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Anion-Induced Electron Transfer

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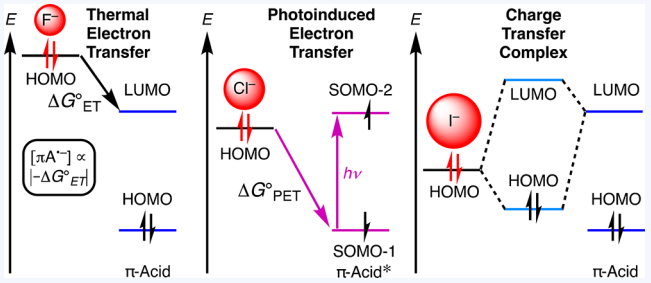
CONSPECTUS: As counterintuitive as it might seem, in aprotic media, electron transfer (ET) from strong Lewis basic anions, particularly F^-, OH^-, and CN^-, to certain π-acids (πA) is not only spectroscopically evident from the formation of paramagnetic $\pi A^{\bullet -}$ radical anions and πA^{2-} dianions, but also thermodynamically justified because these anions' highest occupied molecular orbitals (HOMOs) lie above the π-acids' lowest unoccupied molecular orbitals (LUMOs) creating negative free energy changes ($\Delta G^\circ_{ET} < 0$). Depending on the relative HOMO and LUMO energies of participating anions and π-acids, respectively, the anion-induced ET (AIET) events take place either in the ground state or upon photosensitization of the π-acids. The mild basic and charge-diffuse anions with lower HOMO levels fail to trigger ET, but they often form charge transfer (CT) and anion−π complexes. Owing to their high HOMO levels in aprotic environments, strong Lewis basic anions, such as F^- enjoy much greater ET driving force (ΔG°_{ET}) than mild and non-basic anions, such as iodide. In protic solvents, however, the former become more solvated and stabilized and lose their electron donating ability more than the latter, creating an illusion that F^- is a poor electron donor due to the high electronegativity of fluorine. However, UV−vis, EPR, and NMR studies consistently show that in aprotic environments, F^- reduces essentially any π-acid with LUMO levels of −3.8 eV or less, revealing that contrary to a common perception, the electron donating ability of F^- anion is not dictated by the electronegativity of fluorine atom but is a true reflection of high Lewis basicity of the anion itself. Thus, the neutral fluorine atoms with zero formal charge and F^- anion have little in common when it comes to their electronic properties. The F^- anion can also legitimately act as a Brønsted base when the proton source has a pK_a lower than that of its conjugate acid HF (15), not the other way around, and ET from F^- to a poor electron acceptor is not thermodynamically feasible. While there is no shortage of indisputable evidence and clear-cut thermodynamic justifications for ET from F^- and other Lewis basic anions to various π-acids in aprotic solvents, because of the aforesaid misconception, it had been posited that F^- perhaps formed diamagnetic Meisenheimer complexes via nucleophilic attack, deprotonated an aprotic solvent DMSO against an insurmountably high pK_a (35) leading to a π-acid reduction, or formed [$F^-/\pi A^{\bullet +}$] complexes via a thermodynamically prohibited oxidation of π-acids. Unlike AIET, however, none of these hypotheses was thermodynamically viable nor supported by any experimental evidence.

First, by defining the thermodynamic criteria of AIET pathways and all other alternate hypotheses and then evaluating the spectroscopic signals emanating from the interactions between different anions and π-acids and Lewis acids in the light of these criteria, this Account comes to a conclusion that AIET is the only viable mechanism that can rationalize the reduction of π-acids without violating any thermodynamic rules. The paradigm-shifting discovery of AIET not only exposed a common misconception about the electron donating ability of F^- but also enabled naked-eye detection of toxic anions, electrode-free silver plating, luminescent silver nanoparticle synthesis, light-harvesting, and conductivity enhancement of conjugated polymers, with more innovative applications still to come.



INTRODUCTION

Electron transfer (ET) from an anion to a π-acid is thermodynamically feasible when the anion's highest occupied molecular orbital (HOMO) lies above the ground-state lowest unoccupied molecular orbital (LUMO) or the photogenerated singly occupied molecular orbital-1 (SOMO-1) of the π-acid (Figure 1) creating a negative free energy change ($\Delta G^\circ_{ET} < 0$). Although ET from dithionite, carboxylate, and iodide anions has been long known,[1−3] that from a strong Lewis basic anion, F^- was deemed counterintuitive based on a common misperception that F^- was such a strong electronegative species that it could not donate an electron. Yet, study after study[4−20] unequivocally showed that in aprotic environments where anions are not solvent-stabilized, highly Lewis basic F^-, OH^-, and CN^- anions routinely reduced various π-acids (Figure 2) to paramagnetic $\pi A^{\bullet -}$ radical anions and sometimes to πA^{2-} dianions, whereas the less Lewis basic halides failed to do so. Although these observations were at odds with the common perception, they actually shined a bright spotlight on an obvious but oft-overlooked fact: while neutral fluorine atoms with a zero formal charge are electronegative, the free F^- anion is not, because it can no longer accept or accommodate another electron. Despite originating from the most electro-

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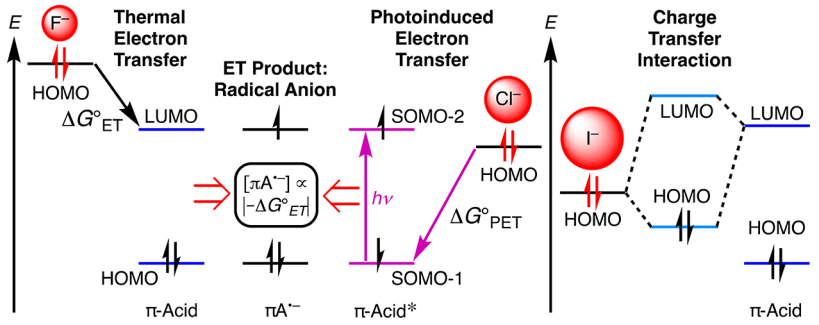

Figure 1. Relative energies of HOMOs of different anions and LUMOs of π-acids depicting thermal ET, PET, and CT complex formation.

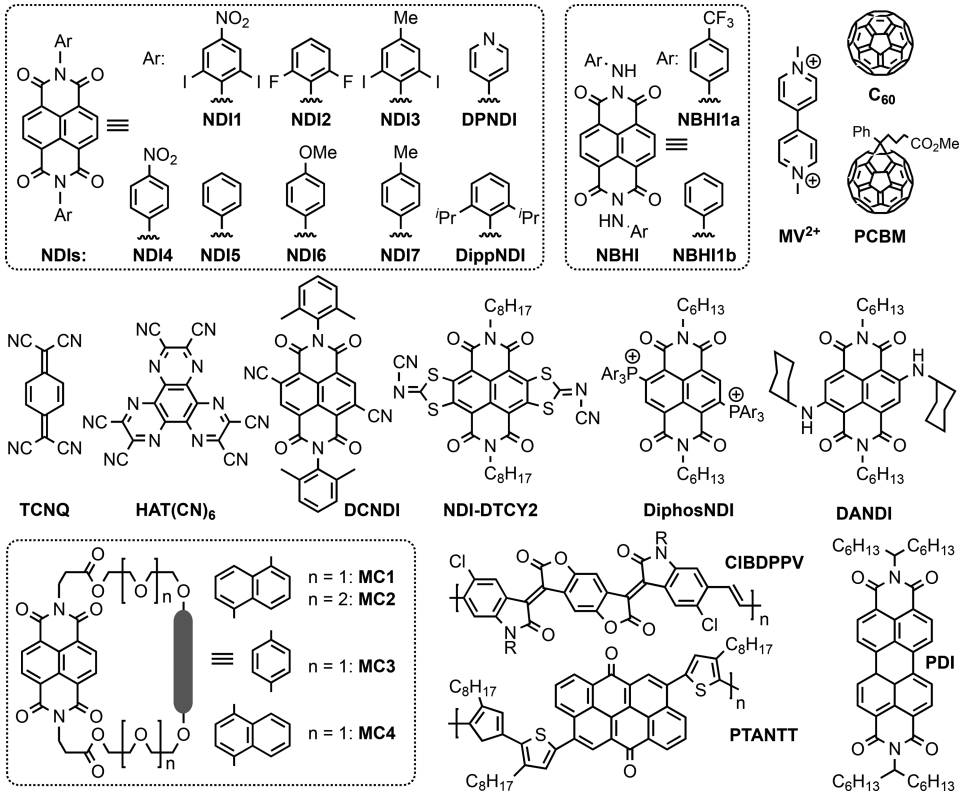

Figure 2. π-Acids that undergo ET from F^- and other Lewis basic anions.

