

## Redox Systems

## Synthesis of Functionalized Naphthalene Diimides and their Redox Properties

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**Abstract:** In this article, we have discussed the recently developed synthetic routes to amplify the electron-poor nature of the naphthalenediimides (NDIs) as well as the integration of electron-rich donor groups towards ambipolar and strongly electron donating NDIs. Non-conventional electron withdrawing groups (EWGs) have been applied, leading to highly electron deficient NDIs. Highly  $\pi$ -acidic molecules with LUMO levels up to  $-5.0$  eV have now been realized. Cationic EWGs have been integrated at the NDI-core resulting in six-electron acceptors called "electron-sponge". Electron donating groups like tetra-thiafulvalene, dicyanomethides, amino-groups, etc. have been

substituted to realize ambipolar NDIs with high HOMO levels and "electron-reservoir" properties. Diverse coupling reactions such as, Suzuki, Sonogashira, Stille, Buchwald–Hartwig, etc. have been performed to achieve attractive redox properties. Double cross-coupling reactions have been successful with metallacyclopentadienes to establish highly extended NDIs. The new synthetic routes to NDIs have significantly extended the electrochemical window, improved their optical properties and have resulted in attractive panchromatic systems and driven new applications.

Arylenediimides have emerged as highly promising class of electron deficient organic scaffolds with high thermal and photochemical stabilities. These have been extensively studied due to their elegant redox activity, charge transport and self-assembly properties.<sup>[1]</sup> These scaffolds find application as the active component in several functional materials.<sup>[2–9]</sup> Among the aryl-

enediimides, naphthalene tetracarboxylic diimides (NDIs) and perylene tetracarboxylic diimides (PDIs)<sup>[10]</sup> appear as the most promising electronic materials because of their large electron deficient  $\pi$ -surface and ability to form self-assembled structures.<sup>[11]</sup> These scaffolds show reversible electrochemical reduction properties to form the one-electron reduced radical anion and the two-electron reduced dianions. Furthermore, the electronic properties of these imides can be easily tuned by the substitution of electron withdrawing groups (EWGs) or/and electron donating groups (EDGs) at the core-positions and to a lesser extent at the axial-positions of the NDI/PDI scaffolds.<sup>[8,12]</sup>

One of the most exquisite aspects of the NDI scaffold is the variety of substitutions possible at its axial-, core- and shoulder-

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positions (Figure 1). The various functionalities at the axial-imide positions of NDI can significantly affect its solubility and

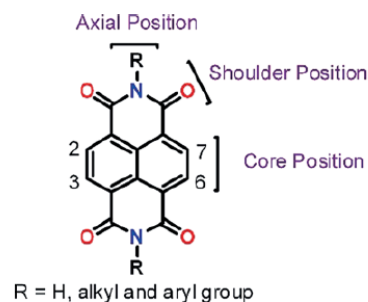


Figure 1. Chemical structure of naphthalenediimide.

molecular organization properties, while having negligible effect on the opto-electronic properties. On the other hand, the chemical modification at the 2, 3, 6 and 7 core-positions of the NDI (c-NDI), can considerably tune their electronic and photo-physical properties.<sup>[8,12–14]</sup> Thus, functionalization of the c-NDI with various groups, such as alkyl or aryl amino, alkoxy, sulfur, cyano, thiophene and metals like Pd,<sup>[15]</sup> have now been possible, which modulates the opto-electronic properties of the NDI scaffold.

Along with this, cationic electron withdrawing groups (EWGs) like bipyridinium, phosphonium, etc. have been integrated resulting in vastly modulated redox properties.<sup>[14]</sup> Notably, the cationic groups have also aided the generation of stable NDI-based radical ions<sup>[16a]</sup> and functional properties.<sup>[16b]</sup> In ad-

Table 1. First Reduction and oxidation potentials, absorption, emission  $\lambda_{\max}$  and HOMO/LUMO energy levels of NDIs.<sup>[a]</sup>

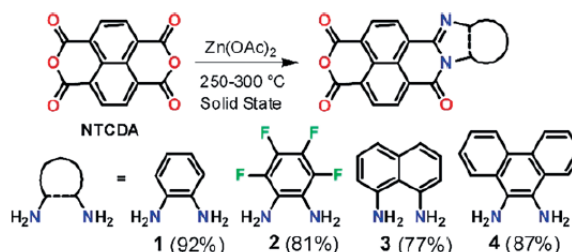
Mol.	Potential (v) vs. SCE		Potential (v) vs. Ag/AgCl		Potential (v) vs. Fc/Fc <sup>+</sup>		LUMO	HOMO	$\lambda_{\max}^{\text{abs}}$ [nm]	$\lambda_{\max}^{\text{em}}$ [nm]
	$E_1^{\text{R}}$	$E_1^{\text{O}}$	$E_1^{\text{R}}$	$E_1^{\text{O}}$	$E_1^{\text{R}}$	$E_1^{\text{O}}$				
1					−1.03	+0.81	−3.78	−5.79	484	585
2					−0.87		−3.92	−6.01	471	549
3					−1.13		−3.63	−5.17	609	
4					−1.08		−3.70	−5.37		
5									380	
6	−0.63	+0.80					−3.77	−5.20	553	705
7	+0.08						−4.41		393	
8									598	
9									613	
11									470	500, 630
12					−1.17		−3.93	−6.11	528	
13	−0.89	+0.98					−3.51	−5.38	613	
14							−3.65	−5.16		
15					−0.19		−4.90		394	
15a						−0.67		−4.42	593	
16	0.03						−4.43			
17	0.07						−4.47			
19					−1.40				423	
20					−1.30				433	
21					−1.17				420	
22					−0.53				389	
24							−3.98	−5.39	658	
25							−3.92	−5.26	686	
26							−3.89	−5.27	667	
28			−1.32	+1.53			−3.32	−5.76	504	521
29			−1.36	+1.74			−3.27	−5.93	480	490
30			−1.27	+1.09			−3.25	−5.30	515	637
31									433	567
32									530	567
33									508	
36					−1.07	+1.11	−3.73	−5.91	622	641
37					−0.96				420	
38									675	
39	−1.14	+0.26 V					−3.26	−4.66	800	
40									503	550
41									481	519
42									534	587
43									645	754
44									439	455
46							−4.0	−6.1		
48							−4.1	−5.9	616	
49							−4.2	−5.8	637	
50									482	
51									498	
52									506	
53									510	

