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ARTICLE *in* EUROPEAN JOURNAL OF ORGANIC CHEMISTRY · JANUARY 2011

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Synthesis and Optical Properties of Molecular Rods Comprising a Central Core-Substituted Naphthalenediimide Chromophore for Carbon Nanotube Junctions

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Keywords: Nanotechnology / Molecular electronics / Nanostructures / Luminescence / Acetylene scaffolding

The synthesis of a series of molecular rods **1–5**, designed to bridge the gap of a carbon nanotube junction in order to emit light as a characteristic signal of integrated molecules, is reported. The molecular rods consist of a central naphthalenediimide (NDI) core, which itself is substituted with benzylamino and benzylsulfanyl groups, providing distinct absorption and emission properties. The NDI core is embedded in an oligo(phenylene ethynylene) (OPE) system providing the rod-like structure required to bridge gaps between nanoelectrodes. The number of repeating units of the OPE is varied to adjust the length of the target compounds between 2.3 and 6.6 nm. The OPE parts are terminally functionalized with polyaromatic hydrocarbon groups (naphthalene, phenanthrene, anthracene or pyrene), which possess affinity with the surface of the carbon nanotubes due to van der Waals interactions. Synthetic protocols based on Sonogashira–Hagihara couplings were developed to build up the OPE backbone.

Bifunctional iodophenyl acetylene derivative **33** served as a key building block in a coupling–deprotecting–coupling sequence. The NDI building block was synthesized by an aromatic nucleophilic substitution reaction of 2,6-dichloro-1,4,5,8-tetracarboxylic acid naphthalenediimide derivative **9** and the corresponding amine and sulfide (i.e., **11**, **12**), respectively. The convergent synthesis allows modular assembly of the NDI and OPE parts in a final Sonogashira–Hagihara coupling reaction. The target structures were fully characterized by NMR spectroscopy and mass spectrometry. Further, the optical properties of compounds **3–5** in solution, and on a graphene surface were qualitatively investigated. A Dexter-type energy transfer from the OPE unit to the NDI unit was observed. The studies of target structures **3–5** revealed that diamino-functionalized compound **3** is ideally suited for the envisaged single molecule electroluminescence experiments.

Introduction

The increasing feature size density of semiconductor electronics requires the continuous size reduction of the subunits comprising the electronic functions. The smallest functional building blocks providing the required diversity to address various electronic functions are single molecules. Their integration and investigation in electronic circuits became within the last decade its own research field entitled “molecular electronics”.^[1–7] Novel investigation techniques like, for example, mechanically controlled break-junctions,^[8–10] scanning-probe based junctions,^[11–13] or electrode pairs made by electromigration,^[14–17] enabled the in-

tegration of single molecules. Molecular features like, for example, symmetry,^[9] the anchor group position,^[18] the coupling between aromatic subunits,^[19–23] the arrangement of mechanically interlinked subunits,^[24] the oxidation state of redox active subunits,^[12,25–28] switching between two transport states,^[29–31] and many others, were observed in the recorded transport currents. However, after its integration in a circuit, the current at a given voltage or the current/voltage (*I/V*) characteristics usually remained the only information pointing at the molecules structure. As additional signals corroborating the molecules structure, inelastic tunneling spectroscopy^[32–35] and surface enhanced Raman spectroscopy^[36–38] were already applied in molecular junctions. A particularly appealing approach to identify the molecule under current would be its electroluminescence signal.^[39–40] However, the excited electrons of a suitably functionalized chromophore would be quenched by the large amount of free electrons of the metal electrode surface, and hence, metal electrodes are not well suited for single molecule electroluminescence experiments. A promising alternative could be metallic carbon nanotubes (CNTs) having excellent conductivity properties but a considerably reduced number of itinerant (delocalized) electrons.

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ejoc.201001415>.

Molecular junctions based on carbon nanotubes were suggested theoretically^[41–45] and already realized as cross-bar junctions^[46] and by covalently immobilizing terminal amine-functionalized molecular rods in oxidatively cleaved carbon nanotube junctions by amide formation.^[47]

We recently reported the formation of an electroluminescent molecular junction formed by immobilizing a suitably functionalized molecular rod by electrostatic trapping between two metallic CNTs.^[48] The pair of nanotube electrodes was formed by applying an electromigration protocol to a metallic single-walled CNT. Here we report the design, synthesis, and optical investigations in solution as well as in the solid state of several molecular rods comprising a central 2,6-core-substituted naphthalenediimide chromophore and terminal anchor groups to enable their integration in a CNT junction.

Core-substituted 1,4,5,8-naphthalenediimides (NDIs) are chromophores with tunable optical properties^[49–53] and have already been used for numerous purposes like, for example, as subunits of supramolecular zippers,^[54] cyclophanes,^[55] anion π -slides,^[56–57] as sensitizers in photovoltaic^[58] and photosynthetic^[59] systems, and as model compounds to study anion π -interactions.^[60]

Results and Discussion

Molecular Design

Several physical boundary conditions have to be considered in the design of a molecular rod for single-molecule electroluminescence experiments. The molecular rod must be long enough to bridge the gap between two electrodes. Both ends of the rod should be functionalized with molecular subunits enabling an immobilizing interaction with the electrode surface in order to stabilize the molecule within

the junction. To allow for electroluminescence, the rod should comprise a fluorescent chromophore on which electrons and holes might recombine radiatively. The backbone structure of the molecular rod should enable the translocation of electrons and holes in order to feed the chromophore with these elementary charges. Finally, there remains the most important chemical boundary conditions, the designed molecular rods have to be synthesizable in reasonable amounts and the chemistry leading to the envisaged structures has to be developed.

Our approach to the design of electroluminescent molecular rods is displayed in Figure 1. A central 2,6-core-substituted naphthalenediimide (NDI) was chosen as fluorophore. The absorption and emission spectra of *N,N'*-diphenyl-1,4,5,8-naphthalenediimides can be tuned by their core substituents in the 2- and 6-positions.^[49–51] While the heteroatoms at the 2- and 6-positions define the position of the longest wavelength absorption and, hence, also of the emission which is usually shifted by about 30–45 nm, the efficiency of the emission is controlled by the chemical nature of the substituents. From a chemical design viewpoint, these core substituents allow the chromophore to be adapted to the experimental requirements. Furthermore, X-ray structures of chromophores comprising the *N,N'*-diphenyl-1,4,5,8-naphthalenediimide motive display almost perpendicular arrangements between the π systems of the central NDI and the terminal phenyl rings,^[50] pointing at an electronic separation between these subunits. This electronic isolation of the NDI fluorophore between two terminal phenyl rings is a particularly appealing feature to enforce the radiative recombination of electrons and holes on the chromophore. In analogy to terminal thiol-functionalized NDI derivatives,^[50] the NDI-based longest wavelength absorption for target structures 1–3 was expected to be slightly above 600 nm due to the benzylamine substitu-

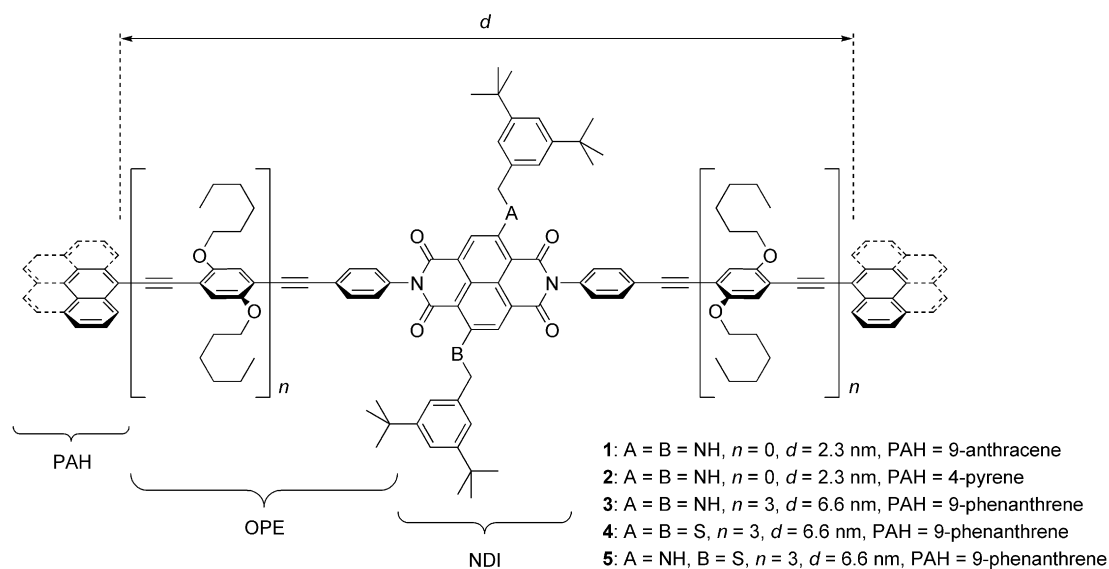


Figure 1. Molecular rod target structures 1–5 consisting of a central 2,6-core-substituted naphthalenediimide (NDI) fluorophore elongated by an oligo(phenylene ethynylene) (OPE) molecular wire comprising a terminal polyaromatic hydrocarbon (PAH) subunit as an anchor group for carbon electrodes.

ents. For benzylsulfanyl-substituted NDI **4**, the longest wavelength absorption was expected to be between 500 and 550 nm, while for asymmetrically substituted NDI **5** comprising one benzylamine and one benzylsulfanyl substituent, the absorption was expected to be in between the values of the former compounds. To reduce the interaction between the NDI π systems and the carbon-based electrode and to increase the processability of the target structures and their precursors, the benzylic core substituents of the NDIs comprise two bulky *tert*-butyl groups.

In order to integrate the NDI chromophore as separated fluorophores in a molecular wire structure, the *para* positions of both terminal phenyl rings had to be functionalized. An oligo(phenylene ethynylene) (OPE) structure as a rigid subunit with delocalized π electrons was chosen as molecular wires. In the case of elongated OPE subunits (**3–5**), the additional phenyl rings were functionalized with two hexyloxy substituents. These side chains were expected to increase the solubility and, hence, also the processability of the rigid rod derivatives without being too bulky to disfavor an interaction of the phenyl ring with the surface of a CNT electrode.

To further increase the affinity of both ends of the molecular rod for carbon-based electrodes, flat polyaromatic hydrocarbons (PAH) like naphthalene, anthracene, phenanthrene or pyrene were attached. The particular hope was that the van der Waals interactions between these PAHs and the surface of a CNT might be large enough to further stabilize a CNT/molecular rod/CNT junction.

The dimensions of the CNT gaps that can be bridged by these NDI rods were estimated by MM2 calculations. The distance (*d*) between the terminal PAH units was estimated to be about 2.3 nm for shorter rods **1** and **2** and about 6.6 nm for elongated rods **3–5**.

Synthetic Strategy

The synthetic strategy is displayed in Figure 2. Parallel assembly of the OPE molecular wire substructure comprising the terminal PAH anchor group and the suitably functionalized central NDI fluorophore was envisaged. The chemistry required to build up the OPE wire is based on Sonogashira coupling reactions,^[61] which are well known for their reliability and efficiency.^[62–63] This stepwise assembly of the OPE wire allowed the length of the molecular rod to be adapted to the dimensions of the junction. Target structures **1–4** are centrosymmetric. From a synthetic strategy point of view, molecular rod **5** is also pseudocentrosymmetric, as the two different core substituents are not expected to affect the linking chemistry between the fluorophore and the molecular wire. Thus, the symmetric assembly of both molecular wires subunits within the same reaction was considered for all five target structures **1–5**. To interlink the NDI chromophore with the OPE molecular wire unit either an ethynyl group or a leaving group allowing for a Sonogashira coupling was required in the *para* position of the terminal phenyl rings of the NDIs. As the

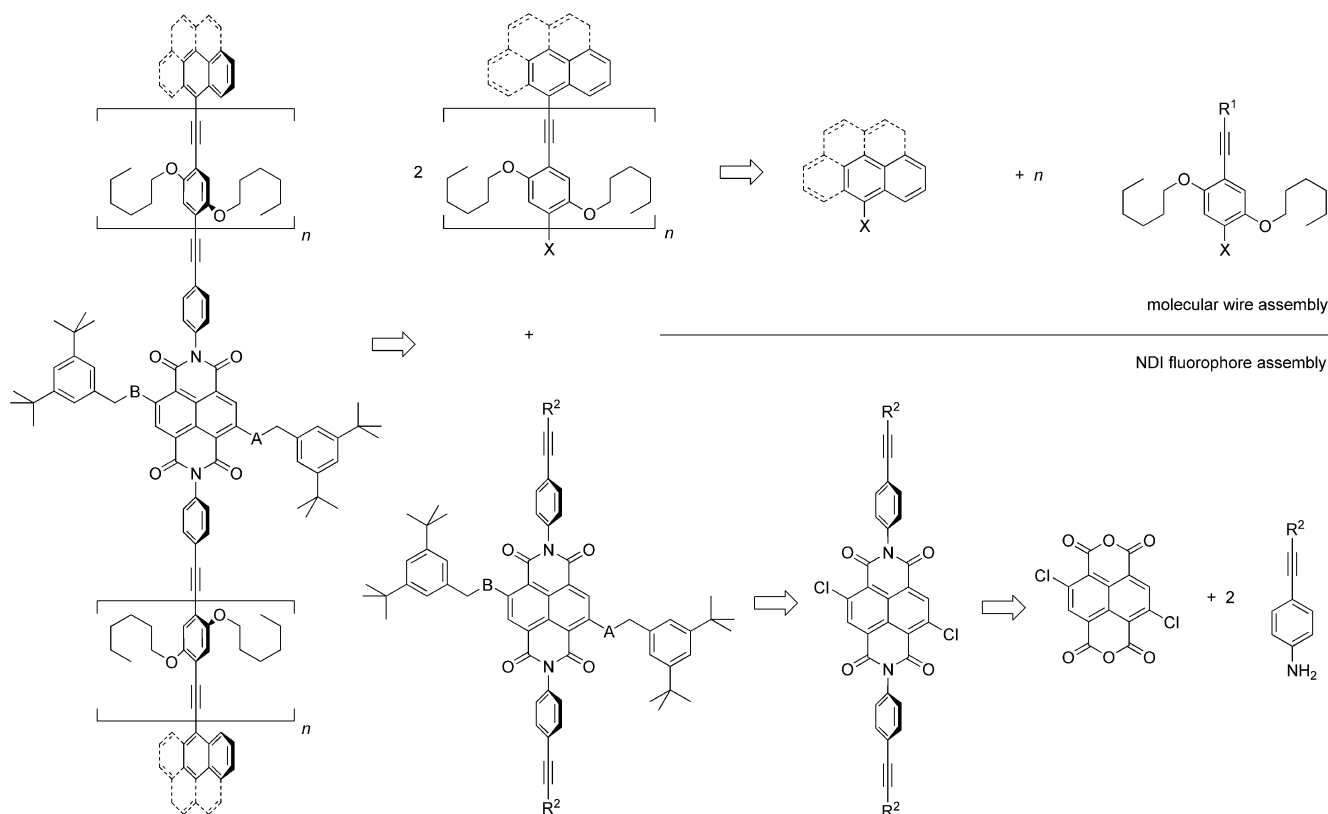


Figure 2. Synthetic strategy for the assembly of electroluminescent molecular rods **1–5**.

benzylhetero core substituents were introduced by a nucleophilic aromatic substitution (S_NAr) also requiring suitable leaving groups, the ethynyl option was favored as a functional group at the periphery of the NDI building block to avoid the competition between different positions functionalized with leaving groups at a later stage of the synthesis. Thus, a 4-ethynylaniline derivative was chosen in the condensation reaction with 2,6-dichloronaphthalene-1,4,5,8-tetracarboxylic acid bisanhydride to provide a correspondingly functionalized NDI building block.

NDI chromophores with different optical properties were intended by varying the core substituents at this stage. Finally, the coupling chemistry between the terminal ethynyl-functionalized NDI chromophore and the OPE molecular wire was envisaged in order to obtain target structures **1–5**.

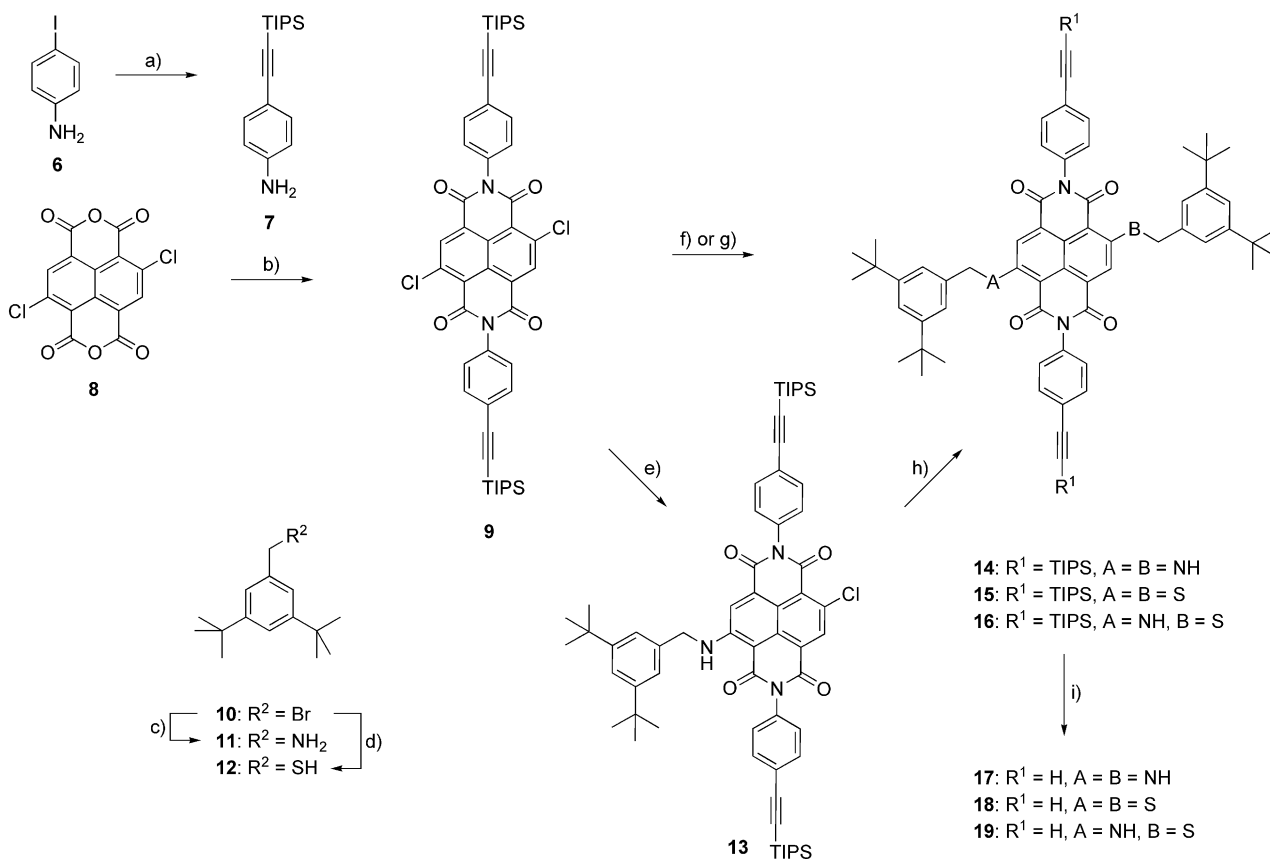
Synthesis

In Scheme 1, the synthesis of the three terminal ethynyl-functionalized NDI fluorophores **17–19** is displayed.

