Core-Tetrasubstituted Naphthalene Diimides by Stille Cross-Coupling Reactions and Characterization of Their Optical and Redox Properties

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Received 18 November 2008; revised 26 January 2009

Abstract: The palladium-catalyzed cross-coupling reaction of 2,3,6,7-tetrabromonaphthalene diimide with various aryl- and alkynylstannanes afforded a series of hitherto unknown tetraaryl- and tetraethynyl-substituted naphthalene diimides (NDIs). UV/Vis spectroscopic studies revealed that the absorption maxima of ethynyl-substituted NDIs are significantly bathochromically shifted compared to those of unsubstituted and tetraaryl-substituted NDIs. Cyclic voltammetry investigations showed that ethynyl substituents shift the reduction potentials of NDIs anodically, thus these NDI derivatives are interesting candidates for air-stable n-channel organic field-effect transistors.

Key words: chromophores, arylenes, cross-coupling, Stille reaction, catalysis

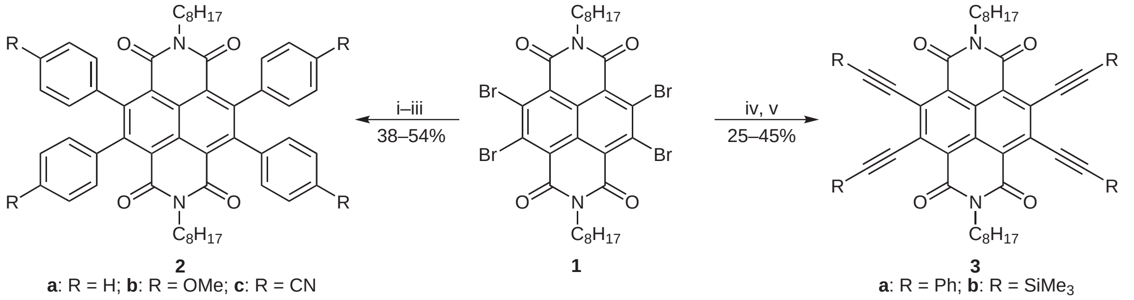
Naphthalene diimides (NDIs) are an important class of chromophores with favorable properties for applications as organic materials and in functional supramolecular systems.[1] For example, NDIs have been used as n-type semiconductors in organic field-effect transistors (OFETs),[2] as electron-acceptor units in photoinduced charge separation arrays,[3] light-harvesting chromophores of synthetic rod antennae,[4] and light-absorbing charge transport units in self-assembled systems for photoproduction of transmembrane proton gradient.[5] In recent years, chemosensors[6,7] and supramolecular switches[8] have been developed based on NDI derivatives. Furthermore, extended supramolecular architectures such as helical nanotubes[9] and synthetic ion channels[10a,b] and zipper assemblies[10c,d] have been constructed using naphthalene diimides.

The electronic properties of naphthalene diimides are decisive for most of the applications mentioned above and they can be tuned by introducing substituents at the naphthalene core.[11] Thus, numerous core-substituted NDIs have previously been reported. Core-disubstituted NDIs were made accessible from the 2,6-dichloro- and 2,6-dibromonaphthalene dianhydride by imidization with amines, followed by subsequent exchange of halogen atoms with nitrogen, oxygen, sulfur, and selenium nucleophiles.[11,12] Core-trisubstituted naphthalene diimides containing triamine or monoalkoxy and diamino groups were obtained by the reaction of 2,6-dichloronaphthalene diimide with ethylenediamine or by successive reactions with ethylenediamine and an alcohol.[13] Nucleophilic substitution of 2,3,6,7-tetrabromonaphthalene diimides, which are accessible by imidization of 2,3,6,7-tetrabromonaphthalene dianhydride,[14,15] with alkoxy, alkylamino, and alkylthio nucleophiles afforded the corresponding core-tetrasubstituted NDI dyes with interesting electronic properties.[14] Very recently, palladium-catalyzed cross-coupling reactions with 2,6-dibromonaphthalene diimides have been performed to afford 2,6-dicyano, diaryl, and diethynyl NDI derivatives,[16a,b] and thiophene-based conjugated polymers of disubstituted NDIs.[16c,d] However, to our knowledge such a cross-coupling reaction of 2,3,6,7-tetrabromonaphthalene diimides has not been reported so far and except a tetrathiophene-NDI derivative that was prepared by Stille reaction of tetrabromonaphthalene dianhydride and subsequent imidization,[17] no further examples of tetraaryl- or tetraethynyl-substituted NDIs are known.[18]

