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### Abstract

Core-substituted naphthalenediimides (NDIs) attract increasing attention to bind, transport, and transform electrons, anions, anionic intermediates, and anionic transition states, and to shine as most colorful rainbow fluorophores. The energy level of their lowest unoccupied molecular orbital (LUMO) is decisive for many of these applications. Here, differential pulse voltammetry (DPV) measurements for a consistent series of NDIs are reported to extract exact LUMO levels under identical conditions. The influence of primary and secondary substituents in the core and on the primary imides is compared with general trends for the reliable prediction of LUMO levels in functional systems. Emphasis is on sulfur redox switches in the NDI core because of their frequent use as isostructural probes for  $\pi$  acidity. The same sulfur redox chemistry is expanded to perylenediimides (PDIs), and LUMO engineering is discussed in a broader context, including also fullerenes, aminonaphthalimides (ANIs), and aminoperyleneimides (APIs). The result is a comprehensive reference table that graphically maps out the LUMO space covered by the leading [...]

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# Core-Substituted Naphthalenediimides: LUMO Levels Revisited, in Comparison with Perylenediimides with Sulfur Redox Switches in the Core

François N. Miros and Stefan Matile\*<sup>[a]</sup>

Core-substituted naphthalenediimides (NDIs) attract increasing attention to bind, transport, and transform electrons, anions, anionic intermediates, and anionic transition states, and to shine as most colorful rainbow fluorophores. The energy level of their lowest unoccupied molecular orbital (LUMO) is decisive for many of these applications. Here, differential pulse voltammetry (DPV) measurements for a consistent series of NDIs are reported to extract exact LUMO levels under identical conditions. The influence of primary and secondary substituents in the core and on the primary imides is compared with general trends for the reliable prediction of LUMO levels in functional

systems. Emphasis is on sulfur redox switches in the NDI core because of their frequent use as isostructural probes for  $\pi$  acidity. The same sulfur redox chemistry is expanded to perylenediimides (PDIs), and LUMO engineering is discussed in a broader context, including also fullerenes, aminonaphthalimides (ANIs), and aminoperyleneimides (APIs). The result is a comprehensive reference table that graphically maps out the LUMO space covered by the leading families of electron-accepting aromatics. This graphical summary of general trends in the  $\pi$ -acidic space is expected to be both inspiring and quite useful in practice.

## Introduction

Core-substituted naphthalenediimides (NDIs)<sup>[1]</sup> are emerging as unique, most compact, and most versatile components in functional systems.<sup>[2–11]</sup> The intrinsically low energy of their lowest unoccupied molecular orbitals (LUMOs) makes them attractive to assemble into complex architectures<sup>[2]</sup> and to transport electrons along face-to-face stacks.<sup>[3]</sup> Related to these low LUMOs, their large intrinsic positive quadrupole moment<sup>[4]</sup> makes them attractive to elaborate on anion- $\pi$  interactions.<sup>[5]</sup> Realized examples with NDIs include anion binding,<sup>[6,7]</sup> transport across lipid bilayer membranes,<sup>[4]</sup> and catalysis of reactions with anionic transition states,<sup>[8]</sup> including enolate chemistry<sup>[9]</sup> and enamine chemistry.<sup>[10]</sup>

The introduction of substituents in their core provides access to an exceptionally rich diversity.<sup>[1]</sup> Withdrawing substituents afford excellent *n*-semiconductors on the one hand<sup>[3]</sup> and anion- $\pi$  transporters<sup>[4]</sup> and catalysts<sup>[8–10]</sup> on the other. With electron-donating substituents in the core, NDI chemistry becomes exceptionally colorful.<sup>[1,11]</sup> Exchange of only atoms suffices to cover the primary colors.<sup>[11,12]</sup> Most of these colorful core-substituted NDIs show symmetry-breaking charge separa-

tion, making them some of the most compact chlorophyll mimics available.<sup>[13]</sup>

Most of these decisive contributions of NDIs to functional systems originate from the change of the energy level of HOMO and LUMO with substituents added in the core and to the imides. Particularly, the LUMO levels are important with regard to applications reaching from optoelectronic devices to anion- $\pi$  catalysis. As such, the determination of these LUMO levels from cyclic voltammetry (CV) or differential pulse voltammetry (DPV) combined with absorption spectroscopy is straightforward. However, differences in data analysis have led to different values appearing in the literature. This is particularly true for CV data, which can come from very broad peaks or barely visible shoulders, and have been taken either at the onset of the wave, at the maximum on one wave, or the midpoint between reduction and oxidation wave. Moreover, the resulting values have been calibrated against different values, for example,  $-4.8$  eV or, more recently,  $-5.1$  eV for the  $\text{Fc}^+/\text{Fc}$  couple against vacuum.<sup>[1,14]</sup> Most importantly, contributions from secondary substituents on the intrinsic imide and primary substituents in the core have been largely neglected.<sup>[1,15]</sup>

Considering this situation, we decided to prepare a focused collection of NDIs and determine their LUMO levels from the unambiguous maximum in their DPV under identical, clearly defined conditions. As a result, we here provide the pertinent data set needed to dissect individual contributions from substituents to the LUMO levels of NDIs. Moreover, we add an extension to sulfur chemistry in the core of perylenediimides (PDIs)<sup>[16–18]</sup> to construct a comparative reference table that outlines general trends in the LUMO space covered by leading