The synthesis of 4-[(triisopropylsilyl)ethynyl]benzenamine (**7**) was achieved in one step by a Sonogashira coupling reaction between commercially available 4-iodoaniline (**6**) and (triisopropylsilyl)acetylene.^[64] 2,6-Dichloronaphth-

alene-1,4,5,8-tetracarboxylic acid bisanhydride (**8**) was synthesized in four steps by following a literature procedure.^[65] NDI core structure **9** was obtained by treating dianhydride **8** with a sixfold excess of aniline **7** in acetic acid at 120 °C. Precipitating NDI derivative **9** was isolated by filtration and obtained as a pink solid in 63% yield after column chromatography (CC). Benzylic amine **11** was synthesized from the corresponding benzyl bromide **10** in a Gabriel synthesis.^[66,67] Treatment of benzyl bromide **10** with phthalimide and potassium carbonate (K_2CO_3) followed by hydrolysis with hydrazine monohydrate provided benzylamine **11** as a white solid almost quantitatively. The second substrate for the core substitution (3,5-di-*tert*-butyl)benzyl sulfide **12** was obtained as a yellow oil in 70% by treating benzyl bromide **10** with potassium thioacetate and subsequent hydrolysis.

Substitution of the chlorine atoms of **9** provided core-substituted NDI building blocks **14–16**. With benzylthiol **12** as nucleophile both chlorine atoms were readily substituted in dimethylformamide (DMF) at room temperature with K_2CO_3 as base, providing benzylsulfanyl-core-substituted NDI derivative **15** as a dark pink solid after aqueous workup and CC in 93% yield. The weaker nucleophilicity of benzylamine **11** required elevated temperature to substi-



Scheme 1. Synthesis of NDI fluorophore building blocks **17–19**. Reagents and conditions: (a) (triisopropylsilyl)acetylene, $\text{Pd(PPh}_3)_2\text{Cl}_2$, CuI , TEA, THF, room temp., 93%; (b) AcOH, **7**, 120 °C, 63%; (c) 1. phthalimide, K_2CO_3 , DMF, room temp., 2. $\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$, THF, room temp. \rightarrow 70 °C, 99%; (d) 1. KSAc, THF, room temp., 2. K_2CO_3 , MeOH, room temp., 72%; (e) **11**, K_2CO_3 , DMF, 40 °C, 54%; (f) **11**, DMI, 100 °C, 73% **14**; (g) **12**, K_2CO_3 , DMF, room temp., 93% **15**; (h) **12**, K_2CO_3 , DMF, room temp., 86% **16**; (i) TBAF, THF, room temp., 67% **17**, 74% **18**, 58% **19**.

tute the chlorine atoms. As DMF is known to react (decompose) at 100 °C in the presence of benzylamines, more robust 1,3-dimethyl-2-imidazolidinone (DMI) was chosen as solvent. Treatment of NDI-dichloride **9** with benzylamine **11** (4 equiv.) in DMI with K_2CO_3 as base at 100 °C for 16 h provided benzylamino-core-substituted NDI derivative **14** as a blue solid in 73% after CC. A stepwise synthesis was applied for the asymmetric NDI fluorophore **16**. Equimolar amounts of **9** and **11** were dissolved in DMF with K_2CO_3 as base, and the reaction mixture was heated to 40 °C for 8.5 h. After aqueous workup and purification by CC, monosubstituted compound **13** was isolated as a red solid in 54% yield. To introduce the sulfanyl substituent, mono-benzylamino-substituted derivative **13** was treated with benzylthiol **12** (2 equiv.) in DMF with K_2CO_3 at room temperature to provide asymmetrically substituted NDI derivative **16** as a violet solid in 86% after CC.

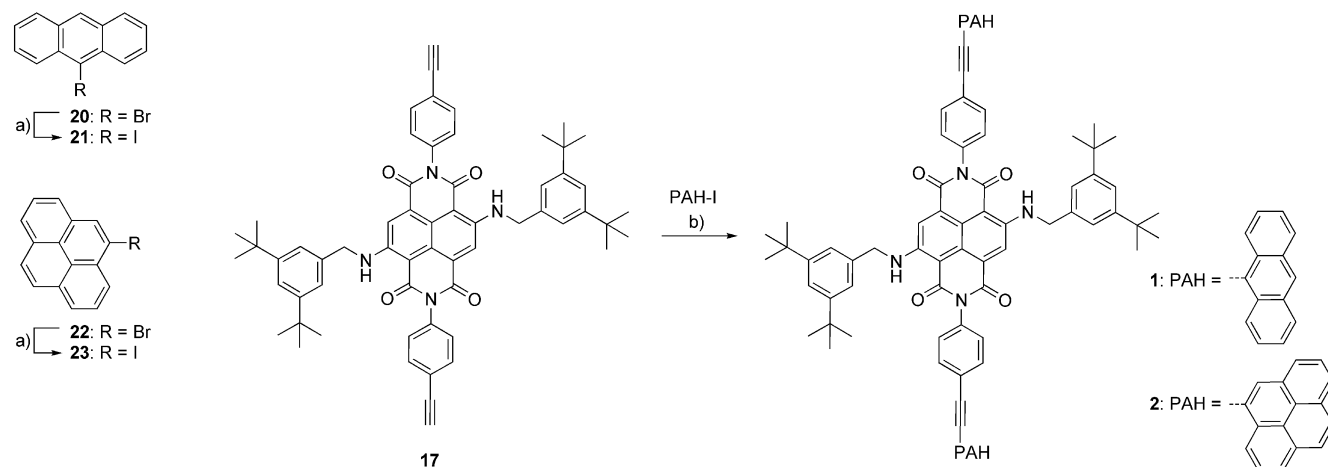
The TIPS protecting groups of the terminal acetylenes in compounds **14–16** were deprotected by using tetrabutylammonium fluoride (TBAF). Therefore, starting materials **14–16** were dissolved in THF and treated with a 1 M TBAF solution in THF containing 5% water. After aqueous workup and purification by CC, free acetylenes **17**, **18**, and **19** were obtained in 67, 74, and 58% yield, respectively (Scheme 1). These free acetylene derivatives displayed reduced stability features compared to their TIPS-protected precursors. Thus, these NDI building blocks were stored in their TIPS protected forms **14–16** and deprotected prior to their use.

To investigate the suitability of terminal ethynyl-functionalized NDI derivatives **17–19** for Sonogashira coupling reactions, short molecular rods **1** and **2** moved into the focus of interest (Scheme 2). Numerous attempts to couple diethynyl **17** with 9-bromoanthracene (**20**) failed. To facilitate the coupling the bromine was substituted with an iodine, which is known to be a superior leaving group in palladium-catalyzed coupling reactions.^[68] Thus, the corresponding bromoaryl derivatives **20** and **22** were treated with potassium iodide and copper iodide in DMI at 160 °C to

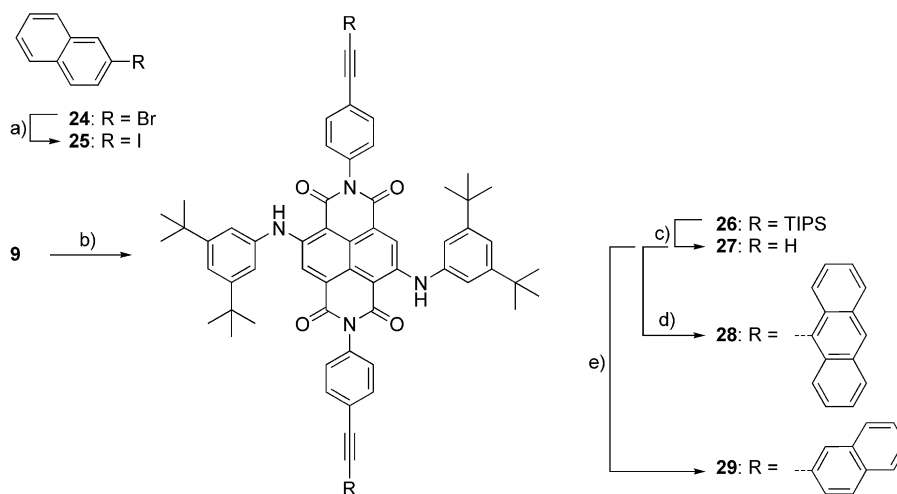
provide iodoaryl compounds **21** and **23** both in 79% yield.^[69] Using these iodoaryl derivatives, the Sonogashira coupling was successful even at room temperature. Treating diethynyl **17** with 9-iodoanthracene (**21**, 3.5 equiv.) in the presence of tetrakis(triphenylphosphane)palladium $[Pd(PPh_3)_4]$ and copper iodide (CuI) as catalysts and Huenigs base $[(iPr)_2NEt]$ in THF at 55 °C for 1 h provided the desired terminal anthracene-functionalized NDI rod **1** as a green-blue solid in a yield of 29% after CC. For the assembly of the pyrene-functionalized derivative **2**, only 2.5 equiv. of the 4-iodopyrene were used and the reaction mixture was stirred for 5 h at room temperature. During the reaction, a blue precipitate was formed, which was collected by filtration and recrystallized from toluene to afford terminal pyrene-functionalized molecular rod **2** as a dark blue solid in 82% yield.

The fluorescence efficiency of the 2,6-core-substituted NDI dyes depends on the chemical nature of the core substituents. While benzylhetero-substituted NDIs are strongly fluorescent, their phenylhetero-substituted analogues are not.^[50,70] Thus, the modular assembly strategy allowed also the assembly of molecular NDI rods **28** and **29** as nonfluorescent analogues with various terminal polyaromatic subunits as potential model compounds for electroluminescence experiments. The assembly of these rods is displayed in Scheme 3.

Again starting from terminal ethynyl-functionalized dichloro NDI **9** as key building block, the two aniline substituents were introduced in an aromatic nucleophilic substitution reaction. Thus, dichloro NDI **9** was treated with 3,5-di-*tert*-butyl aniline in DMF at 110 °C to provide phenylamino-core-substituted NDI derivative **26** as a blue solid in 54% yield after CC. Deprotection of the terminal acetylenes with TBAF in wet THF provided diethynyl NDI derivative **27** in 72% yield after purification by CC. Similar Sonogashira protocols as applied to benzylamino derivative **17** provided poorly fluorescent NDI rods **28** and **29**. Diethynyl **27** was treated with 9-iodoanthracene (4 equiv.) in the presence of $Pd(PPh_3)_4$, CuI, and $(iPr)_2NEt$ in THF at 55 °C



Scheme 2. Synthesis of molecular rods **1** and **2**. Reagents and conditions: (a) KI, CuI, DMI, 160 °C, 79% **21**, 79% **23**; (b) $Pd(PPh_3)_4$, CuI, $(iPr)_2NEt$, THF, **1**: 55 °C and 29%, **2**: room temp. and 82%.



Scheme 3. Synthesis of nonfluorescent NDI rods **28–29**. Reagents and conditions: (a) KI, CuI, DMI, 160 °C, 78%; (b) 3,5-di-*tert*-butylaniline, DMF, 110 °C, 54%; (c) TBAF, THF, room temp., 72%; (d) **21**, Pd(PPh₃)₄, CuI, (*i*Pr)₂NEt, THF, 55 °C, 33%; (e) **25**, Pd(PPh₃)₄, CuI, (*i*Pr)₂NEt, THF, room temp., 58%.

for 4 h to provide the terminal anthracene-functionalized NDI rod **28** as a blue solid in 33% yield after CC. For the assembly of naphthalene-functionalized NDI rod **29**, similar reaction conditions were applied with the difference that in this case the reaction mixture was allowed to stir for 1 h at room temp. Poorly fluorescent NDI rod **29** was isolated as a blue solid by CC in 58% yield.

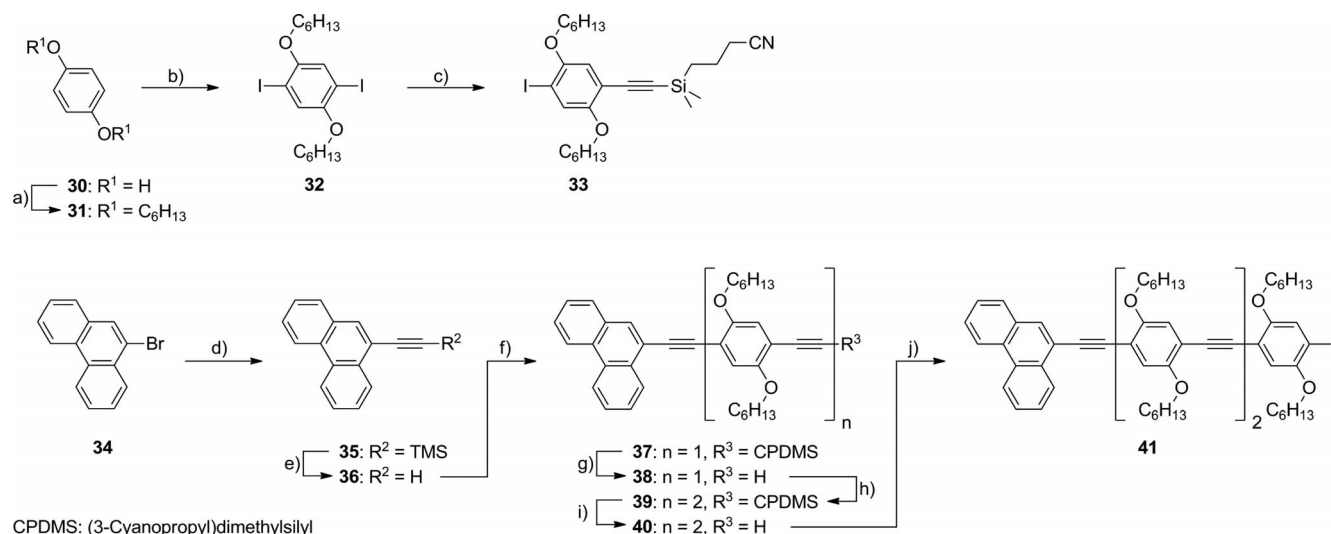
During the development of the synthesis of these about 3-nm long NDI rods comprising polyaromatic terminal groups to increase the interaction with CNT electrodes, the experimental physics team developed techniques to reduce the dimension of the CNT junctions. The key parameter responsible for the separation of both electrodes obtained by electromigration was the oxygen partial pressure. To minimize the oxygen partial pressure, the electromigration process was performed under ultra-high vacuum (UHV) conditions.^[48] Unfortunately, the smallest reliably obtained junctions displayed CNT electrode separations in the order of about 5 nm and were thus wider than the length of this first generation of fluorescent NDI rods **1** and **2**. While these rods were not able to serve the purpose of bridging a gap in a CNT junction, the coupling chemistry developed for NDI building blocks **14** and **26** should enable the straightforward assembly of longer OPE rods comprising a central, electronically decoupled NDI fluorophore.

As the modular rigid molecular wire, an OPE subunit with a polyaromatic hydrocarbon to interact with the surface of a CNT at one end and an aryl iodide for the coupling chemistry with the NDI building blocks at the other end was required. The assembly of suitably functionalized OPE rod **41** is displayed in Scheme 4.

The modular assembly of the OPE wire was based on bifunctional repeating unit **33** comprising an iodine and a masked acetylene. A suspension of hydroquinone **30** in acetonitrile (CH₃CN) containing 1-bromohexane and K₂CO₃ was heated at reflux for 1 d to provide 1,4-bis(hexyloxy)-benzene (**31**) as colorless crystals after recrystallization in 53% yield. Iodination of **31** by standard iodination condi-

tions with potassium iodate and iodine in a 10:1 mixture of concentrated acetic acid and concentrated sulfuric acid, followed by an aqueous workup and purification by recrystallization, provided diiodo derivative **32** as a colorless solid in 95% yield.^[71,72] To substitute one of the two iodine atoms of **32** with an acetylene, a statistical approach was chosen. To facilitate the separation of the statistical mixture, an acetylene with a polar group was required. Systems based on 2-hydroxyprop-2-yl-^[73] or (3-cyanopropyl)dimethylsilyl^[74] (CPDMS)-protected acetylenes were reported to be suitable for OPE syntheses. Thus, equimolar amounts of the CPDMS-acetylene and diiodo derivative **32** were dissolved in degassed piperidine. Dichlorobis(triphenylphosphane)palladium [PdCl₂(PPh₃)₂], triphenylphosphane (PPh₃), and CuI were added, and the reaction mixture was stirred at room temperature. After workup, the desired bifunctional building block **33** was isolated by CC in 32% yield as a beige solid.

