

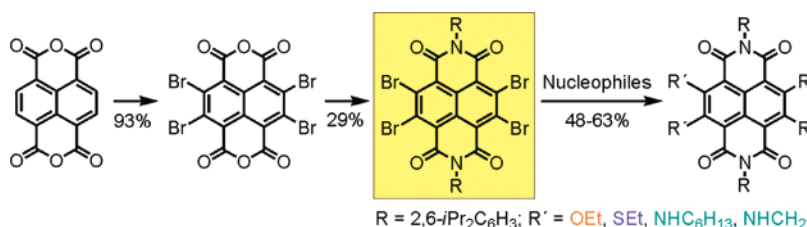
Core-Tetrasubstituted Naphthalene Diimides: Synthesis, Optical Properties, and Redox Characteristics

Cornelia Röger and Frank Würthner*

Universität Würzburg, Institut für Organische Chemie, Am Hubland, 97074 Würzburg, Germany

wuerthner@chemie.uni-wuerzburg.de

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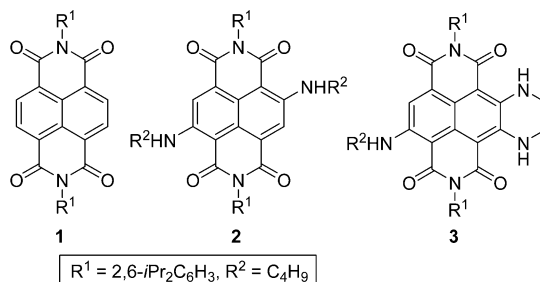


2,3,6,7-Tetrabromonaphthalene dianhydride has been synthesized by the bromination of naphthalene dianhydride with dibromoisocyanuric acid in excellent yield. The condensation of this dianhydride with 2,6-diisopropylaniline yielded the corresponding tetrabromo-substituted naphthalene diimide (NDI), which is a versatile precursor for the synthesis of core-tetrafunctionalized NDIs. Nucleophilic substitution of tetrabromo NDI with alkoxy, alkylthio, and alkylamino nucleophiles afforded a series of core-tetrasubstituted NDI chromophores that complete the series of previously reported di- and trifunctionalized NDI derivatives. The effects of electronic nature and number of core substituents on the optical and electrochemical properties of NDIs have been investigated by UV-vis and fluorescence spectroscopy and cyclic voltammetry. The absorption maxima (629–642 nm) of tetraamino NDIs are strongly bathochromically shifted compared to those of other core-functionalized NDIs.

Introduction

1,4,5,8-Naphthalenetetracarboxylic acid diimides (NDIs) are important compounds for materials and supramolecular chemistry. In past years, core-unsubstituted NDIs (structure **1**, Chart 1) were tailored for applications in numerous research fields. Due to their n-type semiconducting properties, core-unsubstituted NDIs bearing alkyl or fluorinated alkyl groups in the imide positions have been of interest as active layer in organic field-effect transistors (OFETs).¹ Since NDIs are easily reversibly reduced to form stable radical anions, they serve as electron-acceptor units in artificial photosynthetic systems for solar energy conversion.² In supramolecular chemistry, NDI-based catenanes and rotaxanes³ have been designed and very recently a supramolecular switch, which can be turned on and off by heating with a hydrogen-bonding guest molecule, has been

CHART 1. Structures of Core-Unsubstituted NDI **1** and Core-Di- and -Trisubstituted Derivatives **2** and **3**



created.⁴ The propensity of NDIs to form excimers initiated the development of NDI-based fluorescent chemosensors,⁵ and they have been used for DNA intercalating and sensing.⁶ NDIs can form large supramolecular structures through hydrogen bonding, leading to helical organic nanotubes of defined chirality.⁷ Also, supramolecular arrangement by π - π interactions was achieved resulting in rigid-rod π -helical architectures, whose structures are untwisted into open cation channels by intercalation of dialkoxynaphthalene ligands.⁸ Furthermore, anions can be transported over lipid bilayers by anion- π interactions to

* To whom correspondence should be addressed. Tel: + 49 (0)931-8885340. Fax: + 49-(0)931-8884756.