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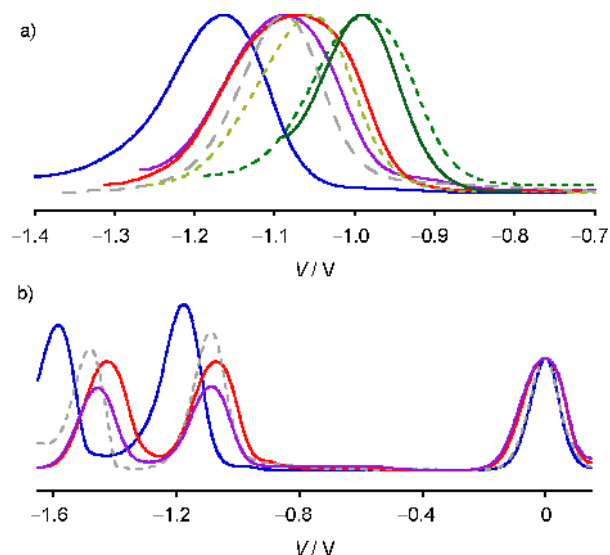
families of electron acceptors, that is, NDIs, PDIs, and fullerenes.

## Results and Discussion

### Secondary substituents on imides

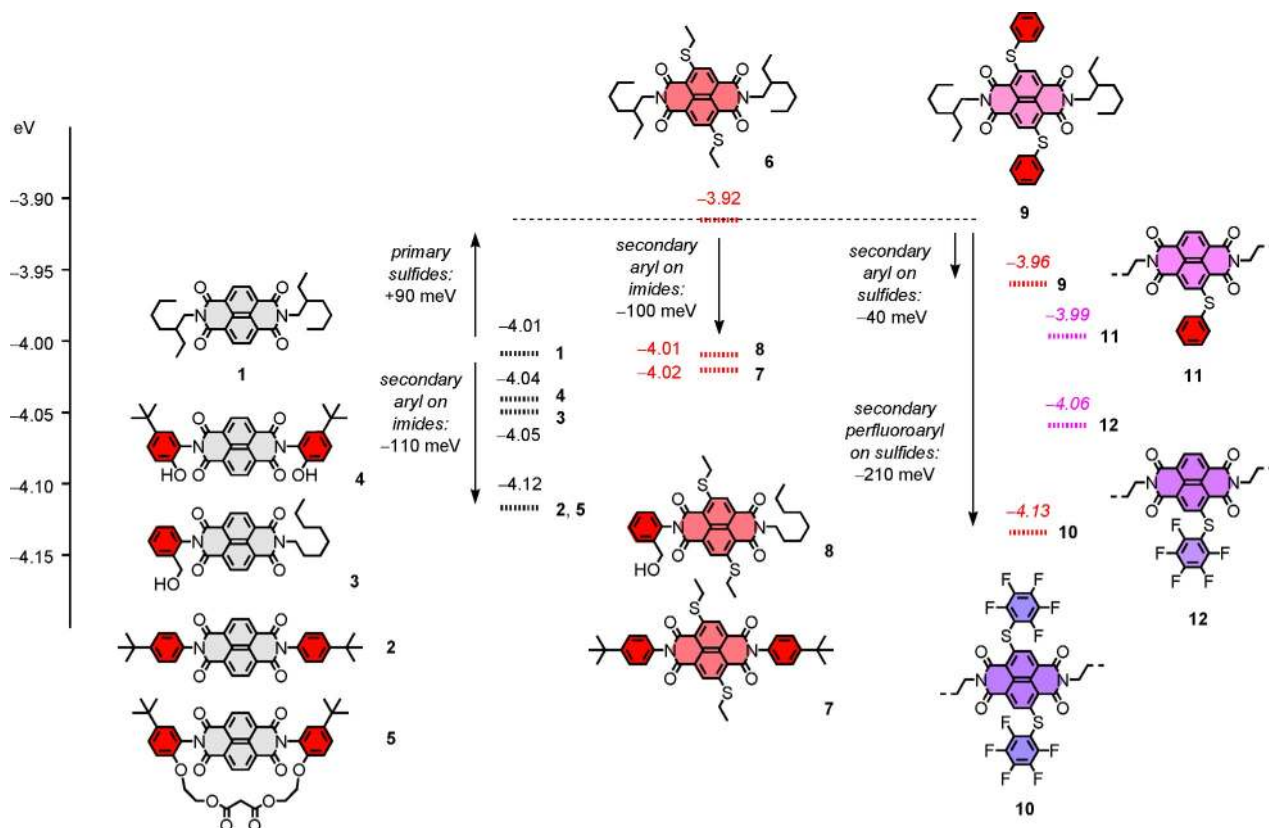
In assessments of the LUMO level of core-substituted NDIs in functional systems, contributions from the secondary substituents of the intrinsic primary imides remain underappreciated.<sup>[1–15]</sup> This seemed justified because these substituents were expected to be largely decoupled at the nitrogen atom. In functional systems, the main difference at the imide periphery concerns aromatic versus aliphatic substituents.<sup>[6–10]</sup> To determine the impact of these secondary substituents on the LUMO levels precisely, model systems 1–5 with unsubstituted NDIs were prepared (Figure 1). Their synthesis was very straightforward; details can be found in the Supporting Information.<sup>[19]</sup>