The assembly of the molecular rod started from the phenanthrene system. Phenanthrene was chosen as a ready available PAH and subsequent integration experiments displayed its suitability as an anchor subunit. Alternative PAH groups were thus no longer considered in the design of elongated NDI rods. 9-Ethynylphenanthrene (**36**) was synthesized starting from commercially available 9-bromophenanthrene (**34**).^[75] In a Sonogashira reaction with TMS-acetylene and Pd(PPh₃)₄, CuI, and triethylamine [N(C₂H₅)₃], TMS-protected 9-ethynylphenanthrene (**35**) was obtained as a beige solid in 95% yield after CC. The acetylene was deprotected with K₂CO₃ in methanol (CH₃OH) to provide **36** as a beige solid in 92% yield. With bifunctional building block **33**, phenanthrene acetylene **36** was elongated stepwise by one phenylethynyl unit at a time by using a sequence of Sonogashira coupling conditions followed by the deprotection of the masked acetylene. Thus, **36** was treated with **33** in the presence of Pd(PPh₃)₄ and CuI in a 5:1 mixture of THF and diisopropylamine [(*i*Pr)₂NH] at 45 °C for about 20 h. After evaporation of the solvent, OPE



Scheme 4. Synthesis of the OPE molecular wire **41**. Reagents and conditions: (a) 6-bromohexane, K_2CO_3 , CH_3CN , 95 °C, 54%; (b) KIO_3 , I_2 , AcOH , H_2SO_4 , 115 °C, 95%; (c) HCC-CPDMS, $\text{PdCl}_2(\text{PPh}_3)_2$, PPh_3 , CuI , piperidine, room temp., 32%; (d) HCC-TMS, $\text{Pd}(\text{PPh}_3)_4$, CuI , NEt_3 , 95 °C, 95%; (e) K_2CO_3 , MeOH , room temp., 92%; (f) **33**, $\text{Pd}(\text{PPh}_3)_4$, CuI , $(i\text{Pr})_2\text{NH}$, THF, 45 °C, 91%; (g) K_2CO_3 , THF/ MeOH , room temp., 63%; (h) **33**, $\text{Pd}(\text{PPh}_3)_4$, CuI , $(i\text{Pr})_2\text{NH}$, THF, 45 °C, 91%; (i) K_2CO_3 , THF/ MeOH , room temp., 90%; (j) **32**, $\text{Pd}(\text{PPh}_3)_4$, CuI , $(i\text{Pr})_2\text{NH}$, THF, 60 °C, 80%.

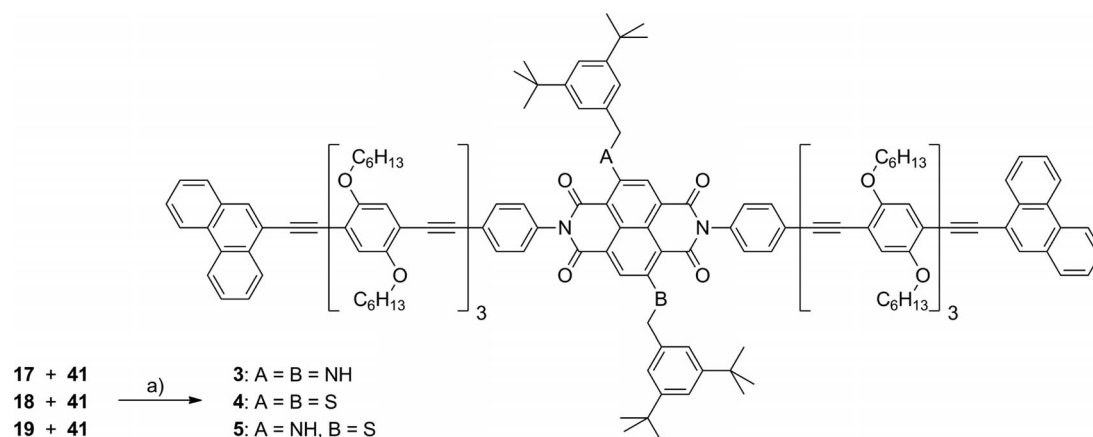
subunit **37** was obtained as a beige solid in 91% yield after CC. CPDMS-protected acetylene **37** was treated with K_2CO_3 (2 equiv.) in THF/ CH_3OH (1:1) to provide free acetylene **38** as a beige solid in 63% yield after CC. Another elongation step followed by applying similar Sonogashira conditions to provide CPDMS-protected acetylene **39** in 91% yield after CC, which was again deprotected as described for **37** to yield free acetylene **40** in 90% after CC.

In order to match the size of the CNT junction another phenyl unit was required, but coupling with the terminal acetylene-functionalized NDI fluorophores is only possible with a rod comprising a terminal iodine leaving group. Thus, the elongation of OPE wire **40** with 1,4-bis(hexyloxy)-2,5-diiodobenzene (**32**) was considered. In order to suppress the coupling at both iodine positions of this bifunctional building block, a tenfold excess of diiodo derivative **32** was used. Thus, **32** (10 equiv.) was added to a solution of acetyl-

ene **40** in THF/ $(i\text{Pr})_2\text{NH}$ (5:1) followed by $\text{Pd}(\text{PPh}_3)_4$ and CuI . After stirring for 3 h at 60 °C, aqueous workup, and CC, desired OPE molecular wire **41** was obtained as a yellow solid in 80% yield.

After the successful completion of both parallel synthetic pathways displayed in Figure 2 both advanced building blocks, namely, the terminal acetylene-functionalized NDI chromophores **17–19** and OPE molecular wire **41** comprising a phenanthrene subunit and an iodine leaving group at one end, respectively, were available and only their merging to target structures **3–5** remained (Scheme 5).

NDI diacetylene **17** and iodide **41** (2 equiv.) were dissolved in THF/ $(i\text{Pr})_2\text{NH}$ (25:2). After addition of catalytic amounts of $\text{Pd}(\text{PPh}_3)_4$ and CuI , the reaction mixture was stirred for 23 h at room temperature. Evaporation of the solvent and purification by CC provided desired target rod **3** as a green solid in 95% yield. Applying similar reaction



Scheme 5. Synthesis of molecular rods **3–5** comprising a central NDI chromophore. Reagents and conditions: (a) $\text{Pd}(\text{PPh}_3)_4$, CuI , $(i\text{Pr})_2\text{NH}$, THF, room temp., 95% **3**, 37% **4**, and 29% **5**.

conditions to diacetylenes **18** and **19** provided NDI rods **4** and **5** as reddish solids in 29 and 37% yield, respectively. The drastically reduced yields in both cases were due to the difficult isolation properties of both benzylsulfanyl-substituted rods **4** and **5**. Already during monitoring of the reaction by thin-layer chromatography (TLC), blurred spots were observed for the target structures resulting in very broad fractions during CC. As only pure fractions were considered, the isolated yields do not reflect the amount of target structures formed during the reaction.

These elongated molecular rods **3–5** and their precursors were fully characterized by ^1H and ^{13}C NMR spectroscopy and mass spectrometry. The NDI rod target structures were further investigated by UV/Vis and fluorescence spectroscopy. In the case of elongated NDI rods **3–5**, particular NMR pulse programs like HMBC, HMQC, TOCSMY, and COSY allowed the assignment of the peaks. The recorded spectra fully corroborated their structural identity. Elemental analysis of NDI rod target structures **3–5** were not performed due to the limited amounts available of these precious samples. Their purity was investigated by gel permeation chromatography (GPC) instead. Single crystals suitable for X-ray analysis were obtained for molecular rod subunit **41** by slow evaporation of the solvent from a chloroform solution further corroborating its structural identity.

The structural identification of the target NDI rods was mainly based on NMR spectra and mass spectrometry. As an example, the structural analysis of elongated molecular rod **3** will be discussed in the following. As displayed in Figure S1 (Supporting Information), the molecular signal of **3** in the matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) displayed an isotopic pattern matching the one expected for its elemental composition ($\text{C}_{208}\text{H}_{244}\text{N}_4\text{O}_{16}$).

A ^1H NMR spectrum of **3** was recorded at 600 MHz and is displayed in Figure 3. The structural assignment of the signals is based on additional HMBC, HMQC, TOCSMY, and COSY experiments (Figure 3).

Due to its symmetry, 94 different carbon signals were expected for **3** in its ^{13}C NMR spectrum. However, not all signals from the various alkyl chains displayed large enough differences to be resolved. Furthermore, the low intensity of the ethynyl carbon atoms as quaternary carbon atoms in conjugated systems was only detected with the help of heteronuclear multiple bond coherence (HMBC) experiments, profiting from a strong ^1H – ^{13}C coupling over three bonds. The technique was ideally suited to identify the ethynyl carbon atoms in NDI rod **3**, as each ethynyl carbon was attached to a phenyl ring with a hydrogen in the *ortho* position. Figure 4 displays the region of the HMBC spec-

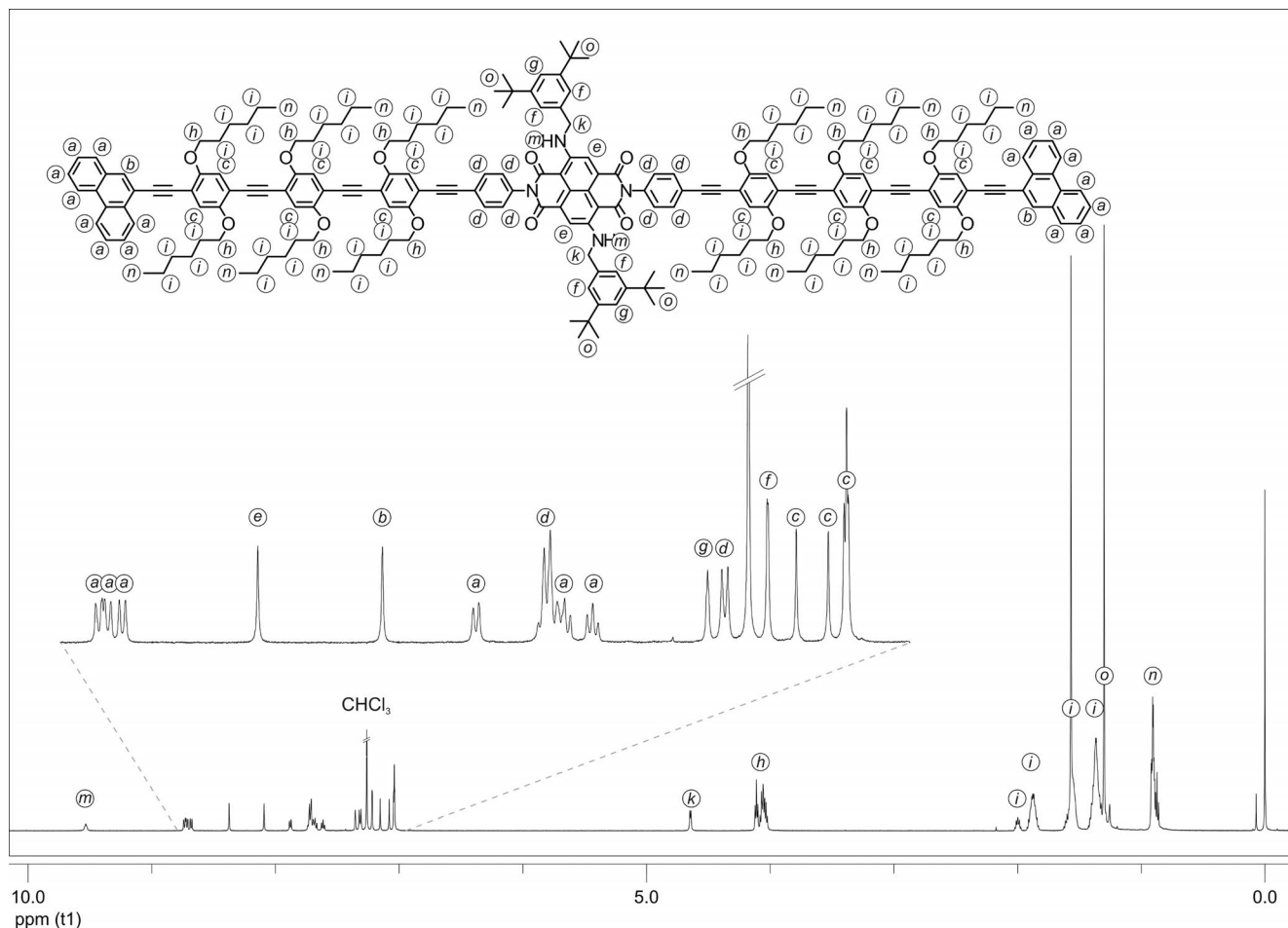


Figure 3. ^1H NMR spectrum of NDI rod **3** in CDCl_3 at room temperature.

trum of **3** in which the ethynyl carbon atoms appear. Clearly, six different ethynyl signals were identified, from which the one at $\delta = 91.3$ ppm was assigned to three ethynyl carbon atoms.

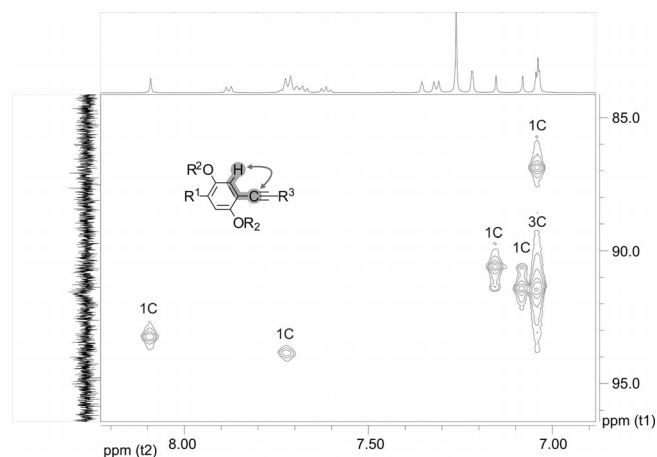


Figure 4. HMBC spectra of **3** to observe the ^{13}C – ^1H coupling over three bonds (displayed as inset). Six peaks are observed; in one of the peaks three carbon signals overlap.

This entire body of spectroscopic data corroborated the identity of NDI rod **3**. With similar spectroscopic experiments the identities of elongated NDI rods **4** and **5** were confirmed. However, considerably less effort was put in the spectroscopic characterization of shorter rods **1** and **2**. These rods were only synthesized in limited quantities and a synthesis at enlarged scale was abandoned when it became obvious that they are too short for the envisaged purpose. Thus, due to the limited amounts available, we were not able to record the ^{13}C NMR spectra for some of these shorter NDI derivatives.

Photophysical Investigations

The electronic absorptions of elongated NDI rods **3–5** were investigated by UV/Vis spectroscopy. Therefore, UV/Vis spectra were recorded in dichloromethane (CH_2Cl_2) at room temperature. In Figure 5, the comparison of the absorption spectrum of NDI rod **3** with those of NDI building block **14** and OPE rod **41** as its precursors shows that the UV/Vis spectrum of **3** is mainly the sum of its components. A longest wavelength absorption band at 609 nm with a shoulder at 563 nm was observed emerging from the central 2,6-benzylamino-core-substituted NDI chromophore. Furthermore, a more intense band at 415 nm was assigned to the OPE rod subunit. Compared to the absorption band of OPE precursor **41** at 407 nm, the corresponding OPE band of **3** is slightly redshifted as expected due to its additional ethynylphenyl subunit compared with the OPE system of **41**.

In Figure 6, the absorption spectra of all three long NDI rods **3–5** are displayed. All three have a comparable OPE absorption band at 415 nm, while the longest wavelength absorption band of the NDI subunit depends, as expected,

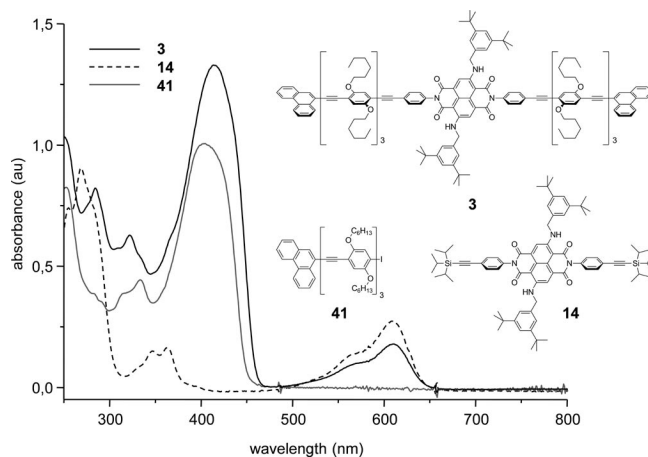


Figure 5. Absorption spectra of NDI rod **3** (black line) and its two precursors: NDI central subunit **14** (dashed line) and OPE molecular wire **41** (grey line). The UV/Vis spectra ($\approx 1 \times 10^{-5}$ M) were recorded in CH_2Cl_2 at room temperature.

strongly on their core substituents. While 2,6-bis(benzylamino)-core-substituted rod **3** displayed a longest wavelength absorption maximum at 609 nm, bis(benzylsulfanyl)-substituted NDI rod **4** had its longest wavelength absorption maximum at 530 nm. Mixed core-substituted NDI rod **5** comprising one benzylamino and one benzylsulfanyl substituent displayed its NDI absorption maximum in between the two at 567 nm.