Here we report on the palladium-catalyzed Stille reactions of 2,3,6,7-tetrabromonaphthalene diimide **1** with electron-rich, electron-poor and neutral organostannanes to afford the new tetraaryl- and tetraethynylnaphthalene diimides **2a**–**c** and **3a**,**b** (Scheme 1). The starting compound 2,3,6,7-tetrabromonaphthalene diimide **1** was prepared by imidization of 2,3,6,7-tetrabromonaphthalene dianhydride with *n*-octylamine according to the literature method.[15]

Stille cross-coupling reaction of tetrabrominated NDI **1** with 6.6 equivalents of tributylphenylstannane in the presence of $Pd(PPh_3)_4$ as catalyst in toluene afforded the tetraphenyl-substituted NDI **2a** in 54% yield. To explore whether electron-rich or electron-poor aryl groups can also be introduced at the naphthalene core by this method, tributyl(4-methoxyphenyl)stannane and tributyl(4-cyanophenyl)stannane were reacted with NDI **1** using $Pd(dba)_2$ and Ph_3As as catalysts. Indeed, the corresponding tetraaryl-substituted NDIs **2b** and **2c** were obtained in 38% and 47% yield, respectively. It is noteworthy that with $Pd(PPh_3)_4$ as catalyst similar results were obtained as for $Pd(dba)_2$ and Ph_3As. The latter combination, however, is easier to handle under ambient conditions. As next, we have investigated the cross-coupling of NDI **1** with ethynylstannanes under Stille conditions. Pleasingly, the reaction of NDI **1** with tributyl(phenylethynyl)stannane and tributyl[(trimethylsilyl)ethynyl]stannane in the presence of $Pd(PPh_3)_4$ catalyst provided the very first examples of tetraethynyl-substituted naphthalene diimides **3a** and **3b** in 25% and 45% yield, respectively. It is noteworthy that,

SYNTHESIS 2009, No. 11, pp 1841–1845
Advanced online publication: 30.04.2009
DOI: 10.1055/s-0029-1216785; Art ID: T20008SS



Scheme 1 Synthesis of tetraaryl- and tetraethynyl-substituted naphthalene diimides **2a**–**c** and **3a**,**b** by Stille coupling reactions under argon atmosphere. *Reagents and conditions*: (i) tributylphenylstannane, Pd(PPh$_3$)$_4$, toluene, reflux, 70 h, yield **2a**: 54%; (ii) tributyl(4-methoxyphenyl)stannane, Pd(dba)$_2$, Ph$_3$As, toluene, reflux, 19 h, yield **2b**: 38%; (iii) tributyl(4-cyanophenyl)stannane, Pd(dba)$_2$, Ph$_3$As, toluene, reflux, 28 h, yield **2c**: 47%; (iv) tributyl(phenylethynyl)stannane, Pd(PPh$_3$)$_4$, toluene, reflux, 21 h, yield **3a**: 25%; (v) tributyl[(trimethylsilyl)ethynyl]stannane, Pd(PPh$_3$)$_4$, toluene, reflux, 24 h, yield **3b**: 45%.

although copper(I)-cocatalyzed Sonogashira reaction of 2,6-dibromo NDI had been previously applied to prepare the respective diethynyl-substituted NDIs,[16b] the reactions of 2,3,6,7-tetrabromo NDI **1** with phenylacetylene and trimethylsilylacetylene under Sonogashira conditions led to a complex mixture and only little amounts (4–8%) of the desired cross-coupling products could be obtained.

The new 2,3,6,7-tetrasubstituted NDIs **2a–c** and **3a**,**b** were characterized by ^{1}H and ^{13}C NMR spectra, UV/Vis spectroscopy, high-resolution mass spectrometry, and elemental analysis.