DPV measurements were done under standard conditions in dichloromethane with the  $\text{Fc}^+/\text{Fc}$  couple as internal standard. From the DPV maxima, LUMO levels were calculated assuming  $E_{\text{LUMO}} = -5.10$  eV for  $\text{Fc}^+/\text{Fc}$  against vacuum. For unsubstituted NDI 1 with two secondary alkyl substituents on the primary imides, an  $E_{\text{LUMO}} = -4.01$  eV was found (Figures 1 and 2). Replacement of these two alkyl by phenyl substituents with *tert*-butyl solubilizers in *para* position in NDI 2 gave  $E_{\text{LUMO}} = -4.12$  eV. Replacement of two secondary alkyls by two aryls on



**Figure 2.** a) Normalized first reduction peaks in the differential pulse voltammogram (DPV) of NDIs 6 (blue), 1 (grey, dashed), 8 (purple), 7 (red), 3 (light green, dashed), 2 (dark green, dashed), and 5 (dark green) in  $\text{CH}_2\text{Cl}_2$ . b) Original DPV data for 6 (blue), 1 (grey, dashed) and 8 (purple), and 7 (red), normalized at the internal standard  $\text{Fc}^+/\text{Fc}$ .

the primary imides thus caused a decrease of  $\Delta E_{\text{LUMO}} = -110$  meV. This decrease, clearly, is not negligible. Only one aryl substituent in NDI 3 gave an intermediate  $E_{\text{LUMO}} = -4.05$  eV. Introduction of two most powerful phenol donors in



**Figure 1.** Selected contributions from substituents in NDI core and periphery to the energy of their LUMOs. Energies  $E_{\text{LUMO}}$  were obtained by differential pulse voltammetry (DPV) in  $\text{CH}_2\text{Cl}_2$ , and are reported in eV relative to  $-5.10$  eV for  $\text{Fc}^+/\text{Fc}$ . Values given in italics are taken from literature<sup>[16]</sup> and are shown for comparison and completion (9–12).

*ortho* position gave with  $E_{\text{LUMO}} = -4.04$  eV a LUMO level for NDI **4** that was still clearly below that of NDI **1** with two secondary alkyls. Conversion of these phenol donors into weaker ethers and bridging of the core of NDI **5** with a malonate dilactone<sup>[7]</sup> returned the LUMO levels to the original  $E_{\text{LUMO}} = -4.12$  eV of NDI **2**. Although the variation of too many parameters prevented strong conclusions, it could be said that neither bridging nor tertiary alkoxy substituents on the secondary phenyls have an important impact on the LUMO level of the central NDI **5**.

### Secondary substituents with sulfides in the NDI core

For NDI **6** with two alkyl substituents at the primary imides, the introduction of two alkyl sulfides in the core, an  $E_{\text{LUMO}} = -3.92$  eV was measured by DPV (Figures 1 and 2). Compared with the native NDI **1** at  $E_{\text{LUMO}} = -4.01$  eV, this calculated to an increase of  $\Delta E_{\text{LUMO}} = +90$  meV caused by two alkyl sulfide donors in the core. This increase demonstrated that ethyl sulfides inject electron density into the naphthalene core. This role of ethyl sulfides as electron donors was in conflict with their slightly positive Hammett  $\sigma_p = +0.03$ . However, this value refers to benzoic acids.<sup>[20]</sup> Recent studies with twisted mechanophores confirmed predictions from theory<sup>[21]</sup> (including  $\sigma_p^+ = -0.60$ )<sup>[20]</sup> that with decreasing electron density in the aromatic system, sulfides transform from weak electron acceptors to quite strong electron donors.<sup>[22]</sup> The  $\Delta E_{\text{LUMO}} = +90$  meV in response to the addition of two ethyl sulfides in the  $\pi$ -acidic core of NDI **6** was thus in full agreement with this concept of turn-on sulfide donors (see below).

Replacement of the secondary alkyl by aryl substituents on the primary imides of NDI **6** with two sulfides in the core reproduced the trends found with the native NDI **1**. A  $\Delta E_{\text{LUMO}} = -100$  meV was found for NDI **7** (Figures 1 and 2). This comparison nicely illustrated that contributions from secondary imide substituents in the periphery are not negligible and deserve full attention for the interpretation of results with functional systems. The  $\Delta E_{\text{LUMO}} = -90$  meV found with only one aryl substituent in NDI **8** exceeded the  $\Delta E_{\text{LUMO}} = -40$  meV of homolog **3** without primary sulfides clearly. However, the central lesson learned was not affected by this quite puzzling but overall minor inconsistency: The  $\Delta E_{\text{LUMO}} \sim -100$  meV for substitution of two secondary alkyls by two aryls on the primary imide is roughly independent of the presence of other primary substituents in the NDI core.