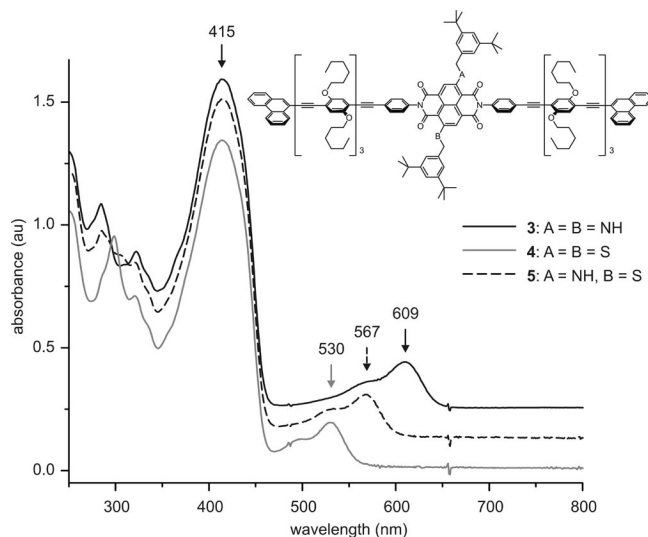


Figure 6. Absorption spectra of elongated NDI rods **3–5** recorded in CH_2Cl_2 ($\approx 1 \times 10^{-5}$ M) at room temperature. The spectra are offset vertically for clarity.

Of particular interest were the fluorescence properties of elongated NDI rods **3–5** and their precursors. Emission spectra of NDI rod **3** and its precursors **14** and **41** were recorded in CH_2Cl_2 at room temperature and are displayed in Figure 7. OPE molecular wire building block **41** displays an emission at 449 nm with a shoulder at 474 nm upon excitation at 415 nm (Figure 7, red line). Bisbenzylamino-core-substituted NDI subunit **14** has an emission at 638 nm

upon excitation at 609 nm (Figure 7, dashed blue line). Excitation of **14** at 415 nm did not result in any detectable emission (Figure 7, blue line). As expected, elongated NDI rod **3** combining both subunits displayed an intense emission at 637 nm upon excitation of the NDI subunit at 609 nm (Figure 7, dashed black line). Interestingly, excitation of the OPE subunit of **3** at 415 nm resulted in only a moderate emission from the OPE subunit at 457 nm and an intense emission at 637 nm (Figure 7, solid black line), pointing at an efficient energy transfer from the OPE subunit to the central NDI chromophore. As the absorption and emission spectra of **3** consisted exclusively of contributions of its subunits, the formation of both charge transfer complexes and excimers was excluded as origin of the shift of the emission over more than 200 nm upon excitation at 415 nm.

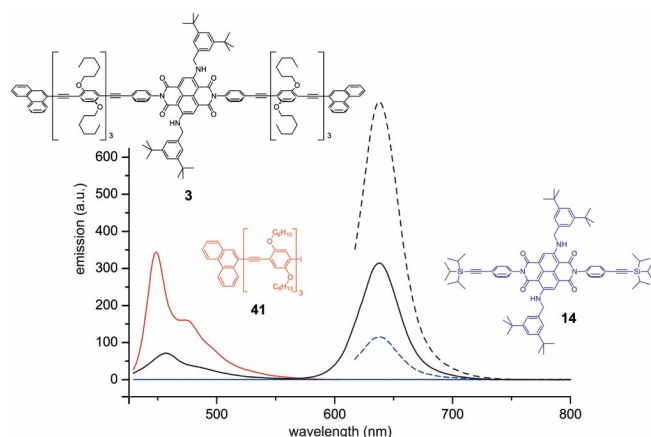


Figure 7. Emission spectra of elongated NDI rod **3** (6.5×10^{-7} M in CH_2Cl_2 , black) and its precursors: central NDI subunit **14** (2.2×10^{-6} M in CH_2Cl_2 , blue) and OPE wire **41** (1.2×10^{-6} M in CH_2Cl_2 , red) at room temperature. Solid lines upon excitation at 415 nm and dashed lines upon excitation at 609 nm.

The emission properties of elongated NDI rods **4** and **5** were also investigated dissolved in CH_2Cl_2 at room temperature. In contrast to NDI rod **3**, a considerably reduced energy transfer from the molecular wire to the central NDI subunit was observed for benzylsulfanyl- and benzylamino-core-substituted rod **5**. As displayed in Figure 8, the excitation of the OPE subunit (415 nm) provided an intense emission at about 458 nm arising from the excited OPE wire and a less intense signal from the NDI chromophore at 593 nm indicating the smaller extent of energy transfer to the central chromophore. As expected, direct excitation of the NDI chromophore at 567 nm resulted in an emission peak at 593 nm. However, even upon direct excitation the intensity of the emission peak of **5** is considerably smaller than that observed for **3**. These trends were even more pronounced for doubly benzylsulfanyl-core-substituted NDI rod **4**, which displayed a hardly observable NDI emission signal at 557 nm upon direct excitation at 530 nm. Excitation at 415 nm provided an emission peak at 451 nm with a more than 100-nm long tailing towards longer wavelength. The expected NDI emission at 557 nm is only observed as a minor shoulder in this tail.

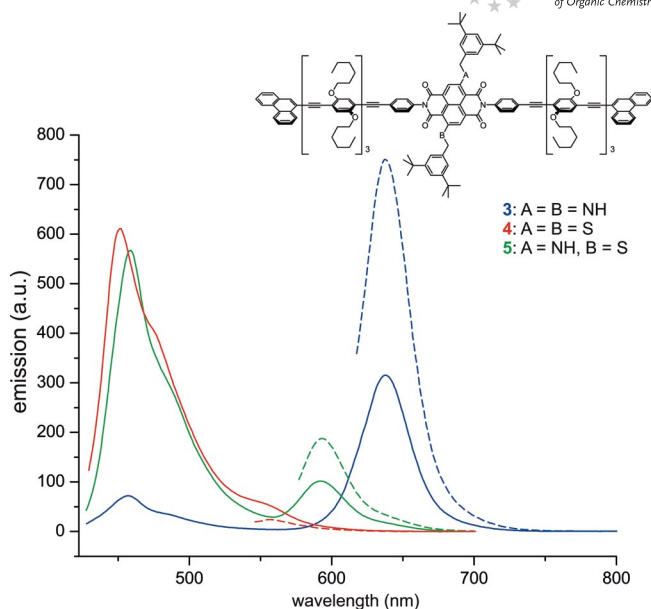


Figure 8. Emission spectra of elongated NDI rods **3–5** ($\approx 6.5 \times 10^{-7}$ M in CH_2Cl_2) at room temperature. Solid lines upon excitation at 415 nm and dashed lines upon excitation at 609 nm for **3** (blue lines), at 530 nm for **4** (red lines), and at 567 nm for **5** (green lines).

Quantum yields of the fluorescence were determined in CHCl_3 by the “optical dilution method”^[76] by using *N,N'*-bis(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxyperylene-3,4,9,10-tetracarboxylic acid bisimide excited at 575 nm as reference ($\Phi_f = 0.96$, CHCl_3).^[77,78] The given quantum yields were averaged from values obtained at five different concentrations all with absorbances below 0.1 at the excitation wavelengths. Long NDI rods **3**, **4**, and **5** were excited at 609, 530 and 567 nm, respectively. While a quantum yield of $\Phi_f = 0.31$ was measured for **3**, the quantum yield of **5** was with $\Phi_f = 0.02$ more than one order of magnitude smaller. Within the concentration range required for the “optical dilution method”, the emission peak of **4** could not be distinguished from the noise of the spectrum. These measured quantum yields confirmed the decrease in fluorescence intensity from **3** over **5** to **4**, which was already observed by the naked eye. While **3** was an intensely shining compound under the UV lamp, the emission of **5** was much less intense, while the one of **4** could hardly be detected. The loss of fluorescence intensity by substituting benzylamino-core substituents with benzylsulfanyl substituents reflects the increased efficiency of the latter in quenching of the NDI excited state due to its larger number of electrons. This loss of fluorescence intensity with core substituents of increasing atomic weight has already been observed for NDI chromophores.^[50]

To investigate the emission properties of elongated NDI rods **3–5** in more detail, excitation versus emission plots were recorded. Mesitylene was chosen as a less volatile solvent for these studies. In Figure 9, the recorded plots of all three NDI rods **3–5** are displayed. Over the entire absorption range of the OPE subunit from 350–450 nm, an ef-

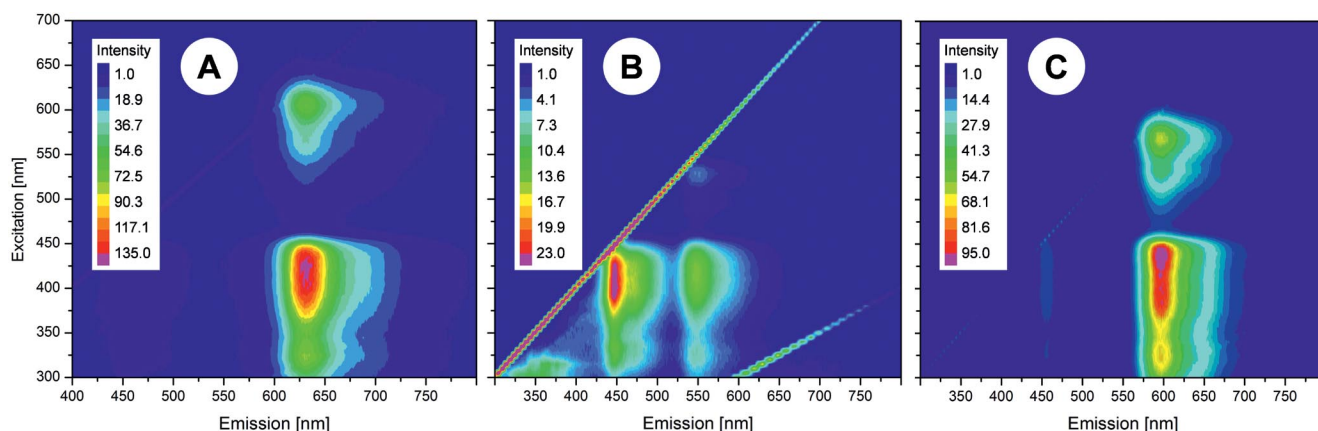


Figure 9. Excitation vs. emission plots of long NDI rods **3** (A), **4** (B), and **5** (C) recorded as 1.7×10^{-6} M solutions in mesitylene. For visibility, the color code of the emission was adjusted to the emission intensity of the samples.

ficient energy transfer to the central NDI chromophore was observed for **3** (A) in Figure 9, while mainly the emission from the OPE subunit at about 450 nm and a much weaker NDI emission at about 550 nm, even under direct excitation, was recorded for **4** (B) in Figure 9. The energy transfer from the OPE subunit to the NDI chromophore in sulfanyl- and amino-core-substituted rod **5** (C) in Figure 9 was increased compared to **4**, but considerably less efficient than the one observed for doubly amino-substituted rod **3**.

While these preliminary optical investigations of the dissolved NDI rods were very promising, the question raised if they were able to maintain their optical feature upon immobilization onto a solid substrate. The elongated NDI rods were designed for CNT junctions and thus homolytically cleaved graphite substrates (HOPG) were chosen as a solid surface with chemical properties comparable to a

CNT. NDI rod **3** was drop casted as a $\approx 1.7 \times 10^{-6}$ M solution in mesitylene on a HOPG substrate. After evaporation of the solvent, the sample was transferred into a high-vacuum optical cryostat comprising the optical set up displayed in Figure 10A and described by Krupke and co-workers.^[79] Upon excitation at 532 nm, a well-resolved emission at 677 nm was observed. Cooling the cryostat with liquid helium enabled the emission of the substrate to be recorded at various temperatures (Figure 10B). At temperatures below 200–150 K, the broad emission peak at 670 nm became better resolved, displaying a pronounced shoulder towards longer wavelengths. The resolved emission peaks resemble strongly the mirror image of the absorption peaks arising from the doubly benzylamino-core-substituted NDI of **3** recorded in CH_2Cl_2 , where the peak at 609 nm has a shoulder towards shorter wavelengths (Figure 6, solid black

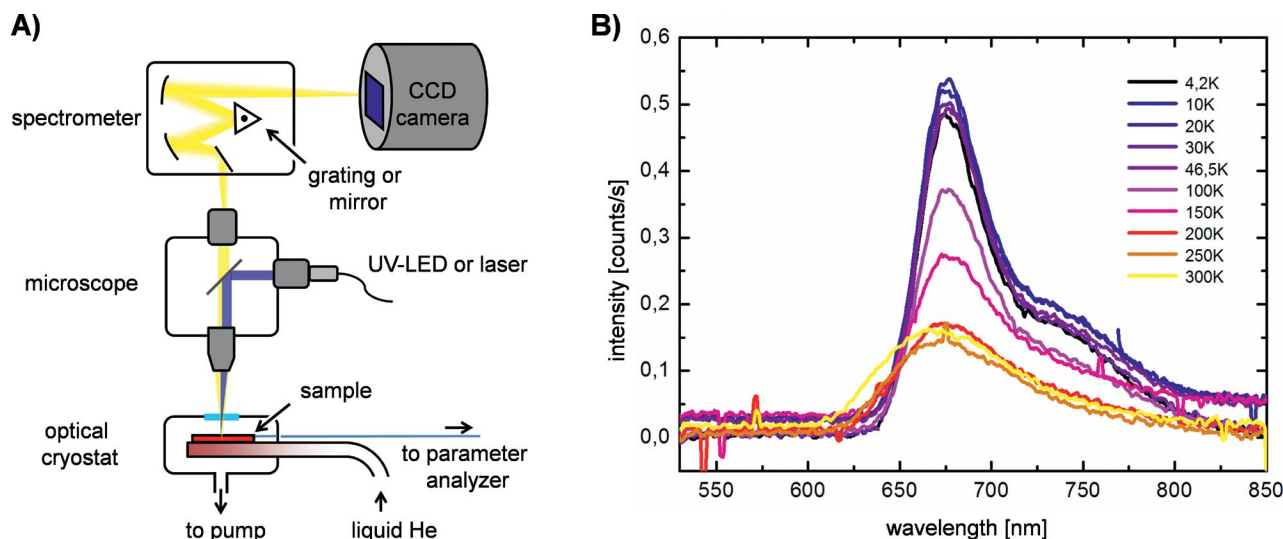


Figure 10. (A) Sketch of the optical set-up in the UHV chamber. (B) Emission recorded of the layer of NDI rods **3** deposited on a HOPG substrate in UHV upon excitation at 532 nm at various temperatures.

line). Obviously, upon deposition on HOPG, the emission from the doubly benzylamino-substituted NDI core is not quenched, but its maximum is shifted towards lower energy by about 32 nm compared to the one observed in CH_2Cl_2 and mesitylene solutions.

Similar solid-state emission experiments were also made with elongated NDI rods **4** and **5**. While an emission from doubly benzylsulfanyl-core-substituted NDI rod **4** could not be detected, benzylsulfanyl- and benzylamino-substituted derivative **5** displayed an emission at 623 nm (Figure 11). With 28 nm, the shift of the drop-casted film of **5** on HOPG in relation with the sample dissolved in CH_2Cl_2 is comparable to the value observed earlier for **3** (32 nm). The failure in recording emission signals from the drop-casted film of **4** was attributed to the poor emitting properties of the central NDI chromophore, which was already observed in solution.

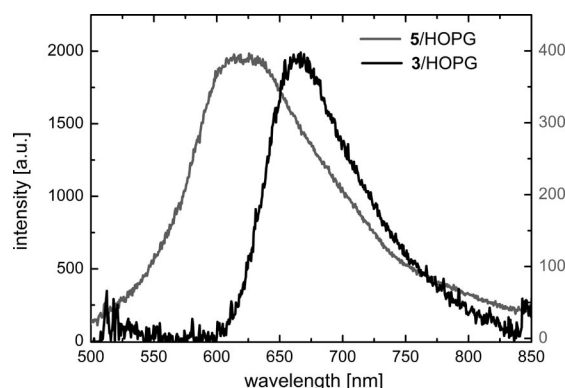


Figure 11. Emission from a drop-casted film of **3** (black line) and **5** (gray line) on HOPG (excited at 532 nm) recorded at room temperature under high vacuum. For visibility the intensity scale was adjusted to the maximum signal of both.

On the basis of our qualitative optical investigations we hypothesized a Dexter-type energy transfer mechanism between the OPE molecular wire as donor subunit and the central NDI fluorophores within rods **3–5**. Förster resonance energy transfer (FRET) was excluded for the following arguments. Due to the structural similarity, all three rods **3–5** have identical OPE donors and comparable donor–acceptor distances (r). Hence, the FRET efficiency is given by Equation (1):^[80]

$$E = \frac{R_0^6}{R_0^6 + r^6} \quad (1)$$

in which the Förster radius (R_0) is a convenient value for the spectral overlap between the donor emission and the acceptor absorption. According to Equation (1), an increased efficiency of the energy transfer would be expected with increasing spectral overlap between the donor and the acceptor. However, exactly the opposed trend was observed in the experiment with the most efficient energy transfer for NDI rod **3** having the poorest spectral overlap between the OPE emission and the absorption of its central NDI fluorophore.

The observation of efficient energy transfer from the OPE part to the NDI core combined with a strong emission signal makes compound **3** a very appealing candidate for single-molecule electroluminescence studies in a carbon nanotube junction.

Conclusions

Several NDI rods as model compounds for single-molecule electroluminescence experiments were designed and synthesized. Using a CNT junction as electrode pairs, molecular rods longer than 5 nm and having terminal PAH units as anchor groups for CNTs were required. The coupling chemistry required to assemble molecular rods consisting of OPE-type molecular wires, an electronically decoupled central 2,6-core-substituted NDI chromophore, and terminal PAH anchor groups was investigated. To develop appropriate reaction conditions, short NDI rods **1** and **2** were synthesized first. Subsequently, by the repetitive introduction of an OPE repeat unit, NDI rods **3–5** with dimensions exceeding 5 nm in length were synthesized. Systematic variation of both NDI core substituents in the series **3–5** allowed not only the tuning of their optical properties for the physical experiment, but also the elucidation of the energy transfer mechanism between the OPE donor and the central NDI acceptor. Qualitative fluorescence studies support a Dexter-type energy transfer mechanism within these elongated NDI rods. In order to investigate the suitability of these NDI rods for CNT junctions, emission spectra of drop-casted films on HOPG were measured in the UHV at various temperatures. Interestingly, shifts of about 30 nm towards longer wavelength were observed for these films compared to dichloromethane solutions.