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oligonaphthalene diimide rods, exhibiting halide selectivity.⁹ Naphthalene diimide organogels were built by noncovalent interactions such as π - π stacking, hydrogen bonding, and van der Waals forces which serve as supramolecular hosts and sensors for different types of electron-rich naphthalene compounds.¹⁰ Moreover, due to their charge-transfer interaction with alkoxy-substituted naphthalenes, NDIs are applicable in flexible foldable polymers forming a stacked charge transfer (CT) donor-acceptor structure.¹¹

Functionalization of NDIs by core substitution triggered an eminent progress in controlling the optical and redox properties of this class of dyes and thus extended the scope of application. NDIs bearing two electron-donating core substituents, such as NDI **2** (Chart 1), have been previously synthesized by our group that show highly brilliant colors and strong fluorescence.¹²

Their interesting electronic properties arise from a new CT transition in the visible wavelength range, which is strongly influenced by the electron-donating strength of the core substituents. Such core-substituted NDIs have attracted interest as light-harvesting chromophores in self-assembled artificial antenna systems,¹³ and they have been used to drive a transmembrane proton gradient caused by a photoinitiated electron-transfer cascade.¹⁴ One potential future application of NDIs with electron-donating core substituents might be the optically triggered transport of currents on the molecular scale in metal-NDI hybrid setups.¹⁵ Recently a core-dicyanated electron-deficient NDI derivative has been reported, which provided high mobility, air-stable, n-type transparent organic field-effect

transistors.¹⁶ Very recently, we have reported the first examples of core-trisubstituted NDI derivatives, such as compound **3** (Chart 1), which show intense color and high fluorescence quantum yield.¹⁷

Core-di- and -trisubstituted NDIs are accessible from 2,6-dichloronaphthalene dianhydride by imidization with primary amines, followed by substitution of the chlorine atoms at the naphthalene core.^{12,17,18} In the past 2 years, several groups have also used 2,6-dibromonaphthalene dianhydride as precursor for core-disubstituted NDIs.^{12c,16,19} Two bromine substituents were introduced at the naphthalene core of 1,4,5,8-naphthalenetetracarboxylic acid dianhydride by electrophilic aromatic substitution under different reaction conditions. Application of a stoichiometric amount of dibromoisocyanuric acid (DBI) in oleum (20% SO₃) at room temperature afforded a mixture consisting of mainly 2,6-dibromonaphthalene dianhydride and small amounts of 2-monobromo and 2,3,6-tribromo compounds, along with some unreacted naphthalene dianhydride.^{12c} Alternatively, bromine has been used as a bromination agent in the presence of catalytic amounts of iodine using oleum as a solvent resulting mainly in desired dibrominated product.¹⁶ Recently, it has been reported that quantitative and selective formation of 2,6-dibromonaphthalene dianhydride can be achieved using DBI in concentrated sulfuric acid at 130 °C.¹⁹

Although a broad variety of core-di- and -trisubstituted NDIs can be synthesized starting from 2,6-dichloro- or 2,6-dibromonaphthalene dianhydride, to our knowledge, no route to NDIs bearing four electron-donating substituents at the naphthalene core has been reported in the literature. To complete the highly interesting series of core-di- and -trisubstituted NDIs, we chose 2,3,6,7-tetrabromonaphthalene dianhydride **4** as a precursor. It had been reported in the Russian literature that compound **4** was observed as a mixture with other brominated products in bromination of naphthalene dianhydride with bromine, but no procedure for the isolation and purification of **4** was given.²⁰

Here we report a highly efficient method for the synthesis of pure 2,3,6,7-tetrabromonaphthalene dianhydride **4**. The latter has been used as a starting material for the synthesis of tetrabromo-substituted NDI **5** which was disclosed in a patent shortly before our work was submitted for publication.²¹ NDI **5** was reacted in good yields with oxygen, nitrogen, and sulfur nucleophiles to give NDIs bearing four electron-donating core-