Table 1. Calculated[13] HOMOs of Anions (in MeCN) and Experimental LUMOs of π-Acids[a]

anions	HOMO[13]	π-acids	LUMO	π-acidsπ-acids	LUMO	π-acids	LUMO
OH^-	−3.3	$HAT(CN)_6$	−4.9[13]	NDI-DTCY2	−4.3[15]	NBHI	−3.9[6]
F^-	−4.3	TCNQ	−4.8[14]	ClBDPPV	−4.2[17]	PDI	−3.9[9]
Cl^-	−5.3	C_{60}	−4.5[14]	NDI1	−4.1[8]	NDI7	−3.8[8]
Br^-	−5.3	PCBM	−4.4[14]	DPNDI	−4.0[4]	DANDI	−3.5[11]
I^-	−5.1	DCNDI	−4.4[8]	MV^{2+}	−3.9[5]	PTANT	−3.4[18]

[a]Values in eV. The calculated HOMO levels of anions are systematically underestimated, but the trend holds true.

negative element fluorine, F^- is one of the most Lewis basic anions because it is more difficult for a small F^- anion to accommodate the extra electron than for larger anions, such as Br^- or I^-. For the same reason, HF is the weakest halogen acid, because F^- forms almost a covalent bond by sharing its extra valence electron with a H^+.

By definition, the stronger Lewis bases have higher HOMO levels and hence, better electron donating ability. Ballester's *in silico* experiments[13] verified this fact by showing that in MeCN, the HOMO levels of anions indeed follow their Lewis basicity trend (Table 1): $OH^- > F^- > Cl^- \approx Br^- \approx I^- > HF_2^-$; that is, F^- does enjoy almost 1 eV greater ET driving force than I^-, a well-known electron donor. Evidently, in a given group of the periodic table, it is the Lewis basicity of anions dictated by their size, not the electronegativity of parent elements, that regulates the anions' HOMO levels and electron donating ability. This is particularly true in aprotic media where they remain naked or sparingly solvated. In water and other strong H-bond forming solvents, the smaller F^- anion with a greater charge density becomes disproportionately more solvated and

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stabilized than the larger charge-diffused anions, losing its electron donating ability more than the latter. To put it in perspective, while the relatively naked F^- anion enjoys a 0.8 eV higher HOMO level than I^- in MeCN,[13] the former becomes ~2.2 eV more stabilized than the latter in water because of their respective hydration energies: −123 and −73 kcal/mol. Thus, their electron donating ability is reversed in water, creating an illusion that F^- would always be an inferior electron donor because of its presumed electronegativity. However, this is not true in aprotic media where the electron donating ability of anions is dictated by their intrinsic HOMO energies, which closely follow their Lewis basicity trend.

The discovery of anion−π complexes[21] in the early 2000s and the subsequent emergence of CT complexes[22−24] involving anions and π-acids inspired us to explore the possibility of formal ET from anions to π-acids because CT and ET interactions belong to the same energy landscape and emerge depending on the HOMO and LUMO levels of electron donors and acceptors, respectively.[25] The renaissance of anion-induced ET (AIET) began earnestly in 2010 when (i) we[4] first recognized formal ET from F^- to a π-acidic naphthalenediimide (NDI) compound in various aprotic solvents (DMF, DMSO, and MeCN) leading to the formation of a paramagnetic $NDI^{\bullet-}$ radical anion and an NDI^{2-} dianion, (ii) Bucher[5] observed F^--induced reduction of methyl viologen (MV^{2+}) to $MV^{\bullet+}$, (iii) Mukhopadhyay[6] reported ET from CN^- to NDI and perylenediimide (PDI) compounds, and (iv) Matile[3] noticed ET from I^- to a highly π-acidic dicyano-NDI (DCNDI) compound, but speculated that F^- perhaps formed a Meisenheimer complex via nucleophilic attack instead of ET. Subsequently, a flurry of investigations[7−20] revealed that other π-acids, such as 1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile ($HAT(CN)_6$), tetracyanoquinodimethane (TCNQ), C_{60}, [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), PTANTT, an n-type conjugated polymer, and a Lewis acid Ag^+ (Figure 2)—practically any electron acceptor with a LUMO level of −3.8 eV or less or a reduction potential of −900 mV or less vs Ag/AgCl—were consistently reduced by F^- and other Lewis basic anions in various aprotic solvents as well as in solid films. The reduced forms of π-acids and Lewis acids display fascinating optical, electrical, and magnetic properties, which have been exploited for colorimetric and fluorimetric anion sensing, light-harvesting, improving electrical conductivity, and luminescent silver nanoparticle synthesis, among other applications.

While there is no dearth of experimental evidence and thermodynamic justification for each observed anion-induced π-acid and Lewis acid reduction, assuming that F^- could not possibly donate an electron, three alternate explanations were offered: (i) a diamagnetic Meisenheimer/σ-complex formation via nucleophilic attack of F^-,[3] although the identified products were always paramagnetic $\pi A^{\bullet-}$ radical anions, (ii) the concurrent formation of $\pi A^{\bullet-}$ and a $[F^-/\pi A^{\bullet+}]$ complex,[26] although the oxidation of π-acids to $\pi A^{\bullet+}$ radical cations in the presence of a strong Lewis base is not thermodynamically feasible, nor can two entirely different species share the same spectra, and (iii) deprotonation of an aprotic solvent DMSO (pK_a 35) by F^- (HF's pK_a 15) against an exceptionally high thermodynamic barrier ($K_{eq} = 10^{-20}$), followed by a π-acid reduction by the resulting $^{\ominus}CH_2SOCH_3$ anion.[27]

By first defining the thermodynamic criteria of AIET events and all other alternate explanations and then evaluating the key spectroscopic data in the light of these criteria, for the first time, this Account depicts a complete picture of how strong Lewis basic anions actually interact with various π-acids and Lewis acids in aprotic environments. The goal here is to help the scientific community to draw an evidence-based conclusion, which may even require us to recognize the incongruity of a common perception.

THERMODYNAMIC CRITERIA OF AIET AND CT INTERACTIONS

For an ET event to be thermodynamically viable, the donor HOMO must be located above the acceptor's LUMO or the photoinduced SOMO-1 (Figure 1).[7,8] Strong Lewis basic OH^-, F^-, and CN^- anions with high HOMO levels[13] and strong π-acids having low LUMO levels fulfill this requirement (Table 1). When an anion's HOMO lies above a π-acid's LUMO, thermal ET transpires in the ground-state.[7,8] Photoinduced ET (PET) occurs when an anion's HOMO falls below the π-acid's LUMO but still lies above its photogenerated SOMO-1. Both thermal and photoinduced AIET pathways produce paramagnetic $\pi A^{\bullet-}$ radical anions and sometimes πA^{2-} dianions, generating the same characteristic UV−vis and EPR/NMR spectra as the electrochemically reduced species. The larger the ET thermodynamic driving force, i.e., the energy gap between the anion's HOMO and the π-acid's LUMO, the more facile are the ET events and the radical anion formations: $[\pi A^{\bullet-}] \propto |-\Delta G^{\circ}_{ET}|$.[7,8] When both thermal and photoinduced AIET pathways are disabled, CT complexes (Figure 1) accompanied by characteristic broad absorption or optically silent anion−π complexes emerge.[23,24,28,29] The anion−π coulombic interaction is so weak that it does not meaningfully perturb the electronic and optical properties of either participant.

Unlike AIET events, none of the other hypotheses fulfilled their respective thermodynamic criteria, nor did they display any supporting spectroscopic signals. (i) The anion-induced formation of paramagnetic $\pi A^{\bullet-}$ radical anions, detected by UV−vis, EPR, and NMR spectra, rules out the formation of diamagnetic σ-complexes via nucleophilic attack.[3] (ii) The formation of a proposed $[F^-/\pi A^{\bullet+}]$ complex[26] would require a thermodynamically prohibited oxidation of electron deficient NDI and PDI compounds in the presence of a strong Lewis base F^-. Having completely different compositions, electronic state, and HOMO−LUMO levels, $\pi A^{\bullet-}$ and $[F^-/\pi A^{\bullet+}]$ cannot share the same spectra. (iii) The proposed F^--induced deprotonation[27] of aprotic DMSO is 10^{-20}-times disfavored ($pK_{eq} = \Delta pK_a$) based on the pK_a values of DMSO (35) and HF (15). To allay this serious inconsistency, an improbable acidification of DMSO by a weak π-acid, *N*,*N*′-di-(2,6-diisopropylphenyl)naphthalene diimide (DippNDI), was invoked.[27] However, in order for DippNDI to adequately acidify DMSO, that is, lower its pK_a from 35 to 15 to enable F^--induced deprotonation, it must significantly drain the electron density from DMSO either by oxidizing it to Me_2SO^+ while being reduced to $DippNDI^{\bullet-}$ or by at least forming a strong $Me_2S\ddot{O}: \rightarrow$ DippNDI CT complex. In these hypothetical scenarios, the absorption spectrum of $DippNDI^{\bullet-}$ or a CT complex would have emerged even in the absence of F^-. But no such spectroscopic evidence of meaningful DMSO/DippNDI electronic interactions has been found that could justify the proposed acidification and subsequent deprotonation of DMSO. Furthermore, F^- also reduced π-acids and Lewis acids in many other aprotic solvents, such as DMF,

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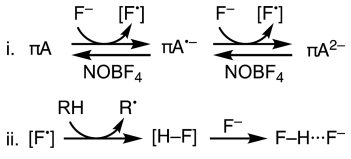
THF, CH_2Cl_2, MeCN, PhCN, and *o*-dichlorobenzene (ODCB),[4−20] as well as in solid films,[14,19] ruling out this claim.

