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Regioselectivity in Sequential Nucleophilic Substitution of Tetrabromonaphthalene Diimides

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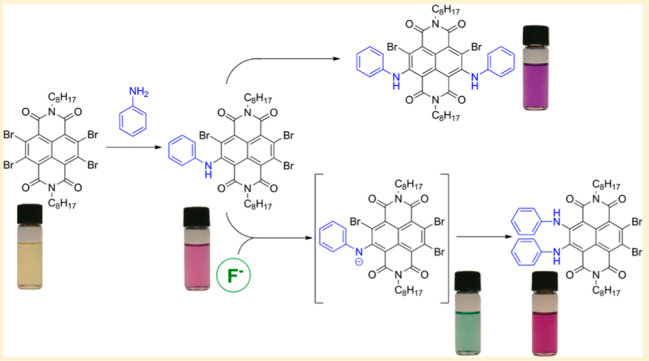
Supporting Information

ABSTRACT: Nucleophilic substitution of tetrabromosubstituted naphthalene diimides (NDIs) with aniline was studied in detail to explore the regioselectivity as three different diamino-substituted regioisomeric products can be formed. We found that the regioselectivity of the nucleophilic disubstitution of 2,3,6,7-tetrabromonaphthalene diimide with aniline is dependent on reaction solvents and additives. In dichloromethane and chloroform without an additive the 2,7-diamino-3,6-dibromo-NDI isomer was formed regioselectively, while in DMF under similar reaction conditions the 2,3-diamino-6,7-dibromo isomer was observed as the major regioisomer. The third possible regioisomer 2,6-diamino-3,7-dibromo product was formed, if at all, in an insignificant amount. Tetrabutylammonium fluoride (TBAF) additive exerts a dramatic effect on the regioselectivity of this reaction, as in dichloromethane without TBAF the 2,7-diamino isomer was formed regioselectively, while without TBAF the 2,3-diamino isomer was formed exclusively. This remarkable effect of TBAF can be rationalized in terms of a deprotonation of the monoamino-tribromo-NDI generated in the first step of this sequential reaction as an intermediate by fluoride ions leading to an anionic species as indicated by UV−vis and NMR experiments whose electronic properties direct the regioselective attack of the second amine molecule. Our efforts led to the exclusively regioselective synthesis of 2,7-diamino-3,6-dibromo- and 2,3-diamino-6,7-dibromo-NDIs for the first time.



INTRODUCTION

Core-substituted 1,4,5,8-naphthalene diimides (NDIs) have been a subject of very intense research activities during the past years.[1−3] In fact, core-disubstituted NDIs have been known for many decades,[4] and those very first examples were obtained from dichloro-1,4,5,8-naphthalene dianhydride, which was prepared in a tedious four-step synthesis starting with the chlorination of pyrene using chlorine gas.[4,5] Therefore, it was the direct bromination of commercially available naphthalene dianhydride[5] that led to a strong push in research activities with core-substituted NDIs. The importance of halogen-substituted NDIs arises from an extensive tunability of the optical and electrochemical properties of NDIs by substitution of the halogen atoms at the naphthalene core with many nucleophiles, making this highly popular class of dyes available in different colors and with easily adjustable HOMO/LUMO levels for numerous applications. For example, the substitution of dihalogenated NDIs with heteroatom nucleophiles at the 2- and 6-positions leads to chromophores with excellent absorption properties, which were used for efficient light harvesting in supramolecular antennae systems based on zinc chlorine-NDI conjugates,[6,7] and as light-absorbing charge transport units in self-assembled systems driving a transmembrane proton gradient caused by a photoinitiated electron-transfer process.[8] On the basis of such core-disubstituted NDI chromophores, n/p heterojunction zipper assemblies[9] and photofunctional multicomponent architectures were created.[10,11] Moreover, distinctly electron-poor 2,6-core-disubstituted NDIs bearing electron-withdrawing substituents such as chlorine or cyano groups are ambient-stable high performance n-type semiconductors.[12,13] The expansion of NDI core leads to excellent n-type performing[14,15] and ambipolar materials.[16] At the core mono- and 2,6-disubstituted NDIs were also used as building blocks for oligomers[17,18] and copolymers[19,20] that exhibit electron-transporting properties.

For most of the previously reported core-disubstituted NDIs, the 2,6-substitution pattern is prevalent since those NDIs were derived from the respective 2,6-dichloro-[4,21] or 2,6-dibromo-naphthalene dianhydrides,[5] which are accessible with high regioisomeric purity. In contrast, the disubstitution of 2,3,6,7-tetrabromo-NDIs (Br_4-NDIs)[22,23] with nucleophiles can lead to different regioisomers. However, the regioselectivity of such disubstitution reactions has not been elucidated so far. The tetrabromo precursor was used to substitute all four bromine atoms by heteroatom[23,24] and carbon nucleophiles[25−27] uniformly, or even to realize a lateral core enlargement of the parent NDI core, where the regioselectivity is obviously not an

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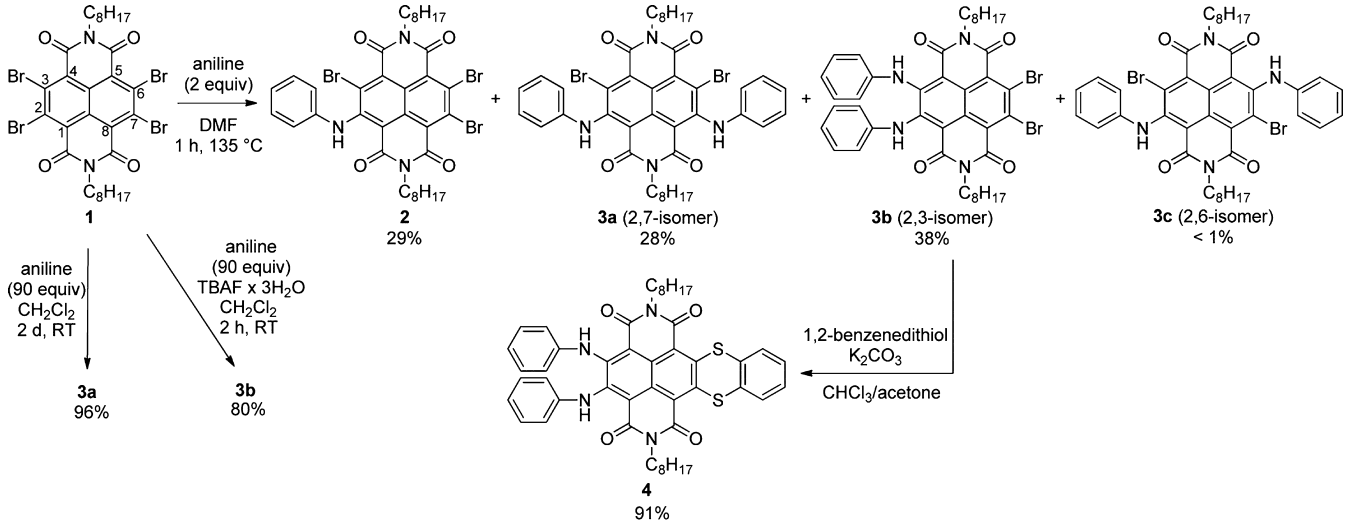
Scheme 1. Reactions of NDI 1 with Aniline under Different Conditions and Derivatization of NDI 3b



issue.[14,28−31] Nucleophilic disubstitution of Br_4-NDIs was previously shown with 1,2-phenylenediamines, where the *ortho*-constitution of the bidentate diamine enforces the 2,3-substitution pattern on the NDI core providing a desymmetrization of the compound.[32] However, the situation gets more complicated when monodentate nucleophiles are involved. In this context, it was reported that the attempted metal-catalyzed percyanation of a Br_4-NDI proceeds via the 2,6-dibromo-3,7-dicyano isomer. However, the regioisomeric pattern of the latter compound was proposed, but not confirmed, on the basis of the crystal structure of another dicyano-di(*tert*-butylphenylthio)-NDI derivative.[33] Very recently a nucleophilic disubstitution of Br_4-NDI **1** (for structure, see Scheme 1) with *n*-octylamine was published by the group of Zhao, and they claimed the formation of the respective 2,6-dibromo-3,7-di(*n*-octyl)amino-NDI, which is a unique triplet photosensitizer.[34] However, with regard to the product characterization, particularly the assignment of substitution pattern, special care has to be taken in this case since the formation of three different regioisomeric products **I**−**III** (Figure 1) with different symmetry elements is conceivable, and hence their identification only by NMR spectroscopy is not necessarily straightforward. Our studies indeed indicate that the above-mentioned regioisomeric assignment needs to be amended (vide infra).

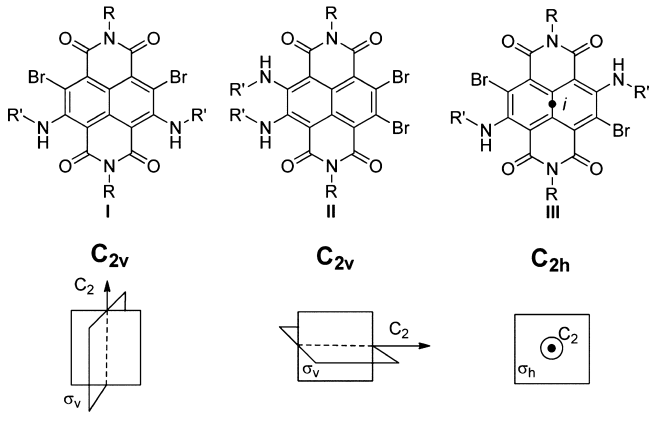


Figure 1. The possible regioisomers of diamino-dibromo-substituted NDIs with their molecular symmetries.

Our extensive literature search did not reveal any systematic study on the regioselectivity of nucleophilic disubstitution of tetrabromo-NDIs. Therefore, we have approached this problem and report herein our detailed studies on the regioselectivity of nucleophilic disubstitution of Br_4-NDI **1** with aniline as nucleophile. We found that the regioselectivity of this reaction is dependent on the conditions applied, and more interestingly, the regioselectivity can be controlled by additives, in particular fluoride anions, which influence the electronic properties of the monoamino-substituted intermediate to regioselectively direct the second bromine substitution by amine. Our studies afforded simple protocols for the highly regioselective synthesis of diamino-dibromo-substituted NDIs from tetrabrominated NDI with monodentate aniline nucleophile.