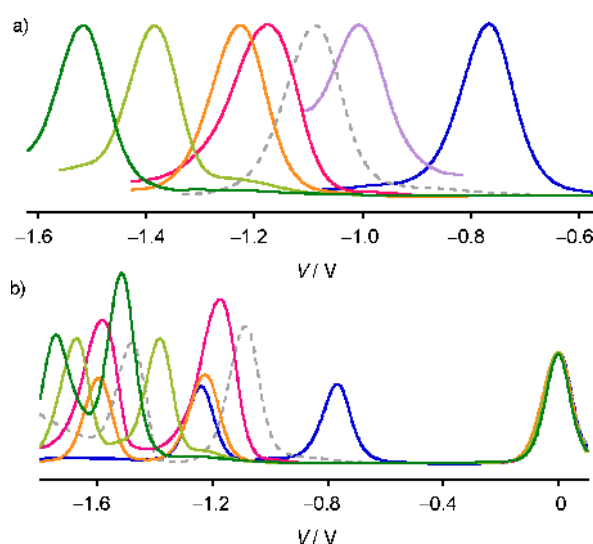
LUMO levels of NDIs **9–12** have been previously reported as part of a comprehensive series on aryl sulfides in the NDI core.<sup>[15]</sup> The  $E_{\text{LUMO}} = -3.96$  eV of phenyl sulfide **9** was found  $\Delta E_{\text{LUMO}} = -40$  meV below the  $E_{\text{LUMO}} = -3.92$  eV of alkyl sulfide **6**. This change with secondary phenyls on primary sulfides in the core was clearly less pronounced than the  $\Delta E_{\text{LUMO}} \sim -100$  meV with secondary phenyls on primary imides in NDI **7**. Secondary pentafluorophenyl substituents on the primary sulfides in NDI **10** lowered to LUMO level to  $E_{\text{LUMO}} = -4.13$  eV. Compared with alkyl sulfides in NDI **6**, this decrease with secondary pentafluorophenyl substituents in NDI **10** calculated to  $\Delta E_{\text{LUMO}} = -210$  meV.

Comparison with unsubstituted alkyl NDI **1** at  $E_{\text{LUMO}} = -4.01$  eV demonstrated that, consistent with the concept of turn-on sulfides,<sup>[22]</sup> phenyl sulfides in **9** remain electron donors. Compared with the ethylsulfides in **6** with  $\Delta E_{\text{LUMO}} = +90$  meV and  $\sigma_p = +0.03$ , the  $\Delta E_{\text{LUMO}} = +50$  meV for phenyl sulfides with  $\sigma_p = +0.07$  in **9** was very reasonable within the context of the concept of turn-on sulfide donors. In clear contrast, pentafluorophenyl sulfides in NDI **10** functioned as electron acceptors. The  $\Delta E_{\text{LUMO}} = -120$  meV below **1** suggested the withdrawing effect from the secondary pentafluorophenyl substituents in NDI **10** overcompensates the donating effect of primary turn-on sulfides.

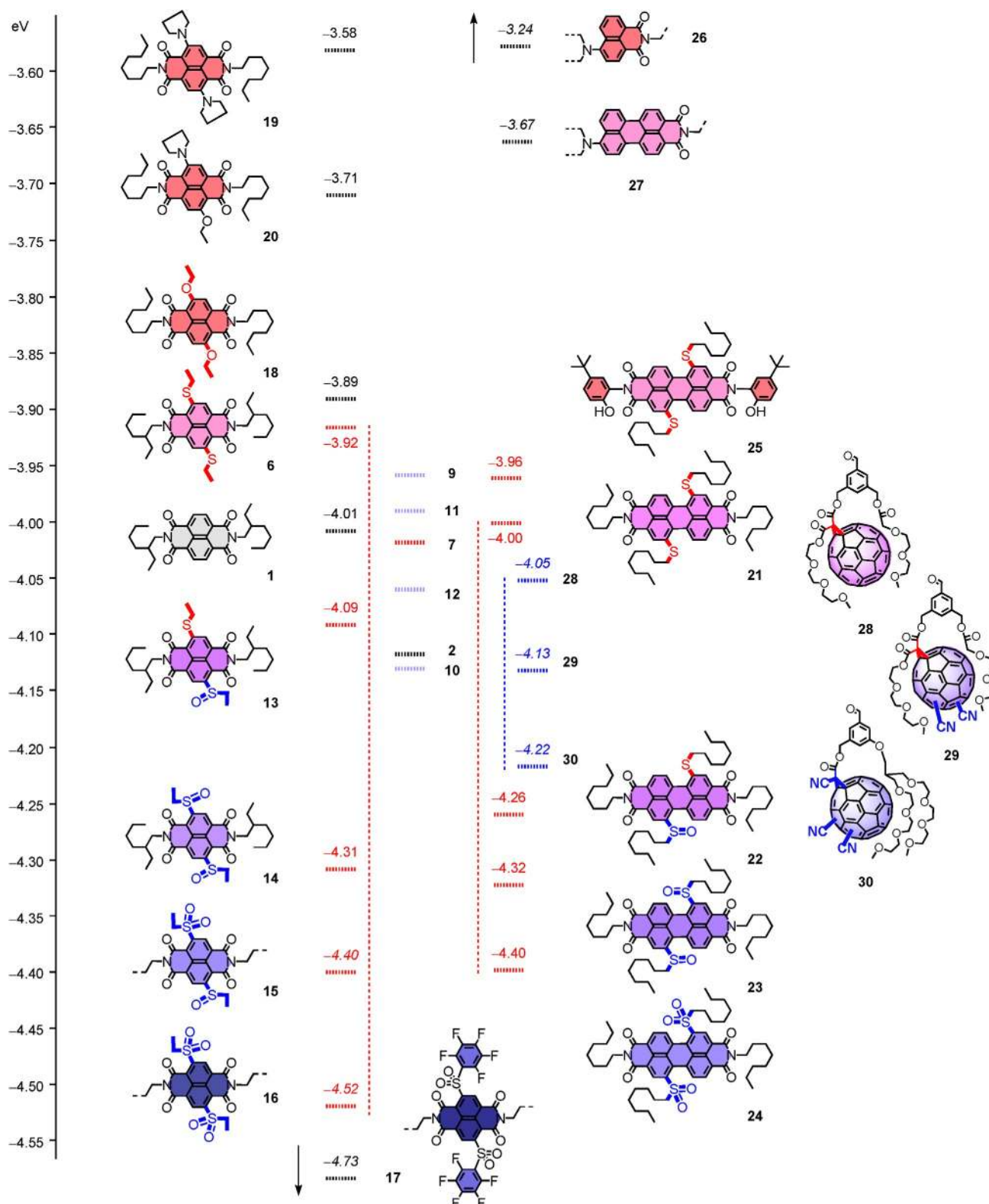
To complete the picture, the previously reported<sup>[15]</sup> LUMO levels for NDIs **11** and **12** with only one arylsulfide in the core were added to the graphical summary in Figure 1. Viewed from unsubstituted NDI **1**, the contributions were nearly additive. The  $\Delta E_{\text{LUMO}} = +20$  meV of NDI **11** with one was almost halfway the  $\Delta E_{\text{LUMO}} = +50$  meV of NDI **9** with two phenyl sulfide donors in the core. The same was true in the pentafluorophenyl series with  $\Delta E_{\text{LUMO}} = -50$  meV for NDI **12** and  $\Delta E_{\text{LUMO}} = -120$  meV for NDI **10**.

