

Synthesis of an Acceptor–Donor–Acceptor Multichromophore Consisting of Terrylene and Perylene Diimides for Multistep Energy Transfer Studies

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Supporting Information

ABSTRACT: Motivated by the results obtained from the investigation of singlet-singlet annihilation in a linear multichromophore comprising terrylene diimides (TDI) and perylene diimide (PDI) in 2010, we report the detailed process toward the successful synthesis of a TDI-PDI-TDI dyad. Ineffective synthetic pathways, which were necessary for the understanding of the step-by-step construction of the complex



multichromophore, are described, leading toward a universal synthetic plan for multicomponent systems containing rylene diimides separated by rigid oligophenylene spacers.

INTRODUCTION

Light-harvesting systems in nature generate a sustainable energy source to support the life of organisms. Complexes of chromophores and proteins have the outstanding ability of efficient energy transfer and conversion after absorption of sunlight, especially in the process of photosynthesis. Until now, the different steps involved in photosynthesis are still not completely understood. Thus, synthetic multichromophores have been used to investigate the fundamentals of excitation energy transfer down to the single-molecule level.^{1,2} In this regard, we have investigated several multichromophoric systems in which a perylene diimide (PDI) donor moiety and terrylene diimide (TDI) acceptor units were linked by rigid para-oligophenylene bridges (Figure 1).³⁻⁶ PDI and TDI had been selected with the consideration of their large absorption cross-section, high fluorescence quantum yields, and outstanding photostability with low photobleaching yields.⁷⁻⁹ In 2010, we reported a TDI-PDI dyad 1, which had a PDI at the center position, two TDIs as end-caps, and two rigid bridges linking the PDI and TDIs (Figure 1).¹⁰ In a first set of experiments, electronic coupling between the two TDI moieties was studied by their selective excitation at 635 nm. In this case, the central PDI moiety solely acted as part of a long rigid spacer and neither contributed to absorption/emission or energy transfer pathways. A photon coincidence setup was implemented to quantitatively reveal the competition between singlet-singlet annihilation (SSA) and simultaneous emission once both TDI chromophores were excited. It turned out that the SSA process between the two TDI molecules in dyad 1 was on average three-times faster than the competing fluorescence.

Unfortunately, further investigation of 1 was limited due to the complex, low-yielding multistep synthesis with difficult purification giving only milligram quantities, which prompted us to explore efficient and facile synthetic routes to such multichromophores. As a consequence of the envisioned applications in single molecule energy transfer studies, even minor variations in the design of each chromophore subunit are relevant, and especially the connection between donor and acceptor needs to be investigated thoroughly with regard to energy transfer efficiency as well as synthetic accessibility. Here we outline the reasons for redesigning the molecular structure of the formerly published dyad 1 together with a new synthetic strategy refined toward greater reproducibility and target structural versatility. One can imagine a variety of different strategies to prepare the well-defined TDI-bridge-PDI-bridge-TDI oligomer, but each with its own special challenges. For instance, (1) while the symmetric PDI core-units are readily available, more complicated syntheses are required to prepare the requisite lower-symmetry TDI building blocks. (2) Preparation and purification of any such extended rigid oligomer of rylene diimides will be hindered to varying degrees by solubility/aggregation. Thus, equipping the dyes with solubilizing groups and diminishing π -stacking are of pivotal importance but require more elaborate synthetic work. We could not turn to tetra-phenoxy bay-functionalized PDI and TDI building blocks for this purpose, because the phenoxy

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Figure 1. TDI-PDI-TDI dyad synthesized for the investigation of SSA of weakly interacting chromophores.



Figure 2. Types of reaction involved in the synthesis of the target structure of TDI-bridge-PDI-bridge-TDI.

Scheme 1. Reaction Scheme of the Cyclodehydrogenation Pathway



groups induce additional radiationless relaxation pathways leading to a decrease in energy transfer efficiency between the chromophores and to stronger electron—phonon coupling in low-temperature experiments. Special attention was therefore focused on the rigid linker between the chromophores. Although the dimension of the bridging unit is of less importance, reactivity, connectivity, and contribution to solubility play major roles. As will be outlined here, not every building block can be combined in standard coupling reactions, revealing the complexity and nontriviality of the dyad. Limited combinatory possibilities of donor, bridge, and acceptor prompted many strategies to fail in the final stage; hence, the most important issue was to find the best balance between solubility, reactivity, and ease of purification. Benefiting from progress in the synthesis of rylene dyes over the past decades, we herein describe the experimental process toward the desired A-D-A structure culminating in the successful synthesis of dyad **26** in high yields.