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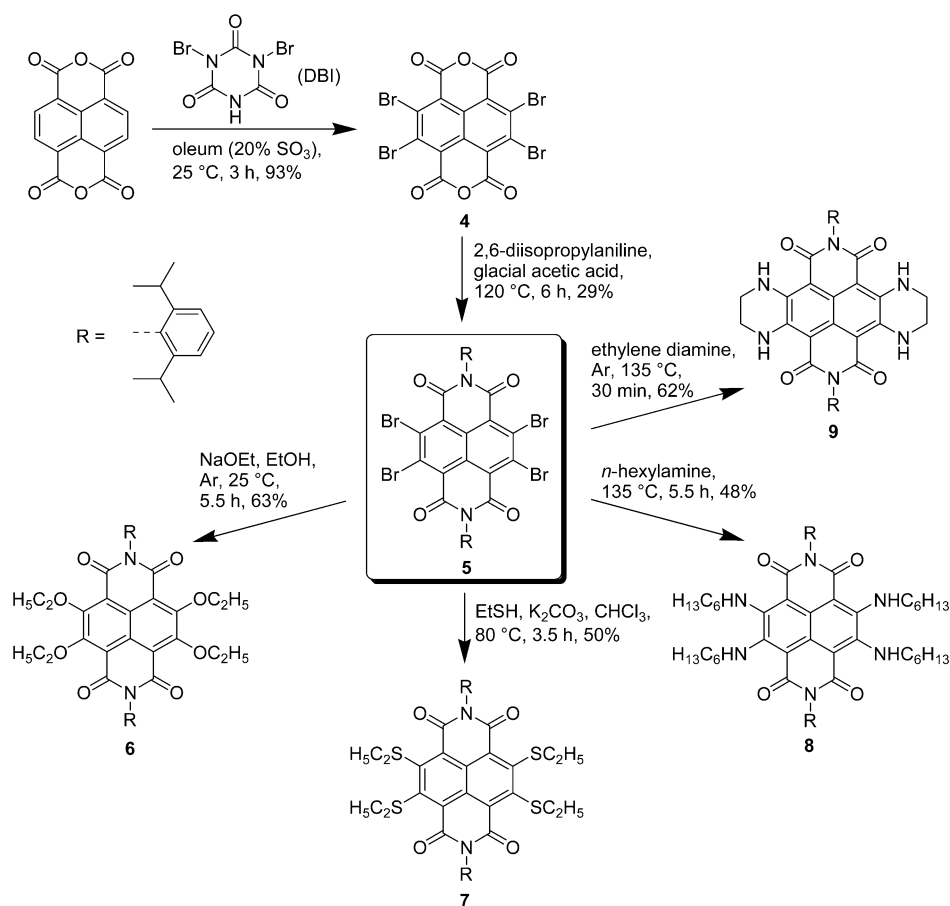
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SCHEME 1. Synthesis of Core-Tetrasubstituted NDIs 5–9



substituents. We have studied the substituent effects on the optical and redox properties for this new series of NDIs and compared those with NDIs 1–3.

Results and Discussion

Synthesis. The starting material for the synthesis of core-tetrasubstituted NDI, 2,3,6,7-tetrabromonaphthalene dianhydride **4**, was prepared by bromination of commercially available naphthalene dianhydride with 2.5 equiv of DBI in oleum (20% SO₃) at room temperature in excellent yield (Scheme 1). This bromination afforded selectively tetrabromonaphthalene dianhydride **4** since the ¹H NMR spectrum (DMSO-*d*₆) of bromination product does not show any proton resonance, indicating absence of lower brominated compounds. The purity of **4** was confirmed by elemental analysis and a correct mass was obtained by EI mass spectrometry.

For the imidization of tetrabromonaphthalene dianhydride **4** the rather bulky, less nucleophilic 2,6-diisopropylaniline was chosen to suppress nucleophilic substitution of bromine atoms. Indeed, the imidization of **4** with 2,6-diisopropylaniline in glacial acetic acid afforded the desired tetrabromonaphthalene diimide **5** as a major product, along with some at core monoaminated byproduct and unreacted naphthalene dianhydride that could be removed by column chromatography.

Tetrabrominated NDI **5** was then used as precursor for the synthesis of core-tetrafunctionalized NDIs by nucleophilic substitution of bromine atoms with alkoxy, alkylthio, or alkylamino nucleophiles (Scheme 1). Reaction of NDI **5** with

sodium ethanolate in ethanol at room temperature afforded the tetraethoxy-substituted NDI **6** in good yield. Similarly, the reaction of **5** with ethanethiol in the presence of potassium carbonate in chloroform at 80 °C yielded the tetraethylthio-substituted NDI **7** in reasonable yield. With *n*-hexylamine as nucleophile, all four bromine atoms of **5** could be replaced, resulting in the corresponding core-tetraamino-functionalized NDI **8**. Likewise, the reaction of NDI **5** with ethylene diamine as a solvent under reflux leads to the formation of tetraamino-substituted ring-closure product NDI **9**.