### Sulfur chemistry in the NDI core

Oxidation of the two sulfides in the core of NDI **6** gradually converted the turn-on donors ( $\sigma_p = +0.03$ ) into strong sulfoxide ( $\sigma_p = +0.48$ ) and even stronger sulfone acceptors ( $\sigma_p = +0.78$ ). This redox switch is of highest importance in functional systems because  $\pi$  acidity<sup>[6–10]</sup> or macrodipoles<sup>[22,23]</sup> can be changed without global structural changes. According to their DPV maxima, the LUMO levels dropped correspondingly from NDI **13** with one sulfoxide in the core at  $E_{\text{LUMO}} = -4.09$  eV to NDI **14** with two sulfoxides at  $E_{\text{LUMO}} = -4.31$  eV (Figures 3 and 4). The  $E_{\text{LUMO}} = -4.09$  eV of NDI **13** with one sulfoxide and one



**Figure 3.** a) Normalized first reduction peaks in the differential pulse voltamogram (DPV) of NDIs **19** (dark green), **20** (light green), **18** (orange), **6** (red), **1** (grey, dashed), **13** (purple), and **14** (blue) in  $\text{CH}_2\text{Cl}_2$ . b) Original DPV data for **1**, **14**, and **18–20** normalized at the internal standard  $\text{Fc}^+/\text{Fc}$  (colors as in a).



**Figure 4.** Reference table for LUMO space covered by leading electron acceptors: NDIs (left), PDIs (middle), and fullerenes (right), compared also with ANIs and APIs (top right). Representative data from Figure 1 (1–12) are transcribed here to show the contribution of secondary aromatic NDI substituents on sulfides (blue) and imides (red, black). LUMO levels were obtained by differential pulse voltammetry (DPV) in  $\text{CH}_2\text{Cl}_2$  and are reported in eV relative to  $-5.10$  eV for  $\text{Fc}^+/\text{Fc}$ . Values given in italics are extrapolated from literature<sup>[15,26,28]</sup> and are shown for comparison and completion (15–17, 26–30).

sulfide in the core was clearly, that is  $\Delta E_{\text{LUMO}} = -80$  meV, below the  $E_{\text{LUMO}} = -4.01$  eV of unsubstituted NDI 1. This finding demonstrated that turn-on sulfide donors are less effective than

conventional sulfoxide acceptors. The LUMO level of mixed sulfide/sulfoxide NDI 13 was  $\Delta E_{\text{LUMO}} = -170$  meV below that of NDI 6 with sulfides and  $\Delta E_{\text{LUMO}} = +220$  meV above that of NDI

**14** with two sulfoxides in the core. These differences showed that the sulfide-to-sulfoxide substitution in the NDI core is a) most significant and b) slightly overadditive.

Less important for this study focusing on precise fine-tuning around unsubstituted NDIs, values extrapolated from the literature for the more extreme LUMOs of mixed sulfoxide/sulfone NDI **15** ( $E_{\text{LUMO}} = -4.40$  eV), NDI **16** with two ethyl sulfone ( $E_{\text{LUMO}} = -4.52$  eV) and NDI **17** with two pentafluorophenyl sulfones ( $E_{\text{LUMO}} = -4.73$  eV) were added in Figure 4 for comparison and completion.<sup>[15]</sup>

### Other donors in the NDI core

The increase of LUMO levels with stronger donors in the core is understood.<sup>[1]</sup> In the current series, two ethoxy donors with  $\sigma_p = -0.24$  in the core of NDI **18** gave  $E_{\text{LUMO}} = -3.89$  eV, two stronger pyrrolidyl donors in the core of NDI **19** gave  $E_{\text{LUMO}} = -3.58$  eV, and the mixed NDI **20** was with  $E_{\text{LUMO}} = -3.71$  eV quite exactly in between (Figures 3 and 4). Most important for this study on small changes, ethoxy NDI **18** with  $\sigma_p = -0.24$  could be firmly placed  $\Delta E_{\text{LUMO}} = +30$  meV above NDI **6** with the turn-on ethyl sulfide donors ( $\sigma_p = +0.03$ , Figure 3a). Compared with unsubstituted NDI **1**, the increase with two turn-on sulfides ( $\Delta E_{\text{LUMO}} = +90$  meV) was not so much weaker than that with strong ethoxy donors ( $\Delta E_{\text{LUMO}} = +120$  meV), that is, +45 mV against +60 mV per donor.