The optical properties of the NDIs **2a**–**c** and **3a**,**b** were studied by UV/Vis spectroscopy in dichloromethane. The phenyl- and 4-cyanophenyl-substituted NDIs **2a** and **2c** are yellow nonfluorescent compounds, exhibiting absorption maxima at 360 and 377 nm, and at 359 and 379 nm, respectively (Figure 1, a). The position and vibronic structure is very similar to that of the core-unsubstituted NDI-C8 with an *n*-octyl substituent at the imide position (359 and 380 nm),[11c,15] indicating a limited conjugation of the phenyl substituents with the naphthalene core. Interestingly, the red NDI **2b** bearing four 4-methoxyphenyl groups at the naphthalene core exhibits an additional broad band with an absorption maximum at 480 nm of weak intensity. This band can be attributed to a charge-transfer transition as previously reported for some di- and tetrasubstituted NDIs.[11a,16b] The broadening of this band (as well as the tailing of the absorption bands of **2a** and **2c**) is attributed to the presence of noncoplanar conformations evoked by steric constraints that distort the chromophore (in particular around the phenyl–naphthalene single bonds). Compared with the aryl-substituted NDIs **2a**–**c**, ethynyl-substituted NDIs **3a** and **3b** exhibit significantly red-shifted well-defined absorption bands (Figure 1, b). This red-shift is the consequence of an extended π-conjugation in the absence of sterical encumbering. For NDI **3a**, a weak fluorescence with a quantum yield of 0.6% was observed. The remaining NDI dyes are nonfluorescent.

The redox properties of the NDIs **2a**–**c** and **3a**,**b** were studied by cyclic voltammetry in dichloromethane with ferrocene as internal standard. The results are summarized in Table 1 and cyclic voltammograms of NDIs **2a** and **3a** are shown in Figure 2 as representative examples. All of these NDIs show two well separated reversible reduction waves, respectively. Comparing with the reduction potentials of the unsubstituted NDI-C8 (–1.10 and –1.51 V vs. Fc/Fc$^+$),[11c] the reduction waves of the phenyl-substituted NDI **2a** (–1.19 and –1.66 V vs. Fc/Fc$^+$) and the methoxyphenyl-substituted NDI **2b** (–1.26 and –1.72 V vs. Fc/Fc$^+$) are shifted to more negative values, while NDI **2c** containing electron-withdrawing 4-cyanophenyl groups displays significantly anodically shifted reduction waves (–0.92 and –1.46 V vs. Fc/Fc$^+$). Likewise the phenylethynyl-substituted NDI **3a** (–0.93 and –1.30 V vs. Fc/Fc$^+$) is more easily reducible than the unsubstituted NDI-C8 and the phenyl-substituted NDI **2a**. This can be attributed to an extension of the LUMO orbitals by four ethynyl substituents.[16b] For NDI **3b** (–0.97 and –1.35 V vs. Fc/Fc$^+$) similar

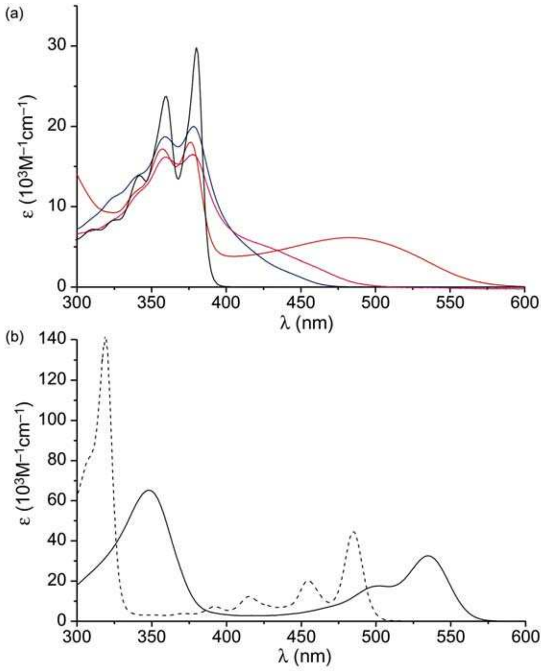


Figure 1 (a) UV/Vis absorption spectra of NDIs **2a** (pink line), **2b** (red line), **2c** (blue line) and, for comparison, of the core-unsubstituted NDI-C8 (black line); and (b) of **3a** (dashed line) and **3b** (solid line)

values are observed. Within the available potential range in dichloromethane only for NDI **2b** an irreversible oxidation could be observed at around 1.16 V.