Scheme 2. Reaction Scheme of the Sonogashira-Hagihara Pathway



Scheme 3. Reaction Scheme of the Stille Pathway versus Suzuki-Miyaura Pathway



RESULTS/DISCUSSION

The symmetry of the target molecule gave rise to several possible synthetic pathways, each of them bearing specific challenges. In general, three key reactions have to be considered for building the scaffold (Figure 2), which are (1) cyclo-dehydrogenation of unfused PDI or TDI precursors; (2) imidization to functionalize the PDI unit; and (3) aryl C–C coupling to connect the PDI and TDI moieties. Because the C–C coupling is aiming to connect two different units, the most common Pd-mediated reactions are used such as Suzuki, Stille, and Sonogashira coupling reactions. The primary obstacle then is to determine the most effective sequence of these steps. As it turns out, in most cases, the final-step reaction is critical. Thus, three overall synthetic strategies can be defined by the type of the final-step reaction: Cyclodehydrogenation, Sonogashira, and Suzuki/Stille pathways.

Cyclodehydrogenation Pathway. Initially, we concentrated on readily accessible building blocks, that is, moderately soluble PDIs and TDIs, for example, **4** and **5**, with major consideration on reducing the number of synthetic steps (Scheme 1). Imidization of commercially available perylenetetracarboxylic dianhydride **2** proceeds readily with various anilines but requires greater synthetic effort with

sterically hindered or less reactive amines or anilines. Aniline 3 was prepared to provide a linker with sterically hindered, twisted terphenyl linkage and solubilizing alkyl chains. By imidization of 2 with bromo-functionalized 4'-bromo-2',5'dioctyl-[1,1'-biphenyl]-4-amine (3), a symmetric, solubilized, and reactive PDI building block 4 was obtained (Scheme 1). Coupling of TDI 5 to PDI 4 was unsatisfactory, mainly giving monocoupled intermediates which partially precipitated from the reaction mixture. We attribute the poor yields to the poor solubility of the intermediate in combination with low reactivity of the TDI-boronic acid ester 5. Suzuki coupling of the same PDI 4 with the unfused TDI precursor 7 alleviates some of the solubility problem and gives better yields but then requires a subsequent cyclodehydrogenation step. During the cyclodehydrogenation reaction, fusion and saponification occurred simultaneously, leading mostly to unwanted reaction products. Attempts to improve this by reducing reaction time or temperature failed as saponification of at least one of the six imide linkages dominated over cyclization.

Sonogashira Pathway. Because of unexpected saponification when cyclodehydrogenation was employed as the final step, we turned to strategies with aryl C–C coupling as the final reaction. The first fruitful attempts yielding the desired A-D- Scheme 4. Left: Failed C–C Cross-Coupling Reactions Targeting Disubstituted Rylenediimides. Ryleneimide Substructure Indicates PDI, TDI, or Unfused TDI. Right: Multi-Suzuki–Miyaura Pathway Successfully Giving the Cross-Coupling Product in High Yields



Scheme 5. Reaction Scheme for the Multi-Suzuki-Miyaura Pathway



A structure 1 made use of Sonogashira coupling of an ethynyl functionalized PDI-moiety 10 with the halo-functionalized TDI 12. The synthetic strategy was geared to generate soluble building blocks with highly reactive and accessible coupling functionality. Studies have shown that coupling of one TDIunit to one PDI-unit can be achieved in some cases,⁴ but connection of two TDI units to a central PDI-moiety failed under those conditions. As a result, more solubilizing groups were introduced, and the Sonogashira-Hagihara reaction was chosen as the final C-C-coupling step (Scheme 2). Both chromophores, PDI 9 and TDI 11, were equipped with 2,6diisopropylphenyl substituents in the imide position to impart steric hindrance to aggregation as well as resistance to saponification. Starting from well-known dibromo-diisopropylphenyl PDI 9 and monobromo diisopropylphenyl TDI 11, the key reaction of the following multistep synthesis was the desymmetrizing monolithiation of the precursor 1,4-dibromo-2,5-dioctylbenzene (13) and subsequent silvlation. Unfortunately, the final Sonogashira-Hagihara coupling of PDI 10 and TDI 12 suffered from poor reproducibility and yield, which is unacceptable given the immense effort in this 20-step synthesis.

Suzuki versus Stille Pathway. Our earlier unsuccessful attempts with cyclodehydrogenation as final step relied on C–