RESULTS AND DISCUSSION

We were interested in the 2-fold nucleophilic substitution of bromine atoms of 2,3,6,7-tetrabromo NDI **1**[22] with a monodentate amine to explore the regioselectivity of this reaction. Therefore, Br_4-NDI **1** was reacted with 2 equiv of aniline in DMF for 1 h at 135 °C, and three main products were isolated after column chromatography in different yields (Scheme 1).

Among the isolated products, the monoamino-substituted compound **2** was obtained with 29% yield, indicating that this compound acts as an intermediate in this nucleophilic disubstitution reaction. Furthermore, two disubstitution products were isolated in 28 and 38% yields, respectively, and their constitution was confirmed by HRMS and elemental analysis. The correct assignment of the substitution pattern for the diamino product with 28% yield was achieved by ^{1}H and ^{13}C NMR spectroscopy, and it was identified as the 2,7-diamino-3,6-dibromo isomer **3a**. The 2,7-diamino substitution pattern of **3a** can be easily deduced from NMR spectra since the imide substituents of this isomer are chemically not equivalent (see structure **I** in Figure 1), and thus they should not exhibit isochronic signals in the ^{1}H and ^{13}C NMR spectra, which is indeed the case as shown in Figures 2, S16 and S17 (Supporting Information). The distinct feature in ^{1}H NMR spectrum of **3a** (Figure 2) is that, in comparison to other two

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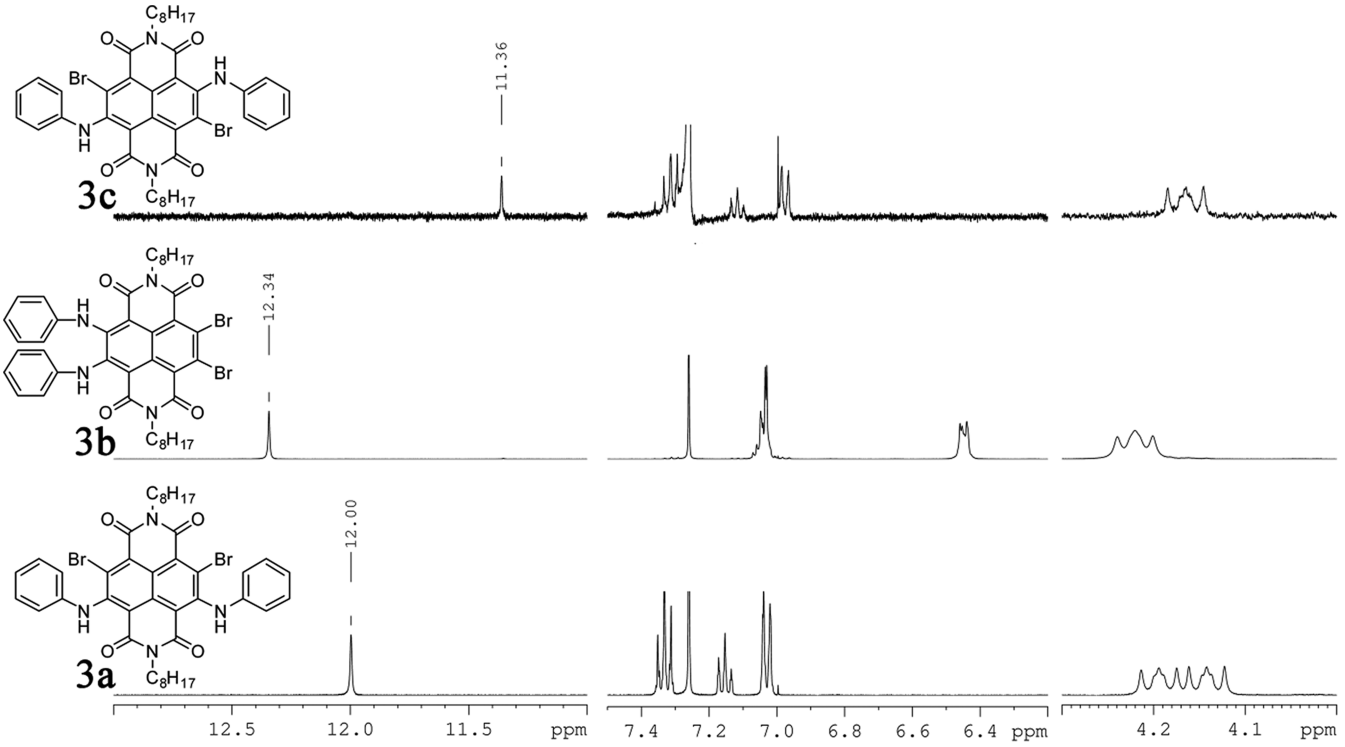

Figure 2. Sections of the ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of the three regioisomers **3a–c** showing the regions for amino NH proton, aromatic, and imide NCH_2 protons.

isomers, the signals for imide NCH_2 protons are split into two separate signals at 4.18 and 4.13 ppm. On the other hand, the identification of the third main product with 38% yield is rather demanding. The substitution of two bromine atoms was proven by high-resolution mass spectrometry, elemental analysis, and the ratio of aromatic and imide protons in the ^{1}H NMR spectrum, but these data cannot differentiate between the two regioisomers **3b** and **3c**. The usefulness of ^{1}H NMR spectroscopy to distinguish between the three regioisomers remains limited to the 2,7-isomer **3a** because, in contrast to the latter, the 2,3- and 2,6-diamino isomers **3b** and **3c** show only one set of signals in ^{1}H (Figure 2) and ^{13}C spectra (Figure S21, Supporting Information), since the imide substituents as well as the amino substituents on the core are chemically equivalent because of the 2-fold rotational C_2 axes in these isomers (Figure 2, **II** and **III** in Figure 1). In order to assign the product with 38% yield to one of the possible isomers (2,3- or the 2,6-diamino), the isolated NDI derivative was reacted with 1,2-benzenedithiol, since only the 2,3-isomer **3b** should be able to react with 1 equiv of 1,2-benzenedithiol to substitute both adjacent bromine atoms. Indeed, the annulated benzo[*b*]-thianthrene NDI derivative **4** was obtained with 91% yield (Scheme 1). This compound was appropriately characterized by ^{1}H and ^{13}C NMR and HRMS. This derivatization reaction confirms unequivocally the identity of the 2,3-isomer **3b** in this reaction. We also found a fourth product in trace amounts (yield <1%) after column chromatography, which was characterized as an additional diamino-dibromo-NDI by HRMS and ^{1}H NMR spectroscopy (Figure 2). Since the other two regioisomers are clearly identified, the regioisomeric assignment of this minor product as 2,6-diamino-3,7-dibromo isomer **3c** is obvious.

We have further performed this reaction in dichloromethane, instead of DMF, with high excess of aniline (90 equiv). After stirring at room temperature for two days, only a new spot on the TLC was detected, and no spot for the starting compound Br_4-NDI **1** was visible, indicating its total conversion. After purification of the crude mixture the disubstitution product **3a** was obtained with a yield of 96% (Scheme 1). More interestingly, we found that the regioselectivity of this reaction can be influenced decisively by using additives. Particularly, the addition of an excess of fluoride ions in form of TBAF (>10 equiv) changes the regioselectivity completely to 2,3-isomer (**3b**) compared to 2,7-isomer (**3a**) formed without this additive. Thus we could establish an easy protocol for the synthesis of 2,3-diamino isomer **3b** in exclusive regioselectivity with an isolated yield of 80% by simply stirring a mixture of Br_4-NDI **1** and aniline (90 equiv) in dichloromethane in the presence of TBAF. It is noteworthy that the presence of fluoride ions not only has a remarkable effect on the regioselectivity of the reaction, but also accelerates the reaction significantly. Thus, in the presence of TBAF the 2,3-isomer **3b** was formed exclusively already after ca. 100 min, and neither the starting compound Br_4-NDI **1** nor monobrominated intermediate **2** could be detected by TLC, while in the absence of TBAF intermediate **2** was the predominant component in the reaction mixture after ca. 100 min, and the latter could still be observed after 18 h (Figure S1, Supporting Information).

In order to get more insight into the regioselectivity of the diamination of Br_4-NDI **1** with aniline, we have performed further experiments in several common aprotic solvents such as chloroform, dichloromethane, toluene, THF, acetonitrile and DMF, and the regioisomeric ratios of the disubstitution products **3a–c** formed in these solvents were determined by ^{1}H NMR analyses of the crude products directly after the reaction. This NMR investigation has the advantage that it avoids unbalanced losses of compounds, as it is obviously the case after chromatographic purification on silica, and hence

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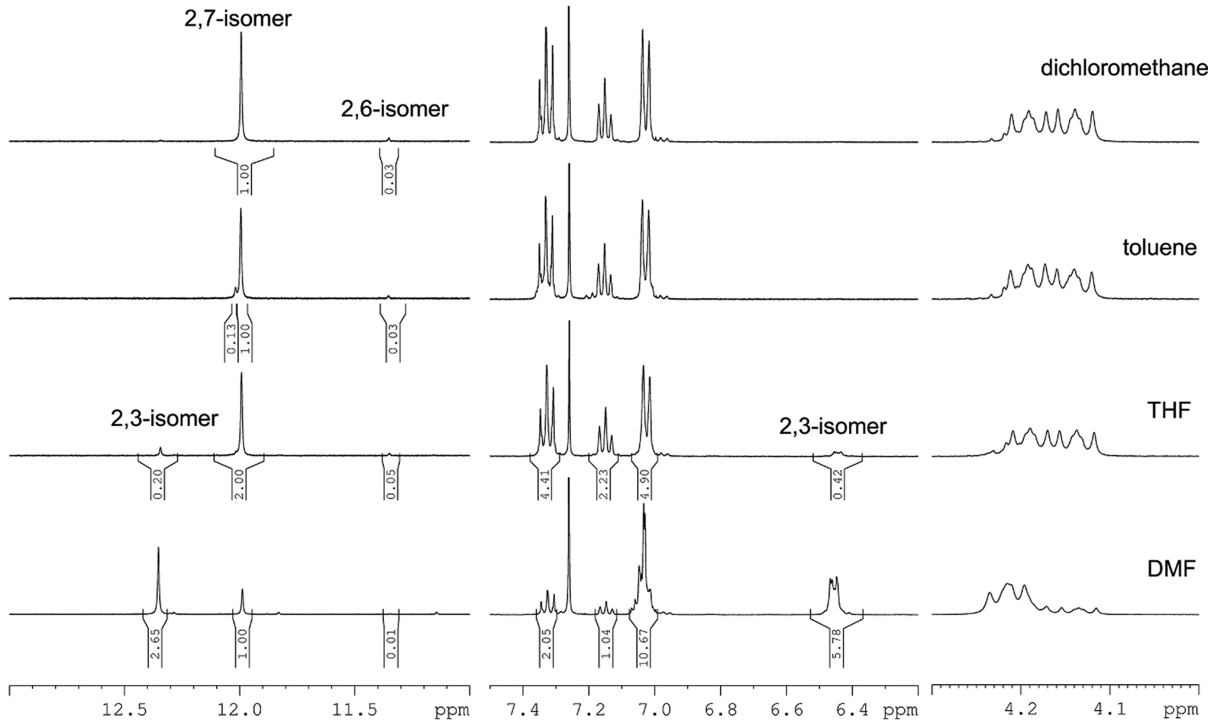

Figure 3. Sections of the ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of the crude reaction products of Br_4-NDI **1** with aniline (90 equiv) in the different solvents indicated above the respective spectrum (entries 4, 6, 7, 12 in Table 1). The ratios of the formed isomers **3a–c** were determined after removal of excess aniline by integration of the signals of amine NH protons 12.34 (**3b**), 12.00 (**3a**), and 11.36 ppm (**3c**).