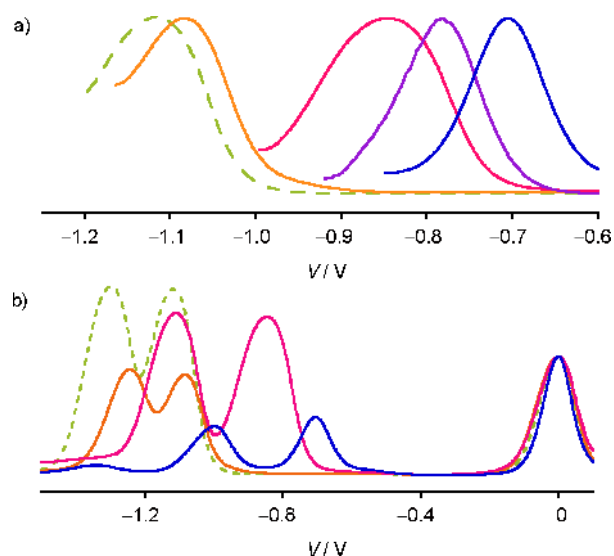
NDI **6** with turn-on sulfide donors is red ( $\lambda_{\text{max}} = 528$  nm), whereas NDI **18** with ethoxy donors is yellow ( $\lambda_{\text{max}} = 469$  nm).<sup>[1,11-14]</sup> The red color of turn-on NDI **6** is similar to that of mixed NDI **20** with one amine and one ether in the core ( $\lambda_{\text{max}} = 552$  nm), whereas diamino NDI **19** is blue ( $\lambda_{\text{max}} = 620$  nm).<sup>[1,11-14]</sup> The red color of sulfide NDI **6** compared with the yellow color of ethoxy NDI **18** suggested that the turn-on anomaly of sulfide substituents<sup>[22]</sup> is more pronounced on the HOMO than on the LUMO level. Estimated from the intercept of absorption and emission spectra,<sup>[1,12-15]</sup> the HOMO level of NDI **6** with turn-on donors ( $\sigma_p = +0.03$ ) approximated to quite remarkable  $\Delta E_{\text{HOMO}} = +270$  mV above the HOMO level of NDI **18** with permanent ethoxy donors ( $\sigma_p = -0.24$ ). A HOMO far above and a LUMO slightly below the conventional alkoxy standards supported that turn-on sulfide donors<sup>[22]</sup> operate more on the HOMO than on the LUMO level. Contributions from 1,5O-S interactions<sup>[24]</sup> to the imide carbonyls are possible.<sup>[25]</sup>

### Sulfur chemistry in the PDI core

Contrary to the situation with NDIs, sulfur chemistry in the core of PDIs has not received much attention.<sup>[17]</sup> To put the results with NDIs into context, we prepared PDI **21** with two octylsulfides in the core (Figure 4). Long alkyl chains were needed also on the primary sulfides to assure good solubility. Controlled oxidation with *meta*-chloroperbenzoic acid (*m*CPBA) and  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  at 0 °C afforded the PDI **22** with one sulfide and one chiral sulfoxide and **23** with two chiral sulfoxides in the core. The two diastereomers of PDI **23** showed very different retentions on thin-layer chromatography (TLC) and could be

easily separated by column chromatography. The pairs of enantiomers in **22** and **23** were not separated. Further oxidation with excess *m*CPBA at room temperature yielded the highly fluorescent PDI **24** with two sulfones in the core.

DPV revealed an  $E_{\text{LUMO}} = -4.00$  eV for PDI **21** with two sulfide donors (Figures 4 and 5). With increasingly strong primary  $\pi$  acceptors in the core, their LUMO levels decreased from  $E_{\text{LUMO}} = -4.26$  eV for the mixed PDI **22** to  $E_{\text{LUMO}} = -4.32$  eV for sulfoxide PDI **23** and  $E_{\text{LUMO}} = -4.40$  eV for sulfone PDI **24** (Figures 4 and 5). For completion, PDI **25** with powerful secondary phenol donors on the primary imides was prepared as well. Compared with the standard alkyl substituents, secondary phenol donors on the imides raised the LUMO level of PDI **25** by  $\Delta E_{\text{LUMO}} = +40$  meV to  $E_{\text{LUMO}} = -3.96$  eV (Figures 4 and 5).



**Figure 5.** a) Normalized first reduction peaks in the differential pulse voltammogram (DPV) of PDIs **25** (light green, dashed), **21** (orange), **22** (red), **23** (purple), and **24** (blue) in  $\text{CH}_2\text{Cl}_2$ . b) Original DPV data for **25** (light green, dashed), **21** (orange), **22** (red), and **24** (blue), normalized at the internal standard  $\text{Fc}^+/\text{Fc}$ .