Currently, we are not only optimizing optical features and the electronic coupling of NDI rods, but we are also synthesizing architectures comprising several NDIs like, for example, cyclophanes, in order to decouple one chromophore from the electrode surface.^[55,81,82]

While exclusively the design, synthesis, and qualitative optical investigations are discussed in this paper, the immobilization of these NDI rods in CNT junctions and the subsequent electroluminescence experiments are reported elsewhere.^[48]

Experimental Section

Reagents and Solvents: All chemicals were directly used for the synthesis without further purification unless otherwise noted. Solvents for chromatography and crystallization were distilled once before use; the solvents for extraction were used in technical grade. Dry THF and dry dichloromethane (DCM) were dispensed from a Pure Solv MD Solvent Purification System. Dry toluene was distilled from Na/benzophenone. Dry DMF and DMI were purchased over molecular sieves from Fluka.

Synthesis: All reactions with reagents that are easily oxidized or hydrolyzed were performed under an argon atmosphere by using Schlenk techniques; only dry solvents were used and the glassware was heated out.

Analytics and Instruments: ^1H NMR: Bruker DRX-600 NMR (600 MHz), Bruker DPX NMR (400 MHz), Bruker BZH NMR (250 MHz), and Bruker Ultra Shield (300 MHz) instruments were used to record the spectra. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent peaks or trimethylsilane (TMS). NMR solvents were obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). The measurements were done at room temperature. Multiplicities are written as: s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintet, m = multiplet, and br. = broad. ^{13}C NMR: Bruker DPX NMR (101 MHz), Bruker DRX-600 NMR (151 MHz), and Bruker Ultra Shield (75 MHz) instruments were used to record the spectra. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent peaks. The measurements were done at room temperature. Mass spectrometry (MS): Mass spectra were recorded with a Bruker Esquire 3000 Olus for electrospray ionization (ESI), a Finnigan MAT 95Q for electron ionization (EI), a Finnigan MAT 8400 for fast atom bombardment (FAB), or a Voyager-DeTM Pro for MALDI-TOF. Elementary Analysis (EA): Elementary analyses were measured with a Perkin-Elmer Analysator 240. Ultraviolet Spectroscopy (UV): UV/Vis spectroscopy was measured in CH_2Cl_2 with an Agilent 8453. Fluorescence Spectroscopy: Emission spectra were recorded with a Shimadzu RF-5301 PC spectrofluorophotometer under normal conditions. Gel Permeation Chromatography (GPC): Shimadzu LC-8A was used to record the chromatogram. The measurements were done at room temperature with an Oligo-Pore 300×7.5 mm column (particle size 6 μm) from Polymer Laboratories, eluting with toluene, with a flow rate of 0.5 mL/min at $\lambda = 220$ nm. Column Chromatography (CC): For CC silica gel 60 (40–63 μm) from Merck or silica gel 60 (40–63 μm) from Fluka was used. Thin-Layer Chromatography (TLC): Silica gel 60 F₂₅₄ glass plates with a thickness of 0.25 mm from Merck were used. Detection was observed with a UV lamp at 254 or 366 nm.

***N,N'*-Bis{4-[2-(triisopropylsilyl)ethynylphenyl]}-2,6-dichloro-1,4,5,8-tetracarboxylic Acid Naphthalenediimide (9):** 2,6-Dichloronaphthalene-1,4,5,8-tetracarboxylic acid bisanhydride (**8**) (3.00 g, 8.90 mmol, 1.0 equiv.) was suspended in glacial acetic acid (140 mL) and heated at reflux. To this mixture was added **7** (14.6 g, 53.4 mmol, 6.0 equiv.), and the reaction mixture was kept at reflux for another 30 min. After the addition of the amine, everything was dissolved and after some minutes a pink solid precipitated. The precipitate was filtered, washed with methanol, and purified by CC (silica gel, $\text{CH}_2\text{Cl}_2/\text{hexane} = 2:1$) to afford the desired product as a yellowish solid (4.73 g, 5.58 mmol, 63%). M.p. >410 °C. ^1H NMR (400 MHz, CDCl_3 , 25 °C): $\delta = 8.86$ (s, 2 H), 7.68 (d, $^3J_{\text{H,H}} = 8.1$ Hz, 4 H), 7.27 (d, $^3J_{\text{H,H}} = 8.1$ Hz, 4 H), 1.16 (s, 36 H), 1.09 (s, 6 H) ppm. ^{13}C NMR (101 MHz, CDCl_3 , 25 °C): $\delta = 161.0$, 160.6, 141.0, 136.6, 134.2, 134.0, 128.5, 127.7, 126.5, 125.2, 122.8, 106.1, 92.8, 18.8, 11.4 ppm. MS (MALDI-TOF): calcd. for $\text{C}_{48}\text{H}_{52}\text{Cl}_2\text{N}_2\text{O}_4\text{Si}_2$ 846.2837; found 848.6842.

***N,N'*-Bis{4-[2-(triisopropylsilyl)ethynylphenyl]}-2-chloro-6-(3,5-di-*tert*-butylbenzylamine)-1,4,5,8-tetracarboxylic Acid Naphthalenediimide (13):** A flask containing **9** (51.4 mg, 0.061 mmol, 1.0 equiv.), **11** (27.2 mg, 0.124 mmol, 2.0 equiv.), K_2CO_3 (16.3 mg, 0.118 mmol, 1.9 equiv.), and dry DMF (2 mL) was heated at 40 °C for 8.5 h. The reaction mixture was then cooled to room temperature and evaporated, giving a solid that was purified by CC (silica gel, 3.5×14 cm, hexane/ $\text{CH}_2\text{Cl}_2 = 1:2$) to afford **13** as a red solid (34 mg, 0.033 mmol, 54%). $R_f = 0.27$ ($\text{CH}_2\text{Cl}_2/\text{hexane} = 2:1$). ^1H NMR (400 MHz, CDCl_3 , 25 °C): $\delta = 10.14$ (t, $^3J_{\text{H,H}} = 5.3$ Hz, 1 H), 8.67 (s, 1 H), 8.46 (s, 1 H), 7.66 (d, $^3J_{\text{H,H}} = 8.5$ Hz, 4 H), 7.37 (t, $^4J_{\text{H,H}} = 1.6$ Hz, 1 H), 7.27 (d, $^3J_{\text{H,H}} = 8.5$ Hz, 4 H), 7.20 (d, $^4J_{\text{H,H}} = 1.6$ Hz, 2 H), 4.68 (d, $^3J_{\text{H,H}} = 5.3$ Hz, 2 H), 1.29 (m, 18

H), 1.16 (br. s, 21 H), 1.14 (br. s, 21 H) ppm. ^{13}C NMR (101 MHz, CDCl_3 , 25 °C): $\delta = 165.9$, 161.8, 161.8, 161.1, 151.7, 135.3, 134.9, 134.4, 134.4, 133.8, 133.2, 133.2, 128.6, 128.5, 127.7, 124.7, 124.7, 124.1, 122.5, 122.4, 122.3, 121.6, 121.4, 106.2, 100.3, 92.2, 48.4, 34.9, 31.4, 29.7, 18.7, 18.7, 11.3, 11.3 ppm. MS (MALDI-TOF): calcd. for $\text{C}_{63}\text{H}_{76}\text{ClN}_3\text{O}_4\text{Si}_2$ 1029.51; found 1030.22.

***N,N'*-Bis{4-[2-(triisopropylsilyl)ethynylphenyl]}-2,6-bis(3,5-di-*tert*-butylbenzylamine)-1,4,5,8-tetracarboxylic Acid Naphthalenediimide (14):** Derivative **9** (2.07 g, 2.44 mmol, 1.0 equiv.) and 3,5-di-*tert*-butylbenzylamine (**11**; 2.14 g, 9.77 mmol, 4.0 equiv.) were dissolved in dry DMI (10 mL). The reaction mixture was heated at 100 °C for 16 h. After cooling to room temperature, it was extracted with toluene/water. The organic phase was dried with MgSO_4 , evaporated, and purified by CC ($\text{CH}_2\text{Cl}_2/\text{hexane} = 2:1$) to give **14** as a blue solid (2.18 g, 1.78 mmol, 73%). M.p. 382–384 °C. ^1H NMR (400 MHz, CDCl_3 , 25 °C): $\delta = 9.45$ (t, $^3J_{\text{H,H}} = 5.1$ Hz, 2 H, NH), 8.26 (s, 2 H), 7.66 (d, $^3J_{\text{H,H}} = 8.7$ Hz, 4 H), 7.30–7.37 (m, 6 H), 7.21 (d, $^4J_{\text{H,H}} = 1.8$ Hz, 4 H), 4.57 (d, $^3J_{\text{H,H}} = 5.1$ Hz, 4 H), 1.29 (s, 36 H), 1.17 (s, 42 H) ppm. ^{13}C NMR (101 MHz, CDCl_3 , 25 °C): $\delta = 166.2$, 162.8, 151.5, 149.2, 135.9, 135.1, 133.3, 128.8, 126.1, 124.5, 122.6, 122.3, 121.6, 119.0, 106.5, 102.0, 92.0, 48.5, 34.9, 31.5, 18.8, 11.4 ppm. MS (MALDI-TOF): calcd. for $\text{C}_{78}\text{H}_{100}\text{N}_4\text{O}_4\text{Si}_2$ 1212.7278; found 1213.0802. UV/Vis: λ_{max} (ϵ , $10^3 \text{ M}^{-1} \text{ cm}^{-1}$) = 566 (11.5), 609 (22.9) nm.

***N,N'*-Bis{4-[2-(triisopropylsilyl)ethynylphenyl]}-2,6-bis(3,5-di-*tert*-butylbenzylsulfanyl)-1,4,5,8-tetracarboxylic Acid Naphthalenediimide (15):** Compound **9** (50 mg, 0.06 mmol, 1.0 equiv.), **12** (56 mg, 0.24 mmol, 4.0 equiv.), and K_2CO_3 (25 mg, 0.18 mmol, 3.0 equiv.) were dissolved in dry and degassed DMF (3 mL). The reaction mixture was stirred at room temperature overnight. The reaction mixture was then evaporated to dryness, giving a dark red residue that was dissolved in CH_2Cl_2 (20 mL) and washed with water (4 mL). The aqueous phase was extracted with CH_2Cl_2 ($3 \times$), and the combined organic layers were evaporated to dryness, giving a violet solid that was purified by CC (silica gel, $\text{CH}_2\text{Cl}_2/\text{hexane} = 1:3$) to afford **15** as a violet solid (68.4 mg, 0.22 mmol, 93%). $R_f = 0.49$ ($\text{CH}_2\text{Cl}_2/\text{hexane} = 2:1$). ^1H NMR (400 MHz, CDCl_3 , 25 °C): $\delta = 8.86$ (s, 2 H), 7.63 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 4 H), 7.31 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 4 H), 7.31 (t, $^4J_{\text{H,H}} = 1.8$ Hz, 2 H), 7.27 (d, $^4J_{\text{H,H}} = 1.8$ Hz, 4 H), 4.43 (s, 4 H), 1.25 (s, 36 H), 1.14 (s, 42 H) ppm. ^{13}C NMR (101 MHz, CDCl_3 , 25 °C): $\delta = 163.1$, 162.0, 151.3, 149.7, 134.2, 133.1, 128.6, 125.0, 124.5, 124.2, 123.8, 123.6, 122.1, 118.5, 106.3, 92.0, 38.2, 34.8, 31.4, 29.7, 18.7, 11.3 ppm. MS (MALDI-TOF): calcd. for $\text{C}_{78}\text{H}_{98}\text{N}_2\text{O}_4\text{S}_2\text{Si}_2$ 1246.65; found 1246.77

***N,N'*-Bis{4-[2-(triisopropylsilyl)ethynylphenyl]}-2-(3,5-di-*tert*-butylbenzylsulfanyl)-6-(3,5-di-*tert*-butylbenzylamine)-1,4,5,8-tetracarboxylic Acid Naphthalenediimide (16):** A flask charged with **13** (32 mg, 0.031 mmol, 1.0 equiv.), **12** (15 mg, 0.062 mmol, 2.0 equiv.), and K_2CO_3 (9 mg, 0.062 mmol, 2.0 equiv.) in dry DMF (2 mL) was stirred at room temperature overnight. The violet reaction mixture was evaporated to dryness, affording a violet solid that was purified by CC (silica gel, 3.5×16 cm, $\text{CH}_2\text{Cl}_2/\text{hexane} = 2:1$) to afford **16** as a violet solid (33 mg, 0.027 mmol, 86%). $R_f = 0.25$ ($\text{CH}_2\text{Cl}_2/\text{hexane} = 2:1$). ^1H NMR (400 MHz, CDCl_3 , 25 °C): $\delta = 9.90$ (t, $^3J_{\text{H,H}} = 5.3$ Hz, 1 H), 8.79 (s, 1 H), 8.38 (s, 1 H), 7.66 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 4 H), 7.62 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 4 H), 7.35 (s, 1 H), 7.31 (s, 1 H), 7.28–7.26 (m, 4 H), 4.65 (d, $^3J_{\text{H,H}} = 5.3$ Hz, 2 H), 4.36 (s, 2 H), 1.28 (s, 18 H), 1.27 (s, 18 H), 1.15 (s, 42 H) ppm. ^{13}C NMR (101 MHz, CDCl_3 , 25 °C): $\delta = 166.4$, 163.9, 163.1, 162.6, 152.0, 151.6, 151.3, 145.0, 135.6, 135.2, 134.8, 134.0, 133.6, 133.5, 129.0, 127.5, 126.9, 124.9, 124.6, 124.2, 123.6, 122.8, 122.3, 122.3, 121.8, 120.7, 119.9, 110.0, 101.0, 92.4, 48.8, 35.3, 35.2, 31.8, 31.8,

31.7, 19.1, 11.7, 0.4 ppm. MS (MALDI-TOF): calcd. for $C_{78}H_{99}N_3O_4SSi_2$ 1229.69; found 1229.93.

***N,N'*-Bis(4-ethynylphenyl)-2,6-bis(3,5-di-*tert*-butylbenzylamine)-1,4,5,8-tetracarboxylic Acid Naphthalenediimide (17):** TIPS-protected **14** (91 mg, 0.075 mmol, 1.0 equiv.) was dissolved in THF (20 mL). Then, TBAF (1 M in THF, 20 μ L, 0.02 mmol, 0.27 equiv.) was added, and the mixture was stirred at room temperature. More TBAF (1 M in THF) was added after 30 min (15 μ L, 0.015 mmol, 0.2 equiv.) and after 1 h (40 μ L, 0.04 mmol, 0.5 equiv.). The reaction mixture was stirred for 2 h and then filtered over a silica plug, evaporated, and purified by CC (silica gel, 1 \times 12 cm, CH_2Cl_2) to give **17** as a dark blue-red fluorescent solid (45 mg, 0.050 mmol, 67%). R_f = 0.55 (CH_2Cl_2). M.p. $\geq 350^\circ C$. 1H NMR (400 MHz, $CDCl_3$, $25^\circ C$): δ = 9.48 (m, 2 H), 8.34 (s, 2 H), 7.67 (d, $^3J_{H,H}$ = 8.5 Hz, 4 H), 7.34 (t, $^4J_{H,H}$ = 1.7 Hz, 2 H), 7.28 (d, $^3J_{H,H}$ = 8.5 Hz, 4 H), 7.19 (d, $^4J_{H,H}$ = 1.8 Hz, 4 H), 4.61 (d, $^3J_{H,H}$ = 5.1 Hz, 4 H), 3.14 (s, 2 H), 1.29 (s, 36 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, $25^\circ C$): δ = 166.6, 163.3, 151.9, 149.8, 136.3, 136.0, 133.7, 129.2, 126.7, 124.6, 123.4, 122.7, 122.5, 122.4, 119.7, 102.7, 90.7, 48.7, 35.3, 31.8 ppm. MS (FAB): m/z (%) = 900.4 (26) $[M]^+$, 203.2 (100). GPC (oligopore 6 μ m, toluene, UV/Vis photodiode array detector): Area = 99.9% (at 16.46 min).

***N,N'*-Bis(4-ethynylphenyl)-2,6-bis(3,5-di-*tert*-butylbenzylsulfanyl)-1,4,5,8-tetracarboxylic Acid Naphthalenediimide (18):** A flask under an argon atmosphere was charged with **15** (64 mg, 0.0513 mmol, 1.0 equiv.) and dry and degassed THF (13 mL). Then, TBAF (1 M in THF with 5% water, 21 μ L, 0.021 mmol, 0.4 equiv.) was added, and the reaction mixture was stirred at room temperature. More TBAF was added after 30 min (15 μ L, 0.015 mmol, 0.3 equiv.) and after 1 h (20 μ L, 0.020 mmol, 0.4 equiv.). After 2.5 h the reaction mixture was filtered over a plug of silica gel, washed with CH_2Cl_2 , and the red filtrate was evaporated, affording a red solid that was purified by CC (silica gel, CH_2Cl_2 , 3.5 \times 18 cm) to give **18** as a red-orange solid (36 mg, 0.038 mmol, 74%). R_f = 0.44 (CH_2Cl_2). 1H NMR (400 MHz, $CDCl_3$, $25^\circ C$): δ = 8.91 (s, 2 H), 7.66 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H), 7.33–7.26 (m, 12 H), 4.39 (s, 4 H), 1.28 (s, 36 H) ppm. MS (MALDI-TOF): calcd. for $C_{60}H_{58}N_2O_4S_2$ 934.38; found 934.82.