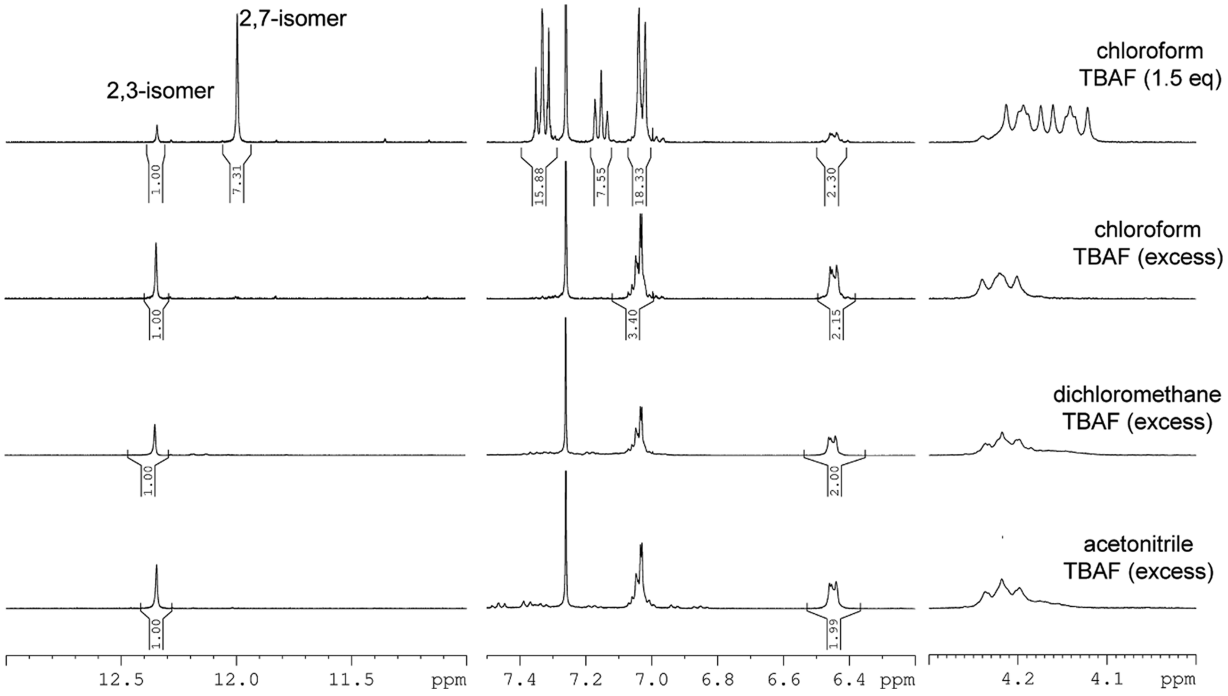

Figure 4. Sections of the ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of the crude reaction products of Br_4-NDI **1** with aniline (90 equiv) in the presence of TBAF in different solvents indicated above the respective spectrum. The ratios of the formed isomers **3a** and **3b** were determined after removal of excess aniline by integration of the NH protons signals.

minimizes systematic errors in the determination of regioisomeric ratios. As shown in Figure 2, the chemical shifts of the amine NH signals in the range of 11.0–12.5 ppm of the three isomers **3a–c** are distinctly different. Therefore, the identity of these isomers and their ratios in crude product mixtures could be easily determined by ^{1}H NMR spectroscopy from the integrals of the NH proton signals at 12.34 (**3b**), 12.00 (**3a**) and 11.36 ppm (**3c**) (Figures 3 and 4, Figure S2, Supporting Information). The regioisomeric ratios obtained under different reaction conditions are summarized in Table 1.

The data collected in Table 1 reveal that, in most of the solvents used, the regioselectivity of the disubstitution of Br_4-

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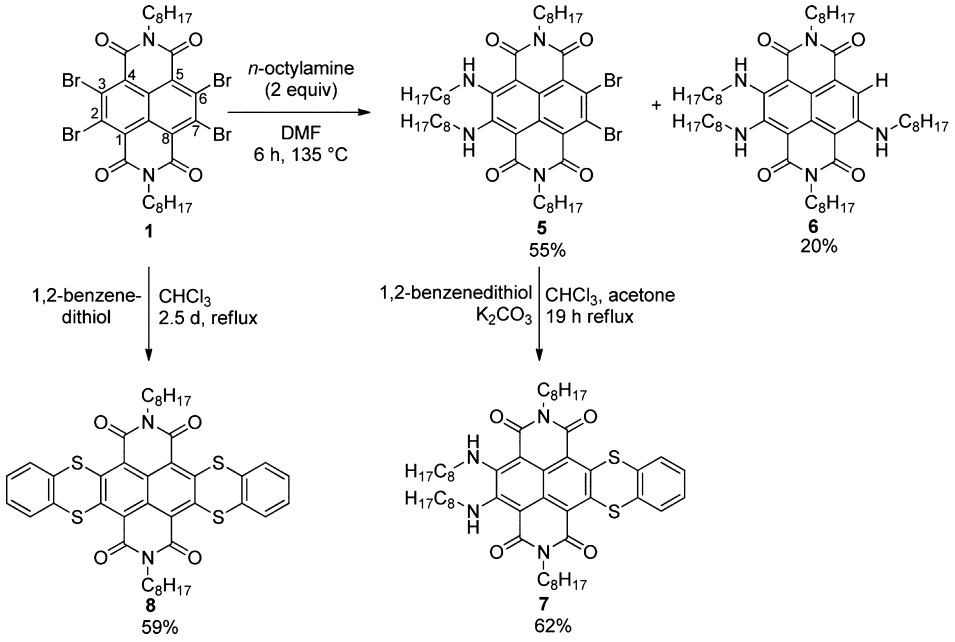
Table 1. Nucleophilic Disubstitution of Br_4-NDI 1 with Aniline (90 equiv) in Different Solvents under the Given Reaction Conditions and the Ratios of the Regioisomeric Diamino-dibromo-NDIs 3a (2,7-Diamino), 3b (2,3-Diamino), and 3c (2,6-Diamino) Determined by Integration of the Amine NH Proton Integrals in ^1H NMR Spectra Recorded in $CDCl_3$

	reaction conditions				ratio of regioisomers		
entry	solvent	temperature (°C)	time[a]	TBAF (equiv)	3a	3b	3c
1	$CHCl_3$	rt	16 h	–	1	0.02	0.02
2	$CHCl_3$	rt	14.5 h	1.5	1	0.14	0.03
3	$CHCl_3$	rt	7 h	10	[b]	1	[b]
4	CH_2Cl_2	rt	66 h	–	1	[b]	0.03
5	CH_2Cl_2	rt	18 h	16	[b]	1	[b]
6	toluene	rt	16 h	–	1	[b]	0.03
7	THF	rt	16 h	–	1	0.1	0.03
8	THF	65	1.5 h	–	1	0.02	[b]
9	CH_3CN	rt	7 d	–	1[c]	0.3[c]	[b]
10	CH_3CN	rt	3 h	18	[b]	1	[b]
11	CH_3CN	65	1 h	–	1	0.2	[b]
12	DMF	rt	14.5 h	–	1	2.7	0.01
13	DMF	65	2 h	–	1	2.6	[b]

[a]The reaction times were not optimized. The reactions were monitored by TLC and terminated when monoamino-substituted NDI **2** intermediate was nearly consumed. [b]Not observed. [c]Because of the low solubility of Br_4-NDI **1** and intermediate **2** in acetonitrile at rt, the reaction was slow and incomplete, and thus a superposition of the NH proton signals of **3a** and residual **2** obstructs their proper integration.

Scheme 2. Reaction of Br_4-NDI 1 with 2 equiv of *n*-Octylamine in DMF under the Same Conditions Reported in Ref 34 and Subsequent Transformation of the Major Product 5 to NDI 7 with 1,2-Benzenedithiol[a]



[a]The reaction of Br_4-NDI **1** with 1,2-benzenedithiol to NDI **8** is shown for comparison.

NDI **1** with aniline without TBAF additive is very high with 2,7-isomer (**3a**) as the major product (entries 1, 4, 6–8, 9 and 11), except for DMF in which 2,3-isomer (**3b**) dominates (entries 12, 13). The regioselectivity is very similar in chloroform, dichloromethane and toluene in the absence of TBAF with the nearly exclusive formation of 2,7-isomer (entries 1, 4 and 6). In THF and acetonitrile the selectivity is not that pronounced as in above-mentioned solvents since 2,3-isomer (**3b**) was formed in appreciable amounts in these solvents. However, the 2,7-isomer (**3a**) is still the major product with a **3a**/**3b** ratio of 10:1 for THF (entry 7) and 10:3 for acetonitrile (entry 9). Interestingly, an appreciable temperature effect on the regioselectivity was observed in THF, as **3a** was formed nearly exclusively at 65 °C (entry 8).