### The big picture

The  $E_{\text{LUMO}} = -4.00$  eV of PDI **21** with two turn-on sulfide donors in the core was found  $\Delta E_{\text{LUMO}} = -80$  meV below the  $E_{\text{LUMO}} = -3.92$  eV of the homologous NDI **6** (Figure 4). This  $\Delta E_{\text{LUMO}} = -80$  meV was clearly significant yet relatively small considering the structural modifications involved. Already the replacement of normal alkyl by aryl substituents at the imine periphery of NDI **7** was sufficient to lower the LUMO below this level. The  $E_{\text{LUMO}} = -4.00$  eV of PDI **21** with two primary sulfides was roughly identical with that of unsubstituted NDI **1**. Interestingly, the most powerful secondary phenol donors on the imides raised the LUMO from PDI **21** to PDI **25** by  $\Delta E_{\text{LUMO}} = +40$  meV, whereas the same secondary phenols lowered the LUMO of the original NDI **1** to NDI **4** by  $\Delta E_{\text{LUMO}} = -30$  meV (Figure 4).

The  $E_{\text{LUMO}} = -4.26$  eV of the mixed sulfide/sulfoxide PDI **22** was  $\Delta E_{\text{LUMO}} = -170$  meV below the  $E_{\text{LUMO}} = -4.09$  eV of the homologous NDI **13** (Figure 4). Further oxidation to sulfoxides

strongly decreased this difference to nearly negligible  $\Delta E_{\text{LUMO}} = -10$  meV for PDI **23** below NDI **14**. Complete oxidation to sulfones made PDI **24** appear  $\Delta E_{\text{LUMO}} = +120$  meV above NDI **16**. Overall, the expansion of the aromatic system from naphthalene to perylene decreased the responsiveness to oxidation of turn-on sulfide donors to sulfoxide and sulfone acceptors down to 67%.

For completion, we point out that similar trends can be extracted for strong donors. NDI **19** with two amines in the core reaches  $E_{\text{LUMO}} = -3.58$  eV. The formal removal of one imide acceptor and one amine donor leads to push-pull amino-naphthalimide (ANI) **26** at  $E_{\text{LUMO}} = -3.24$  eV (Figure 4).<sup>[26,27]</sup> The homologous amino peryleneimide (API) **27** appears at  $E_{\text{LUMO}} = -3.67$  eV.<sup>[26]</sup> Compared with the standard NDI **6** ( $\Delta E_{\text{LUMO}} = +720$  meV) and PDI **21** ( $\Delta E_{\text{LUMO}} = -330$  meV), this calculated to a decrease in the responsiveness to 50% for APIs compared with ANIs. This observation was intriguing because compared with the ideal NDIs, the reduced responsiveness of PDIs to primary acceptors might question their usefulness to integrate anion- $\pi$  interactions into functional systems.<sup>[4-10]</sup> With APIs and ANIs compared with PDIs and NDIs, however, the reversed conclusion applies: an even more decreased responsiveness to the primary donor could eventually increase the appeal of APIs for studies on ionpair- $\pi$  interactions.<sup>[26,27]</sup>

To provide a general overview for LUMO engineering with the arguably most popular families of electron-accepting aromatics, selected data from the recently reported nine-component gradient of fullerenes were added to Figure 4 as well.<sup>[28]</sup> These data were obtained under identical conditions, that is, from DPV maxima calibrated against  $\text{Fc}^+/\text{Fc}$  at  $-5.10$  eV. Fullerene **28** with one cyclopropane substituent, that is, the classical motif obtained by fullerene modification with the Bingel reaction, was found at  $E_{\text{LUMO}} = -4.05$  eV. This is just below unsubstituted NDI **1** with alkyl substituents on the imides ( $E_{\text{LUMO}} = -4.01$  eV) and PDI **21** with turn-on sulfides in the core ( $E_{\text{LUMO}} = -4.00$  eV).

The addition of two cyano acceptors as primary substituents lowers the LUMO level of **28** by  $\Delta E_{\text{LUMO}} = -80$  meV to  $E_{\text{LUMO}} = -4.13$  eV for **29**. With  $\Delta E_{\text{LUMO}} = -90$  meV, the impact of one secondary cyano acceptor in **30** exceeded the moderate  $\Delta E_{\text{LUMO}} = -80$  meV from two primary acceptors in **29** slightly. The  $\Delta E_{\text{LUMO}} = -80$  meV of fullerenes in response to two strong primary acceptors with  $\sigma_p = +0.66$  was small compared with NDIs. Two strong primary acceptors with  $\sigma_p = +0.48$  gave an  $\Delta E_{\text{LUMO}} = -300$  meV, primary sulfone acceptors with  $\sigma_p = +0.77$  an  $\Delta E_{\text{LUMO}} = -510$  meV. The responsiveness of fullerenes to primary substituents thus calculated to  $\sim 20\%$  of that of NDIs. The response of comparable NDIs to two primary cyano groups is even more impressive:  $E_{\text{LUMO}} = -4.80$  eV,  $\Delta E_{\text{LUMO}} = -280$  meV below disulfone **16**,  $-790$  meV below unsubstituted **1** has been estimated under similar conditions.<sup>[1]</sup> Compared with these dicyano NDIs, the responsiveness of fullerenes drops to  $\sim 10\%$ . In any case, the poor responsiveness of fullerenes to primary acceptors was also clearly below the 67% observed for PDIs.