Table 1 Half-Wave Reduction Potentials of Core-Tetrasubstituted NDIs **2a**–**c** and **3a**,**b** and Reference Compound NDI-C8 in Volt (V) vs. Fc/Fc$^+$

$E_{1/2}$	**2a**	**2b**	**2c**	**3a**	**3b**	**NDI-C8**
X/X^-	–1.19	–1.26	–0.92	–0.93	–0.97	–1.10
X^-/X^{2-}	–1.66	–1.72	–1.46	–1.30	–1.35	–1.51

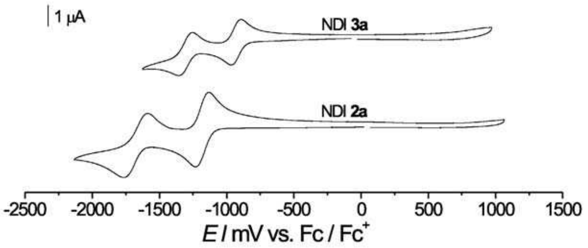


Figure 2 Cyclovoltammograms for NDIs **2a** and **3a**

In conclusion, our present study has revealed that the Stille cross-coupling reaction is a convenient method for the synthesis of tetraaryl- and tetraethynyl-substituted naphthalene diimides which has not previously been applied to tetrabromonaphthalene diimides. In aryl-substituted NDIs the π-conjugation between the NDI core and the four substituents is apparently restricted due to steric constraints, while in ethynyl-substituted NDI extended π-conjugation is given as reflected in bathochromically shifted absorption maxima and lower (less negative) reduction potentials of latter derivatives. Because of their electron-deficient character, these tetraethynyl NDIs should be interesting n-type semiconductors for air-stable n-channel organic field-effect transistors.[19,20]

The starting compound tetrabromonaphthalene diimide **1** was prepared according to the literature.[15] Tributylphenylstannane was obtained from commercial sources. Tributyl(4-methoxyphenyl)stannane,[21] tributyl(4-cyanophenyl)stannane,[22] tributyl(phenylethynyl)stannane and tributyl[(trimethylsilyl)ethynyl]stannane[23] were prepared as described in the literature. All other reagents and solvents were obtained from commercial suppliers and purified and dried according to standard procedures.[24] Column chromatography was performed on silica gel (Merck Silica 60, particle size 0.040–0.063 mm). Solvents for spectroscopic studies were of spectroscopic grade and used as received. Elemental analyses were performed on a CHNS 932 analyzer (Leco Instruments GmbH, Mönchengladbach, Germany). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 400 or on a Bruker DMX 600 spectrometer. Residual undeuterated solvent was used as internal standard (7.26 ppm for ^{1}H and 77.23 ppm for ^{13}C spectra). High-resolution ESI-TOF mass spectrometry was carried out on a microTOF focus instrument (Bruker Daltronik GmbH). UV/Vis measurements were performed in a conventional quartz cell (light pass 10 mm) on a PerkinElmer Lambda 950 spectrometer. Emission spectra were measured in a conventional rectangular quartz cell (10 × 10 × 40 mm) on a PTI QM4-2003 fluorescence spectrometer and are corrected against photomultiplier and lamp intensity. A long wavelength range emission-corrected photomultiplier R928 was used. Fluorescence quantum yields were determined under dilute conditions in CH_2Cl_2 ($<10^{-6}$ M) versus *N*,*N*′-(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetracarboxylic acid bisimide (Φ_{fl} = 0.96 in $CHCl_3$).[25] For cyclic voltammetry, a standard commercial electrochemical analyzer (EC epsilon; BAS Instruments, UK) with a three electrode single-compartment cell was used. CH_2Cl_2 (HPLC grade) was dried over CaH_2 under argon and degassed before using. The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAHFP) was prepared according to the literature,[26] and recrystallized from EtOH–H_2O. The measurements were carried out in CH_2Cl_2 at a concentration of about 10^{-4} M with ferrocene (Fc) as internal standard for the calibration of the potential. Ag/AgCl reference electrode was used. A Pt disc and a Pt wire were used as working and auxiliary electrodes, respectively.

Attention! Because of their high toxicity, organostannanes must be handled with caution!

N,*N*′-Di-(*n*-octyl)-2,3,6,7-tetraphenyl-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (2a)

Compound **1** (210 mg, 0.26 mmol), tributylphenylstannane (635 mg, 1.73 mmol), and $Pd(PPh_3)_4$ (14.0 mg, 12.1 µmol) were combined in toluene (10 mL) and heated under reflux in an argon atmosphere for 70 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (*n*-hexane–THF, 96:4). A yellow solid was obtained (111 mg, 54%); mp 198–200 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, ^3J = 7.0 Hz, 6 H), 1.12–1.29 (m, 20 H), 1.30–1.41 (m, 4 H), 3.86 (t, ^3J = 7.6 Hz, 4 H), 6.86–6.93 (m, 8 H), 7.14–7.23 (m, 12 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.3, 22.8, 27.2, 28.2, 29.4, 29.5, 31.9, 41.2, 124.2, 126.9, 127.2, 127.7, 128.8, 139.4, 149.1, 162.2.