***N,N'*-Bis(4-ethynylphenyl)-2-(3,5-di-*tert*-butylbenzylsulfanyl)-6-(3,5-di-*tert*-butylbenzylamine)-1,4,5,8-tetracarboxylic Acid Naphthalenediimide (19):** Compound **16** (78.5 mg, 0.0638 mmol) was dissolved in dry and degassed THF (16 mL). TBAF (1 M in THF with 5% water, 25 μ L, 0.025 mmol) was added, and the violet reaction mixture was stirred at room temperature. More TBAF was added after 1 h (15 μ L, 0.015 mmol), after 2 h (20 μ L, 0.020 mmol), and after 2.5 h (10 μ L, 0.010 mmol). After 3 h, the reaction mixture was filtered over a silica plug and washed with CH_2Cl_2 , and the filtrate was evaporated to afford a violet solid. Purification by CC (silica gel, hexane/ CH_2Cl_2 = 1:2) gave **19** as a violet solid (34 mg, 0.037 mmol, 58%). 1H NMR (400 MHz, $CDCl_3$, $25^\circ C$): δ = 9.93 (t, $^3J_{H,H}$ = 5.3 Hz, 1 H), 8.83 (s, 1 H), 8.42 (s, 1 H), 7.69 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H), 7.64 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H), 7.36 (s, 1 H), 7.31 (s, 1 H), 7.26 (m, 6 H), 4.65 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H), 4.36 (s, 2 H), 1.28 (s, 18 H), 1.27 (s, 18 H) ppm. MS (MALDI-TOF): calcd. for $C_{60}H_{59}N_3O_4S$ 917.42; found 917.88.

***N,N'*-Bis[4-[2-(9-anthracene)ethynylphenyl]]-2,6-bis(3,5-di-*tert*-butylbenzylamine)-1,4,5,8-tetracarboxylic Acid Naphthalenediimide (1):** Compound **17** (72.1 mg, 0.08 mmol, 1.0 equiv.), 9-iodoanthracene (**21**; 84.9 mg, 0.28 mmol, 3.5 equiv.), $Pd(PPh_3)_4$ (32.4 mg, 0.028 mmol), CuI (5.3 mg, 0.028 mmol), and (*i*Pr)₂NEt (1 mL) were mixed in dry and degassed THF (10 mL). It was heated at $55^\circ C$ for 1 h. Then all solvents were removed, and the residue was

absorbed on silica gel and purified by CC (silica gel, CH_2Cl_2 /hexane = 7:3) and further with a second column (silica gel, $CHCl_3$) to afford compound **1** as a green-blue solid (28.8 mg, 0.023 mmol, 29%). 1H NMR (300 MHz, $C_2D_2Cl_4$, $100^\circ C$): δ = 9.65 (s, 2 H), 8.72 (d, $^3J_{H,H}$ = 7.2 Hz, 4 H), 8.50 (s, 2 H), 8.46 (s, 2 H), 8.08 (d, $^3J_{H,H}$ = 6.9 Hz, 4 H), 7.98 (s, 4 H), 7.68 (s, 4 H), 7.58 (s, 4 H), 7.44–7.51 (m, 6 H), 7.31 (s, 4 H), 4.77 (s, 4 H), 1.40 (s, 36 H) ppm. MS (MALDI-TOF): calcd. for $C_{88}H_{76}N_4O_4$ 1253.5894; found 1251.8996.

***N,N'*-Bis[4-[2-(1-pyrene)ethynylphenyl]]-2,6-bis(3,5-di-*tert*-butylbenzylamine)-1,4,5,8-tetracarboxylic Acid Naphthalenediimide (2):** A mixture of compound **17** (110.2 mg, 0.122 mmol, 1.0 equiv.), 1-iodopyrene (**23**; 103 mg, 0.314 mmol, 2.6 equiv.), $Pd(PPh_3)_4$ (21.2 mg, 0.018 mmol, 15 mol-%), CuI (70 mg, 0.0368 mmol, 30 mol-%), and diisopropylethylamine (1.5 mL) in degassed and dry THF (125 mL) was stirred for 5 h at room temperature. During the reaction a blue precipitate was formed, which was filtered and crystallized from toluene to afford product **2** as a blue solid (131 mg, 0.101 mmol, 82%). M.p. $< 305^\circ C$ (decomp.). 1H NMR (300 MHz, $C_2D_2Cl_4$, $100^\circ C$): δ = 9.65 (m, 2 H), 8.75 (d, $^3J_{H,H}$ = 9.3 Hz, 2 H), 8.47 (s, 2 H), 8.24–8.32 (m, 8 H), 8.21 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 8.15 (d, $^3J_{H,H}$ = 6.89 Hz, 2 H), 8.04–8.12 (m, 4 H), 7.94 (d, $^3J_{H,H}$ = 8.1 Hz, 4 H), 7.46 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H), 7.43 (s, 2 H), 7.30 (s, 4 H), 4.77 (d, $^3J_{H,H}$ = 4.8 Hz, 4 H), 1.39 (s, 36 H) ppm. MS (MALDI-TOF): calcd. for $C_{92}H_{76}N_4O_4$ 1300.59; found 1301.88. UV/Vis: λ_{max} = 619, 393, 369, 286 nm.

***N,N'*-Bis[4-[2-(triisopropylsilyl)ethynylphenyl]]-2,6-bis(3,5-di-*tert*-butylphenyl)amine]-1,4,5,8-tetracarboxylic Acid Naphthalenediimide (26):** Dichloronaphthalene bisimide **9** (2.20 g, 2.60 mmol, 1.0 equiv.) and 3,5-di-*tert*-butylaniline (3.20 g, 15.6 mmol, 6.0 equiv.) were suspended in dry DMF (60 mL), and the reaction mixture was heated at $110^\circ C$ for 16 h. The solvent was removed, and the product was purified by CC (silica gel, CH_2Cl_2 /hexane = 1:1) to give compound **26** as a blue solid (1.67 g, 1.40 mmol, 54%). M.p. $> 410^\circ C$. 1H NMR (300 MHz, $CDCl_3$, $25^\circ C$): δ = 11.08 (s, 2 H, NH), 8.74 (s, 2 H), 7.67 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H), 7.26–7.30 (m, 6 H), 7.15 (d, $^4J_{H,H}$ = 1.8 Hz, 4 H), 1.32 (s, 36 H), 1.14 (s, 42 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, $25^\circ C$): δ = 166.6, 162.7, 152.8, 147.7, 137.6, 135.1, 133.3, 128.7, 126.4, 124.7, 122.9, 121.2, 120.1, 118.2, 106.4, 103.0, 92.2, 35.1, 31.6, 18.8, 11.5 ppm. MS (MALDI-TOF): calcd. for $C_{76}H_{96}N_4O_4Si_2$ 1184.6965; found 1184.7116.

***N,N'*-Bis[4-(2-ethynylphenyl)-2,6-bis(3,5-di-*tert*-butylphenyl)amine]-1,4,5,8-tetracarboxylic Acid Naphthalenediimide (27):** Compound **26** (1.59 g, 1.34 mmol, 1.0 equiv.) was dissolved in degassed THF (200 mL) and then TBAF (1 M in THF, 1.34 mL, 1.34 mmol, 1.0 equiv.) was added in one portion. After 30 min, the reaction was complete, and the mixture was filtered through silica gel with CH_2Cl_2 to give a crude blue product that was purified by CC (silica gel, hexane/ CH_2Cl_2 = 3:7) to give compound **27** as a blue solid (844 mg, 0.965 mmol, 72%). M.p. $> 410^\circ C$. 1H NMR (300 MHz, $CDCl_3$, $25^\circ C$): δ = 11.09 (s, 2 H, NH), 8.73 (s, 2 H), 7.70 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H), 7.32 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H), 7.29 (t, $^4J_{H,H}$ = 1.5 Hz, 2 H), 7.16 (d, $^4J_{H,H}$ = 1.5 Hz, 4 H), 3.14 (s, 2 H), 1.33 (s, 36 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, $25^\circ C$): δ = 166.6, 162.8, 152.8, 147.8, 137.6, 135.6, 133.5, 128.9, 126.4, 123.3, 122.9, 121.3, 120.2, 118.2, 103.0, 83.0, 78.5, 35.1, 31.5 ppm. MS (MALDI-TOF): calcd. for $C_{58}H_{56}N_4O_4$ 872.4296; found 872.5438.

***N,N'*-Bis[4-[2-(9-anthracene)ethynylphenyl]]-2,6-bis(3,5-di-*tert*-butylphenyl)amine]-1,4,5,8-tetracarboxylic Acid Naphthalenediimide (28):** A mixture of compound **27** (65.6 mg, 0.075 mmol, 1.0 equiv.),

9-iodoanthracene (**21**; 80 mg, 0.263 mmol, 3.5 equiv.), Pd(PPh₃)₄ (30.4 mg, 0.0363 mmol), CuI (12 mg, 0.063 mmol), and diisopropylethylamine (1 mL) in degassed and dried THF (30 mL) was heated for 4 h at 55 °C. Then, all solvents were removed, and the residue was absorbed on silica gel and purified by CC (silica gel, CH₂Cl₂/hexane = 7:3) to afford the desired product **28** as a green solid (31.0 mg, 0.025 mmol, 33%). M.p. >410 °C. ¹H NMR (300 MHz, C₂D₂Cl₄, 60 °C): δ = 11.04 (s, 2 H, NH), 8.76 (s, 2 H), 8.70 (d, ³J_{H,H} = 8.7 Hz, 4 H), 8.52 (s, 2 H), 8.09 (d, ³J_{H,H} = 8.4 Hz, 4 H), 8.01 (d, ³J_{H,H} = 8.4 Hz, 4 H), 7.69 (t, ³J_{H,H} = 8.0 Hz, 4 H), 7.59 (t, ³J_{H,H} = 8.0 Hz, 4 H), 7.50 (d, ³J_{H,H} = 8.1 Hz, 4 H), 7.38 (br. s, 2 H), 7.25 (s, 4 H), 1.41 (s, 36 H) ppm. ¹³C NMR (75 MHz, C₂D₂Cl₄, 100 °C): δ = 166.1, 162.4, 152.8, 147.9, 137.6, 135.3, 132.7, 131.2, 130.7, 129.1, 128.5, 127.8, 126.7, 126.6, 126.3, 125.6, 124.2, 122.7, 121.3, 120.1, 118.1, 116.9, 103.2, 99.9, 87.6, 34.8, 31.2 ppm. C₈₆H₇₂N₄O₄ (1224.56): calcd. C 84.28, H 5.92, N 4.57; found C 83.98, H 5.69, N 4.47. MS (MALDI-TOF): calcd. for C₈₆H₇₂N₄O₄ 1224.5548; found 1223.8708.

N,N'-Bis[4-[2-(2-naphthalene)ethynylphenyl]-2,6-bis[(3,5-di-*tert*-butylphenyl)amine]-1,4,5,8-tetracarboxylic Acid Naphthalenediimide (29**):** A mixture of compound **27** (37.8 mg, 0.043 mmol, 1.0 equiv.), 2-iodonaphthalene (**25**; 33 mg, 0.13 mmol, 3.0 equiv.), Pd(PPh₃)₄ (14.1 mg, 0.012 mmol), CuI (12 mg, 0.063 mmol), and diisopropylethylamine (1 mL) in degassed and dried THF (20 mL) was stirred for 1 h at room temperature. Then, all solvents were removed, and the residue was absorbed on silica gel and purified by CC (silica gel, CH₂Cl₂/hexane = 7:3) to afford desired product **29** as a blue solid (28.30 mg, 0.025 mmol, 58%). M.p. >410 °C. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 11.10 (s, 2 H, NH), 8.75 (s, 2 H), 8.09 (s, 2 H), 7.85 (t, ⁴J_{H,H} = 3.1 Hz, 4 H), 7.82 (d, ⁴J_{H,H} = 1.8 Hz, 2 H), 7.78 (d, ³J_{H,H} = 8.7 Hz, 4 H), 7.60 (dd, ³J_{H,H} = 8.6 Hz, ⁴J_{H,H} = 1.6 Hz, 2 H), 7.53 (d, ⁴J_{H,H} = 3.3 Hz, 2 H), 7.50 (d, ⁴J_{H,H} = 3.0 Hz, 2 H), 7.36 (d, ³J_{H,H} = 8.4 Hz, 4 H), 7.29 (t, ⁴J_{H,H} = 1.5 Hz, 2 H), 7.17 (d, ⁴J_{H,H} = 1.5 Hz, 4 H), 1.33 (s, 36 H) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 166.1, 162.4, 152.6, 147.7, 137.4, 134.9, 132.9, 132.8, 132.5, 131.5, 128.9, 128.3, 127.9, 127.7, 126.7, 126.6, 126.1, 124.0, 122.6, 121.20, 121.17, 120.2, 120.1, 118.1, 103.0, 91.0, 88.9, 34.8, 31.3 ppm. MS (MALDI-TOF): calcd. for C₇₈H₆₈N₄O₄ 1124.5235; found 1124.7321.

1,4-Bis(hexyloxy)-2-iodo-5-[(3-cyanopropyl)dimethylsilyl]acetylene Benzene (33**):** Compound **32** (5.92 g, 11.2 mmol, 1.0 equiv.), Pd(PPh₂)Cl₂ (79.21 mg, 0.112 mmol), PPh₃ (79.07 mg, 0.301 mmol), and CuI (44.34 mg, 0.223 mmol) were dissolved in piperidine (40 mL). The mixture was degassed for 15 min and then [3-(cyanopropyl)dimethylsilyl]acetylene (1.69 g, 11.2 mmol, 1.0 equiv.) was added. The reaction mixture was stirred at room temperature for 4 h. The reaction mixture was mixed with CH₂Cl₂ and water in a separatory funnel, and the organic phase was separated, extracted with water, 10% acetic acid, water, 10% aqueous NaOH, and brine, and it was then dried with Na₂SO₄ and filtered. The yellow filtrate was evaporated to dryness. A yellow solid was obtained. The residue was taken up with CH₂Cl₂ and filtered over silica gel. The filtrate was evaporated, affording a yellow liquid that was purified by CC (silica gel, CH₂Cl₂/hexane = 1:1 to 1:0) to give a yellow oil that solidified at room temperature (1.96 g, 3.55 mmol, 32%). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.25 (s, 1 H), 6.82 (s, 1 H), 3.93 (t, ³J_{H,H} = 6.5 Hz, 2 H), 3.92 (t, ³J_{H,H} = 6.5 Hz, 2 H), 2.42 (t, ³J_{H,H} = 7.1 Hz, 2 H), 1.79 (m, 6 H), 1.48 (m, 4 H), 1.34 (m, 8 H), 0.91 (m, 6 H), 0.83 (m, 2 H), 0.25 (br. s, 6 H) ppm. ¹³C NMR (101 MHz, CDCl₃, 25 °C): δ = 155.3, 152.1, 123.9, 120.1, 116.7, 113.2, 102.6, 97.6, 88.8, 70.5, 70.0, 32.0, 31.9, 29.6, 29.5, 26.1, 26.0, 23.1, 23.0, 21.1, 20.9, 16.1, 14.5, 14.5, -1.4 ppm.

9-[(4-[(3-Cyanopropyl)dimethylsilyl]ethynyl)-2,5-dihexyloxyphenyl]ethynyl]phenanthrene (37**):** Acetylene **36** (390 mg, 1.93 mmol, 1.09 equiv.) and iodide **33** (983 mg, 1.78 mmol, 1.0 equiv.) were dissolved in THF (40 mL) and diisopropylamine (7 mL). The mixture was degassed for 15 min, and then Pd(PPh₃)₄ (200 mg, 0.173 mmol, 9.7 mol-%) and CuI (33 mg, 0.173 mmol, 9.8 mol-%) were added. The reaction mixture was stirred for 20 h at 45 °C. The reaction mixture was then evaporated, and the crude was purified by CC (silica gel, 3 × 12 cm, hexane/CH₂Cl₂ = 1:2) to give product **37** as a yellow solid (1.01 g, 1.61 mmol, 91%). M.p. 87.6–89.0 °C. *R*_f = 0.45 (hexane/CH₂Cl₂ = 1:2). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 8.73–8.66 (m, 3 H), 8.08 (s, 1 H), 7.87 (d, ³J_{H,H} = 7.8 Hz, 1 H), 7.74–7.65 (m, 3 H), 7.61 (m, 1 H), 7.10 (s, 1 H), 7.00 (s, 1 H), 4.09 (t, ³J_{H,H} = 6.6 Hz, 2 H), 4.04 (t, ³J_{H,H} = 6.5 Hz, 2 H), 2.45 (t, ³J_{H,H} = 7.0 Hz, 2 H), 1.98 (quint., ³J_{H,H} = 7.1 Hz, 2 H), 1.86 (m, 4 H), 1.58 (m, 4 H), 1.43–1.27 (m, 8 H), 0.94 (m, 3 H), 0.88 (m, 5 H), 0.29 (s, 6 H) ppm. ¹³C NMR (101 MHz, CDCl₃, 25 °C): δ = 154.2, 153.7, 131.6, 131.3, 131.2, 130.3, 130.1, 128.6, 127.5, 127.3, 127.1, 126.9, 122.7, 122.6, 119.9, 119.7, 116.6, 116.5, 114.4, 113.2, 102.7, 97.9, 93.6, 90.6, 69.41, 69.36, 31.64, 31.59, 29.5, 29.3, 25.8, 25.7, 22.7, 22.6, 20.7, 20.5, 15.7, 14.1, 14.0, -1.8 ppm. MS (EI): *m/z* (%) = 627.3 (100) [M]⁺. GPC (oligopore 6 μm, toluene, UV/Vis photodiode array detector): Area = 99.9% (at 17.32 min).