It is remarkable that even with 90 equiv of aniline, no further substitution of diamino-dibromo-NDIs to triamino product was observed in all these solvents, except in DMF, after longer reaction time at room temperature. In DMF further trisubstitution was observed. Furthermore, in DMF the regioisomeric product distribution is changed in favor of 2,3-isomer (**3b**), while in all other solvents 2,7-isomer (**3a**) prevails in the absence of TBAF. In DMF, a **3a**/**3b** ratio of about 1:2.7 was observed, independent of whether the reaction was conducted at room temperature (entry 12) or at 65 °C (entry 13).

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We have further studied the effect of TBAF as an additive on the regioselectivity of the nucleophilic disubstitution of Br_4-NDI **1** with aniline. The addition of a small excess of fluoride ions (1.5 equiv of TBAF) to the reaction mixture of Br_4-NDI **1** and aniline (90 equiv) in chloroform significantly increased (7-fold) the formation of 2,3-isomer, compared to the reactions without TBAF (entry 1), leading to a **3a**/**3b** ratio of 10:1.4 (entry 2), whereas a large excess of fluoride ions (>10 equiv) completely reversed the regioselectivity in favor of **3b**, and the latter isomer was formed exclusively (entry 3). Under the reaction conditions of entry 3, not only in chloroform but also in dichloromethane (entry 5) and acetonitrile (entry 10), exclusive formation of 2,3-isomer (**3b**) was observed as revealed by ^{1}H NMR spectra (Figure 4).

As already mentioned in the Introduction, very recently a similar reaction of Br_4-NDI **1** with *n*-octylamine as a nucleophile was reported.[34] Therein the authors describe that the 2,6-diamino-3,7-dibromo-NDI (identical with the 2,6-dibromo-3,7-diamino-NDI as the authors named this compound) was obtained with 44% yield with 2 equiv of *n*-octylamine in DMF at 135 °C. However, this is not in agreement with our observations that we have made with aniline as a nucleophile under similar reaction conditions as described before. Therefore, we have repeated the reaction of Br_4-NDI **1** with *n*-octylamine, instead of aniline, under the same conditions described in this publication,[34] and found that two main products were formed: the 2,3-diamino-substituted product **5**, as mentioned in the publication, with a yield of 55% and a 3-fold amino-substituted and monodehalogenated NDI **6** with a yield of 20% (Scheme 2). A comparison of the ^{1}H NMR spectrum of **5** (Figure S25, Supporting Information) with that published by the authors suggests that we have isolated the same diamino-substituted compound as reported in the earlier publication.

However, as stated before, on the basis of only ^{1}H NMR analysis it is not possible to distinguish between the 2,3- and 2,6-diamino regioisomers. Therefore, in the absence of a crystal structure, for the regioisomeric assignment of the obtained diamino product independent method needs to be applied. Thus, we have reacted the diamino-dibromo-NDI **5** with 1,2-benzenedithiol and obtained the dithiolated product **7**, which was characterized by NMR spectroscopy and HRMS. This chemical derivatization clearly indicates that the diamino product obtained from the reaction of Br_4-NDI **1** with *n*-octylamine, under the identical conditions reported previously, must be the 2,3-diamino isomer **5** with two adjacent bromine atoms and not the claimed 2,6-diamino-isomer with the two diagonally placed bromine atoms,[34] because the latter simply cannot form an annulated product with 1,2-benzenedithiol. For comparison, we have reacted Br_4-NDI **1** with 1,2-benzenedithiol leading to the symmetrically annulated tetrathiolated compound **8** that constitutes a derivative of the NDI recently reported by Wang and co-workers.[31]

We next studied the optical properties of the isolated NDIs. The absorption spectra of the NDIs **2**, **3a** and **3b** in dichloromethane are displayed in Figure 5. As reported previously, the introduction of amino groups to the NDI core evokes a redshift of the absorption maxima compared to that of halogenated NDIs.[23] The substitution of one bromine atom in Br_4-NDI **1** by a phenylamino group results in a broad absorption band with a maximum at 536 nm for the monoaminated product NDI **2**. The incorporation of a second phenylamino group induces a further bathochromic shift with a higher absorption coefficient. The two diamino-substituted regioisomers **3a** and **3b** show similar, but not identical absorption bands with maxima at 564 and 563 nm, respectively. The dithiolate annulated compound **4** displays a further redshift with an absorption maximum at 608 nm. A similar trend was observed for the NDIs **5**–**7** (Figure S3, Supporting Information). The absorption maximum of **5** appears at 530 nm and that of the dithiolated NDI **7** at 569 nm, while the tetrathiolated NDI **8** exhibits a broad and less intense absorption band with a maximum at 588 nm. The octylamino substituents in **5** and **7** provoke blueshifts of 33 and 39 nm compared to the absorption maximum of phenylamino derivatives **3b** and **4**, respectively.

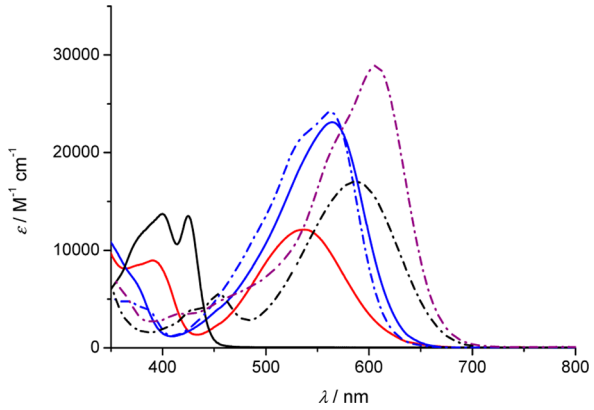

Figure 5. UV–vis absorption spectra of NDI derivatives **2** (red), **3a** (blue), **3b** (blue dash-dotted), **4** (violet dash-dotted), **8** (black dash-dotted), and for comparison, Br_4-NDI **1** (black) in dichloromethane (10^{-5} M) at 25 °C.

Next, we have approached the question what are the reasons for the different regioselectivities of the nucleophilic disubstitution of Br_4-NDI **1** with aniline in different solvents and in the absence or presence of TBAF additive. As mentioned before, the monoaminated NDI **2** is clearly involved as an intermediate in this reaction (Scheme 1), and thus this intermediate should play a crucial role in regioselectivity of the second nucleophilic bromine substitution. Therefore, isolated NDI **2** was subjected to further UV–vis spectroscopic investigations to get insights into the reaction processes under various conditions. First, we have investigated the effect of TBAF addition to the solution of NDI **2** in dichloromethane and acetonitrile by UV–vis spectroscopy. Figure 6 shows the absorption behavior of NDI **2** after successive addition of up to 10 equiv of TBAF to a 4.9×10^{-5} M solution of **2** in dichloromethane. As the spectra in Figure 6a show, the initial absorption band at 536 nm diminishes gradually with increasing amounts of TBAF with concomitant emergence of a new absorption band at 674 nm, and a successive color change of the solution from violet to green was observed. A clear isosbestic point can be seen at 594 nm during the titration experiment, indicating the involvement of two species at an equilibrium. In acetonitrile a similar effect was observed since addition of TBAF generated a green solution with a new red-shifted absorption band with a maximum at 665 nm and an isosbestic point at 586 nm (Figure 6b). The same effect with an identical isosbestic point and absorption maximum was observed by adding the non-nucleophilic base DBU, and subsequent addition of trifluoroacetic acid (TFA) reversed this process (Figure 6c).

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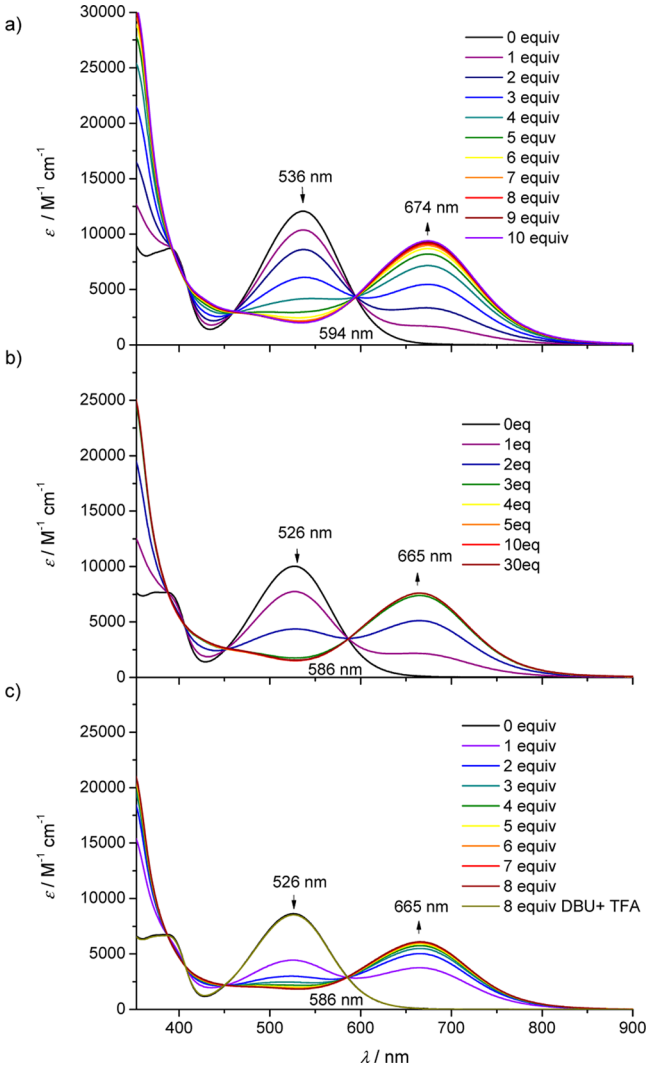

Figure 6. Titration of NDI **2** monitored by UV−vis absorption spectroscopy at 25 °C (a) in dichloromethane (4.9×10^{-5} M) with TBAF × $3H_2O$, (b) in acetonitrile (5.4×10^{-5} M) with TBAF × $3H_2O$, and (c) in acetonitrile (7.0×10^{-5} M) with DBU and subsequent regeneration of the initial absorption band upon addition of TFA.