Optical Properties. The tetrabromo-substituted NDI **5** is a light yellow, nonfluorescent compound exhibiting an electronic transition in the range of 350–440 nm (Figure 1). Compared to the colorless core-unsubstituted NDI **1**, the absorption maximum of **5** is bathochromically shifted from 381 to 402 nm and the absorption band of the latter is less structured which is in accord with the previously reported dichlorinated NDIs.¹² The absorption band of the light yellow tetraethoxy derivative **6** appears in the same wavelength region as NDI **5**. In contrast to **5**, the tetraethoxy-substituted NDI **6** is weakly fluorescent with a quantum yield of about 2%. The fluorescence band of NDI **6** is not in mirror-image relation to the absorption band, indicating that the absorption band of **6** at 350–440 nm comprises not only the S₀–S₁ absorption but presumably overlaps with the next higher transition. Introduction of four ethylthio substituents at the naphthalene core causes a new electronic transition in the visible region with a maximum at 563 nm providing a violet color. As the tetrabromo derivative **5**, tetraethoxy NDI **7** is not fluorescent.

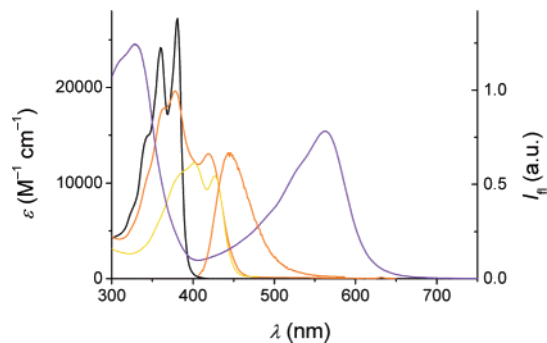


FIGURE 1. Absorption spectra of tetrabromo NDI **5** (yellow line) and tetraethylthio NDI **7** (violet line) and absorption and emission spectra (excitation at 375 nm) of tetraethoxy derivative **6** (orange lines) in dichloromethane. For comparison, the absorption spectrum of core-unsubstituted NDI **1** (black line) is depicted.

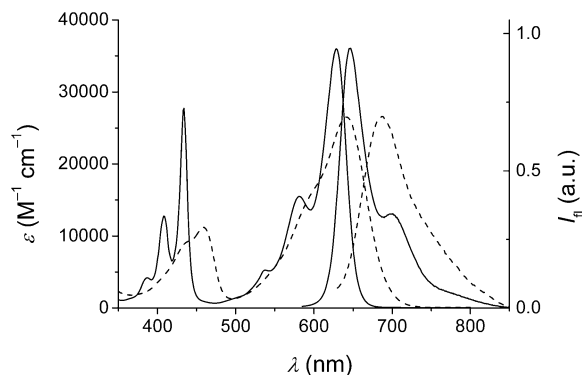


FIGURE 2. Absorption and emission spectra (excitation at 570 nm) of NDIs **8** (dashed lines) and **9** (solid lines) in dichloromethane.

The absorption and emission spectra of tetraalkylamino NDIs **8** and **9** are depicted in Figure 2. The strongly electron-donating alkylamino substituents at the naphthalene core evoke a further red-shift of the S_0 – S_1 absorption band compared to the tetraethylthio NDI **7** to 642 (for **8**) and 629 nm (for **9**), respectively. The absorption band of NDI **9** shows a much more pronounced vibronic fine structure than that of NDI **8**, which results from the higher rigidity of the former chromophore bearing ethylene-bridged substituents. NDIs **8** and **9** exhibit a second absorption band located between 380 and 440 nm which can be attributed to the electronic S_0 – S_2 transition. In particular for NDI **9**, we note a close resemblance in the vibronic structure and position of this band with that of the unsubstituted NDI **1** (Figure 1). The presence of two absorption bands in the visible region provides the bluish-green color of NDIs **8** and **9**. For both of these tetraalkylamino-substituted derivatives, fluorescence bands are observed matching the mirror image of the respective longest wavelength absorption band.