THE INTERACTIONS OF STRONG LEWIS BASIC ANIONS WITH π-ACIDS AND LEWIS ACIDS

The ET from strong Lewis basic anions, especially F^- first came to light in 2010 when we[4] and others[3,5,6] reported anion-induced reduction of π-acidic NDI, PDI, and MV^{2+} in different aprotic solvents (Scheme 1).

Scheme 1. Electron Transfer from F^- Anion to π-Acids[a]



[a]RH represents generic hydrogen atom sources, such as solvents, counterions, or water of crystallization present in organic F^- salts.

We discovered[4] that (Figure 3) the colorless solutions of a π-acidic *N,N′*-di(4-pyridyl)-1,4,5,8-naphthalenetetracarboxy-

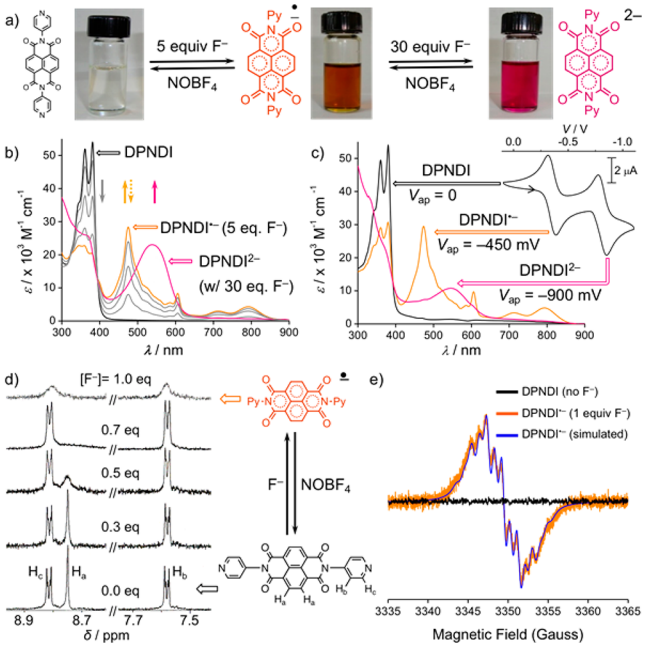


Figure 3. (a) The F^--induced reduction of colorless DPDNI to orange $DPNDI^{\bullet-}$ and pink $DPNDI^{2-}$. (b, c) The UV−vis spectra of (b) F^--generated and (c) electrochemically generated $DPNDI^{\bullet-}$ and $DPNDI^{2-}$. The F^--induced (d) ^1H NMR and (e) EPR spectra of $DPNDI^{\bullet-}$ radical anion. Adapted with permission from ref 4. Copyright 2010 American Chemical Society.

diimide (DPNDI) (LUMO −3.9 eV) in DMF, DMSO, and MeCN first turned orange and then pink with an increasing amount of F^- (Bu_4NF, Et_4NF, and CsF (as Cs^+@18-crown-6·F^-)) but remained silent to all other halides, acetate, phosphates, nitrate, and charge-diffuse anions. The UV−vis spectra of the orange solution generated by a small amount of F^- and the pink solution by an excess F^- were identical to those displayed by electrochemically generated $DPNDI^{\bullet-}$ radical anion and $DPNDI^{2-}$ dianion, respectively, confirming that thermal ET from F^- to DPNDI was responsible for its stepwise reductions (Figure 3a−c). The same clean isosbestic points emerged during the electrochemical and F^--induced reductions of DPNDI, indicating that only $DPNDI^{\bullet-}$ and $DPNDI^{2-}$ were formed in both cases and no other intermediate or product, such as a σ-complex was involved during the latter. Although a [F^-·DPNDI] complex formation prior to formal ET could be a possibility, it is not a prerequisite for ET because the second reduction leading to $DPNDI^{2-}$ formation cannot plausibly involve a [F^-/$DPNDI^{\bullet-}$] complex due to electrostatic repulsion.

In the presence of 1 equiv of F^-, the ^1H NMR signal of the NDI core disappeared and a characteristic EPR spectrum with hyperfine lines[4] appeared, unequivocally confirming the formation of paramagnetic $DPNDI^{\bullet-}$ radical anion and ruling out a diamagnetic Meisenheimer complex formation (Figure 3d,e). The NMR peaks of the pyridine rings also became broad but did not disappear completely because the radical anion was delocalized only within the NDI core, not through the noncoplanar pyridyl groups. This is why, irrespective of the terminal groups, practically all $NDI^{\bullet-}$ radical anions display very similar UV−vis absorption and hyperfine EPR spectra.[31] The fact that the NMR signals did not shift or split during F^- titration ruled out the formation of a nonsymmetric diamagnetic Meisenheimer complex[3] via nucleophilic attack. The F^--generated $DPNDI^{\bullet-}$ was easily oxidized back to the neutral form by $NOBF_4$, further ruling out the formation of a practically irreversible covalent C−F bond (D_{C-F}, 130 kcal/mol). While the reduction of DPNDI was a reversible process, F^- acted as a highly reactive, transient electron donor, generating a sacrificial $F^\bullet$ radical, which abstracted a H atom from the medium, first forming HF and ultimately, a stable HF_2^- anion via a [FH···F^-] H-bond formation (Scheme 1). The conversion F^- to HF_2^- in the presence of electron acceptors has been observed by ^{19}F NMR spectroscopy.[14]

The possibility of E2 elimination of Bu_4NF, followed by the reduction of DPNDI by the resulting Bu_3N was ruled out because (i) Bu_3N itself did not produce any $DPNDI^{\bullet-}$ and (ii) CsF and Et_4NF also performed the same reduction. The deprotonation of DPNDI or the aprotic solvents by F^- was not feasible either because of their remarkably high pK_a values. Furthermore, the NDI compounds containing amide groups were first reduced by F^- before the −CONH groups ($pK_a \approx 22$) interacted with excess F^- (*vide infra*).[4] Therefore, a F^--induced deprotonation of aprotic DMSO (pK_a 35) would be thermodynamically even more unrealistic. In the presence of more than 5% H_2O, no $DPNDI^{\bullet-}$ was formed, as ET from hydrated F^- was turned OFF.

To manipulate the thermodynamic driving force of AIET, that is, the $HOMO_{anion}$—$LUMO_{\pi\text{-acid}}$ gap that controls how facile an AIET event would be, we introduced a library of NDI compounds equipped with different electron withdrawing and donating groups attached to their naphthalene cores and imide rings that defined their LUMO levels (Table 1).[7,8] In CH_2Cl_2, ODCB, THF, and MeCN, the most π-acidic candidate DCNDI (LUMO −4.4 eV) was easily reduced by F^- (Bu_4NF, Et_4NF, and CsF with 18-crown-6) and OH^- to $DCNDI^{\bullet-}$ and $DCNDI^{2-}$ in two steps, but produced only $DCNDI^{\bullet-}$ with excess I^- (Figure 4).[8] These results clearly demonstrated that in aprotic solvents F^- is a much stronger electron donor than I^-. Later on, Ballester's computational studies[13] attested that in MeCN, F^- indeed has a 0.8 eV higher HOMO level than I^- (Table 1).

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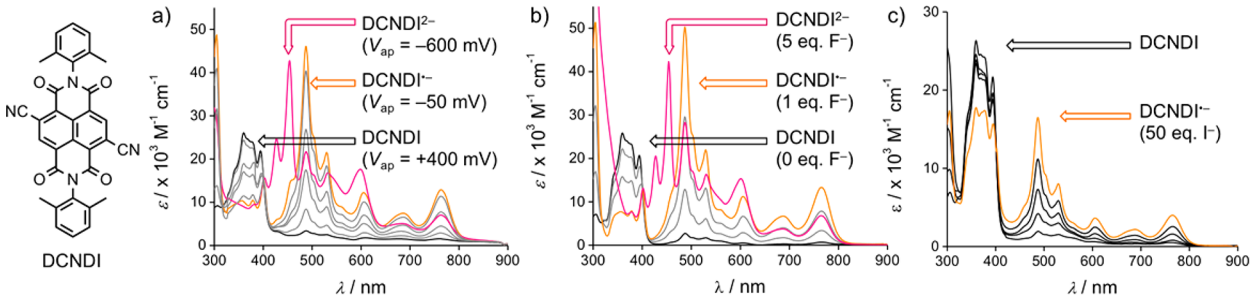

Figure 4. UV–vis spectroscopic changes of DCNDI upon its (a) electrochemical, (b) F^--induced, and (c) I^--induced reductions in MeCN. Adapted with permission from ref 8. Copyright 2012 American Chemical Society.