On the basis of the results of these UV−vis titration experiments, we can conclude that the new species emerged in the presence of TBAF or DBU should be crucial for the observed 2,3-regioselectivity in the second substitution step, and therefore, the elucidation of this species is of significant importance for the rationalization of the observed regioselectivity. The interaction of NDI **2** with a strong Lewis-basic anion like fluoride might, for instance, suggest the formation of radical anions by a thermal electron transfer as proposed by Saha and co-workers for core-unsubstituted NDIs and electron-poor 2,6-dicyano-NDI derivative,[35,36] and by Ballester et al. for the 1,4,5,8,9,12-hexaazatriphenylene (HAT) derivative HAT-$(CN)_6$.[37] To verify this possibility, we have investigated the redox behavior of the monoamino-substituted NDI **2** by cyclic voltammetry (CV) with ferrocene as internal standard in dichloromethane and estimated the LUMO energy. NDI **2** reveals a reversible reduction with a half wave potential at −0.99 V, which is similar to the one observed for the parent NDI (−1.10 V)[5] and about 0.19 V lower than that for Br_4-NDI **1** (see Figure S6 and Table S1, Supporting Information). This corresponds to a LUMO energy of −3.8 eV for NDI **2**, when 4.80 eV is used as the ionization potential for ferrocene. Since the LUMO energy for NDI **2** (−3.8 eV) is higher than the HOMO energy of fluoride (ca. −4.3 eV),[37] the reduction of NDI **2** by fluoride and hence the formation of radical species is not very likely. Additionally, spectroelectrochemistry experiments were performed with NDI **2** in dichloromethane (Figure S7, Supporting Information). The recorded spectrum shows a different spectral response upon electrochemical reduction compared to that of the UV−vis titration experiments of NDI **2** in the presence of TBAF or DBU shown in Figure 6. These results are also not supportive of radical anion formation. Moreover, for NDI **2** we could not observe any EPR signal in the presence of TBAF in dichloromethane, which likewise excludes the possibility of radical species formation.

An alternative scenario might be the formation of a σ complex through covalent bonding of fluoride to the NDI core. However, in such a situation the addition of DBU to NDI **2** should not give the same UV−vis absorption spectrum as in the presence of TBAF. A more likely explanation for the formation of the new species would be an interaction between the amino group of NDI **2** with the fluoride anion. Because fluoride is a strong base in aprotic solvents (HF has a pK_a value of 15 in DMSO),[38] it should be able to deprotonate the phenylamino group at the NDI core, as DBU (pK_a value of 12) may also do. Since the UV−vis titration experiments (Figure 6a) indicated that 7 equiv of TBAF are sufficient for the full transformation of NDI **2** to the new species, we also performed NMR experiments under similar conditions to get more information on structural features of the new species. Figure 7 displays the changes of the aromatic region of the ^{1}H NMR spectra in CD_2Cl_2 after addition of 2 and 7 equiv of TBAF to NDI **2** (see Figure S9, Supporting Information, for the complete spectrum after addition of 7 equiv of TBAF). The disappearance of the NH proton signal after addition of 7 equiv of TBAF (Figure S9, Supporting Information) indicates that the amine proton is involved in the interaction with the fluoride ions, suggesting a deprotonation of the secondary amino group at the NDI core. Moreover, the addition of 7 equiv of fluoride ions results in a high-field shift of the aromatic phenyl protons displaying sharp signals. Addition of only 2 equiv of TBAF causes moderately high-field-shifted and broadened signals, presumably due to an equilibrium between **2** and the new species. These observations are in accordance with those of the UV−vis experiments. It is remarkable that the high-field shift observed for the protons of the phenylamino group in the presence of excess TBAF is more pronounced for the *para* (0.45 ppm) and *ortho* protons (0.32 ppm) than that for *meta* protons (0.27 ppm). This difference in high-field shift is in accordance with a higher shielding effect induced by the higher charge density after deprotonation at the *para* and *ortho* proton as illustrated in Figure 7 inset. Moreover, the nitrogen-bound methylene groups at imide positions experience also a high-field shift of ca. 0.1 and 0.45 ppm in the presence of 2 and 7 equiv of TBAF, respectively (Figure S8, Supporting Information). This effect is also in accordance with an anionic species, resulting in a lower electron-withdrawing character of the imide group. In ^{13}C NMR spectra, particularly the phenyl ^{13}C signals show a similar effect as observed for the phenyl protons in the ^{1}H NMR spectra, i.e., a high-field shift for the carbon atoms at *ortho* and *para* positions, and merely no effect on the *meta* carbons (Figures S10−S12, Supporting Information). A pronounced low-field shift of ca. 13 ppm was

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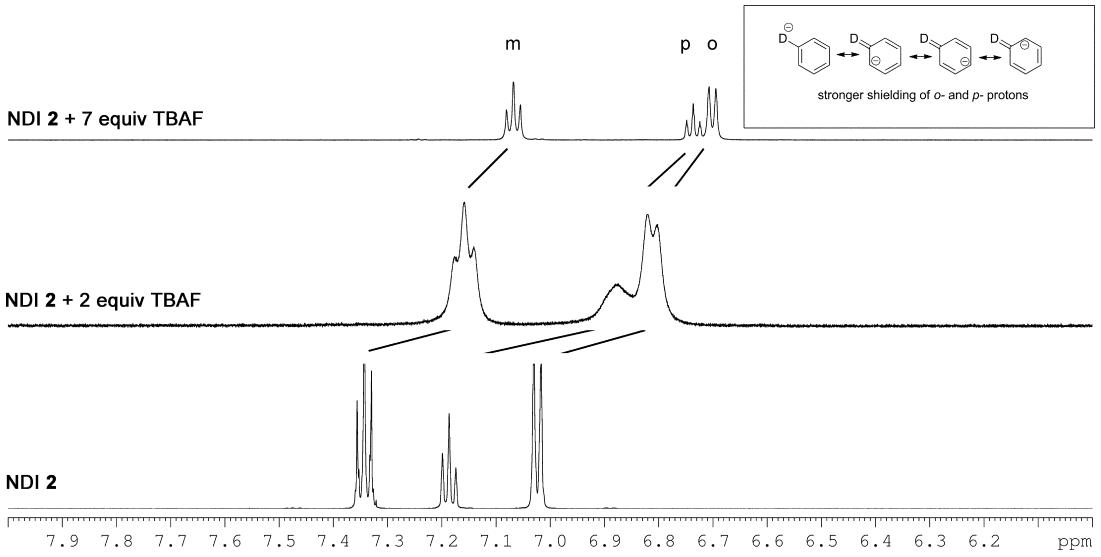

Figure 7. Aromatic region of ^{1}H NMR (CD_2Cl_2, 600 MHz) spectrum of NDI **2** before and after addition of 2 and 7 equiv of TBAF × 3 H_2O. Inset: Resonance structures of negatively charged donor-substituted benzene illustrating high electron density at *ortho* and *para* positions.

observed for the nitrogen-bound carbon atom of phenylamino group after addition of 7 equiv of TBAF to NDI **2** (Figure S11, Supporting Information). Similar low-field shift in carbon resonances was reported for diphenylamide anions.[39] The results of our NMR investigations (Figures S8−S14, Supporting Information) corroborate the existence of an anion species [**2** − **H**]$^-$.

Moreover, ^{13}C NMR experiments also rule out the possibility of a covalent bond between fluorine and the naphthalene core since no $^{19}F-^{13}C$ coupling was observed. Furthermore, the treatment of Br_4-NDI **1** and 2,7-diamino-3,6-dibromo-NDI **3a** with TBAF, respectively, provided indications for the involvement of phenylamino group in the generation of new species from NDI **2** in the presence of TBAF. After addition of up to 15 equiv of TBAF to Br_4-NDI **1**, no changes in the UV−vis spectra were observed, and only very high excess of fluoride ions (>60 equiv) entails a new absorption band (Figure 8). Since this new band could not be reversed by addition of TFA and Br_4-NDI **1** lacks an amino group at the core, a different process than the generation of an anion species should be responsible for the emergence of this band. In contrast, during the titration experiment of diamino-substituted NDI **3a** with TBAF a color change of the solution and emergence of a new absorption band were observed (Figure 9). The occurrence of

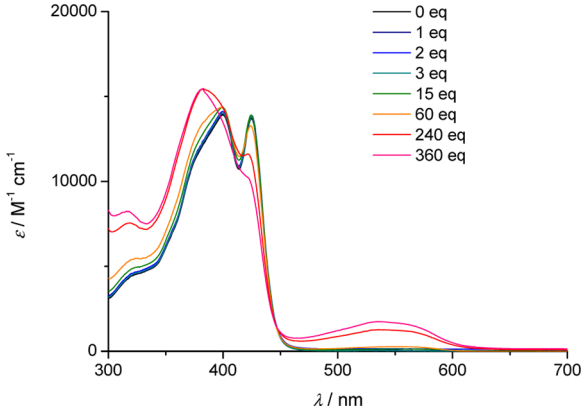

Figure 8. Titration of Br_4-NDI **1** in dichloromethane (2.2×10^{-5} M) with TBAF × 3H_2O monitored by UV−vis absorption spectroscopy at 25 °C.

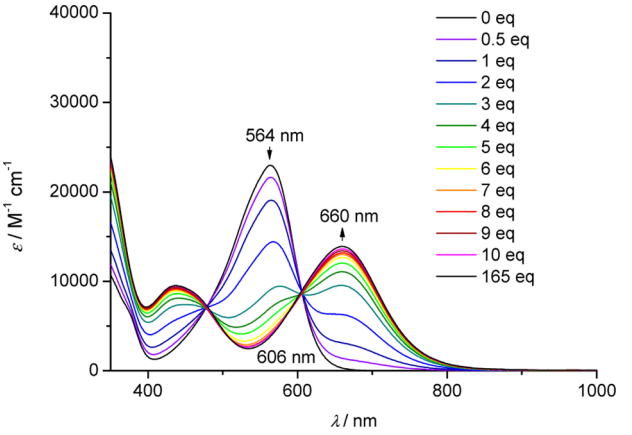

Figure 9. Titration of NDI **3a** in dichloromethane (8.9×10^{-5} M) with TBAF × 3H_2O monitored by UV−vis absorption spectroscopy at 25 °C.

an isosbestic point suggests the existence of only one new species formed upon addition of TBAF. Even a very large excess of 165 equiv of TBAF does not indicate the formation of a second new species. ^{1}H NMR experiments with **3a** in the presence of 14 equiv of TBAF finally showed that, indeed, only one amino group is involved in this process because the new species formed still exhibits one NH proton signal (Figure S15, Supporting Information). Consequently, chemically equivalent phenyl groups become nonequivalent after reaction with TBAF giving rise to two sets of proton signals with different high-field shifts. This observation could be explained in terms of a single deprotonation that obviously hampers the removal of the second proton.

