally, these types of Lewis base π-acid interactions are weak enough that they do not impact the charge carrier properties of organic π-systems. This study showed for the first time that electron-deficient organic semiconductors can act as strong enough π-acids such that strong Lewis bases can act as n-dopants (Figure 11). When mixed with fluoride ions, PDI derivatives showed optical absorbances and EPR spectra distinct for radical anions of PDI. The authors looked at PDI derivatives of varying π-acidity and anions of varying Lewis basicity, and showed that the magnitude of n-doping depended on both the strength of the π-acid and Lewis base. While fluoride ions are not typically expected to reduce PDI due to the high electronegativity of fluorine, the authors discussed in depth how the electronegativity of an element does not correlate to the Lewis basicity of its ion in aprotic solvents. The authors observed that aprotic conditions were required for the n-doping effect to occur. This keeps stabilization of the anion *via* solvation to a minimum, and the electron donating abilities of anions are determined solely by their Lewis basicity. This study did not measure any electronic properties of n-doped PDI derivatives, however π-acid:Lewis base interactions were observed earlier on a PDI having tethered ammonium hydroxide groups. In this case, hydroxide is acting as a Lewis-basic n-dopant and the conductivity of intrinsic PDI films increases by more than five orders of magnitude as the concentration of ammonium hydroxide-PDI increased (Figure 12). [69] The exact mechanism was not investigated therein, but when combined with the later work by Guha *et al.,* shows how Lewis-basic dopants can be powerful n-type dopants for organic semiconductors. Russ *et al.* extended this work and showed hydroxide doped PDI was a high-performance thermoelectric material, having the high conductivities and the highest power factors observed for any n-type organic thermoelectric material. [70]