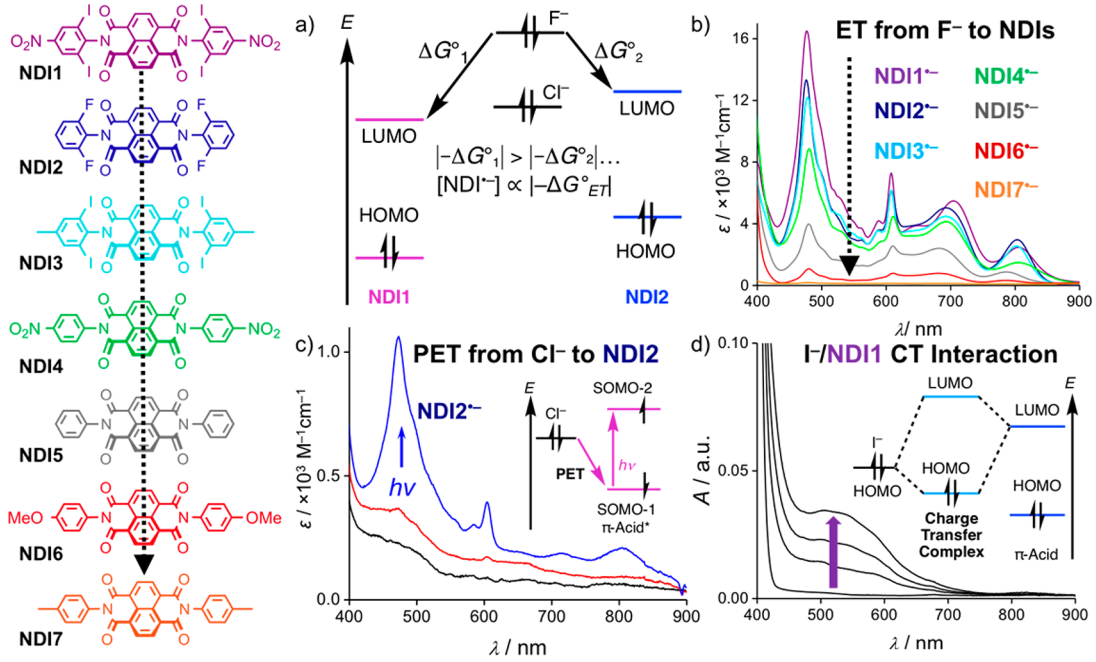

Figure 5. A library of decreasingly π-acidic NDI compounds. (a) As the LUMO levels of NDIs rise gradually, the ΔG°_{ET} values shrink and the amount of resulting $NDI^{\bullet-}$ radical anions diminishes. The UV–vis spectra of (b) $NDI^{\bullet-}$ radical anions produced by thermal ET from F^- to NDI1–7 in ODCB, (c) $NDI2^{\bullet-}$ generated via PET from Cl^- in MeCN, and (d) an I^-/NDI1 CT complex formed in MeCN. Adapted with permission from refs 7 and 8. Copyright 2011 and 2012 American Chemical Society.

As the π-acidity of NDIs decreased systematically from NDI1 through NDI7,[7,8] their LUMO levels rose commensurately, shrinking the $HOMO_{anion}$—$LUMO_{\pi\text{-acid}}$ gap. As a result, the amounts of different $NDI^{\bullet-}$ radical anions produced by F^--induced ET decreased gradually until it failed to reduce the least π-acidic NDI7 (Figure 5). Thus, the electron accepting ability of different NDI derivatives varies significantly, and one is reduced by a given anion only when the thermodynamic criteria of AIET are satisfied. Having a much lower HOMO level, Cl^- could still reduce DCNDI and NDI1, but barely generated any $NDI2^{\bullet-}$ radical anion in the absence of light. Upon irradiation of a solution mixture of NDI2 and excess Cl^-, the characteristic absorption spectrum of $NDI2^{\bullet-}$ intensified and the ^1H NMR signals of the NDI-core disappeared due to PET from Cl^- to the SOMO-1 of ^{1}*NDI2 excited state. For the same reason, other weak Lewis basic anions, such as AcO^- and $H_2PO_4^-$ were only able to partially reduce the strongest π-acidic NDI derivatives via thermal or photoinduced ET generating weak $NDI^{\bullet-}$ signals.[6–8] In contrast, non-Lewis basic I^- anion only formed a CT complex with NDI1 but could not reduce it, conceding again that it is a weaker electron donor than F^- in aprotic media.

We subsequently demonstrated[9] that (Figure 6) in THF, DMSO, and MeCN, another π-acid, PDI (LUMO −3.9 eV), was also reduced to a paramagnetic $PDI^{\bullet-}$ radical anion and PDI^{2-} dianion by an increasing amount of OH^-, but only to $PDI^{\bullet-}$ by excess F^-. These results demonstrated that the more Lewis basic OH^- with a higher HOMO level[13] acted as a stronger electron donor than F^-. The anion-generated $PDI^{\bullet-}$ and PDI^{2-} displayed the same characteristic spectra as the electrochemically reduced PDI. The fact that excess amounts of F^- generated only $PDI^{\bullet-}$ radical anion while excess OH^- reduced PDI all the way to PDI^{2-} dianion further indicated that F^- did not deprotonate the H_2O (in DMSO, the pK_a of H_2O is 32 vs 15 for HF) of crystallization in Bu_4NF salt, because the resulting OH^- would have yielded PDI^{2-} dianion in the former case as well.

Through X-ray crystallography, we demonstrated that (Figure 7) in coordination polymers, charge-diffuse anions, such as $CF_3SO_3^-$ and ClO_4^-, interacted with the DPNDI ligands through weak anion–π and CH···anion H-bonding

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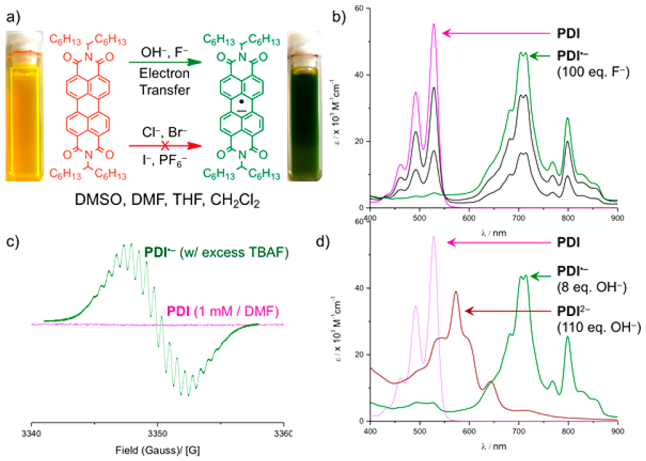

Figure 6. (a) The color change, (b) UV−vis transitions, and (c) EPR spectra of $PDI^{\bullet-}$ produced by F^--induced reduction of PDI in DMF. (d) OH^- produced $PDI^{\bullet-}$ and PDI^{2-} via a two-step one-electron reduction. Adapted with permission from ref 9. Copyright 2013 Royal Society of Chemistry.

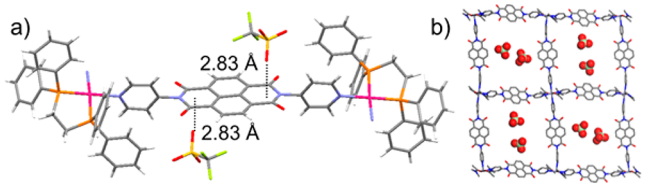

Figure 7. DPNDI binds (a) $CF_3SO_3^-$ and (b) ClO_4^- anions via anion−π and CH···anion interactions. Adapted with permission from refs 28 and 29. Copyright 2012 and 2013 Royal Society of Chemistry.

interactions.[28,29] These weak interactions did not meaningfully perturb the electronic properties of DPNDI nor engender any spectroscopic changes.

We further demonstrated[10] that F^- (Bu_4NF, Et_4NF, and CsF) also reduced Lewis acidic Ag^+ to Ag^0 in MeCN, PhCN, CH_2Cl_2, and DMSO but not in H_2O, generating metallic silver films and blue-luminescent Ag^0 nanoparticle solutions (Figure 8). The other halides formed corresponding Ag^I−halide precipitates but not metallic Ag^0. The ^{19}F NMR studies showed that in the presence of Ag^+, F^- was converted to HF_2^- plausibly through the formation of a transient $F^\bullet$ radical, followed by a fast H atom abstraction by $F^\bullet$ from the medium and a FH···F^- H-bond formation.[10] The F^--induced solvent deprotonation was unrealistic because of their insurmountably high pK_a values and the lack of HF_2^- formation without Ag^+. These results revealed the fate of F^- anion upon its oxidation.

Bucher et al.[5] observed that (Figure 9) F^- turned colorless DMF and DMSO solutions of MV^{2+} (LUMO −3.9 eV) to blue generating the characteristic UV−vis and EPR spectra of $MV^{\bullet+}$. An excess amount of F^- reduced it further to a colorless $MV^{2\bullet}$. In contrast, I^- only formed a CT complex but could not reduce MV^{2+}, demonstrating once again that F^- is indeed a stronger electron donor than I^- in aprotic mediums.