Our further UV−vis spectroscopic investigations revealed that the absorption spectrum of the monoamino-substituted NDI **2** in DMF is markedly different than those in chloroform, dichloromethane and acetonitrile. As shown in Figure S4,

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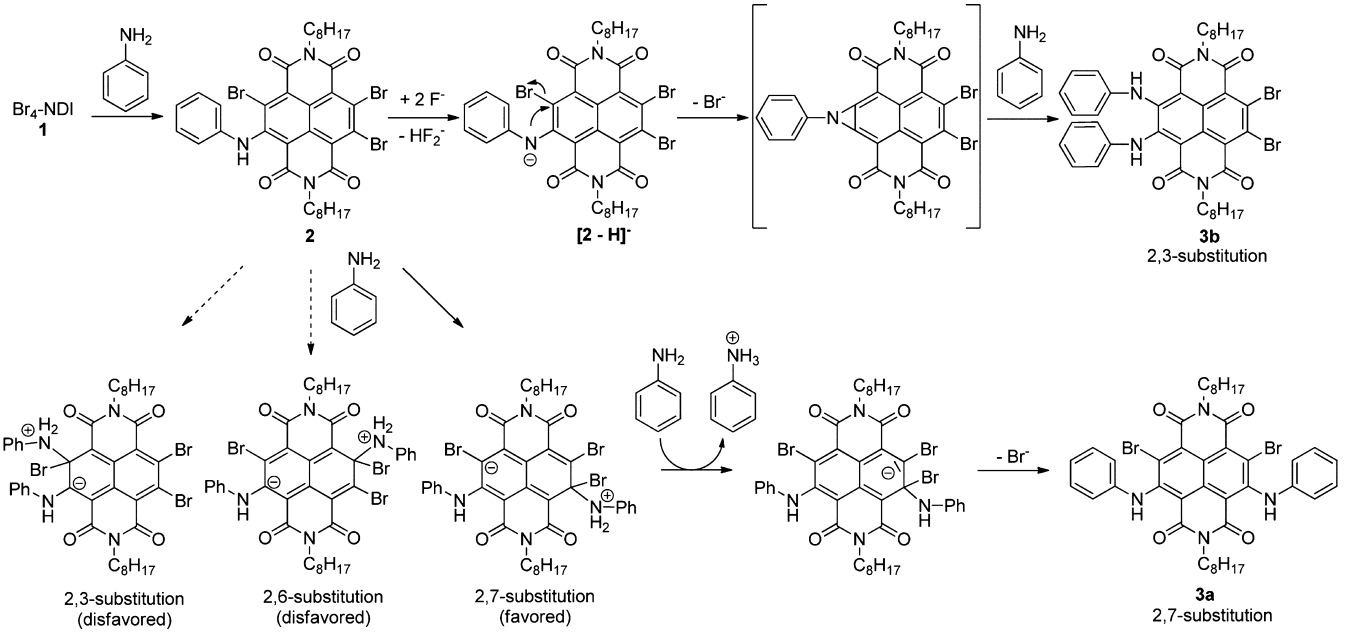
Scheme 3. Proposed Mechanisms for the Regioselective Formation of 2,7-Diamino and 2,3-Diamino Isomers in the Reaction of Br_4-NDI 1 with Aniline in the Absence and Presence of TBAF × 3 H_2O, Respectively



Supporting Information, in DMF an additional bathochromically shifted broad absorption maximum at 671 nm was observed. When comparing this new absorption to that of the aforementioned fluoride anion induced spectral changes in other solvents, it appears to be reasonable that the same species is generated in DMF without the additive. Since NDI **2** is poorly soluble in DMF, we have repeated these experiments with a better soluble analogous derivative **2′** bearing 2,6-diisopropylphenyl groups, instead of *n*-octyl group as in NDI **2** in the imide positions, which shows very similar absorption properties to those of NDI **2**. A freshly prepared solution of NDI **2′** in DMF shows an absorption maximum at 535 nm and a red-shifted shoulder as well (Figure S5, Supporting Information). To corroborate the hypothesis that DMF and fluoride ions induce the formation of the same new species, we added TBAF to the DMF solution of **2′**. Indeed, this causes a decrease of the hypsochromic band and a simultaneous appearance of a new band with an absorption maximum at 666 nm. After addition of TFA to the former solution, the bathochromic band disappears completely, regenerating the initial absorption spectrum of pure NDI **2′**. During this experiment an isosbestic point at 594 nm was observed as well (Figure S5, Supporting Information).

On the basis of what we discussed before, we propose that two different mechanisms are possibly involved in the reaction of Br_4-NDI **1** with aniline depending on the reaction conditions employed (Scheme 3). The 2,7-selectivity observed in pure solvents such as chloroform and dichloromethane is in good agreement with the simple consideration that a nucleophilic aromatic substitution (S_NAr) mechanism with a Meisenheimer-type intermediate is involved. The regioselectivity can be rationalized in terms of the zwitterionic Meisenheimer-type complex generated after addition of an aniline molecule to the monoamino-substituted intermediate NDI **2**. From the three possible regioisomeric complexes, one with the amino groups at the 2,7-positions is favored, while the remaining two with the amino groups at 2,6- and 2,3-positions, respectively, are disfavored because of the repulsion of nitrogen lone pair with the adjacent negatively charged carbon (see Scheme 3). Therefore, the 2,7-diamino regioisomer is formed in the absence of a base. The change of regioselectivity from the 2,7- to the 2,3-disubstitution in the presence of TBAF additive can be explained by the generation of an anionic species $[\mathbf{2} - \mathbf{H}]^-$ from the intermediate **2** (Scheme 3, upper part). Since a nucleophilic attack of a second aniline molecule on this anionic species is rather unlikely, we suggest that the reaction runs via a highly reactive, short-lived intermediate possessing an 1*H*-azirine ring,[40,41] generated by intramolecular nucleophilic substitution of the adjacent bromine atom. This is in agreement with the exclusive 2,3-selectivity in the presence of TBAF and also with the qualitatively observed enhanced reaction rate.

As mentioned before, the regioselectivity switch of the nucleophilic disubstitution of Br_4-NDI **1** was changed by the solvent from 2,7-diamino isomer in chloroform, dichloromethane, toluene and THF to 2,3-diamino isomer in DMF. This regioselectivity switch cannot be explained on the basis of high polarity of DMF (ε_r = 37.8) because such a change was not observed for acetonitrile, which is of similar polarity (ε_r = 35.9). Since the UV−vis spectral behavior of monoamino-NDI **2** intermediate is similar to that observed in other solvents (dichloromethane, acetonitrile) in the presence of fluoride ions, it is suggestive that a deprotonation of **2** by dimethylamine, which is a common decomposition product of DMF present in trace amounts, provokes the observed change in regioselectivity in this solvent. Thus, the observed regioselectivity in DMF is apparently not due to the inherent properties of this solvent.

■ CONCLUSION

A remarkable regioselectivity has been revealed for the nucleophilic disubstitution of 2,3,6,7-tetrabromo NDI **1** with aniline by varying reaction conditions. The reaction in dichloromethane, as well as in chloroform, without any additive leads to the regioselective formation of 2,7-diamino-3,6-dibromo-NDI, while in the presence of TBAF as an additive the regioselectivity is completely changed to 2,3-diamino-6,7-dibromo-NDI as the latter is formed exclusively. Thus, simple

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protocols for the complete regioselective synthesis of these two tetrasubstituted NDIs have been developed. The third possible regioisomer 2,6-diamino-3,7-dibromo-NDI barely plays a role in these reactions under the applied conditions. The clear assignment of the regioisomers of diamino-dibromo-NDIs brought to light that the previously reported diamino-dibromo-substituted NDI[34] should be the 2,3-diamino-6,7-dibromo rather than the 2,6-diamino-3,7-dibromo regioisomer. The observed compelling effect of fluoride ions (in the form of TBAF) on the regioselectivity of nucleophilic disubstitution of tetrabrominated NDI can be attributed to a deprotonation of the NH proton in the monoamino-tribromo-NDI, which acts as an intermediate in this reaction, leading to the respective anionic species whose electronic properties supposed to change the course of regioselectivity compared to the reaction without TBAF. Our unique results may lead to the regioselective synthesis of further new unsymmetrical core-substituted NDI compounds with desired functional properties.

EXPERIMENTAL SECTION

Materials and Methods. *N,N′*-Di-(*n*-octyl)-2,3,6,7-tetrabromo-naphthalenetetracarboxylic acid diimide (**1**) and *N,N′*-bis-(2′,6′-diisopropylphenyl)-2,3,6,7-tetrabromo-naphthalenetetracarboxylic acid diimide were synthesized according to the literature procedures.[22,23] Aniline was distilled under argon and stored under exclusion of light. TBAF × 3 H_2O was purchased from Aldrich and stored under exclusion of moisture. DMF was dried over P_2O_5 and stored under argon and exclusion of light. THF was freshly distilled over sodium. All other reagents and solvents were obtained from commercial suppliers and purified and dried according to standard procedures.[42] All reactions were performed without exclusion of oxygen or humidity. Column chromatography was performed on silica gel (particle size 0.040−0.063 mm). A preparative recycling GPC with 2H + 2.5H columns was used. Solvents for spectroscopic studies were of spectroscopic grade and used as received. ^{1}H and ^{13}C spectra were recorded in CD_2Cl_2 or $CDCl_3$ on a 400 or 600 MHz spectrometer. Residual undeuterated solvent was used as internal standard (CD_2Cl_2: 5.32 ppm for ^{1}H, 53.80 ppm for ^{13}C; $CDCl_3$: 7.26 ppm for ^{1}H, 77.23 for ^{13}C). High-resolution ESI-TOF mass spectrometry was carried out on a microTOF focus instrument. UV−vis measurements were performed in a conventional quartz cell (light pass 10 mm) on a standard, commercial spectrometer. For cyclic voltammetry measurements, a standard commercial electrochemical analyzer with a three electrode single-compartment cell was used. Dichloromethane (HPLC grade) was dried over calcium hydride under argon and degassed before using. The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAHFP) was prepared according to the literature[43] and recrystallized from ethanol/water. The measurements were carried out in dichloromethane at a concentration of about 10^{-4} M with ferrocene (Fc) as an internal standard for the calibration of the potential. A Ag/AgCl reference electrode was used. A Pt disc and a Pt wire were applied as working and auxiliary electrodes, respectively. Spectroelectrochemistry measurements were performed in a specially designed sample compartment consisting of a cylindrical quartz cell, a platinum disc (ø = 6 mm), a gold-covered metal (V2A) plate as the auxiliary electrode, and a Ag/AgCl pseudoreference electrode. All spectra were recorded in reflection mode, and the optical path length was varied by adjusting the vertical position of the working electrode with a micrometer screw. A standard, commercial spectrometer was used for recording UV/vis/NIR absorption spectra.