In Figure 3, the absorption spectrum of tetraalkylamino NDI **8** is shown together with the spectra of di- and trialkylamino NDIs **2** and **3**. The S_0 – S_1 band of NDI **2** exhibits a maximum at 620 nm,^{12a} while this band is shifted to shorter wavelengths for NDI **3** to 579 nm.¹⁷ Interestingly, the introduction of a fourth alkylamino substituent provokes again a red-shift to 642 nm for NDI **8**. Thus, tetraalkylamino-substituted derivative **8** shows the longest wavelength absorption maximum known for core-substituted NDI chromophores so far. In contrast to core-unsubstituted NDIs such as NDI **1**, which do not exhibit any

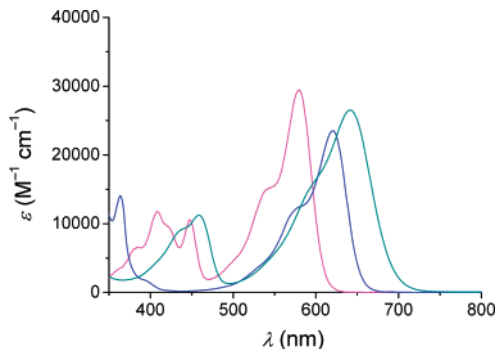


FIGURE 3. Absorption spectra of dialkylamino NDI **2** (blue line),^{12a} trialkylamino NDI **3** (pink line),¹⁷ and tetraalkylamino NDI **8** (bluish-green line) in dichloromethane.

TABLE 1. Absorption Maxima (λ_{abs}), Absorption Coefficients (ϵ), Emission Maxima (λ_{em}), and Fluorescence Quantum Yields (Φ_{fl}) of Core-Substituted NDIs **2**,^{12a} **3**,¹⁷ and **5**–**9** in Dichloromethane

	color ^a	λ_{abs} (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	λ_{em} (nm)	Φ_{fl}
2	blue	620	23 300	650	0.42
3	violet	579	29 400	605	0.70
5	light yellow	427	10 900	^b	^b
6	light yellow	419	12 200	477	0.02
7	violet	563	15 400	^b	^b
8	turquoise	642	26 500	687	0.13
9	turquoise	629	36 000	646	0.19

^a The colors are given for the solid. ^b Not fluorescent.

TABLE 2. Redox Properties of at Core Diamino- and Triaminosubstituted NDIs **2** and **3** and Tetrasubstituted NDIs **5**–**9** in Dichloromethane^d

	$E_{1/2}$ (V vs Fc/Fc ⁺)			
	X ⁻ /X ²⁻	X/X ⁻	X/X ⁺	X ⁺ /X ²⁺
2	-1.90	-1.41	0.65	1.10
3	^b	-1.69	0.41	0.92
5	-1.16	-0.75	1.52 ^c	^b
7	-1.50	-1.10	0.97 ^c	^b
6	-1.77	-1.27	^b	^b
8	-2.12	-1.69	0.01	0.36
9	^b	-1.85	-0.01	0.59

^a All measurements were conducted in dichloromethane; scan rate 100 mV s⁻¹; concentration ca. 1.0 mM; supporting electrolyte: tetrabutylammonium hexafluorophosphate (NBu₄PF₆, 100 mM). ^b Not observed. ^c Peak potentials of irreversible oxidation.

emission, all alkylamino-substituted derivatives are fluorescent. The dialkylamino derivative **2** exhibits a quantum yield of 42%, and it is increased for the trialkylamino compound **3** to 70%.^{12a,17} Introduction of a fourth amino substituent, however, decreases the quantum yield to 13% for NDI **8**. The optical properties of diamino and triamino NDIs **2** and **3** and newly synthesized tetrasubstituted NDIs **5**–**9** are summarized in Table 1.

Redox Properties. The examination of the optical properties of tetrasubstituted NDIs **5**–**9** (Table 1) reveal that the electronic nature of the core substituents strongly influences the respective absorption and emission properties of these chromophores. To gain further insight into the electronic properties of core-tetrasubstituted NDIs, cyclic voltammetry was performed in dichloromethane. The observed reduction and oxidation potentials are collected in Table 2. The cyclic voltammogram of NDI **5** bearing four bromo substituents at the core showed two reversible reduction waves at -0.75 and -1.16 V vs Fc/Fc⁺ (Fc: ferrocene) and irreversible oxidation was detected at 1.52

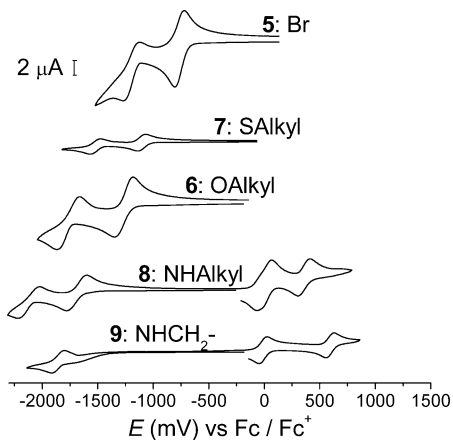


FIGURE 4. Cyclic voltammograms of core-tetrasubstituted NDIs 5–9.