Mukhopadhyay et al.[6,12] reported that (Figure 10) in DMF, F^- reduced colorless NBHI-1a first to an EPR-active brown $NBHI\text{-}1a^{\bullet-}$ radical anion and then to a blue $NBHI\text{-}1a^{2-}$ dianion, whereas CN^- produced only $NBHI\text{-}1a^{\bullet-}$. Unlike nonemissive NDI and $NDI^{\bullet-}$, the NDI^{2-} dianions are highly fluorescent.[4,12] Although CN^- is a stronger nucleophile than F^-, no evidence of a covalent Meisenheimer complex was

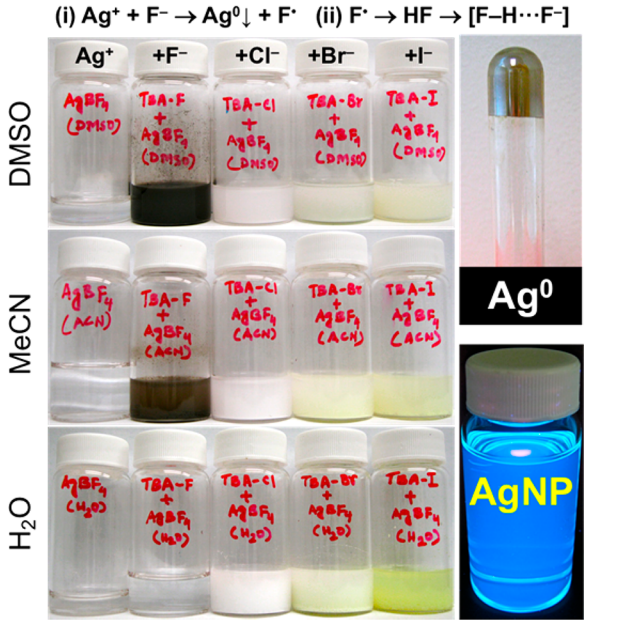

Figure 8. Fluoride reduced Ag^+ to metallic silver and luminescent Ag nanoparticles in aprotic solvents but not in H_2O, while other Ag^+ halides precipitated out of solutions. Adapted with permission from ref 10. Copyright 2015 American Chemical Society.

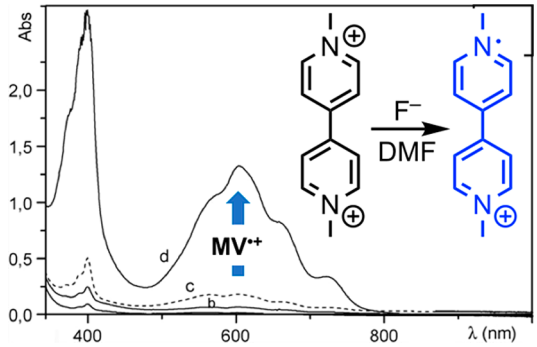

Figure 9. UV−vis spectrum of a $MV^{\bullet+}$ radical cation formed via F^--induced reduction of MV^{2+}. Adapted with permission from ref 5. Copyright 2010 Royal Society of Chemistry.

found in either case. Only in the presence of a large excess of F^- in dry DMF, the hydrazimide groups of NBHI-1a were deprotonated yielding a green solution that displayed an intramolecular CT band distinct from the characteristic radical anion and dianion spectra. F^- could not deprotonate the less acidic NH-groups of NBHI-1b, but reduced its NDI core to yield $NBHI\text{-}1b^{\bullet-}$. Thus, ET from F^- to NBHIs was favored over deprotonation of the hydrazimide groups, suggesting that F^- is unlikely to deprotonate[27] DMSO against a much greater thermodynamic barrier ($K_{Deprotonation}$ 10^{-20}).

Mukhopadhyay et al.[6] further demonstrated that (Figure 11) a blue diamino-NDI (DANDI) having modest oxidation and reduction potentials (E^1_{Ox} = +980 mV and E^1_{Red} = −890 mV vs SCE) was oxidized to a turquoise $DANDI^{\bullet+}$ radical cation by Cu^{II} and reduced to a brown $DANDI^{\bullet-}$ radical anion by CN^-, generating distinct UV−vis absorption spectra. Notably, CN^- (pK_a of HCN = 13 in DMSO) did not deprotonate the NH-groups of DANDI ($pK_a \approx 25$), showing that anions do not randomly deprotonate any group without fulfilling the thermodynamic requirements. These authors later demon-

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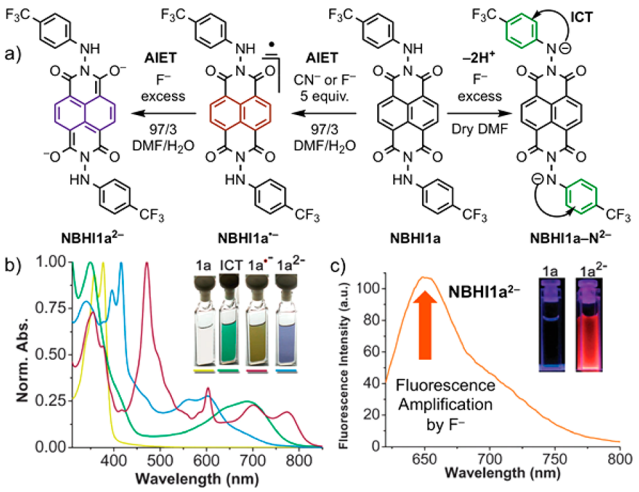

Figure 10. (a) The F^- and CN^--induced ET to NBHI1a. The UV–vis (b) and fluorescence (c) spectra of $NBHI1a^{\bullet-}$ and $NBHI1a^{2-}$.[6,12] Adapted with permission from ref 12. Copyright 2013 Royal Society of Chemistry.

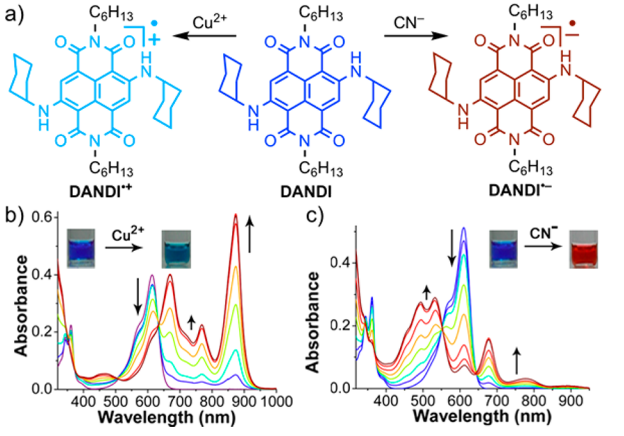

Figure 11. DANDI was oxidized by Cu^{2+} to $DANDI^{\bullet+}$ and reduced by CN^- to $DANDI^{\bullet-}$ generating distinct color and absorption spectra. Adapted with permission from ref 11. Copyright 2012 American Chemical Society.

strated that CN^- could also reduce highly π-acidic TCNQ to $TCNQ^{\bullet-}$ radical anion and a dicationic NDI derivative (LUMO −4.8 eV) carrying two electron-withdrawing phosphonium groups on the naphthalene core to a stable radical cation.[15,17]

Ballester et al.[13] demonstrated that (Figure 12) in MeCN, both F^- and OH^- reduced a highly π-acidic pale-orange $HAT(CN)_6$ (LUMO −4.4 eV) first to a green $[HAT(CN)_6]^{\bullet-}$ radical anion and then to an orange $[HAT(CN)_6]^{2-}$ dianion, generating the same UV–vis, ^{13}C NMR, and EPR spectra as the electrochemically reduced species. $[HAT(CN)_6]$ was previously known to form CT complexes with other halides.[23] Photoirradiation of a solution mixture of $[HAT(CN)_6]$ and excess Cl^- triggered PET, reducing it all the way to the dianion. Not surprisingly, a preformed F^-@calix[4]pyrrole inclusion complex could not reduce $HAT(CN)_6$ in MeCN because the H-bonded F^- ion was stabilized and lost its electron donating ability, just like the hydrated F^- ions. Notably, F^- did not deprotonate the −NH groups of calix[4]pyrrole ($pK_a \approx 23$), which would have generated an N-centered anion capable of reducing $[HAT(CN)_6]$. Since this

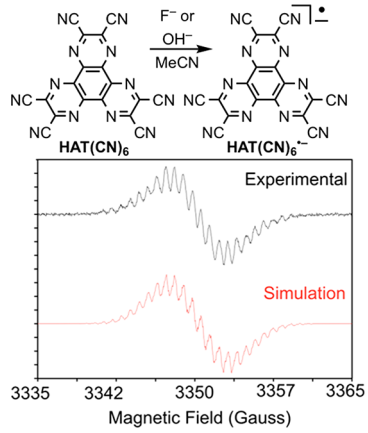

Figure 12. F^--induced reduction of $HAT(CN)_6$ and the EPR spectrum of resulting $HAT(CN)_6^{\bullet-}$. Adapted with permission from ref 13. Copyright 2013 American Chemical Society.

did not happen, the F^--induced deprotonation of DMSO[27] (pK_a 35) would be thermodynamically even more inconceivable. Ballester also estimated[13] that in MeCN, OH^- and F^- have much higher HOMO levels and ΔG°_{ET} than I^-, a potent electron donor. It is worth noting that density functional theory calculations systematically underestimate the HOMO levels of anions but maintain the trend, that is, the actual HOMO levels of anions are higher than the calculated values. In practice, F^- consistently reduces electron acceptors having LUMOs $\leq$ −3.8 eV or $E^1_{Red} \geq$ −900 mV vs Ag/AgCl. The HOMO levels of anions vary with solvents and temperature.