9-[(4-Ethynyl-2,5-dihexyloxyphenyl)ethynyl]phenanthrene (38**):** Starting material **37** (865 mg, 1.38 mmol, 1.0 equiv.) was dissolved in THF (40 mL) and methanol (40 mL). The mixture was degassed for 15 min, and then K₂CO₃ (390 mg, 2.82 mmol, 2.04 equiv.) was added. The reaction mixture was stirred for 30 min at room temperature and 1 h at 0 °C. It was then quenched with water and extracted with CH₂Cl₂. The aqueous phase was washed with CH₂Cl₂ (2 ×). The combined organic phases were washed with water, dried with MgSO₄, and concentrated. The crude was absorbed on silica and purified by CC (silica gel, 3 × 12 cm, hexane/CH₂Cl₂ = 5:1 to 1:1) to give product **38** as a yellow solid (440 mg, 0.875 mmol, 63%). M.p. 79.5–81.5 °C. *R*_f = 0.20 (hexane/CH₂Cl₂ = 5:1). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 8.73–8.66 (m, 3 H), 8.09 (s, 1 H), 7.87 (d, ³J_{H,H} = 7.8 Hz, 1 H), 7.74–7.63 (m, 3 H), 7.61 (m, 1 H), 7.13 (s, 1 H), 7.04 (s, 1 H), 4.07 (m, 4 H), 3.38 (s, 1 H), 1.97 (quint., ³J_{H,H} = 7.1 Hz, 2 H), 1.86 (quint., ³J_{H,H} = 7.1 Hz, 2 H), 1.55 (m, 4 H), 1.38 (m, 8 H), 0.93 (m, 3 H), 0.86 (t, ³J_{H,H} = 7.2 Hz, 3 H) ppm. ¹³C NMR (101 MHz, CDCl₃, 25 °C): δ = 154.6, 154.1, 132.0, 131.7, 131.6, 130.8, 130.5, 129.0, 127.9, 127.8, 127.5, 127.4, 123.11, 123.07, 120.3, 117.54, 117.51, 117.2, 114.9, 113.1, 93.9, 90.9, 82.8, 80.5, 70.1, 69.9, 32.1, 32.0, 29.9, 29.6, 26.2, 26.0, 23.1, 23.0, 14.5, 14.4 ppm. MS (EI): *m/z* (%) = 502.3 (100) [M]⁺. GPC (oligopore 6 μm, toluene, UV/Vis photodiode array detector): Area = 99.0% (at 18.66 min).

9-[(4-4-[(3-Cyanopropyl)dimethylsilyl]ethynyl)-2,5-dihexyloxyphenyl]ethynyl-2,5-dihexyloxyphenyl]ethynyl]phenanthrene (39**):** Acetylene **38** (355 mg, 0.706 mmol, 0.98 equiv.) and iodide **33** (400 mg, 0.723 mmol, 1.00 equiv.) were dissolved in THF (20 mL) and diisopropylamine (5 mL). The mixture was degassed for 15 min, and then Pd(PPh₃)₄ (92 mg, 0.0796 mmol, 11 mol-%) and CuI (13.8 mg, 0.0723 mmol, 10 mol-%) were added. The reaction mixture was stirred for 16 h at 45 °C, then cooled to room temperature, quenched with water, and extracted with CH₂Cl₂ and water. The aqueous phase was washed with CH₂Cl₂ (×2). The combined organic phases were dried with MgSO₄, and the solvents were evaporated. The crude was purified by CC (silica gel, 4 × 12 cm, CH₂Cl₂/hexane = 2:1 to 5:1) to give **39** as a yellow solid (590 mg, 0.701 mmol, 91%). M.p. 85.8–86.5 °C. *R*_f = 0.28 (hexane/CH₂Cl₂ = 1:2). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 8.75–8.66 (m, 3 H), 8.09 (s, 1 H), 7.88 (d, ³J_{H,H} = 7.8 Hz, 1 H), 7.74–7.65 (m, 3

H), 7.61 (m, 1 H), 7.15 (s, 1 H), 7.07 (s, 1 H), 7.00 (s, 1 H), 6.96 (s, 1 H), 4.10 (t, $^3J_{\text{H,H}} = 6.6$ Hz, 4 H), 4.04 (t, $^3J_{\text{H,H}} = 6.6$ Hz, 2 H), 4.00 (t, $^3J_{\text{H,H}} = 6.5$ Hz, 2 H), 2.44 (t, $^3J_{\text{H,H}} = 7.0$ Hz, 2 H), 1.99 (quint., $^3J_{\text{H,H}} = 7.1$ Hz, 2 H), 1.87–1.78 (m, 8 H), 1.63–1.48 (m, 8 H), 1.42–1.30 (m, 16 H), 0.91 (m, 14 H), 0.28 (s, 6 H) ppm. ^{13}C NMR (101 MHz, CDCl_3 , 25 °C): $\delta = 154.2, 153.9, 153.5, 153.3, 131.5, 131.3, 131.2, 130.3, 130.1, 128.5, 127.41, 127.35, 127.0, 126.9, 122.7, 122.6, 120.0, 119.7, 117.4, 116.9, 116.7, 116.4, 114.9, 114.2, 113.9, 113.1, 102.6, 97.8, 93.5, 91.8, 91.4, 90.8, 69.74, 69.67, 69.3, 69.2, 31.64, 31.61, 31.59, 31.56, 29.5, 29.27, 29.25, 25.8, 25.7, 22.6, 20.6, 20.4, 15.7, 14.1, 14.03, 13.99, -1.8$ ppm. MS (EI): m/z (%) = 927.6 (100) $[\text{M}]^+$. GPC (oligopore 6 μm , toluene, UV/Vis photodiode array detector): Area = 99.9% (at 15.86 min).

9-{{4-(4-Ethynyl-2,5-dihexyloxyphenyl)ethynyl-2,5-dihexyloxyphenyl}ethynyl}phenanthrene (40): CPDMS-protected acetylene **39** (120 mg, 0.129 mmol, 1.0 equiv.) was dissolved in THF (5 mL) and methanol (5 mL). K_2CO_3 (68 mg, 0.49 mmol, 3.8 equiv.) was then added, and the mixture was stirred for 12 h at room temperature. The reaction mixture was then extracted with water and TBME. The aqueous phase was washed with TBME (3×20 mL). The combined organic phases were washed with brine, dried with MgSO_4 , and concentrated. The crude was purified by CC (silica gel, 2×12 cm, $\text{CH}_2\text{Cl}_2/\text{hexane} = 1:2$ to $1:1$) to give compound **40** as a yellow solid (87.0 mg, 0.108 mmol, 90%). $R_f = 0.46$ ($\text{CH}_2\text{Cl}_2/\text{hexane} = 1:1$). M.p. 98.5–100 °C. ^1H NMR (400 MHz, CDCl_3 , 25 °C): $\delta = 8.74\text{--}8.67$ (m, 3 H), 8.09 (s, 1 H), 7.87 (d, $^3J_{\text{H,H}} = 8.0$ Hz, 3 H), 7.61 (t, $^3J_{\text{H,H}} = 7.9$ Hz, 1 H), 7.14 (s, 1 H), 7.06 (s, 1 H), 7.01 (s, 1 H), 6.99 (s, 1 H), 4.10 (t, $^3J_{\text{H,H}} = 6.6$ Hz, 4 H), 4.02 (m, 8 H), 3.35 (s, 1 H), 1.99 (quint., $^3J_{\text{H,H}} = 7.1$ Hz, 2 H), 1.92–1.79 (m, 6 H), 1.63–1.47 (m, 6 H), 1.41–1.25 (m, 18 H), 0.90 (m, 18 H) ppm. ^{13}C NMR (101 MHz, CDCl_3 , 25 °C): $\delta = 154.1, 153.9, 153.5, 153.3, 131.5, 131.3, 131.2, 130.3, 130.1, 128.6, 127.42, 127.37, 127.05, 126.9, 122.7, 122.6, 120.0, 117.9, 117.0, 116.5, 114.9, 114.3, 113.9, 112.6, 93.5, 91.6, 91.3, 90.8, 82.3, 80.1, 69.8, 69.7, 69.6, 69.4, 31.7, 31.62, 31.60, 31.5, 29.5, 29.3, 29.2, 29.1, 25.8, 25.68, 25.67, 25.6, 22.64, 22.58, 14.04, 14.01$ ppm. MS (EI): m/z (%) = 802.5 (100) $[\text{M}]^+$. GPC (oligopore 6 μm , toluene, UV/Vis photodiode array detector): Area = 99.0% (at 16.69 min).

9-{{4-(4-(4-Iodo-2,5-dihexyloxyphenyl)ethynyl-2,5-dihexyloxyphenyl)ethynyl}ethynyl}phenanthrene (41): Iodide **32** (530 mg, 1.00 mmol, 10.0 equiv.) and acetylene **40** (80.0 mg, 0.0996 mmol, 1.0 equiv.) were dissolved in THF (10 mL) and diisopropylamine (2 mL). The mixture was degassed for 15 min before $\text{Pd}(\text{PPh}_3)_4$ (12.0 mg, 0.010 mmol, 10 mol-%) and CuI (2 mg, 0.01 mmol, 10 mol-%) were added. It was then stirred for 3 h at 60 °C. The reaction mixture was evaporated, absorbed on silica gel, and purified by chromatography (silica gel, 2×12 cm, $\text{CH}_2\text{Cl}_2/\text{hexane} = 1:2$ to $1:1$) to give compound **41** as a yellow solid (96.0 mg, 0.0796 mmol, 80%). M.p. 119.9–120.9 °C. $R_f = 0.29$ ($\text{CH}_2\text{Cl}_2/\text{hexane} = 1:1$). ^1H NMR (400 MHz, CDCl_3 , 25 °C): $\delta = 8.75\text{--}8.67$ (m, 3 H), 8.09 (s, 1 H), 7.88 (dd, $^4J_{\text{H,H}} = 1.2$ Hz, $^3J_{\text{H,H}} = 7.9$ Hz, 1 H), 7.74–7.65 (m, 3 H), 7.61 (td, $^4J_{\text{H,H}} = 1.1$ Hz, $^3J_{\text{H,H}} = 7.4$ Hz, 1 H), 7.31 (s, 1 H), 7.15 (s, 1 H), 7.08 (s, 1 H), 7.04 (s, 1 H), 7.02 (s, 1 H), 4.10 (t, $^3J_{\text{H,H}} = 6.6$ Hz, 4 H), 4.06–3.99 (m, 6 H), 3.96 (t, $^3J_{\text{H,H}} = 6.5$ Hz, 2 H), 2.00 (quint., $^3J_{\text{H,H}} = 7.1$ Hz, 2 H), 1.85 (m, 10 H), 1.62–1.48 (m, 12 H), 1.42–1.30 (m, 24 H), 0.90 (m, 18 H) ppm. ^{13}C NMR (101 MHz, CDCl_3 , 25 °C): $\delta = 154.2, 153.9, 153.5, 153.47, 151.8, 131.5, 131.3, 131.2, 130.3, 130.1, 128.6, 127.42, 127.37, 127.1, 126.9, 124.0, 122.6, 120.0, 117.22, 117.2, 117.0, 116.4, 116.1, 114.4, 114.3, 114.2, 113.9, 113.8, 93.5, 91.64, 91.61, 91.1, 90.82, 90.79, 87.9, 70.06, 69.99, 69.8, 69.7, 69.6, 69.4, 31.7, 31.63, 31.61, 31.58, 31.5, 29.5, 29.3, 29.23, 29.16, 25.78, 25.75, 25.68, 25.67, 25.6, 22.7, 22.63, 22.59, 14.1, 14.03, 14.01$ ppm. MS (EI): m/z (%) =

1205.6 (29), 1204.6 (29) $[\text{M}]^+$, 77.0 (100). UV/Vis: λ_{max} (ϵ , $10^3 \text{ m}^{-1} \text{ cm}^{-1}$) = 407 (169.9) nm. GPC (oligopore 6 μm , toluene, UV/Vis photodiode array detector): Area = 99.0% (at 15.44 min).

***N,N'*-Bis[9-{{4-(4-(4-iodo-2,5-dihexyloxyphenyl)ethynyl-2,5-dihexyloxyphenyl)ethynyl}ethynyl}phenanthrenyl]-2,6-bis(3,5-di-*tert*-butylbenzylamine)-1,4,5,8-tetracarboxylic Acid Naphthalenediimide (3):** Blue acetylene **17** (20.7 mg, 0.0230 mmol, 1.0 equiv.) and yellow iodide **41** (57 mg, 0.0470 mmol, 2.04 equiv.) were dissolved in THF (25 mL) and diisopropylamine (2 mL). The mixture was degassed for 15 min, and then $\text{Pd}(\text{PPh}_3)_4$ (6 mg, 23 mol-%) and CuI (1 mg, 23 mol-%) were added. It was then stirred for 23 h at room temperature. The reaction mixture was evaporated and purified by CC (silica gel, 1×12 cm, CH_2Cl_2) to give compound **3** as a green, red-fluorescent solid (67 mg, 0.0219 mmol, 95%). $R_f = 0.31$ ($\text{CH}_2\text{Cl}_2/\text{hexane} = 2:1$). ^1H NMR (600 MHz, CDCl_3 , 25 °C): $\delta = 9.53$ (m, 2 H, NH), 8.73 (d, $^3J_{\text{H,H}} = 7.9$ Hz, 2 H, phenanthrene), 8.71 (d, $^3J_{\text{H,H}} = 8.7$ Hz, 2 H, phenanthrene), 8.68 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 2 H, phenanthrene), 8.37 (s, 2 H, NDI), 8.09 (s, 2 H, phenanthrene), 7.88 (d, $^3J_{\text{H,H}} = 7.1$ Hz, 2 H, phenanthrene), 7.72 (d, $^3J_{\text{H,H}} = 8.3$ Hz, 4 H, phenyl), 7.73–7.66 (m, 6 H, phenanthrene), 7.61 (t, $^3J_{\text{H,H}} = 7.7$ Hz, 2 H, phenanthrene), 7.36 (s, 2 H, NDI substituent), 7.32 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 4 H, phenyl), 7.22 (d, $^4J_{\text{H,H}} = 1.7$ Hz, 4 H, NDI substituent), 7.15 (s, 2 H, OPE), 7.08 (s, 2 H, OPE), 7.044 (s, 2 H, OPE), 7.039 (m, 4 H, OPE), 7.035 (s, 2 H, OPE), 4.64 (d, $^3J_{\text{H,H}} = 5.1$ Hz, 4 H, N-CH₂), 4.11 (t, $^3J_{\text{H,H}} = 6.6$ Hz, 8 H, OCH₂), 4.06 (m, 16 H, OCH₂), 2.00 (quint., $^3J_{\text{H,H}} = 7.1$ Hz, 4 H, CH₂), 1.88 (m, 20 H, CH₂), 1.57 (m, 24 H, CH₂), 1.37 (m, 48 H, CH₂), 1.30 (s, 36 H, *t*Bu), 0.91 (m, 36 H, CH₃) ppm. ^{13}C NMR (151 MHz, CDCl_3 , 25 °C): $\delta = 166.2$ (2 C, Cq, C=O), 162.8 (2 C, Cq, C=O), 153.8 (2 C, Cq, C-O), 153.7 (2 C, Cq, C-O), 153.4 (6 C, Cq, C-O), 153.3 (2 C, Cq, C-O), 151.2 (4 C, Cq, NDI substituent), 149.3 (2 C, Cq, C-N), 135.7 (2 C, Cq, NDI substituent), 134.8 [2 C, Cq, C(phenyl)], 132.4 [4 C, Ct, CH(phenyl)], 131.3 [2 C, Ct, CH(phenanthrene)], 131.1 [2 C, Cq, C(phenanthrene)], 131.0 [2 C, Cq, C(phenanthrene)], 130.2 [2 C, Cq, C(phenanthrene)], 129.9 [2 C, Cq, C(phenanthrene)], 128.6 [4 C, Ct, CH(phenyl)], 128.4 [2 C, Ct, CH(phenanthrene)], 127.2 [2 C, Ct, CH(phenanthrene)], 127.1 [2 C, Ct, CH(phenanthrene)], 126.9 [2 C, Ct, CH(phenanthrene)], 126.8 [2 C, Ct, CH(phenanthrene)], 126.72 [2 C, Ct, CH(phenanthrene)], 126.2 (2 C, Cq, NDI), 124.2 [2 C, Cq, C(phenyl)], 122.5 [2 C, Ct, CH(phenanthrene)], 122.4 [2 C, Ct, CH(phenanthrene)], 122.1 (4 C, Ct, NDI substituent), 121.9 (2 C, Ct, NDI substituent), 121.8 (2 C, Cq, NDI), 119.8 [2 C, Cq, C(phenanthrene)], 119.2 [2 C, Ct, CH(NDI)], 117.0 [8 C, Ct, CH(OPE)], 116.8 [2 C, Ct, CH(OPE)], 116.3 [2 C, Ct, CH(OPE)], 114.4 [2 C, Cq, C(OPE)], 114.3 [2 C, Cq, C(OPE)], 114.1 [4 C, Cq, C(OPE)], 113.6 [2 C, Cq, C(OPE)], 113.5 [2 C, Cq, C(OPE)], 102.1 (2 C, Cq, NDI), 93.9 (2 C, Cq, C \equiv C), 93.3 (2 C, Cq, C \equiv C), 91.4 (2 C, Cq, C \equiv C), 91.3 (6 C, Cq, C \equiv C), 90.6 (2 C, Cq, C \equiv C), 86.9 (2 C, Cq, C \equiv C), 69.6 (2 C, Cs, OCH₂), 69.5 (8 C, Cs, OCH₂), 69.2 (2 C, Cs, OCH₂), 61.6 (2 C, Ct, alkyl- β -CH₂), 48.1 (2 C, Cs, N-CH₂), 34.6 (4 C, Cq, *t*Bu), 31.69 (2 C, Ct, alkyl- β -CH₂), 31.66 (6 C, Ct, alkyl- β -CH₂), 31.65 (2 C, Ct, alkyl- β -CH₂), 31.3 (12 C, Cp, *t*Bu), 29.6 (2 C, Ct, alkyl- γ -CH₂), 29.37 (2 C, Ct, alkyl- γ -CH₂), 29.34 (6 C, Ct, alkyl- γ -CH₂), 29.31 (2 C, Ct, alkyl- γ -CH₂), 25.81 (2 C, Ct, alkyl- δ -CH₂), 25.77 (2 C, Ct, alkyl- δ -CH₂), 25.72 (6 C, Ct, alkyl- δ -CH₂), 25.70 (2 C, Ct, alkyl- δ -CH₂), 22.68 (4 C, Ct, alkyl- ϵ -CH₂), 22.67 (4 C, Ct, alkyl- ϵ -CH₂), 22.66 (2 C, Ct, alkyl- ϵ -CH₂), 22.65 (2 C, Ct, alkyl- ϵ -CH₂), 14.08 (2 C, Cp, alkyl-CH₃), 14.072 (4 C, Cp, alkyl-CH₃), 14.065 (4 C, Cp, alkyl-CH₃), 14.03 (2 C, Cp, alkyl-CH₃) ppm. MS (MALDI-TOF): m/z (%) = 3058.24 (24), 3057.26 (51), 3056.27 (85), 3055.27 (100), 3054.27 (87), 3053.26 (40) $[\text{M}]^+$; calcd. for $\text{C}_{208}\text{H}_{244}\text{N}_4\text{O}_{16}$:

3058.86 (22), 3057.85 (48), 3056.85 (82), 3055.85 (100), 3054.84 (90), 3053.84 (40). UV/Vis: λ_{max} (ϵ , $10^3 \text{ M}^{-1} \text{ cm}^{-1}$) = 609 (27.2), 563 (15.1), 415 (204) nm. GPC (oligopore 6 μm , toluene, UV/Vis photodiode array detector): Area = 99.5% (at 12.34 min).