For completion, all newly determined LUMO levels were listed together with the measured first reduction potentials in

**Table 1.** Summary of newly measured differential pulse voltammetry (DPV) data.<sup>[a]</sup>

Entry	Compound <sup>[a]</sup>	$E_{\text{LUMO}}$ [eV] <sup>[b]</sup>	$E_{\text{red1}}$ [V] <sup>[c]</sup>	$E_{\text{red2}}$ [V] <sup>[d]</sup>
1	<b>1</b>	-4.01	-1.09	-1.48
2	<b>2</b>	-4.12	-0.98	-1.40
3	<b>3</b>	-4.05	-1.05	-1.37
4	<b>4</b>	-4.04	-1.06	-1.37
5	<b>5</b>	-4.12	-0.98	-1.54
6	<b>6</b>	-3.92	-1.18	-1.58
7	<b>7</b>	-4.02	-1.08	-1.46
8	<b>8</b>	-4.01	-1.09	-1.43
9	<b>13</b>	-4.09	-1.01	-1.46
10	<b>14</b>	-4.31	-0.79	-1.37
11	<b>18</b>	-3.89	-1.21	-1.59
12	<b>20</b>	-3.71	-1.39	-1.69
13	<b>19</b>	-3.58	-1.52	-1.75
14	<b>21</b>	-4.00	-1.10	-1.24
15	<b>22</b>	-4.26	-0.84	-1.01
16	<b>23</b>	-4.32	-0.78	-1.09
17	<b>24</b>	-4.40	-0.70	-1.00

[a] See Figure 1–5 for structures, original data, and conditions. [b] Energies  $E_{\text{LUMO}}$  in eV relative to  $-5.10$  eV for  $\text{Fc}^+/\text{Fc}$ . [c] DPV maxima for first NDI/PDI reduction, in V relative to 0 V for  $\text{Fc}^+/\text{Fc}$ . [d] DPV maxima for second NDI/PDI reduction, in V relative to 0 V for  $\text{Fc}^+/\text{Fc}$ .

DPV (Table 1). Although less important for most applications, the second reduction potentials were added as well. The influence of primary and secondary substituents on first and second reduction potentials was similar overall.

## Conclusion

The objective of this study was to produce a comprehensive reference table for quantitative LUMO engineering of NDIs, in comparison with PDIs, fullerenes, as well as ANIs and APIs. The responsiveness of NDIs to primary substituents is shown to exceed that of PDIs (67%) and fullerenes ( $\sim 20\%$ ) by far. These trends confirm the most responsive NDIs as ideal to integrate anion- $\pi$  interactions into functional systems,<sup>[4-10]</sup> whereas the less responsive APIs could be of interest to explore ionpair- $\pi$  interactions.<sup>[25,26]</sup>

With primary substituents in the NDI core, the comparison of sulfides and ethers deserves particular attention. With electron-rich aromatics, ethyl sulfides are weak acceptors ( $\sigma_p = +0.03$ ), but they transform into quite strong donors with electron-poor aromatics such as NDIs.<sup>[21,22]</sup> In contrast, ethoxy substituents are conventional donors ( $\sigma_p = -0.24$ ). The LUMO level of NDIs with ethyl sulfides in the core ( $E_{\text{LUMO}} = -3.92$  eV) could be firmly localized right below that of NDIs with alkoxy substituents ( $E_{\text{LUMO}} = -3.89$  eV) but clearly above that of unsubstituted NDIs ( $E_{\text{LUMO}} = -4.01$  eV). However, their HOMO levels show inversion of this order: The red NDIs with ethyl sulfides in the core appear far above the yellow NDIs with ethoxy substituents ( $\Delta E_{\text{HOMO}} = +135$  meV per donor). This particular impact of turn-on sulfides<sup>[22]</sup> on the HOMO level invites for computational analysis<sup>[21,24]</sup> and could be of use to elaborate on the nature of anion- $\pi$  interactions.<sup>[5]</sup>

Secondary aryl in place of alkyl substituents for the intrinsic primary imide substituents of NDIs lowers their LUMO levels by  $\Delta E_{\text{LUMO}} \sim -100$  meV. Aryl in place of alkyl substituents for primary turn-on sulfides in the NDI core lowers their LUMO levels by  $\Delta E_{\text{LUMO}} = -40$  meV (perfluorophenyl):  $\Delta E_{\text{LUMO}} = -210$  meV). As a result, NDIs with primary sulfides in the core can be more or less  $\pi$  acidic than unsubstituted NDIs, depending on the secondary substituents on imides and sulfides. The availability of comparable values for different primary and secondary substituents is thus most important for design and analysis of functional systems. For example, the answer to the question whether the dependence of anion- $\pi$  catalysts on their  $\pi$  acidity is linear or exponential can change, depending on the LUMO energies used.<sup>[7,9,29,30]</sup>

The graphical summary of general trends with primary and secondary substituent effects for NDIs, PDIs, and fullerenes provided in Figure 4 is obviously far from complete. Nearly endless possibilities exist to refine the collection with more, or less, subtle structural modifications. However, the data set provided in Figure 4 identifies the relevant trends needed to clarify open questions and map out the LUMO space for electron-accepting aromatics with appreciable certainty and completeness. It could be quite useful.

## Experimental Section

For details of the materials, methods and synthetic procedures, and characterization data for all new compounds, see the Supporting Information.

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