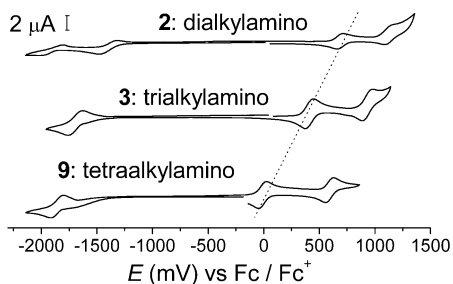


FIGURE 5. Cyclic voltammograms of dialkylamino and trialkylamino derivatives 2 and 3 and tetraalkylamino-substituted NDI 9.

V (Figure 4). Within the series of core-tetrasubstituted NDIs 5–8, a gradual shift of the two reduction potentials to more negative values was observed, indicating a strong influence of the electron-donating character of the respective core substituents on the redox properties. For the tetrathio-substituted derivative 7, reversible reduction (–1.10 and –1.50 V) and irreversible oxidation (0.97 V) took place, while for tetraethoxy NDI 6 (–1.27 and –1.77 V), no oxidation could be detected within the available potential range in dichloromethane. For the most electron-rich NDI within this series, namely the tetraalkylamino-substituted NDI 8, not only significantly lower reduction potentials (–1.69 and –2.12 V) but also two reversible oxidations (0.01 and 0.36 V) were observed, implying the formation of stable radical cationic species. For NDI 9 bearing the cyclic diaminoethyl core substituents, two reversible oxidation waves at –0.01 and 0.59 V were detected, while only one reversible reduction potential (–1.85 V) could be observed within the available potential range.

We further examined the influence of the number of core substituents on the electrochemical properties of NDIs by comparing the CV data of derivatives 2, 3, and 9 bearing two, three, or four alkylamino substituents, respectively, at the naphthalene core (Figure 5 and Table 2). Among this series of alkylamino-substituted NDIs, derivative 2 shows the most positive oxidation (0.65 and 1.10 V) and reduction potentials (–1.41 and –1.90 V). With increasing number of alkylamino substituents a gradual decrease of reduction (–1.69 V for 3, –1.85 V for 9) and oxidation potentials (0.41 and 0.92 V for 3, –0.01 and 0.59 V for 9) is observed. The fact that only one reversible reduction wave was observed for NDI 9 within the available potential range suggests that the second reduction potential of this NDI should be lower than –2.2 V; thus, the tetrasubstituted NDI 9 is the most electron-rich NDI dye known so far.

Conclusion

Bromination of 1,4,5,8-naphthalenetetracarboxylic acid dianhydride by electrophilic aromatic substitution with DBI in oleum provided a convenient and highly efficient method for the preparation of 2,3,6,7-tetrabromonaphthalene dianhydride 4, which is a valuable starting material for the synthesis of core-tetrasubstituted NDIs. Imidization of 4 with amines, in the present case 2,6-diisopropylaniline, afforded the tetrabromo-substituted NDI 5, the latter being a versatile precursor for the synthesis of tetrafunctionalized NDI chromophores by nucleophilic aromatic substitution with a variety of nucleophiles. Thus, at the naphthalene core tetraalkoxy-, tetraalkylthio-, and tetraalkylamino-substituted NDIs 6–9 could be made available. The present tetrasubstituted NDI derivatives now complete the series of di- and trifunctionalized NDI chromophores. Our studies have further revealed that not only the nature but also the number of core substituents has a strong effect on the electronic properties of NDIs; thus, with increasing number of alkylamino substituents, the redox potentials gradually shift to more negative values. The tetraalkylamino-substituted NDI 8 showed the most red-shifted absorption maximum known for NDIs, while for NDI 9 the lowest oxidation potential could be observed. Such electron-rich NDI dyes might enable entirely new applications of NDI chromophores, i.e., as electron-donating components in artificial photosynthesis and solar energy conversion devices^{2,14} or as p-type organic semiconductors. Along this line, we are currently exploring the possibility to extend the aromatic core by using tetrabromo NDI 5 to develop ambipolar organic semiconductor materials.²²