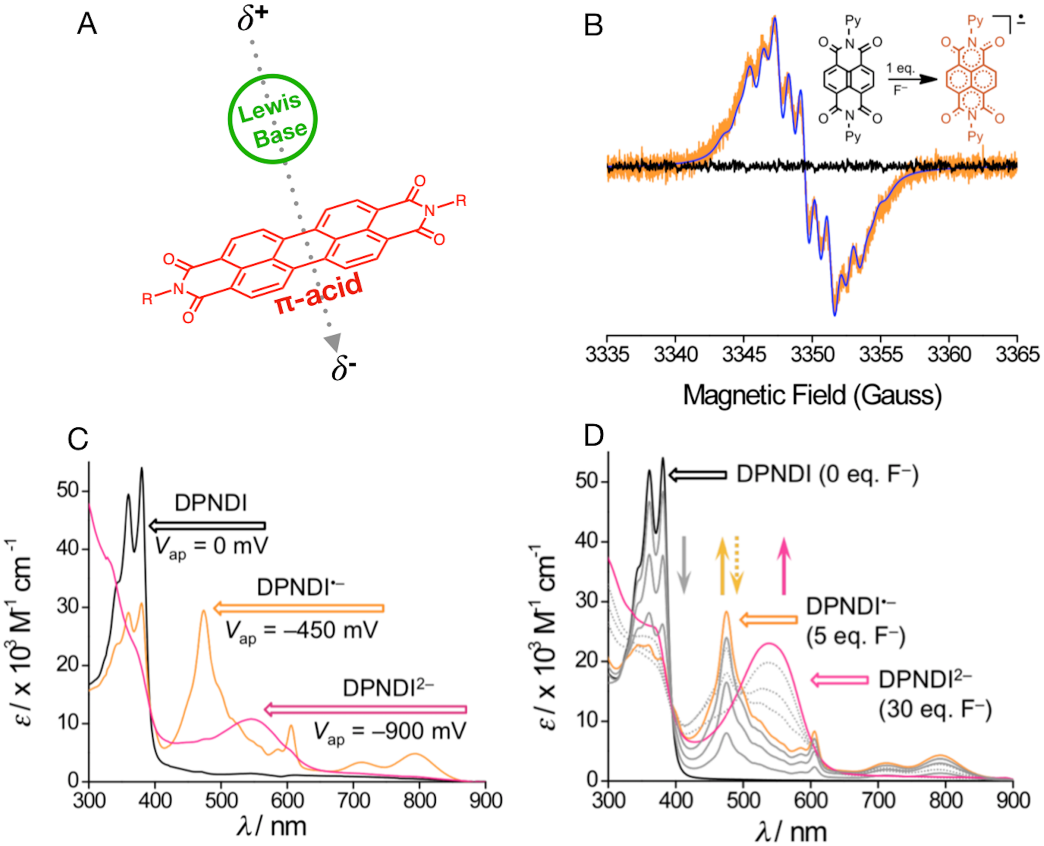


FIGURE 11 Diagram showing how Lewis bases interact with π-acidic organic semiconductors (A). EPR spectra of a strongly π-acidic PDI derivative after interactions with fluoride anions (B). Optical absorbance of a PDI derivative that has been n-doped *via* electron transfer using an applied potential (C) and *via* interaction with a Lewis base (D). The low energy absorbances indicate radical anions and a dianion form upon reduction, which are the same absorbances seen after Lewis base interactions. This indicates Lewis base-π-acid interactions induce n-type charge carriers in the same way as electron transfer. Reproduced with permission from ref. 68. Copyright 2012 American Chemical Society.

Kim *et al.* measured the output characteristics of thin-film transistors as a practical method of measuring the transport properties of carriers induced by Lewis base doping. The authors used TBAF and TBAOH as sources of fluoride and hydroxide for an organic semiconducting polymer having a π-acidic PDI backbone. [71] TBAF and TBAOH cause the Fermi energy of the organic semiconductor to rise, unambiguously showing that these Lewis bases are acting as n-type dopants. This was coupled with a change in optical absorption, and most notably the electron mobility and conductivity showed a monotonic increase with Lewis base dopant up to 0.5 wt. %; a decrease in turn-on voltage and an almost complete turn-off of any hole mobility was also observed (Figure 12). This is the first measured incidence of an organic semiconductor showing ambipolar transport being converted to a solely n-type transistor using Lewis-base doping. These results are akin to n-doping in classical silicon semiconductors and show Lewis-base doping facilitates the formation of free n-type charge carriers in organic semiconductors.

Russ *et al.* later extended Lewis-basic doping to a variety of electron-deficient organic semiconductors (fullerenes, diketopyrrolopyrroles, naphthalene diimides) and showed that weaker Lewis bases like the lone pair on tertiary amines were still strong enough to induce this type of π-acid Lewis base doping interaction. [72] This n-type doping effect has since been generally observed with π-acidic organic semiconductors in transistors and solar cells using a variety of anions including lithium benzoate, [73] hexafluorophosphate, [74] borates, [75, 76] acetates, [77] and all tetrabutylammonium-halogen salts. [78, 79] In all cases the performance of these devices was shown to increase due to expected increases in conductivity and carrier concentration consistent with n-type doping.