C coupling of halo-functionalized PDI central units with TDIboronate coupling partners. As described here, we then evaluated a few routes with the reactivity "inverted" according to Scheme 3. Coupling of the unfused brominated TDIprecursor 16 to boronated PDI 15a via Suzuki coupling (Scheme 3, left) was superior to the coupling of the respective fused TDI moiety 11, but yields were still unsatisfactory. We then turned to a better-solubilized TDI, (Scheme 3, right) but surprisingly, no reaction was observed at all with 15a. Electrostatic repulsion of the shielding octyl-chains with the neighboring functionalities could explain the unsatisfyingly low reaction yields (<5%) but does not explain the high amounts of monocoupled intermediates, whereas two-fold coupling was rarely observed (Scheme 1). Since the poor outcomes could be related to the increasingly hydrophobic environments immediately surrounding the reactive sites under biphasic Suzuki coupling conditions, we attempted Stille coupling. However, in accordance with the analogous Suzuki-reaction of 15a and 12, no reaction between 15b and 12 could be observed, proving the above suggestions wrong. These results point toward steric problems in the C-C-coupling step at the octyl-chain bearing phenylene within the para-terphenylene spacer, regardless of which reaction type was utilized. As will be shown later,

Scheme 6. Reaction Scheme for the Synthesis of the Bridging Dioctyl-Substituted Terphenylene



Scheme 7. Reaction Scheme of the Synthesis of the Donor Unit PDI 9. Upper Part Showing the Reported Four-Step Procedure, Lower Part Displaying Our Novel Two-Step Procedure



sterically unhindered and electronically activated moieties do indeed react with the dioctyl-substituted phenylene system in very high yields (Scheme 6).

Multi-Suzuki Pathway. After the unsuccessful Stille and Suzuki pathways (Scheme 3), we reconsidered the synthetic strategy and tried to solve the reactivity problem of the aryl C-C coupling pairs (e.g., 4 and 5, 11 and 15a, 12 and 15). Regardless of the substitution pattern at the dioctylphenylenespacer and the diisopropylphenyl-group in the imide-position, yields of direct aryl-aryl coupling of any rylene diimide 19 to any dioctyl substituted oligo para-phenylene bridge 20 were very low (Scheme 4, left). In our final synthetic procedure described herein, the coupling reaction center was separated by one unhindered phenylene spacer from the sterically hindered bridging parts, which proved to be of crucial importance (Scheme 4, right). Shifting the center of reaction away from the dioctylphenyl-moiety enabled two-fold cross-coupling of the bridge 22 with the respective rylene diimide, even in the case of the less soluble fused TDI 11. With this finding, we identify the right balance of solubility and reactivity as essential feature of the final synthesis.

On the basis of this result, a convergent synthesis was developed using two symmetric and one unsymmetric unit, yielding the final dyad in decent amounts. All three final building blocks, that is, dibromo di*iso*propylphenyl PDI 9, monobromo-di*iso*propylphenyl TDI 11, and dioctyl-substituted terphenyl diboronic acid pinacolester 24, can be synthesized in up to a gram scale (Scheme 5).

SYNTHESIS

Our synthetic procedure includes the synthesis of the bisfunctionalized PDI 9, attachment of a solubilizing linker via 24, and final coupling to the asymmetric TDI-units 11 (Scheme 5). The bis-functionalized PDI 9 was synthesized by a new, palladium-free method in only two steps via the tetraester of perylenetetracarboxylic acid in high overall yields of 73%. For reasons of solubility, a terphenylene-linker with *n*-octyl chains was introduced. These linear substituents not only had a positive effect on solubility, but also were needed to increase the interphenylene twisting angle. According to the literature, ortho-unsubstituted poly(para-phenylenes) show a twist of 23° between consecutive repeating units along the phenylene backbone, which allow for non-negligible π -overlap and are greatly decreased upon ortho-substitution, thus reducing the degree of conjugation of the bridging unit.^{11,12} The syntheses of the individual building blocks are described below.

Spacer. Oligo *para*-phenylenes are ideal building blocks as rigid, nonconjugated spacer moieties up to a spacer-length of approximately 30 phenylene-units.¹³ The intrinsic twist between the phenylene units was enhanced by introduction of two *n*-octyl chains, thus optimizing solubility and minimizing conjugation. By using symmetric 1,4-dibromo-2,5-diocytlbenzene (13), the *para*-difunctionalized terphenylene unit was synthesized by palladium catalyzed coupling reaction with *p*-(trimethylsilyl)phenylboronic acid (Scheme 6). Subsequent exchange of the TMS group gave the corresponding *para*-diiodo terphenylene **28** in excellent yields, which was further converted into the boronic acid pinacolester **24** via Miyauraborylation reaction. Conversion of TMS into the pinacolester

Scheme 8. Reaction Scheme for the Synthesis of the Acceptor Unit TDI 11



via the aryl iodide was found to be superior to the direct conversion of TMS into the boronic acid for reasons of purification.