HRMS (ESI, +): *m*/*z* [M + H]$^+$ calcd for $C_{54}H_{55}N_2O_4$: 795.4156; found: 795.4156.

UV/Vis (CH_2Cl_2): λ_{max} (ε) = 253 (62500), 360 (15900), 377 nm (16300 M^{-1} cm^{-1}).

CV (CH_2Cl_2, 0.1 M TBAHFP, vs. Fc/Fc$^+$): E_{red} (X^-/X^{2-}) = –1.66 V, E_{red} (X/X^-) = –1.19 V.

Anal. Calcd for $C_{54}H_{54}N_2O_4$: C, 81.58; H, 6.85; N, 3.52. Found: C, 81.36; H, 6.99; N, 3.51.

N,*N*′-Di-(*n*-octyl)-2,3,6,7-tetrakis(4-methoxyphenyl)-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (2b)

Compound **1** (108 mg, 0.134 mmol), tributyl(4-methoxyphenyl)stannane (384 mg, 0.967 mmol), $Pd(dba)_2$ (7.90 mg, 13.7 µmol), and Ph_3As (8.30 mg, 27.1 µmol) were combined in toluene (10 mL) and heated under reflux in an argon atmosphere for 19 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (CH_2Cl_2). An orange solid was obtained (46.8 mg, 38%); mp 229–230 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, ^3J = 7.0 Hz, 6 H), 1.14–1.43 (m, 20 H), 1.43–1.51 (m, 4 H), 3.78 (s, 12 H), 3.88 (t, ^3J = 7.5 Hz, 4 H), 6.71–6.81 (m, 16 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.3, 22.8, 27.2, 28.3, 29.5, 29.6, 32.0, 41.2, 55.2, 113.4, 124.3, 127.0, 130.0, 131.8, 149.1, 158.4, 162.6.

HRMS (ESI, +): *m*/*z* [M + H]$^+$ calcd for $C_{58}H_{63}N_2O_8$: 915.4579; found: 915.4579.

UV/Vis (CH_2Cl_2): λ_{max} (ε) = 249 (68800), 358 (17200), 376 (18000), 480 nm (6200 M^{-1} cm^{-1}).

CV (CH_2Cl_2, 0.1 M TBAHFP, vs. Fc/Fc^+): E_{red} (X^-/X^{2-}) = –1.72 V, E_{red} (X/X^-) = –1.26 V.

Anal. Calcd for $C_{58}H_{62}N_2O_8$: C, 76.12; H, 6.83; N, 3.06. Found: C, 75.60; H, 6.76; N, 3.17.

N,N′-Di-(*n*-octyl)-2,3,6,7-tetrakis(4-cyanophenyl)-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (2c)

Compound **1** (111 mg, 0.138 mmol), tributyl(4-cyanophenyl)stannane (394 mg, 1.00 mmol), $Pd(dba)_2$ (8.10 mg, 14.0 μmol), and Ph_3As (9.00 mg, 29.4 μmol) were combined in toluene (14 mL) and heated under reflux in an argon atmosphere for 28 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (CH_2Cl_2). A yellow solid was obtained (58.5 mg, 47%); mp 350–352 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, ^3J = 7.0 Hz, 6 H), 1.13–1.29 (m, 20 H), 1.36–1.49 (m, 4 H), 3.82 (t, ^3J = 7.6 Hz, 4 H), 6.97–7.02 (m, 8 H), 7.50–7.55 (m, 8 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.3, 22.8, 27.1, 28.0, 29.36, 29.37, 31.9, 41.6, 111.8, 118.5, 124.3, 127.7, 129.2, 131.9, 143.5, 147.0, 161.3.

HRMS (ESI, +): *m*/*z* [M + Na]$^+$ calcd for $C_{58}H_{50}N_6O_4$ + Na: 917.3785; found: 917.3780.

UV/Vis (CH_2Cl_2): λ_{max} (ε) = 257 (116700), 359 (18200), 379 nm (19400 M^{-1} cm^{-1}).