Jen et al.[14] demonstrated that (Figure 13) in ODCB, $CHCl_3$, and THF, as well as in solid films, electron deficient TCNQ, C_{60}, and PCBM were reduced by F^- but not by other halides. While F^- readily reduced the highly π-acidic TCNQ (LUMO −4.8 eV) and C_{60} (−4.5 eV) to corresponding radical anions in all three solvents, it could not reduce a weaker π-acid, PCBM (LUMO −4.4 eV) in $CHCl_3$. Upon removal of $CHCl_3$, the resulting solid film displayed the characteristic EPR signal of $PCBM^{\bullet-}$ indicating that ET from the naked F^- anion was activated. While the lack of $PCBM^{\bullet-}$ stabilization in less polar $CHCl_3$ could be a possible explanation for this phenomenon, a potentially more significant factor was the stabilization of F^- via a $F^-\cdots H-CCl_3$ H-bond formation (unlike other aprotic solvents, $CHCl_3$ forms a strong H-bond with its fairly acidic proton), which prevented ET from the solvated F^- ions to PCBM, the weakest electron acceptor among the three. These AIET events were exploited in polymer solar cells.

Hu et al.[16] demonstrated that (Figure 14) in CH_2Cl_2 and ODCB, F^- easily reduced a yellow NDI-DTYC2 (LUMO −4.3 eV) to an EPR-active pink $NDI\text{-}DTYC2^{\bullet-}$ radical anion while other halides did not. All these results repeatedly and indisputably show that the reductions of π-acid in the presence of F^- are not caused by thermodynamically disfavored F^--induced deprotonation of DMSO, followed by ET from $^{\ominus}CH_2SOCH_3$.[27]

Langford et al.[18] demonstrated (Figure 15) ET from F^- to different NDI-based macrocycles (MC1–4), each containing a different π-donor: 1,4-dihydroquinone, 1,5-dioxynaphthalene, or 1,4-dioxynaphthalene. Depending on the π-donor strength and location, they were engaged in varied degrees of intramolecular CT interactions with the π-acidic NDI unit, affecting the NDI's electron accepting ability accordingly. Similar to our observations with a library of NDIs having

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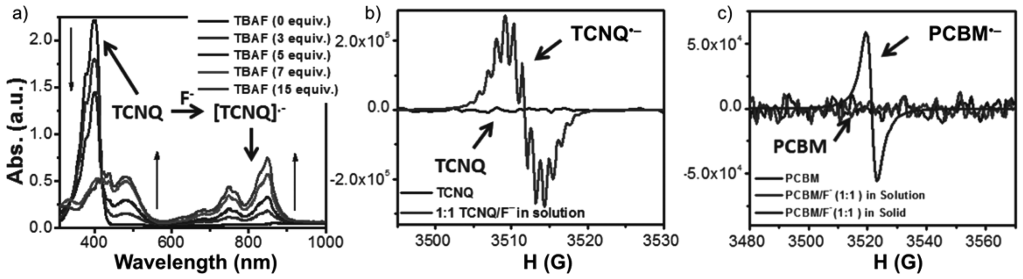

Figure 13. UV−vis (a) and EPR (b) spectra of $TCNQ^{\bullet-}$ produced by F^- in $CHCl_3$. (c) The EPR spectrum of F^--induced $PCBM^{\bullet-}$ formed in a solid film. Adapted with permission from ref 14. Copyright 2013 John Wiley and Sons.

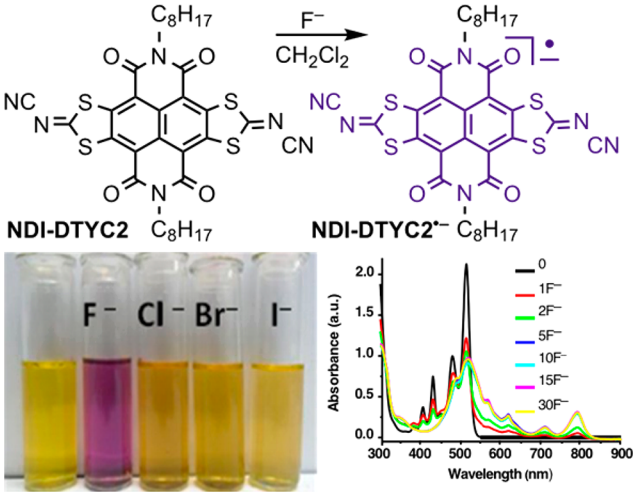

Figure 14. Color and absorption changes upon F^--induced reduction of NDI-DTYC2 in CH_2Cl_2. Adapted with permission from ref 16. Copyright 2013 Elsevier.

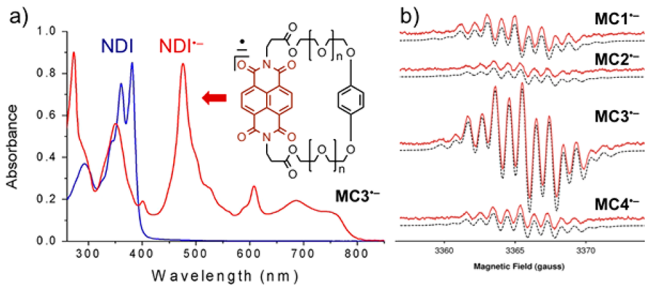

Figure 15. UV−vis and EPR spectra of F^--generated $NDI^{\bullet-}$ in NDI/π-donor macrocycles. Adapted with permission from ref 18. Copyright 2017 John Wiley and Sons.

variable LUMO levels (Figure 5),[7,8] the F^--induced reduction of the NDI unit was most facile in MC3 featuring the weakest π-donor 1,4-dihydroquinone, which formed the weakest CT complex and least quenched the NDI's π-acidity. Together, these results demonstrate that the F^--induced ET to NDIs and other π-acids is thermodynamically driven.

Katz et al.[19] showed that (Figure 16) in THF/PhCl solutions and solid films, an n-type conjugated polymer, ClBDPPV (LUMO −4.2 eV) was reduced by F^- to a paramagnetic $ClBDPPV^{\bullet-}$ radical anion, engendering the characteristic UV−vis and EPR spectra. The F^--generated $ClBDPPV^{\bullet-}$ film displayed higher electrical conductivity than the neutral form, exemplifying another benefit of AIET events. The possibility of an intermediate σ-complex formation via a nucleophilic attack by F^- was contemplated, but no evidence

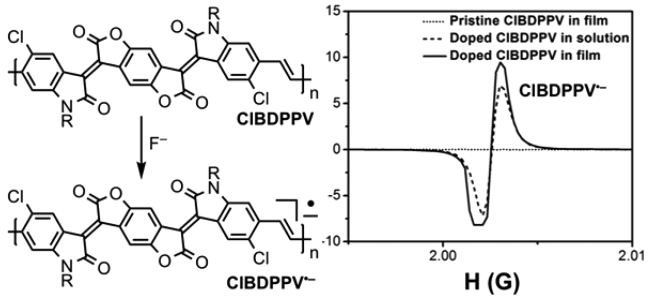

Figure 16. EPR spectra of F^--generated $ClBDPPV^{\bullet-}$ in solutions and solid films. Adapted with permission from ref 19. Copyright 2017 John Wiley and Sons.

of such was found. Moreover, the conversion of an intermediate σ-complex to $ClBDPPV^{\bullet-}$ would require a practically impossible homolysis of a polar C−F bond (D_{C-F}, 130 kcal/mol) involving the departure of the electronegative F atom leaving the both bonded electrons on the C atom without any impetus. The σ-complex formation has been ruled out previously based on the UV−vis and NMR data (*vide supra*).[4,5,7−9,12]

Morin et al.[20] demonstrated that (Figure 17) although F^- could not reduce a very weak π-acid PTANTT (LUMO −3.4

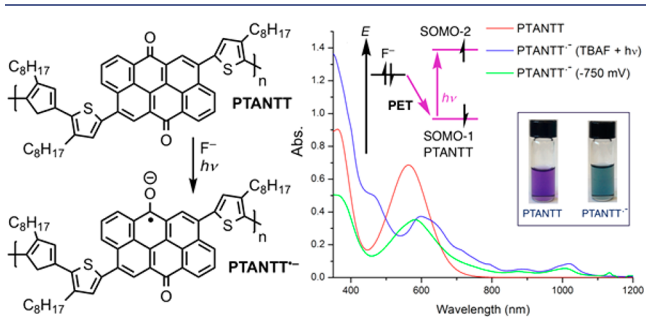

Figure 17. UV−vis changes upon PET from F^- to PTANTT. Adapted with permission from ref 20. Copyright 2015 American Chemical Society.

eV) in the ground-state ($\Delta G^{\circ}_{ET} > 0$), upon photoirradiation PET from F^- produced $PTANTT^{\bullet-}$ radical anion turning the purple solution to blue. Wang et al.[24] reported a CT complex formation between F^- and a mild π-acidic triazine-based calix[4]arene. Thus, depending on the electron accepting ability of different π-acids, F^- can engage them in either thermal ET, PET, or CT interactions in aprotic solvents.