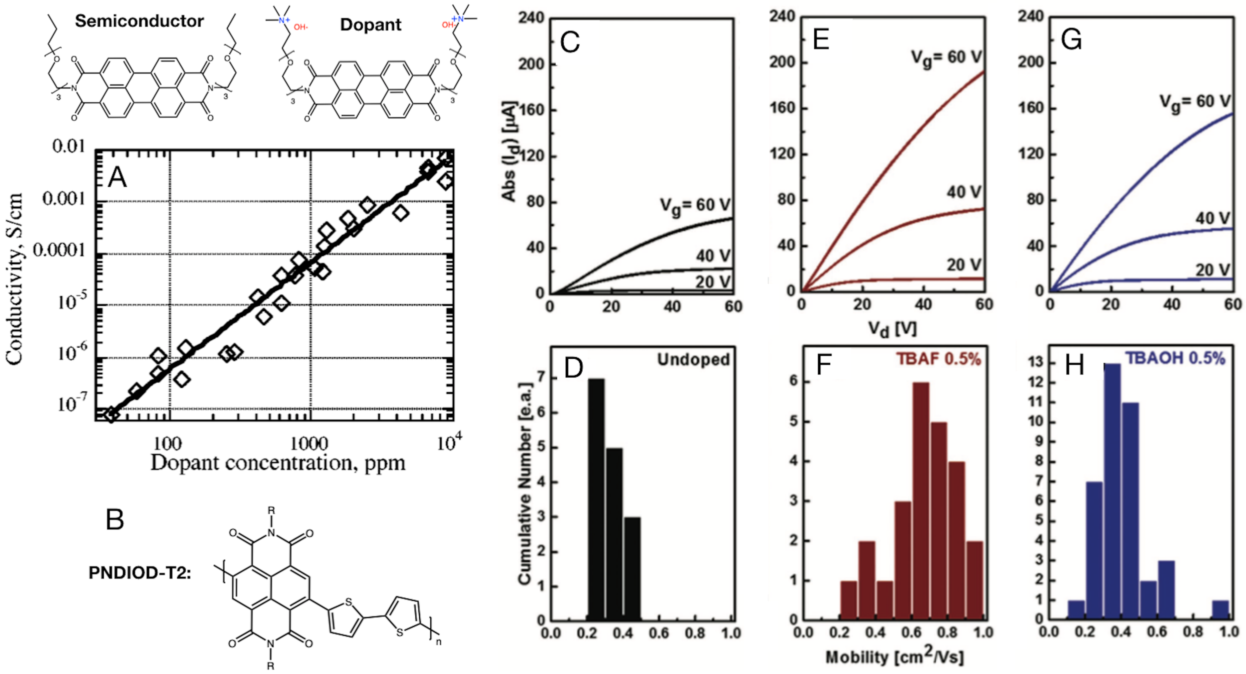


FIGURE 12 Conductivity of a PDI film with increasing amounts of PDI having a tethered hydroxide ion acting as an n-type dopant (A). Reproduced with permission from ref. 69. Copyright 2001 American Chemical Society. The conductivity increases by over 5 orders of magnitude as the dopant concentration increases from 1 ppm to the 1 mol %. Performance of PNDIOD-T2 (B) as an undoped transistor (C, D), and as a transistor n-doped using TBAF (E, F) and TBAOH (G, H). R = 2-octyldodecyl. The pristine material exhibits moderate hole mobility and lower n-type current. Upon doping, significant increases in electron mobility and n-type current are observed. Reproduced with permission from ref. 71. Copyright 2016 John Wiley and Sons.

P-type doping using Lewis acids was shown to occur using π-bases (electron rich π-systems) and Lewis bases incorporated into organic semiconductors, while n-type doping using Lewis bases has so far been shown only to occur through π-acid-Lewis base interactions. Overall the mechanism for Lewis-basic n-dopants has been less controversial, and most results seem to confirm the concept of organic semiconductors acting as π-acids with Lewis bases to account for the n-doping effect *via* induction or orbital hybridization. This mechanism is analogous to initial observations with Lewis-acid doping and does lend credence to the idea that organic semiconductors can also act as π-bases when combined with strong Lewis acids to induce p-type carriers in materials. Both the p-doping and n-doping effects have been only recently observed, and further optimization of organic semiconductors as π-acids and exploration of more structurally diverse Lewis bases is required to fully realize how Lewis acids and bases control the carrier concentration of organic semiconductors.

3 Conclusions

It has been difficult to find direct analogues for doping organic semiconductors that followed the same rules for p-type and n-type semiconductors. In silicon, free electrons and holes can be injected by doping with electron-rich or electron-deficient elements. In organic semiconductors, Brønsted-acid doping only allows for p-type doping. Doping using hydrated Lewis acids has emerged as a promising alternative to Brønsted acid doping and seems to be more effective at controlling the p-type electronic properties of organic semiconductors. Electron-transfer doping allows for both p-type and n-type doping, but it is incredibly difficult to find stable n-type dopants via the electron-transfer mechanism due to the high HOMO levels required for the dopants. Lewis-acid/base doping may be the closest analogue for doping that we observe for organic semiconductors in that it seems to be applicable to both p-type and n-type doping and it has been observed using Lewis acids and Lewis bases centered on group 13 and 15 elements. Indeed, Lewis acids and bases have recently been observed to be some of the most effective p-type and n-type dopants available for organic semiconductors. The exact mechanism is still open for debate, but some studies show Lewis acids may be reacting with trace water impurities to form strong Brønsted-acid dopants. Under anhydrous conditions Lewis doping may occur as either electron donation or electron withdrawal from a π-system forming highly polarized complexes. These polarized π-complexes form filled or vacant hybrid orbitals within the HOMO-LUMO gap of the organic semiconductor, allowing for facile injection of p-type or n-type charge carriers. There is still significant work to be done; only a few organic semiconductor scaffolds have been explored as π-acids or π-bases and relatively few Lewis acids or bases have been explored. With all these successes, there are some open questions regarding Lewis doping: since p-doping was observed using a Lewis-basic organic semiconductor and Lewis acid, can n-doping be achieved using a Lewis-acidic organic semiconductor and a Lewis base? This is especially relevant to the notion that FLPs can be used to induce mobile charge carriers on organic semiconductors, and whether the doping is p-type or n-type would depend on the organic semiconductor being either a frustrated Lewis acid or a frustrated Lewis base (Figure 10C). To date, π-acids have been optimized for n-doping using Lewis bases, whereas considering organic semiconductors as π-bases has not been explored as a method of optimizing p-doping using Lewis acids. Most importantly: how does the accumulation of polarized π-complexes result in free carriers? Mechanisms suggesting mid-gap orbitals appearing as a result of Lewis-base doping could accomplish this, but this has yet to be directly observed. Designing organic semiconductors that are optimized to act as π-acids or π-bases may increase the efficiency of this class of doping. Lewis acids may be the critical missing piece in the somewhat mysterious lack of doping efficacy for organic semiconductors compared to elemental doping in inorganic semiconductors. The future of Lewis acid/base doping will hopefully allow for more fine control over the carrier properties of organic semiconductors and allow them to fulfill the huge potential they showed over the past few decades.