CV (CH_2Cl_2, 0.1 M TBAHFP, vs. Fc/Fc^+): E_{red} (X^-/X^{2-}) = –1.46 V, E_{red} (X/X^-) = –0.92 V.

Anal. Calcd for $C_{58}H_{50}N_6O_4$: C, 77.83; H, 5.63; N, 9.39. Found: C, 77.60; H, 5.68; N, 9.31.

N,N′-Di-(*n*-octyl)-2,3,6,7-tetrakis(phenylethynyl)-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (3a)

Compound **1** (86.1 mg, 0.107 mmol), tributyl(phenylethynyl)stannane (278 mg, 0.710 mmol), and $Pd(PPh_3)_4$ (7.00 mg, 6.06 μmol) were combined in toluene (10 mL) and heated under reflux in an argon atmosphere for 21 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (CH_2Cl_2–*n*-pentane, 7:3). A red solid was obtained (24.3 mg, 25%); mp 315–316 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 7.1 Hz, 6 H), 1.25–1.49 (m, 20 H), 1.77–1.90 (m, 4 H), 4.26 (t, ^3J = 7.7 Hz, 4 H), 7.33–7.45 (m, 12 H), 7.71–7.76 (m, 8 H).

^{13}C NMR (151 MHz, $CDCl_3$, 40 °C): δ = 14.1, 22.7, 27.2, 28.0, 29.28, 29.34, 32.0, 53.4, 88.9, 108.0, 123.1, 125.4, 125.6, 128.5, 129.6, 130.9, 132.6, 160.1.

HRMS (ESI, –): *m*/*z* [M]$^-$ calcd for $C_{62}H_{54}N_2O_4$: 890.4089; found: 890.4090.

UV/Vis (CH_2Cl_2): λ_{max} (ε) = 348 (65200), 535 nm (32600 M^{-1} cm^{-1}).

Fluorescence (CH_2Cl_2, λ_{ex} = 490 nm): λ_{max} = 560 nm.

Fluorescence quantum yield (CH_2Cl_2): Φ_{fl} = 0.6%.

CV (CH_2Cl_2, 0.1 M TBAHFP, vs. Fc/Fc^+): E_{red} (X^-/X^{2-}) = –1.30 V, E_{red} (X/X^-) = –0.93 V.

Anal. Calcd for $C_{62}H_{54}N_2O_4$: C, 83.57; H, 6.11; N, 3.14. Found: C, 83.29; H, 6.16; N, 3.40.

N,N′-Di-(*n*-octyl)-2,3,6,7-tetrakis[(trimethylsilyl)ethynyl]-1,4,5,8-naphthalenetetracarboxylic Acid Diimide (3b)

Compound **1** (130 mg, 0.161 mmol), tributyl[(trimethylsilyl)ethynyl]stannane (600 mg, 1.55 mmol), and $Pd(PPh_3)_4$ (8.80 mg, 7.61 μmol) were combined in toluene (9 mL) and heated under reflux in an argon atmosphere for 24 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (*n*-hexane–THF, 96:4). A yellow solid was obtained (65.0 mg, 45%); mp 207–209 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.39 (s, 36 H), 0.88 (t, ^3J = 7.1 Hz, 6 H), 1.25–1.70 (m, 20 H), 1.70–1.78 (m, 4 H), 4.18 (t, ^3J = 7.6 Hz, 4 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 0.1, 14.3, 22.9, 27.3, 28.0, 29.38, 29.42, 32.1, 42.4, 101.9, 116.0, 125.3, 126.8, 130.7, 160.6.

HRMS (ESI, +): *m*/*z* [M + H]$^+$ calcd for $C_{50}H_{71}N_2O_4Si_4$: 875.4485; found: 875.4482.

UV/Vis (CH_2Cl_2): λ_{max} (ε) = 319 (140100), 455 (20100), 485 nm (44000 M^{-1} cm^{-1}).

CV (CH_2Cl_2, 0.1 M TBAHFP, vs. Fc/Fc^+): E_{red} (X^-/X^{2-}) = –1.35 V, E_{red} (X/X^-) = –0.97 V.

Anal. Calcd for $C_{50}H_{70}N_2O_4Si_4$: C, 68.60; H, 8.06; N, 3.20. Found: C, 68.35; H, 8.25; N, 3.18.

Acknowledgment

We thank Ms. Ana-Maria Krause for the cyclic voltammetry measurements, and the BMBF for financial support within the program ‘Organische Photovoltaik’.

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