Li et al.[26] observed that (Figure 18) in the presence of F^-, the deoxygenated DMF solutions of NDI and PDI displayed characteristic UV−vis absorption spectra and hyperfine EPR

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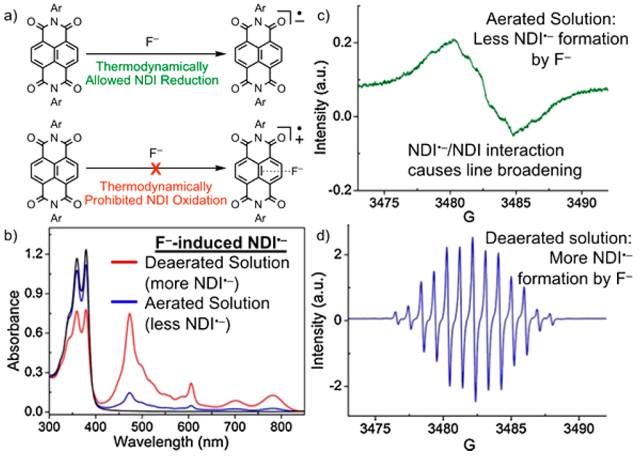

Figure 18. F^- produced more $NDI^{\bullet-}$ via thermal ET in the absence of O_2 than in its presence. Adapted with permission from ref 26. Copyright 2014 Elsevier.

spectra of $NDI^{\bullet-}$ and $PDI^{\bullet-}$ radical anions, but the aerated solutions showed much weaker absorption and broad EPR spectra. While there was no doubt about the complete reduction of the π-acids into corresponding radical anions in the former, and the latter displayed characteristic signs of incomplete π-acid reduction and $\pi A^{\bullet-}/\pi A$ self-exchange, surprisingly, the authors claimed that $[\pi A^{\bullet+}/F^-]$ complexes were formed in the latter. This interpretation has two major flaws: (i) the oxidation of electron deficient NDI and PDI compounds (E^1_{ox} > +1.5 V vs Ag/AgCl) in the presence of a strong Lewis base F^- is not thermodynamically feasible and (ii) since $\pi A^{\bullet-}$ and $[\pi A^{\bullet+}/F^-]$ have totally different compositions, redox states, and HOMO/LUMO levels, which define their absorption spectra, they cannot display the same spectral features. For reference, $DANDI^{\bullet-}$ and $DANDI^{\bullet+}$ displayed distinct absorption spectra (Figure 11).[8] Therefore, utmost care must be taken to ensure that the characteristic $\pi A^{\bullet-}$ spectra generated by F^- and other Lewis basic anions revealing the AIET events are not misinterpreted.

Gabbai et al.[27] employed an extremely weak π-acidic DippNDI having a relatively high LUMO level similar to our previously studied NDI7 (−3.8 eV), which was not reduced by F^-.[7,8] Since the F^--induced reduction of different NDI compounds, or any π-acids for that matter, becomes less facile with their diminishing π-acidity and rising LUMO levels (Figure 5),[7,8,18] it was not at all surprising that in CH_2Cl_2, F^- produced only ∼5% $DippNDI^{\bullet-}$, while a much stronger electron donor, cobaltocene (HOMO −3.5 eV), generated more $DippNDI^{\bullet-}$ (Figure 19). In DMSO, F^- produced significantly more $DippNDI^{\bullet-}$ because the radical anion was better stabilized in the more polar solvent. However, assuming that F^- could not donate an electron, the authors posited that F^- perhaps deprotonated DMSO and the resulting $^{\ominus}CH_2SOCH_3$ caused the DippNDI reduction. As explained above, based on the pK_a values of DMSO (35) and HF (15), this claim is not thermodynamically feasible ($K_{Deprotonation}$ = 10^{-20}). In an effort to address this incongruity, authors postulated that DippNDI acidified DMSO to facilitate the deprotonation. In order for this claim to be viable, DippNDI must significantly drain the electron density away from DMSO either by forming a CT complex or by oxidizing it to Me_2SO^+ while getting reduced to $DippNDI^{\bullet-}$ even before the F^- addition. However, no evidence of such DMSO/DippNDI

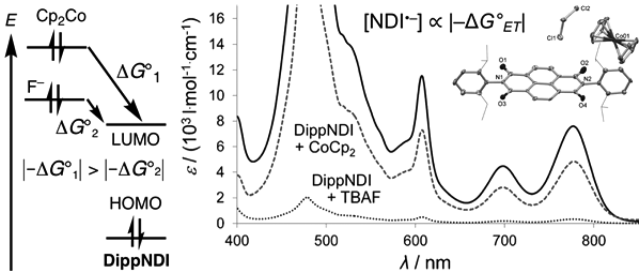

Figure 19. A less facile reduction of DippNDI formation by F^- than by Cp_2Co in CH_2Cl_2. Adapted with permission from ref 27. Copyright 2017 John Wiley and Sons.

CT complex or $DippNDI^{\bullet-}$ formation was found without F^-, revealing that the DMSO/DippNDI interaction was insignificant at best. Furthermore, the fact that F^- was able to reduce various π-acids in several aprotic solvents having much higher pK_a values than DMSO (e.g., ODCB, toluene, THF, CH_2Cl_2, and CCl_4), as well as in solid films devoid of any solvents,[14] clearly suggested that the F^--induced deprotonation of DMSO was not responsible for these π-acid reductions. Just like F^- was converted to HF_2^- by Ag^+ (*vide supra*),[10] the same happened in the presence of DippNDI in both $(CD_3)_2SO$ and CD_2Cl_2, with noticeably more HF_2^- (DF_2^-) being generated in $(CD_3)_2SO$ where more $DippNDI^{\bullet-}$ was formed via facile ET from F^-. These results again suggested that ET from F^- to DippNDI, followed by H atom abstraction by the resulting $F^{\bullet}$ radical and subsequent FH···F^- H-bonding interaction, not a direct F^--induced solvent deprotonation, led to yield HF_2^- formation (Scheme 1). A direct solvent deprotonation by F^- would have readily converted all F^- to HF_2^- even in the absence of any Lewis or π-acid, which never happened. The authors also speculated about a potential involvement of impurities in the π-acid reduction. However, no more than 0.02% of I_3^- impurity was found in colorless Bu_4NF salts,[30] and the direct addition of excess I^- or I_3^- did not reduce Ag^+ and most π-acids (except highly electron deficient DCNDI and TCNQ) because of unfavorable ΔG°_{ET} but stoichiometric amount of F^- did (ΔG°_{ET} < 0),[7−10,13−15] ruling out this possibility as well.

In the presence of both Cp_2Co and F^-, the ^1H NMR signal of the NDI core disappeared and the same characteristic hyperfine EPR spectra appeared showing that the $NDI^{\bullet-}$ radical anion was delocalized only within the naphthalene and imide rings whereas, the noncoplanar terminal aryl groups were not involved in resonance.[31] Interestingly, the NMR signals of diisopropylphenyl groups also disappeared only in the presence of Cp_2Co possibly because of their proximity with the resulting Cp_2Co^+, as seen from the crystal structure (Figure 19), not because they were involved in resonance with the NDI core, which would have produced a different hyperfine EPR pattern than that was observed.[31] In addition to an EPR-active $DippNDI^{\bullet-}$, F^- also produced an NMR-active by-product possibly through a facile H atom abstraction by the resulting $F^{\bullet}$ radical from the *ortho*-isopropyl groups, followed by cyclization of the ensuing benzylic radicals with the carbonyl-C of the $NDI^{\bullet-}$ core, similar to one demonstrated by Griesbeck,[32] or via a yet-unidentified radical reaction.