Reaction of *N,N′*-Di-(*n*-octyl)-2,3,6,7-tetrabromo-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (1) with Aniline. Br_4-NDI **1** (84.0 mg, 0.104 mmol) was dissolved in DMF (3 mL), and aniline (0.20 mL of a solution in DMF; *c* = 97.0 g/mL; 0.21 mmol) was added. The resulting mixture was stirred at 135 °C for 1 h. After cooling to room temperature the solvent was removed under reduced pressure, and the residue was purified by column chromatography (dichloromethane/pentane 1:1) yielding the following compounds.

***N,N′*-Di-(*n*-octyl)-2,3,6-tribromo-7-phenylamino-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (2).** Red solid (24.5 mg, 29%); mp 160−162 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): 11.90 (s, 1H), 7.40−7.28 (m, 2H), 7.23−7.15 (m, 1H), 7.07−6.97 (m, 2H), 4.22−4.10 (m, 4H), 1.78−1.66 (m, 4H), 1.49−1.21 (m, 20H), 0.93-0.83 (m, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2): 164.5, 160.7, 160.6, 160.3, 150.9, 141.9, 135.0, 129.9, 129.6, 128.4, 127.3, 126.1, 125.7, 125.3, 124.2, 123.5, 122.0, 107.9, 42.7, 42.2, 32.1, 29.61, 29.59, 29.57, 28.2, 28.0, 27.47, 27.46, 23.00, 22.99, 14.22, 14.21. HRMS (ESI, acetonitrile, neg. mode): *m*/*z* 814.0485 $(M - H)^-$, calculated for $C_{36}H_{39}Br_3N_3O_4$: 814.0496. Anal. Calcd. for $C_{36}H_{40}Br_3N_3O_4$: C, 52.83; H, 4.93; N, 5.13. Found: C, 52.36; H, 4.96; N, 5.14. UV−vis (CH_2Cl_2): λ_{max}/nm (ε/M^{-1} cm^{-1}) = 536 (12100).

***N,N′*-Di-(*n*-octyl)-2,7-dibromo-3,6-diphenylamino-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (3a).** Dark blue solid (23.5 mg, 28%); mp 178−179 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 11.98 (s, 2H, NH) 7.36−7.28 (m, 4H), 7.18−7.10 (m, 2H), 7.05−6.97 (m, 4H), 4.18 (t, ^3J = 7.7 Hz, 2H), 4.13 (t, ^3J = 7.7 Hz, 2H), 1.82−1.64 (m, 4H), 1.46−1.17 (m, 20H), 0.90−0.82 (m, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2): 165.0, 161.2, 151.2, 142.5, 129.5, 128.9, 127,4, 124.8, 121.7, 119.7, 109.0, 42.5, 41.6, 32.23, 32.21, 29.71, 29.68, 29.66, 29.6, 28.3, 28.1, 24.6, 23.1, 23.0, 14.3, 14.2. HRMS (ESI, acetonitrile/chloroform 1:1, pos. mode): *m*/*z* 829.1962 (M + H^+), calculated for $C_{42}H_{47}Br_2N_4O_4$: 829.1959. Anal. Calcd. for $C_{42}H_{46}Br_2N_4O_4$: C, 60.73; H, 5.58; N, 6.74. Found: C, 61.01; H, 5.73; N, 6.81. UV−vis (CH_2Cl_2): λ_{max}/nm = (ε/M^{-1} cm^{-1}) 564 (23000).

***N,N′*-Di-(*n*-octyl)-2,3-dibromo-6,7-diphenylamino-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (3b).** Dark violet solid (32.4 mg, 38%); mp 212−214 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): 12.32 (s, 2H), 7.17−6.92 (m, 6H), 6.49−6.46 (m, 4H), 4.20 (t, ^3J = 7.6 Hz, 4H), 1.80−1.71 (m, 4H), 1.49−1.24 (m, 20H), 0.88 (t, ^3J = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2): 165.8, 161.1, 143.3, 138.4, 128.5, 128.2, 125.2, 124.8, 123.5, 121.5, 105.2, 41.9, 32.2, 29.8, 29.7, 28.3, 27.6, 23.1, 14.3. HRMS (ESI, acetonitrile/chloroform 1:1, pos. mode): *m*/*z* 829.1960 (M + H^+), calculated for $C_{42}H_{47}Br_2N_4O_4$: 829.1959. Anal. Calcd. for $C_{42}H_{46}Br_2N_4O_4$: C, 60.73; H, 5.58; N, 6.74. Found: C, 60.91; H, 5.66; N, 6.92. UV−vis (CH_2Cl_2): λ_{max}/nm (ε/M^{-1} cm^{-1}) = 563 (24200).

***N,N′*-Di-(*n*-octyl)-2,6-dibromo-3,7-diphenylamino-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (3c).** After further purification by HPLC (dichloromethane/hexane 1:1), trace amounts of this compound were obtained (<1 mg, <1%), sufficient for a ^{1}H NMR and HRMS analysis. ^{1}H NMR (400 MHz, CD_2Cl_2): 11.25 (s, 2H, NH), 7.36−7.27 (m, 4H), 7.15−7.09 (m, 2H), 7.00−6.94 (m, 4H), 4.15 (t, ^3J = 7.7 Hz, 4H), 1.76−1.64 (m, 4H), 1.46−1.17 (m, 20H), 0.90−0.82 (m, 6H). HRMS (ESI, acetonitrile/chloroform 1:1, pos. mode): *m*/*z* 829.1958 (M + H^+), calculated for $C_{42}H_{47}Br_2N_4O_4$: 829.1959.

***N,N′*-Di-(*n*-octyl)-8,9-diphenylamino-6,7,10,11-benzo[*b*]-thianthrenetetracarboxylic Acid Diimide (4).** NDI **3b** (12.0 mg, 14.4 μmol) and potassium carbonate (9.0 mg, 65 μmol) were placed in a mixture of chloroform (5 mL) and acetone (3 mL). After addition of 1,2-benzenedithiol (10 μL, 84 μmol) the mixture was refluxed for 14 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (dichloromethane/pentane 1:1) yielding a dark blue solid (10.6 mg, 91%); mp 178−181 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 12.05 (s, 2H), 7.49−7.46 (m, 2H), 7.29−7.26 (m, 2H), 7.03−7.00 (m, 6H), 6.45−6.43 (m, 4H), 4.22 (t, ^3J = 7.7 Hz, 4H), 1.82−1.73 (m, 4H), 1.49−1.22 (m, 20H), 0.89 (t, ^3J = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): 165.8, 162.6, 142.3, 140.4, 138.3, 135.4, 128.8, 128.5, 128.1, 124.2, 123.0, 121.1, 121.0, 105.7, 41.5, 32.0, 29.5, 29.4, 28.2, 27.5, 22.8, 14.2. HRMS (ESI, acetonitrile/chloroform 1:1, pos. mode): *m*/*z* 811.3341 (M + H^+), calculated for $C_{48}H_{51}N_4O_4S_2$: 811.3346. UV−vis (CH_2Cl_2): λ_{max}/nm (ε/M^{-1} cm^{-1}) = 608 (28900).

Reaction of *N,N′*-Di-(*n*-octyl)-2,3,6,7-tetrabromo-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (1) with *n*-Octylamine. Br_4-NDI **1** (50.0 mg, 62.0 μmol) was placed in DMF (1.5 mL). After addition of *n*-octylamine (100 μL of a solution in DMF, 0.16 g/mL) the mixture was stirred at 135 °C for 6 h. The DMF was

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distilled off, and the residue was purified by column chromatography (dichloromethane/pentane 2:3) yielding the following compounds.

***N,N′*-Di-(*n*-octyl)-2,3-dibromo-6,7-di(*n*-octyl)amino-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (5).** Orange solid (30.7 mg, 55%); mp 93−97 °C (Lit.[34] 92−95 °C). ^{1}H NMR (400 MHz, $CDCl_3$): 10.48 (s, 2H), 4.17 (t, ^3J = 8.0 Hz, 4H), 3.57 (bs, 4H), 1.80−1.67 (m, 4H), 1.64−1.51 (m, 4H), 1.47−1.13 (m, 40H), 0.88 (t, ^3J = 6.8 Hz, 6H), 0.84 (t, ^3J = 7.1 Hz, 6H). HRMS (ESI, acetonitrile/chloroform, pos. mode): m/z 901.3828 (M + H$^+$), calculated for $C_{46}H_{71}Br_2N_4O_4$: 901.3827. UV−vis (CH_2Cl_2): λ_{max}/nm (ε/M^{-1} cm^{-1}) = 530 (25500).

***N,N′*-Di-(*n*-octyl)-2,3,6-tri-(*n*-octyl)-amino-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (6).** Violet solid (10.8 mg, 20%); mp 78−80 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): 10.29 (t, ^3J = 6.0 Hz, 1H), 9.59 (t, ^3J = 5.4 Hz,1H), 9.14 (t, ^3J = 6.0 Hz, 1H), 7.75 (s, 1H), 4.21−4.07 (m, 4H), 3.65−3.56 (m, 2H), 3.48−3.40 (m, 2H), 3.40−3.32 (m, 2H), 1.83−1.73 (m, 2H), 1.74−1.62 (m, 4H), 1.60−1.30 (m, 60H), 1.93−1.78 (m, 15H). ^{13}C NMR (101 MHz, CD_2Cl_2): 167.0, 166.3, 166.0, 163.7, 152.5, 150.6, 146.8, 126.6, 125.6, 122.9, 100.3, 108.8, 105.5, 102.0, 46.0, 45.7, 43.5, 40.7, 40.3, 32.20, 32.19, 32.18, 32.09, 32.08, 31.8, 31.6, 29.8, 29.72, 29.67, 29.64, 29.60, 29.59, 29.58, 29.54, 29.52, 29.50, 29.49, 28.33, 28.28, 27.6, 27.53, 27.51, 27.3, 27.2, 23.02, 23.01, 23.00, 22.96, 22.95, 14.22, 14.21, 14.18. HRMS (ESI, acetonitrile/chloroform, pos. mode): m/z 872.6983 (M + H$^+$), calculated for $C_{54}H_{90}N_5O_4$: 872.6987. UV−vis (CH_2Cl_2): λ_{max}/nm (ε/M^{-1} cm^{-1}) = 596 (23680).