Experimental Section

2,3,6,7-Tetrabromo-1,4,5,8-naphthalenetetracarboxylic Acid Dianhydride (4). A solution of dibromoisocyanuric acid (3.59 g, 12.5 mmol) in oleum (20% SO₃, 25 mL) was poured into a solution of 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (1.34 g, 4.99 mmol) in oleum (20% SO₃, 40 mL), and the reaction mixture was stirred vigorously for 3 h at room temperature. The resulting orange suspension was poured into ice (400 g), and water was added (600 mL). The yellow precipitate was filtered, washed with water (100 mL), and dried over potassium hydroxide. Yield: 2.70 g (93%). mp > 350 °C. MS (EI) *m/z* (%): 579.7 (17.3), 581.7 (67.7), 583.6 (100) (calcd 583.63874), 585.7 (66.7), 587.7 (16.0). ¹H NMR (400 MHz, DMSO-*d*₆): No proton signal was observed. Anal. Calcd for C₁₄Br₄O₆: C, 28.81; Br, 54.75. Found: C, 29.06; Br, 54.61.

***N,N'*-Bis-(2',6'-diisopropylphenyl)-2,3,6,7-tetrabromo-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (5).** To a stirred suspension of dianhydride 4 (200 mg, 0.343 mmol) in glacial acetic acid (5 mL) 2,6-diisopropylaniline (425 mg, 2.40 mmol) was added. After stirring for 6 h at 120 °C, the reaction mixture was cooled to room temperature. Then, water (50 mL) was added and the reaction mixture was neutralized with saturated NaHCO₃ solution and extracted with chloroform (3 × 100 mL). The combined organic phases were dried over anhydrous Na₂SO₄, and the solvent was evaporated. Purification of the crude product by column chromatography (*n*-pentane/CH₂Cl₂ = 2:1, silica gel) and subsequent HPLC (CH₂Cl₂/MeOH = 16:84; flow rate = 10 mL min^{–1}) afforded compound 5 (93 mg, 29%) as a light yellow solid. mp = 346–349 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.52 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 7.7 Hz, 4H), 2.68 (sept, *J* = 6.9 Hz, 4H), 1.20 (d, *J* = 6.9 Hz, 24H). HRMS (ESI) *m/z*: calcd for C₃₈H₃₅Br₄N₂O₄ 902.9295, found 902.9245. UV/vis (CH₂Cl₂): λ_{max}/nm (ε/M^{–1} cm^{–1}) = 427 (10 900), 402 nm (12 100).

(22) Zaumseil, J.; Sirringhaus, H. *Chem. Rev.* **2007**, *107*, 1296–1323.

***N,N'*-Bis-(2',6'-diisopropylphenyl)-2,3,6,7-tetra(ethoxy)-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (6).** An ethanolic solution of sodium ethoxide was prepared from sodium (28 mg, 1.2 mmol) and ethanol (3 mL). To this solution NDI **5** (32 mg, 0.035 mmol) was added and the mixture was stirred at room temperature for 5.5 h under an argon atmosphere. Then, 1 N HCl (20 mL) and dichloromethane (50 mL) were added and the phases were separated. The aqueous phase was extracted with dichloromethane (2 × 50 mL), and the combined organic phases were dried over anhydrous Na₂SO₄. After removal of solvent, further purification by column chromatography (CH₂Cl₂/*n*-pentane = 11:8, silica gel) afforded compound **6** (17 mg, 63%) as a yellow solid. mp > 350 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.49 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 7.7 Hz, 4H), 4.28 (q, *J* = 7.0 Hz, 8H), 2.73 (sept, *J* = 6.9 Hz, 4H), 1.49 (t, *J* = 7.0 Hz, 12H), 1.18 (d, *J* = 6.9 Hz, 24H). HRMS (ESI) *m/z*: calcd for C₄₆H₅₅N₂O₈ 763.3958, found 763.3937. UV/vis (CH₂Cl₂): λ_{max}/nm (ε/ M⁻¹ cm⁻¹) = 419 (12 200), 378 nm (18 200). Fluorescence (CH₂Cl₂): λ_{max} = 477 nm (λ_{ex} = 375 nm); fluorescence quantum yield: Φ_f = 0.02.