FLUORIDE AS A BRØNSTED BASE

F^- also forms H-bonds and even deprotonates acidic groups that have pK_a values lower than that of HF, and ET is not

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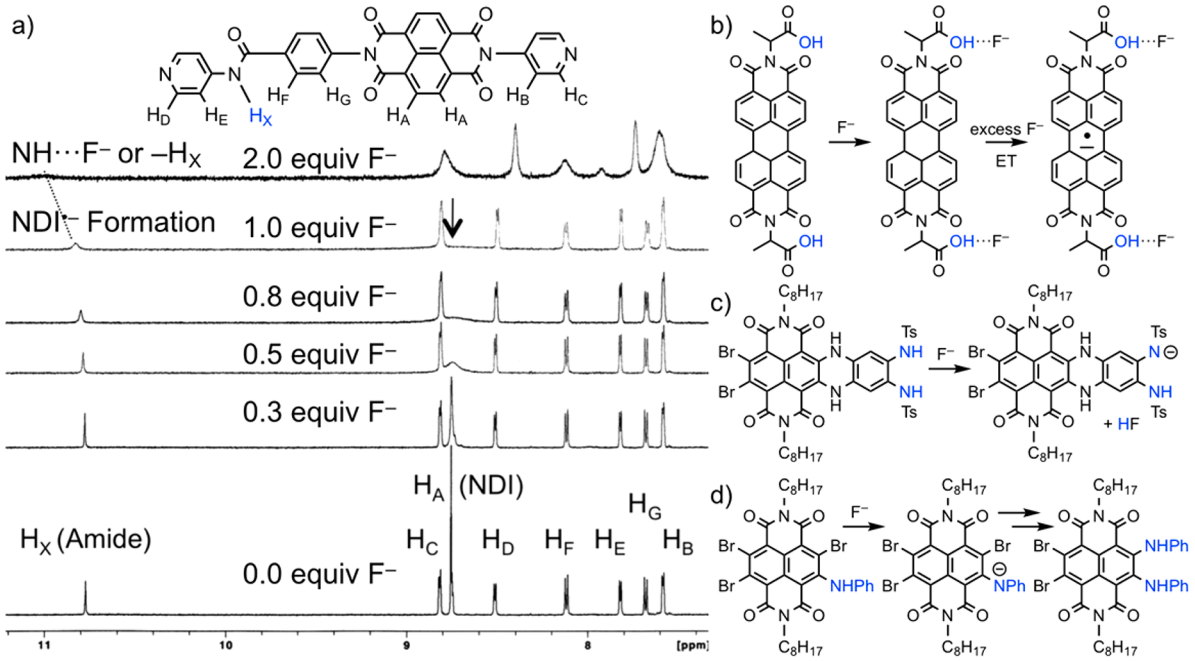

Figure 20. (a) A ^{1}H NMR titration experiment showed that a F^--induced ET to NDI was favored over a −CONH···F^- H-bond formation or deprotonation.[4] (b) Fluoride formed H-bonds with the −COOH groups before reducing a PDI unit.[33] (c,d) F^- deprotonated the acidic groups when ET was not possible to amine-functionalized electron-rich NDI units.[34,35] Adapted with permission from ref 4. Copyright (2010) American Chemical Society.

thermodynamically feasible. When both electron acceptor and proton donor sites coexist in a molecule, the competition between the thermodynamic driving force of each process (ΔG°_{ET} vs ΔpK_a) determines which interaction would precede or dominate. For example, we[4] and Mukhopadhyay[12] demonstrated that F^- first reduced the NDI core to $NDI^{\bullet-}$ before it interacted with amide and hydrazimide groups at higher equivalents (Figure 20a), verifying that ET was thermodynamically more favored over H-bond formation or deprotonation in these cases. By contrast, Chen et al.[33] showed that F^- first interacted with the highly acidic −COOH groups attached to a PDI unit before forming $PDI^{\bullet-}$ at higher concentrations (Figure 20b), as the preference for the two competing pathways flipped based on the respective thermodynamic driving forces. Furthermore, Langford et al.[34] demonstrated that in DMSO, F^- could only deprotonate the acidic sulfonamide groups ($pK_a \approx 13$ in DMSO, $K_{Deprotonation} = 10^2$) attached to an electron rich diamino-NDI core (Figure 20c), which was not reduced, turning the solution from blue to green and quenching its fluorescence. Similarly, Suraru and Würthner[35] found that F^- only deprotonated the PhNH group attached to a tribromo-NDI core, controlling the regioselectivity of a subsequent reaction (Figure 20d). In both cases, F^- failed to reduce electron-rich amino-NDI cores due to unfavorable ΔG°_{ET}. In all these cases, F^- only deprotonated fairly acidic protons attached to heteroatoms, not the C−H bonds of aprotic solvents with extremely high pK_a values. The F^--induced ET is also deactivated when it serves as a desilylation agent forming a strong Si−F covalent bond.[36]

As discussed above, the F^--induced reduction of π-acidic NDI units was thermodynamically more favored and preceded its interactions (i.e., H-bonding or deprotonation) with fairly acidic amide and hydrazimide groups ($pK_a \approx 21-25$) in DMSO, MeCN, and other aprotic solvents (Figure 20a).[4,12] However, in the absence of potent Lewis/π-acids, that is, when F^- was not readily oxidized by a fast ET event, it slowly deprotonated CD_3CN (pK_a 31) over the course of several hours forming stable DF_2^- anions.[37,38] Notably, no DF_2^- was found in $(CD_3)_2SO$ under the same condition,[37] indicating that the F^--induced DMSO deprotonation was even more difficult. Thus, in contrast to instantaneous F^--induced reduction of strong Lewis and π-acids enabled by thermodynamically allowed fast ET process ($K_{ET} \propto |-\Delta G^\circ_{ET}|$), the F^--induced deprotonation of MeCN was extremely slow due to an unfavorable ΔpK_a ($K_{Deprotonation} \approx 10^{-16}$); that is, the rates of these two processes were justifiably quite different. Therefore, once a F^- anion was readily oxidized by a Lewis/π-acid via fast ET, the resulting $F^\bullet$ radical could no longer abstract a H^+ from MeCN, but it could still abstract a H atom from the medium forming HF and ultimately HF_2^- via FH···F^- H-bonding (Scheme 1).[10] Conversely, the F^- anions consumed by slow MeCN deprotonation and stable HF_2^- (HOMO −6.4 eV) formation[13] could not trigger ET, explaining why it often required a little more than 1 equiv of F^- to complete the first reduction of π-acids.

CONCLUSIONS AND OUTLOOK

The foregoing discussions critically evaluated the viability of all potential interactions between Lewis basic anions and π-acids and Lewis acids, namely, (i) AIET leading to π-acid reduction, (ii) Meisenheimer complex formation, (iii) solvent deprotonation, and (iv) [$F^-/\pi A^{\bullet+}$] complex formation, in the light of their respective thermodynamic criteria and the spectroscopic signals. These mutually exclusive events have distinct thermodynamic requirements and spectroscopic signatures.

In summary, the UV−vis, EPR, and NMR spectroscopic data conclusively show that in aprotic environments, F^-, OH^-, and CN^- consistently reduce various electron acceptors, while the less Lewis basic anions form CT or anion−π complexes. Since the HOMOs of strong Lewis basic anions lie above the

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LUMOs of π-acids providing the thermodynamic driving force for ET, the formation of intermediate anion–π, CT, or σ-complexes is not necessary. Furthermore, the formation of πA^{2-} dianions cannot involve an intermediate [$\pi A^{\bullet-}$/anion] complex due to electrostatic repulsion. Nevertheless, the CT and ET interactions belong to the same energy landscape, and one transpires depending on the relative energy levels of electron donors and acceptors, which vary with solvent, temperature, and light. Therefore, an anion–π or CT complex may surface at low temperatures or in the dark when the HOMO of the anion lies below the LUMO of a π-acid and switch to formal ET at higher temperatures or under light similar to a temperature-dependent CT/ET interconversion observed in π-donor/acceptor systems.[25] F^- may also act as a Brønsted base if deprotonation of an acid is feasible based on the ΔpK_a value or as a desilylation agent, in which case it loses the ET capability. Unlike AIET, none of the alternate explanations was thermodynamically feasible, nor spectroscopically supported, but they were based on an unfounded notion that F^- could not donate electron even in aprotic environments. Until this misconception is completely eradicated, and the scientific evidence and facts are embraced, the chemistry community will likely encounter occasional outbursts of interesting but inconsistent speculations. Since there is no shortage of spectroscopic evidence and clear thermodynamic justification of each observed AIET event, at this point, it is up to the individuals to decide whether or not to accept the facts and exploit diverse potentials of this newly discovered phenomenon.

The most important takeaways from these studies are (i) unlike fluorine atoms with zero formal charge, the F^- anion is not an electronegative species but a strong Lewis base having a high HOMO level and strong electron donating ability in aprotic mediums and (ii) the feasibility of an AIET event and the amount of the reduced π-acids ($\pi A^{\bullet-}$ and πA^{2-}) depend on the thermodynamic driving force of ET, defined by the HOMO and LUMO levels of anions and electron acceptors, respectively. These parameters vary with solvent, temperature, and light. The paradigm-shifting discovery of AIET enabled naked-eye detection and discrimination of anions on the basis of their electronic properties, luminescent silver-nanoparticle synthesis, electrode-free silver plating, light-harvesting, and conductivity enhancement of conjugated polymers, with more fascinating applications likely to come.

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The author declares no competing financial interest.

Biography

Born and raised in India, **Sourav Saha** earned his M.Sc. degree from Indian Institute of Technology, Kanpur, Ph.D. (2005) from UCLA under the tutelage of Sir Fraser Stoddart, and postdoctoral experience in Professor Andrew Hamilton's laboratory at Yale University. He began his independent career at Florida State University where he first discovered and established F^--induced electron transfer to π-acids and Lewis acids. In 2016, he joined Clemson University as an Associate Professor. He was recognized as a Kavli Fellow at the 2016 Chinese-American Kavli Frontiers in Science Symposium in Irvine, California, organized by the US National Academy of Sciences and Chinese Academy of Sciences.

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