[a] Only first reduction/oxidation potentials are given in the table other values have been given in the text.

dition, several NDI derivatives have been synthesized and evaluated for their bio-medical applications such as DNA intercalators, antimalarial and as anticancer agents.<sup>[17]</sup>

In this review article, we firstly focus on the synthetic methodologies that have been recently developed to obtain new generation of redox systems utilizing the not so common shoulder positions of the NDI. Our next topic of discussion would be the most widely explored 2,6-core-substituted c-NDIs, followed by the mono- and the tetra-substituted NDIs. The NDIs integrated with EWGs show strong electron acceptor properties and the ones integrated with EDGs show electron donating abilities. We have tabulated the reduction and oxidation potentials (Table 1, Table 2) as well as their absorption and emission wavelengths to provide an overview of their opto-electronic properties. As can be seen, the EWGs/EDGs at the NDI-core modulate the frontier molecular orbitals considerably resulting in attractive redox properties as well as significant extension of the presently accessible electrochemical window.

Anzenbacher et al. reported a high-yielding green synthetic procedure to afford the polycyclic benzimidazole derivatives (**1–4**), by reacting 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) with arylene-diamines at high temperatures (250–300 °C) in the presence of zinc acetate (Scheme 1).<sup>[18]</sup> The reaction effectively utilizes the shoulder position of the NTCDA scaffold. Notably, the reaction was carried out in the solid state.



Scheme 1. Synthetic procedure and structure of compounds **1–4**.

Table 2. First reduction and oxidation potentials, absorption, emission  $\lambda_{\text{max}}$  and HOMO/LUMO energy levels of NDIs.<sup>[a]</sup>

Mol.	Potential (v) vs. SCE $E_1^R$	Potential (v) vs. SCE $E_1^O$	Potential (v) vs. Ag/AgCl $E_1^R$	Potential (v) vs. Ag/AgCl $E_1^O$	Potential (v) vs. Fc/Fc <sup>+</sup> $E_1^R$	Potential (v) vs. Fc/Fc <sup>+</sup> $E_1^O$	LUMO	HOMO	$\lambda_{\text{max}}^{\text{abs}}$ [nm]	$\lambda_{\text{max}}^{\text{em}}$ [nm]
54	−0.54	+1.08					−3.96	−5.35	604	
55	−0.77	+1.00					−3.76	−5.29	663	
56	−0.79	+0.96					−3.77	−5.20	677	
57	−0.87	+0.75					−3.63	−5.04	719	
58	−0.78	+0.46					−3.76	−4.74	799	
59	−0.93	+0.24					−3.60	−4.55	830	
60									672	
61									430	
62					−1.03				381	
63					−1.00				383	
64									454	
68							−4.3		627	
69			−0.40				−4.0		506	
70							−4.1		543	
71							−3.9		582	
72					−1.69	+0.01			642	687
73					−1.85	−0.01			629	646
74					−1.27				419	477
75					−1.10	+0.97			563	
77			−1.31	+0.57			−3.18	−4.87	590	
78									563	
79									608	
80									564	
81							−3.77	−5.10	796	801
82	−0.08 <sup>[a]</sup>						−4.22		591	
83	−0.03 <sup>[a]</sup>						−4.25		608	
84	−0.16						−4.28	−6.28	551	
85 & 86	0.19						−4.63	−.83	545	
87	−0.21						−4.23	−6.23	582	
88	−0.08						−4.36	−6.45	573	
89					−1.15	+1.06	−3.74		589	
90					−0.36		−4.74	−7.70	376	
92			−0.35	+0.59			−4.10	−5.1		
93			−0.40				−4.06	−5.54	756	
94			−0.35				−4.12	−5.68	737	
95					−0.53		−4.41	−5.56	950	
96							−3.06	−4.49	778	793
97									611/642	647
98	+0.260				+0.100		−5.00			
99			−0.56							
100			−0.36							

[a] Only first reduction/oxidation potentials are given in the table other values have been given in the text.