***N,N'*-Bis-(2',6'-diisopropylphenyl)-2,3,6,7-tetra(ethylthio)-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (7).** A mixture of compound **5** (20 mg, 0.022 mmol), potassium carbonate (30 mg, 0.22 mmol), ethanethiol (2.5 mL), and chloroform (1 mL) was refluxed for 3.5 h. The solvent was evaporated, and the remaining solid was subjected to column chromatography (CHCl₃/*n*-hexane = 1:1, silica gel) and subsequent HPLC (MeOH; flow rate = 10 mL min⁻¹) to give the violet compound **7** (9 mg, 50%). mp = 323–325 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.49 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 4H), 3.00 (q, *J* = 7.5 Hz, 8H), 2.70 (sept, *J* = 6.8 Hz, 4H), 1.25–1.18 (m, 36H). HRMS (ESI) *m/z*: calcd for C₄₆H₅₄N₂NaO₄S₄ 849.2864, found 849.2863. UV/vis (CH₂-Cl₂): λ_{max}/nm (ε/M⁻¹ cm⁻¹) = 563 (15 400), 329 nm (24 400).

***N,N'*-Bis-(2',6'-diisopropylphenyl)-2,3,6,7-tetra(*n*-hexylamino)-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (8).** NDI **5** (74 mg, 0.082 mmol) was heated in *n*-hexylamine (10 mL) at 135 °C for 5.5 h. Subsequently, *n*-hexylamine was removed under reduced pressure at the rotary evaporator. The solid residue was dissolved in dichloromethane (30 mL), and 1 N HCl (100 mL) was added. The aqueous phase was extracted with dichloromethane (2 × 30 mL), and the combined organic phases were washed with water

(100 mL). Upon concentration under reduced pressure at room temperature, a turquoise solid precipitated which was purified by column chromatography (CH₂Cl₂/*n*-pentane = 1:2, silica gel) to give compound **8** (38 mg, 48%). mp = 238–242 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.51 (t, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 4H), 3.42 (t, *J* = 7.3 Hz, 8H), 2.69 (sept, *J* = 6.8 Hz, 4H), 1.49 (m, 8H), 1.28–1.17 (m, 48H), 0.80 (t, *J* = 6.9 Hz, 12H). HRMS (ESI) *m/z*: calcd for C₆₂H₉₁N₆O₄ 983.7170, found 983.7072. UV/vis (CH₂Cl₂): λ_{max}/nm (ε/ M⁻¹ cm⁻¹) = 642 (26 500), 459 nm (11 200). Fluorescence (CH₂Cl₂): λ_{max} = 687 nm (λ_{ex} = 570 nm); fluorescence quantum yield: Φ_f = 0.13.

***N,N'*-Bis-(2',6'-diisopropylphenyl)-5,6,11,12-(1,4,7,10-tetraaza-1,2,3,4,7,8,9,10-octahydroanthracene)tetracarboxylic Acid Diimide (9).** NDI **5** (42 mg, 0.047 mmol) was heated under argon in ethylene diamine (5 mL) at 135 °C for 30 min. After the addition of water (30 mL) and dichloromethane (30 mL), the aqueous phase was separated and extracted with dichloromethane (2 × 30 mL). The combined organic phases were washed with 1 N HCl (30 mL), and the solvent was removed under vacuum. Further purification of the residue by column chromatography (CH₂Cl₂, silica) yielded compound **9** (20 mg, 62%) as a bluish-green solid. mp > 350 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.82 (*br s*, 4H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 4H), 3.65 (*br s*, 8H), 2.71 (m, 4H), 1.17 (d, *J* = 6.7 Hz, 24H). HRMS (ESI) *m/z*: calcd for C₄₂H₄₆N₆O₄ 698.3580, found 698.3578. UV/vis (CH₂Cl₂): λ_{max}/nm (ε/ M⁻¹ cm⁻¹) = 629 (36 000), 581 (15 500), 538 (5300), 432 (25 700), 408 (12 700), 387 nm (4200). Fluorescence (CH₂Cl₂): λ_{max} = 698, 646 nm (λ_{ex} = 570 nm); fluorescence quantum yield: Φ_f = 0.19.

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Supporting Information Available: General experimental methods, EI mass spectrum of compound **4**, and ¹H NMR spectra of NDIs **5–9**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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