***N,N'*-Bis[9-(4-[4-(4-iodo-2,5-dihexyloxyphenyl)ethynyl]-2,5-dihexyloxyphenyl)ethynyl]-2,5-dihexyloxyphenyl]phenanthrenyl]-2,6-bis(3,5-di-*tert*-butylbenzylsulfanyl)-1,4,5,8-tetracarboxylic Acid Naphthalenediimide (4):** Violet acetylene **18** (16.5 mg, 0.0176 mmol, 1.0 equiv.) and yellow iodide **41** (44 mg, 0.0365 mmol, 2.07 equiv.) were dissolved in THF (25 mL) and diisopropylamine (2 mL). The mixture was degassed for 15 min, then Pd(PPh₃)₄ (5 mg, 0.0043 mmol, 24 mol-%) and CuI (0.7 mg, 20 mol-%) were added. It was then stirred for 21 h at room temperature. The reaction mixture was evaporated and purified by CC (silica gel, 1 \times 12 cm, hexane/CH₂Cl₂ = 1:2 to 1:10) to give compound **4** as a reddish solid (16 mg, 0.0051 mmol, 29%). R_f = 0.86 (CH₂Cl₂). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ = 8.95 (s, 2 H, NDI), 8.73 (d, ³*J*_{H,H} = 7.8 Hz, 2 H, phenanthrene), 8.71 (d, ³*J*_{H,H} = 8.7 Hz, 2 H, phenanthrene), 8.67 (d, ³*J*_{H,H} = 8.3 Hz, 2 H, phenanthrene), 8.08 (s, 2 H, phenanthrene), 7.87 (d, ³*J*_{H,H} = 7.3 Hz, 2 H, phenanthrene), 7.71 (d, ³*J*_{H,H} = 8.3 Hz, 4 H, phenyl), 7.73–7.66 (m, 6 H, phenanthrene), 7.61 (t, ³*J*_{H,H} = 7.6 Hz, 2 H, phenanthrene), 7.34 (d, ⁴*J*_{H,H} = 1.6 Hz, 2 H, NDI substituent), 7.33 (d, ³*J*_{H,H} = 8.5 Hz, 4 H, phenyl), 7.30 (d, ⁴*J*_{H,H} = 1.5 Hz, 4 H, NDI substituent), 7.16 (s, 2 H, OPE), 7.08 (s, 2 H, OPE), 7.05 (s, 2 H, OPE), 7.042 (m, 4 H, OPE), 7.038 (s, 2 H, OPE), 4.43 (s, 4 H, S-CH₂), 4.11 (t, ³*J*_{H,H} = 6.6 Hz, 8 H, OCH₂), 4.09–4.03 (m, 16 H, OCH₂), 2.00 (quint., ³*J*_{H,H} = 7.1 Hz, 4 H, CH₂), 1.88 (m, 20 H, CH₂), 1.57 (m, 24 H, CH₂), 1.37 (m, 48 H, CH₂), 1.30 (s, 36 H, *t*Bu), 0.91 (m, 30 H, CH₃), 0.87 (m, 6 H, CH₃) ppm. ¹³C NMR (151 MHz, CDCl₃, 25 °C): δ = 163.4 (2 C, Cq, C=O), 162.3 (2 C, Cq, C=O), 153.9 (2 C, Cq, C-O), 153.8 (2 C, Cq, C-O), 153.5 (8 C, Cq, C-O), 151.2 (4 C, Cq, NDI substituent), 149.4 (2 C, Cq, C-S), 134.0 (2 C, Cq, phenyl), 133.2 (2 C, Cq, NDI substituent), 132.4 (4 C, Ct, phenyl), 131.3 (2 C, Ct, phenanthrene), 131.1 (2 C, Cq, phenanthrene), 131.0 (2 C, Cq, phenanthrene), 130.1 (2 C, Cq, phenanthrene), 128.8 (2 C, Ct, NDI), 128.5 (4 C, Ct, phenyl), 128.4 (2 C, Ct, phenanthrene), 127.2 (2 C, Ct, phenanthrene), 126.81 (2 C, Cq, phenanthrene), 126.8 (4 C, Ct, phenanthrene), 126.7 (2 C, Ct, phenanthrene), 125.3 (2 C, Cq, NDI), 124.4 (2 C, Cq, phenyl), 123.8 (2 C, Cq, NDI), 123.5 (4 C, Ct, NDI substituent), 122.5 (2 C, Ct, phenanthrene), 122.4 (2 C, Ct, phenanthrene), 122.2 (2 C, Ct, phenanthrene), 121.9 (2 C, Ct, NDI substituent), 119.7 (2 C, Cq, phenanthrene), 118.9 (2 C, Cq, NDI), 117.0 [8 C, Ct, CH(OPE)], 116.8 [2 C, Ct, CH(OPE)], 116.3 [2 C, Ct, CH(OPE)], 114.5 [2 C, Cq, C(OPE)], 114.2 [2 C, Cq, C(OPE)], 114.1 [4 C, Cq, C(OPE)], 113.6 [2 C, Cq, C(OPE)], 113.5 [2 C, Cq, C(OPE)], 93.8 (2 C, Cq, C≡C), 93.2 (2 C, Cq, C≡C), 91.5 (6 C, Cq, C≡C), 91.4 (2 C, Cq, C≡C), 90.6 (2 C, Cq, C≡C), 87.9 (2 C, Cq, C≡C), 69.82 (2 C, Cs, OCH₂), 69.75 (2 C, Cs, OCH₂), 69.7 (4 C, Cs, OCH₂), 69.6 (2 C, Cs, OCH₂), 69.4 (2 C, Cs, OCH₂), 38.2 (2 C, Cs, S-CH₂), 34.8 (4 C, Cq, *t*Bu), 31.6 (12 C, Cs, alkyl- β -CH₂), 31.4 (12 C, Cp, *t*Bu), 29.5 (2 C, Cs, alkyl- γ -CH₂), 29.3 (10 C, Cs, alkyl- γ -CH₂), 25.79 (2 C, Cs, alkyl- δ -CH₂), 25.75 (2 C, Cs, alkyl- δ -CH₂), 25.70 (8 C, Cs, alkyl- δ -CH₂), 22.7 (12 C, Cs, alkyl- ϵ -CH₂), 14.1 (10 C, Cp, alkyl-CH₃), 14.0 (10 C, Cp, alkyl-CH₃) ppm. MS (MALDI-TOF): m/z (%) = 3093.10 (13), 3092.09 (27), 3091.08 (58), 3090.10 (94), 3089.11 (100), 3088.11 (81), 3087.10 (37)[M]⁺; calcd. for C₂₀₈H₂₄₂N₂O₁₆S₂: 3093.78 (12), 3092.78 (28), 3091.78 (57), 3090.77 (15), 3089.77 (100), 3088.77 (90), 3087.76 (40). UV/Vis: λ_{max} (ϵ , $10^3 \text{ M}^{-1} \text{ cm}^{-1}$) 530 (29.7), 497 (17.8), 415 (223) nm. GPC (oligopore 6 μm , toluene, UV/Vis photodiode array detector): Area = 99.0% (at 12.30 min).

***N,N'*-Bis[9-(4-[4-(4-iodo-2,5-dihexyloxyphenyl)ethynyl]-2,5-dihexyloxyphenyl)ethynyl]phenanthrenyl]-2-(3,5-di-*tert*-butylbenzylsulfanyl)-6-(3,5-di-*tert*-butylbenzylamine)-1,4,5,8-tetracarboxylic Acid Naphthalenediimide (5):** Pink acetylene **19** (25.0 mg, 0.0272 mmol, 1.0 equiv.) and yellow iodide **41** (68.0 mg, 0.0564 mmol, 2.07 equiv.) were dissolved in THF (28 mL) and diisopropylamine (2.8 mL). The mixture was degassed for 15 min, and then Pd(PPh₃)₄ (7 mg, 0.0061, 22 mol-%) and CuI (1 mg, 20 mol-%) were added. It was then stirred for 15 h at room temperature. The reaction mixture was evaporated and purified by CC (silica gel, 2 \times 12 cm, hexane/CH₂Cl₂ = 1:2 to 1:5) to give compound **5** as a reddish solid (31 mg, 0.0101 mmol, 37%). R_f = 0.70 (CH₂Cl₂/hexane = 5:1). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ = 9.98 (s, 1 H, NH), 8.88 (s, 1 H, NDI), 8.73 (d, ³*J*_{H,H} = 7.7 Hz, 2 H, phenanthrene), 8.71 (d, ³*J*_{H,H} = 8.1 Hz, 2 H, phenanthrene), 8.68 (d, ³*J*_{H,H} = 8.3 Hz, 2 H, phenanthrene), 8.44 (s, 1 H, NDI), 8.09 (s, 2 H, phenanthrene), 7.88 (d, ³*J*_{H,H} = 7.5 Hz, 2 H, phenanthrene), 7.74–7.66 (m, 10 H), 7.61 (t, ³*J*_{H,H} = 7.5 Hz, 2 H, phenanthrene), 7.38 (s, 1 H, NDI substituent), 7.34 (d, ³*J*_{H,H} = 8.2 Hz, 2 H, phenyl), 7.33 (d, ⁴*J*_{H,H} = 1.3 Hz, 1 H, NDI substituent), 7.32 (d, ³*J*_{H,H} = 8.3 Hz, 2 H, phenyl), 7.30 (d, ⁴*J*_{H,H} = 1.4 Hz, 2 H, NDI substituent), 7.22 (d, ⁴*J*_{H,H} = 1.4 Hz, 2 H, NDI substituent), 7.16 (s, 2 H, OPE), 7.08 (s, 2 H, OPE), 7.05 (m, 8 H, OPE), 4.70 (d, ³*J*_{H,H} = 5.3 Hz, 2 H, N-CH₂), 4.39 (s, 2 H, S-CH₂), 4.11 (t, ³*J*_{H,H} = 6.6 Hz, 8 H, OCH₂), 4.09–4.03 (m, 16 H, OCH₂), 2.00 (quint., ³*J*_{H,H} = 7.1 Hz, 4 H, CH₂), 1.88 (m, 20 H, CH₂), 1.57 (m, 24 H, CH₂), 1.37 (m, 48 H, CH₂), 1.31 (s, 18 H, *t*Bu), 1.30 (s, 18 H, *t*Bu), 0.911 (m, 30 H, CH₃), 0.908 (m, 6 H, CH₃) ppm. ¹³C NMR (151 MHz, CDCl₃, 25 °C): δ = 166.496 (1 C, Cq, C=O), 166.301 (1 C, Cq, C=O), 162.784 (1 C, Cq, C=O), 162.393 (1 C, Cq, C=O), 153.993 (2 C, Cq, C-O), 153.602 (8 C, Cq, C-O), 153.406 (2 C, Cq, C-O), 151.257 (1 C, Cq, N-C), 151.257 (4 C, Cq, NDI substituent), 144.42 (1 C, Cq, S-C), 135.237 (1 C, Cq, NDI substituent), 134.847 (1 C, Cq, phenyl), 134.456 (1 C, Cq, phenyl), 133.675 (1 C, Cq, NDI substituent), 132.435 (2 C, Ct, phenyl), 132.269 (2 C, Ct, phenyl), 131.33 [2 C, Cq, C(phenanthrene)], 131.273 [2 C, Ct, CH(phenanthrene)], 131.135 [2 C, Cq, C(phenanthrene)], 130.158 [2 C, Cq, C(phenanthrene)], 128.45 (1 C, Ct, NDI), 128.45 (4 C, Ct, phenyl), 128.367 [2 C, Ct, CH(phenanthrene)], 127.228 (1 C, Cq, NDI), 127.205 [2 C, Ct, CH(phenanthrene)], 127.205 [2 C, Ct, CH(phenanthrene)], 127.032 [2 C, Cq, C(phenanthrene)], 126.79 [4 C, Ct, CH(phenanthrene)], 126.707 [2 C, Ct, CH(phenanthrene)], 126.641 (1 C, Cq, NDI), 123.906 (2 C, Cq, phenyl), 123.552 (2 C, Ct, NDI substituent), 123.32 (1 C, Cq, NDI), 122.473 [2 C, Ct, CH(phenanthrene)], 122.39 [2 C, Ct, CH(phenanthrene)], 122.141 (1 C, Ct, NDI substituent), 121.975 (2 C, Ct, NDI substituent), 121.725 (1 C, Ct, NDI substituent), 121.562 (1 C, Cq, NDI), 120.314 (1 C, Ct, NDI), 119.999 [2 C, Cq, C(phenanthrene)], 119.804 (1 C, Cq, NDI), 116.91 [8 C, Ct, CH(OPE)], 116.827 [2 C, Ct, CH(OPE)], 116.27 [2 C, Ct, CH(OPE)], 114.333 [2 C, Cq, C(OPE)], 113.943 [8 C, Cq, C(OPE)], 113.747 [2 C, Cq, C(OPE)], 100.853 (1 C, Cq, NDI), 94.015 (2 C, Cq, C≡C), 93.429 (2 C, Cq, C≡C), 91.671 (2 C, Cq, C≡C), 91.476 (6 C, Cq, C≡C), 90.89 (2 C, Cq, C≡C), 87.178 (2 C, Cq, C≡C), 69.797 (2 C, Cs, O-CH₂), 69.722 (2 C, Cs, O-CH₂), 69.662 (4 C, Cs, O-CH₂), 69.56 (2 C, Cs, O-CH₂), 69.376 (2 C, Cs, O-CH₂), 48.086 (1 C, Cs, N-CH₂), 37.875 (1 C, Cs, S-CH₂), 34.82 (4 C, Cq, *t*Bu), 31.667 (2 C, Cs, CH₂ alkyl β), 31.635 (8 C, Cs, CH₂ alkyl β), 31.596 (2 C, Cs, CH₂ alkyl β), 31.394 (12 C, Cp, *t*Bu), 29.531 (2 C, Cs, CH₂ alkyl γ), 29.304 (8 C, Cs, CH₂ alkyl γ), 29.277 (2 C, Cs, CH₂ alkyl γ), 25.784 (2 C, Cs, CH₂ alkyl δ), 25.749 (2 C, Cs, CH₂ alkyl δ), 25.689 (8 C, Cs, CH₂ alkyl δ), 22.648 (12 C, Cs, CH₂ alkyl ϵ), 14.053 (10 C, Cs, CH₃ alkyl), 14.01 (2 C, Cs, CH₃ alkyl) ppm. MS (MALDI-TOF): found

m/z (%) = 3075.39 (21), 3074.40 (50), 3073.40 (83), 3072.39 (100), 3071.39 (86), 3070.39 (41) $[M]^+$; calcd. for $C_{208}H_{243}N_3O_{16}S$: 3075.81 (25), 3074.81 (51), 3073.81 (85), 3072.81 (100), 3071.81 (90), 3070.80 (40). UV/Vis: λ_{max} (ϵ , 10^3 M $^{-1}$ cm $^{-1}$) = 567 (27.2), 530 (17.8), 415 (212) nm. GPC (oligopore 6 μ m, toluene, UV/Vis photodiode array detector): Area = 99.0% (at 12.28 min).

Supporting Information (see footnote on the first page of this article): The synthesis of compounds **7**, **11**, **12**, **31**, **32**, **35**, and **36**; MALDI-TOF-MS of **3**; NMR spectra of **1–5**, **9**, **13**, **14–19**, **26–29**, and **37–41**; and the GPC chromatograms of **14**, **41**, and **3–5**.

Acknowledgments

Financial support by the Swiss National Science Foundation (SNSF) and the National Center of Competence in Research “Nanoscale Science” is gratefully acknowledged. Dr. Daniel Häussinger is acknowledged for NMR experiments. The research was funded by the Initiative and Networking Fund of the Helmholtz-Gemeinschaft Deutscher Forschungszentren (VH-NG-126). The ongoing support by the University of Basel and the Karlsruhe Institute of Technology (KIT) is gratefully acknowledged.

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Received: October 16, 2010

Published Online: December 7, 2010