***N,N′*-Di-(*n*-octyl)-8,9-di-(*n*-octyl)-amino-6,7,10,11-benzo[*b*]-thianthrenetetracarboxylic Acid Diimide (7).** NDI **5** (20.6 mg, 22.8 μmol) and potassium carbonate (14.0 mg, 101 μmol) were placed in a mixture of chloroform (5 mL) and acetone (3 mL). After addition of 1,2-benzenedithiol (0.02 mL, 0.17 mmol) the mixture was refluxed for 19 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (dichloromethane/pentane 1:1) yielding a violet wax-like substance (12.6 mg, 62%). ^{1}H NMR ($CDCl_3$, 400 MHz): 10.21 (t, ^3J = 6.0 Hz, 2H), 7.50−7.43 (m, 2H), 7.24−7.19 (m, 2H), 4.22 (t, ^3J = 8.0 Hz, 4H), 3.55 (dt, ^3J = 6.8 Hz, ^3J = 6.6 Hz, 4H), 1.85−1.67 Hz (m, 4H), 1.60−1.10 (m, 44H), 0.89 (t, ^3J = 7.1 Hz, 6H), 0.82 (t, ^3J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): 165.8, 162.8, 151.0, 138.6, 136.1,128.7, 128.2, 130.1, 120.6, 104.1, 46.5, 41.2, 32.0, 31.8, 31.7, 29.54, 29.45, 29.2, 28.2, 27.4, 27.0, 22.8, 22.7, 14.24, 14.17. HRMS (ESI, acetonitrile/chloroform, pos. mode): m/z 883.5234 (M + H$^+$), calculated for $C_{52}H_{75}N_4O_4S_2$: 883.5224. UV−vis (CH_2Cl_2): λ_{max}/nm (ε/M^{-1} cm^{-1}) = 569 (23600).

***N,N′*-Di-(*n*-octyl)-6,7,14,15-tetrathianthreno[2,3-b]-thianthrenetetracarboxylic Acid Diimide (8).** Br_4-NDI **1** (41.0 mg, 50.7 μmol) and 1,2-benzenedithiol (104 mg, 0.731 mmol) in chloroform (5 mL) were refluxed for 61 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (dichloromethane/pentane 1:1) affording a dark blue solid (23 mg, 59%); mp 274 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): 7.44−7.38 (m, 4H), 7.29−7.22 (m, 4H), 4.22 (t, ^3J = 7.6 Hz, 4H) 1.79 (t, ^3J = 7.6 Hz, 4H), 1.49−1.23 (m, 20 H), 0.90 (t, ^3J = 7.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): 165.8, 162.8, 151.0, 138.6, 136.1,128.7, 128.2, 130.1, 120.6, 104.1, 46.5,41.2, 32.0, 31.8, 31.7, 29.54, 29.45, 29.2, 28.2, 27.4, 27.0, 22.8, 22.7, 14.24, 14.17. HRMS (ESI, acetonitrile/chloroform, neg. mode): m/z 766.2033 (M$^-$) calculated for $C_{42}H_{42}N_2O_4S_4$: 766.2033. UV−vis (CH_2Cl_2): λ_{max}/nm (ε/M^{-1} cm^{-1}) = 583 (17000).

***N,N′*-Bis-(2′,6′-diisopropylphenyl)-2,3,6-tribromo-7-phenyl-amino-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (2′).** *N,N′*-Bis-(2′,6′-diisopropylphenyl)-2,3,6,7-tetrabromo-naphthalenetetracarboxylic acid diimide (38.5 mg, 42.7 μmol) was placed in chloroform (6 mL), and aniline (1.5 mL of a solution in chloroform; c = 2.65 g/mL; 42.7 μmol) was added. The resulting mixture was stirred at room temperature for 16 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (dichloromethane/pentane 1:1) yielding a red solid (20.3 mg, 52%); mp 321−324 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 12.0 (s, 1H), 7.47−7.38 (m, 2H), 7.31−7.22 (m, 6H), 7.14−7.08 (m, 1H), 6.98−6.92 (m, 2H), 2.65 (sept, ^3J = 6.8 Hz, 2H), 2.58 (sept, ^3J = 6.8 Hz, 2H), 1.17−1.05 (m, 24 H). ^{13}C NMR (101 MHz, CD_2Cl_2): 165.0. 161.2, 160.7, 151.4, 146.8, 146.1, 141.4, 135.5, 131.1, 130.4, 130.2, 130.1, 129.6, 129.3, 128.6, 126.9, 125.8, 125.5, 124.7, 124.6, 123.8, 122.4, 107.3, 29.9, 29.7, 24.2, 24.1, 24.02, 23.99. HRMS (ESI, acetonitrile/chloroform, pos. mode): m/z 912.0639 (M + H$^+$), calculated for $C_{44}H_{41}Br_3N_3O_4$: 912.0642. UV−vis (CH_2Cl_2): λ_{max}/nm (ε/M^{-1} cm^{-1}) = 540 (5000).

Procedures for Regioselective Synthesis of 3a and 3b in Dichloromethane. **3a**: *N,N′*-Di-(*n*-octyl)-2,3,6,7-tetrabromonaphthalenetetracarboxylic acid diimide (31.4 mg, 38.9 μmol) was placed in dichloromethane (4 mL). After addition of aniline (320 μL, 3.58 mmol) the mixture was stirred at room temperature for 2 days. The mixture was directly purified by column chromatography (dichloromethane/pentane 1:1) yielding **3a** as a dark blue solid (31.0 mg, 96%).

3b: *N,N′*-Di-(*n*-octyl)-2,3,6,7-tetrabromo-naphthalenetetracarboxylic acid diimide (32.0 mg, 39.7 μmol) and TBAF × 3 H_2O (85.0 mg, 0.269 mmol) were placed in dichloromethane (4 mL). After addition of aniline (326 μL, 3.58 mmol) the mixture was stirred at room temperature for 2 h. The mixture was directly purified by column chromatography (dichloromethane/pentane 1:1) yielding **3b** as a dark violet solid (26.4 mg, 80%).

Reactions of Br_4-NDI 1 with Aniline for NMR Analysis. Br_4-NDI **1** was dissolved in the respective solvent, and aniline was added. The reaction was conducted under the conditions stated in Table 1. Volatile solvents such as $CHCl_3$, CH_2Cl_2, toluene, THF and acetonitrile were removed after the reaction under reduced pressure, whereas in the case of DMF the reaction mixture was dissolved in diethyl ether and washed with water. The organic phases were collected, and diethyl ether was removed under a vacuum. The crude mixture was subjected to GPC purification prior to NMR analysis, to remove aniline without changing the ratio of the regioisomeric products. If TBAF × 3 H_2O was used as an additive, the fluoride salt was washed out with water prior to GPC purification.

Entry 1: Br_4-NDI **1** (89.0 mg, 0.110 mmol) and aniline (0.9 mL, 1 mmol) were stirred in chloroform (10 mL) at room temperature for 16 h.

Entry 2: Br_4-NDI **1** (12.0 mg, 14.9 μmol), TBAF × 3 H_2O (7.0 mg, 22.2 μmol) and aniline (122 μL 1.34 mmol) were stirred in chloroform (4 mL) at room temperature for 14.5 h.

Entry 3: Br_4-NDI **1** (8.60 mg, 10.7 μmol), TBAF × 3 H_2O (35.0 mg, 111 μmol) and aniline (90 μL 0.96 mmol) were stirred in chloroform (2 mL) at room temperature for 7 h.

Entry 4: Br_4-NDI **1** (12.0 mg, 14.9 μmol) and aniline (122 μL, 1.34 mmol) were stirred in dichloromethane (4 mL) at room temperature for 66 h

Entry 5: Br_4-NDI **1** (11.8 mg, 14.6 μmol), TBAF × 3 H_2O (76.2 mg, 242 μmol) and aniline (120 μL 1.32 mmol) were stirred in dichloromethane (4 mL) at room temperature for 18 h.

Entry 6: Br_4-NDI **1** (8.80 mg, 10.9 μmol) and aniline (90 μL, 0.99 mmol) were stirred in toluene (2 mL) at room temperature for 16 h.

Entry 7: Br_4-NDI **1** (9.10 mg, 11.3 μmol) and aniline (93 μL, 1.02 mmol) were stirred in dry THF (2 mL) at room temperature for 16 h.

Entry 8: Br_4-NDI **1** (9.40 mg, 11.7 μmol) and aniline (860 μL of a 1.22 M aniline solution in dry THF, 1.05 mmol) were stirred in dry THF (2 mL) at room temperature for 1.5 h.

Entry 9: Br_4-NDI **1** (10.6 mg, 13.1 μmol) and aniline (108 μL, 1.18 mmol) were stirred in acetonitrile (20 mL) at room temperature for 7 days.

Entry 10: Br_4-NDI **1** (11.1 mg, 13.8 μmol), TBAF × 3 H_2O (79.7 mg, 253 μmol) and aniline (113 μL, 1.23 mmol) were stirred in acetonitrile (4 mL) at room temperature for 3 h.

Entry 11: Br_4-NDI **1** (9.2 mg, 11.4 μmol) and aniline (1.3 mL of a 0.752 M aniline solution in acetonitrile, 1.34 mmol) were stirred in acetonitrile (2 mL) at 65 °C for 1 h.

Entry 12: Br_4-NDI **1** (55.5 mg, 68.8 μmol) and aniline (565 μL, 0.712 mmol) were stirred in dry DMF (5 mL) at room temperature for 14.5 h.

Entry 13: Br_4-NDI **1** (14.5 mg, 14.28 μmol) and aniline (1.2 mL of a 1.07 M aniline solution in dry DMF) were stirred in dry DMF (2 mL) at 65 °C for 2 h.

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■ ASSOCIATED CONTENT

Supporting Information

Figures S1−S15 and Table S1 mentioned in the text, and additional NMR spectra (Figures S16−S35) and ESI-HRMS spectra (Figures S36−S45). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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