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AUTHOR INFORMATION

Corresponding Authors

*Email Thomas Baumgartner: tbaumgar@yorku.ca
*Email Colin Bridges: cbridges@yorku.ca

Conflicts of interest

There are no conflicts to declare.

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AUTHOR BIOGRAPHIES:

Colin Bridges graduated in Materials Chemistry from the University of British Columbia, and received his Ph.D. in Polymer Chemistry from the University of Toronto (2015). Since then he has worked in the Materials Research Lab at the University of Santa Barbara, California researching the structure and thermodynamics of liquid crystalline semiconducting polymers for thin film transistors, and at York University researching the electronic properties of organophosphorus compounds and their applications in energy storage. His current research interests are doping organic semiconductors, energy storage, and the electrochemistry of heteroatom containing aromatics.

Thomas Baumgartner received his Ph.D. degree in 1998 from the University of Bonn, Germany, working in the group of Edgar Niecke. From 1999 to 2002 he was a postdoctoral fellow at the University of Toronto with Ian Manners. Afterwards, he started his independent career as habilitand at the University of Mainz and RWTH Aachen University, Germany under the mentorship of Jun Okuda before moving to the University of Calgary, Canada in 2006. Since 2017, he is a Full Professor and Canada Research Chair at York University, Toronto, Canada. His research interests are focused on molecular organophosphorus π-conjugated materials, as well as supramolecules and polymers for sustainable energy applications.

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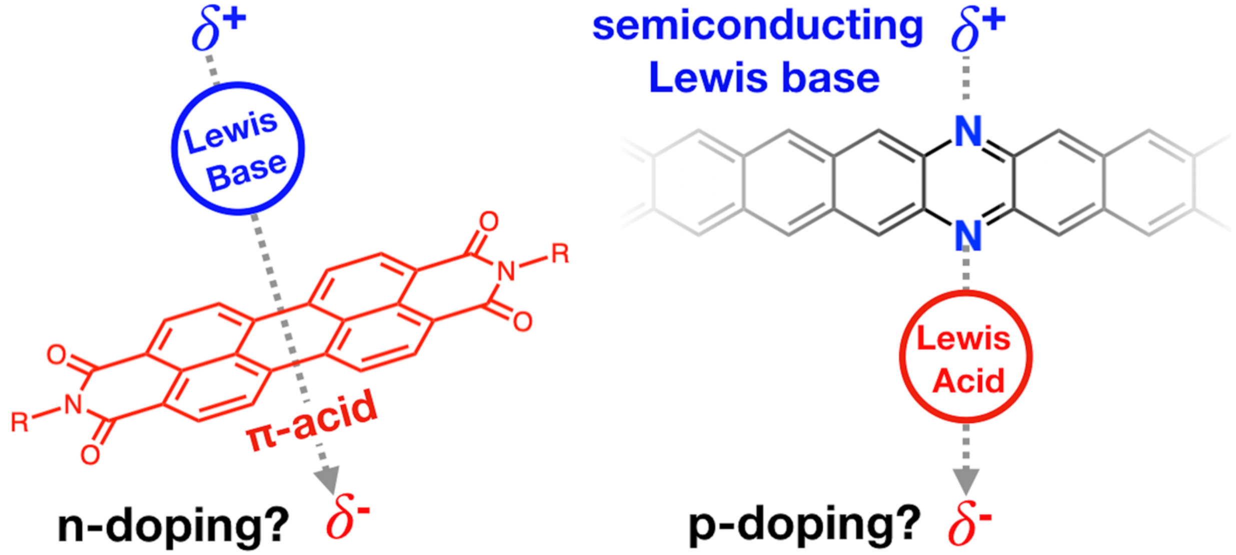
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