PDI (Donor). The central element of the dyad is the bisfunctionalized perylenediimide 9. For reasons of stability and solubility during all following steps, we chose the diisopropylphenyl imide. Therefore, a quick and easy synthetic procedure was introduced to yield dibromo-PDI 9 in only two steps making use of readily available compounds (Scheme 7). PDI 9 has previously been prepared by a four-step procedure via esterification of 4-chloro naphthalic anhydride (29), nickel catalyzed homocoupling followed by imidization with aniline 33, and final cyclodehydrogenation.^{14,15} We instead converted 3,4,9,10-perylenetetracarboxylic dianhydride (PDA, 2) in two easy steps to PDI 9. Since low reactivity of 4-bromo-2,6diisopropylaniline in combination with the insolubility of PDA 2 limits their direct conversion to 9, the esterification and accompanying increase of solubility was of crucial importance.¹⁶ By starting with the hydrolysis of PDA 2 and base induced ester formation, a highly soluble perylene tetracarboxylic-tetrabutylester 34 was obtained, which only needed to be precipitated from its chloroform solution to yield clean compound 34 in high yields (89%). Imidization of the tetraester 34 with the respective aniline 33 and stoichiometric amounts of ZnCl₂ in imidazole gave target dibromo PDI 9 on a multigram scale.

TDI (Acceptor). The acceptor-unit employed is the wellestablished diisopropylphenyl-TDI 11.17 Synthetic procedures (Scheme 8) and purification methods have been developed and optimized by our group. Bromination of N-diisopropylphenylperylene-3,4-dicarboxylic imide (PMI, 35) gave isomerically pure monobrominated 36 in almost quantitative yields. After borylation of 36 under Miyaura-reaction conditions and subsequent Suzuki-Miyaura coupling with 4-bromo-1,8-naphthalic anhydride, the precursor 38 for the synthesis of the TDIcore was obtained. Because of the comparably good solubility of the unfused TDI precursor 38 and the higher reactivity of the naphthalene monoimide-subunit compared to the former case of PDA 2, the imidization reaction of 38 with p-bromo-2,6diisopropylaniline (33) could be executed in propionic acid at elevated temperature. Reaction temperature and time both were regulated to minimize the debrominated sideproduct. Oxidative cyclodehydrogenation of 16 was conducted in monoethanolamine with solid potassium carbonate as base. Owing to the poor solubility of the starting compound 16 in monoethanolamine, finely powdered substance led to improved

yields due to shorter reaction times, thus minimizing the risk of saponification or debromination, which can cause serious losses in isolated yield.

Dyad (A–D–A). The final coupling of the three building blocks, dibromo PDI 9, boronic acid ester functionalized terphenylene 24, and monobromo TDI 11, was performed from the inside out (Scheme 5). By using a slight excess of 1.5 equiv of the terphenylene 24 for each bromo-functionality, the terphenylene-elongated PDI 25 could be obtained without any higher oligomers. Purification of 25 was done by column chromatography on silica as well as on GPC-gel. Finally, both TDI-groups were attached by standard Suzuki–Miyaura coupling of PDI 25 with a slight excess of the TDI-moiety 11. By displacing the reaction center of the final C–C-coupling by one phenylene group from the dioctylphenyl-moiety, the final dyad 26 could be obtained in comparatively high yields of 32% after purification.

Absorption and Emission Spectra. Photophysical investigation of target compound 26 proves that a donor–acceptor system containing PDI and TDI has been established. Absorption and emission spectra (Figure 3) were recorded in toluene at concentrations ranging from 10^{-6} M to 10^{-8} M. The emission spectrum of PDI (Figure 3, left) shows very good overlap with the absorption of TDI, which is necessary for



Figure 3. Absorption and emission spectra of PDI 9 and TDI 11 in toluene. Red line, absorption of PDI 9; green line, emission of PDI 9; blue line, absorption of TDI 11. Shaded area displaying the spectral overlaps of PDI-emission and TDI-absorption for Förster energy transfer.

efficient Förster energy transfer. The absorption spectrum of dyad **26** (Figure 4) appears as the superposition of the



Figure 4. Absorption and emission spectra of dyad 26 in toluene. Black line, absorption of dyad 26; green line, emission of dyad 26; red line, absorption of PDI 9; blue line, absorption of TDI 11.

absorptions of PDI and TDI in very good agreement with the absorption spectra of the individual chromophores (red and blue lines in Figure 4). The emission spectra were independent of the excitation wavelength, giving rise to the same spectral characteristics when excited at the PDI site ($\lambda_{exc.} = 460$ nm) or the TDI site ($\lambda_{exc.} = 600$ nm). Upon excitation of PDI, fast and efficient energy transfer from PDI to TDI occurs since the distance between PDI and TDI is well within the Förster radius.³

CONCLUSION

After pursuing different strategies of PDI- and TDI-based A-D-A synthesis, we presented a successful procedure for the formation of a photophysically important compound consisting of two TDI chromophores connected to a central PDI moiety via a rigid terphenylene linker. A balance between solubility, reactivity, and complexity of the synthesis was found, leading to a reproducible strategy toward acceptor-donor systems containing rylene diimides. By designing the chromophores and linkers separately and combining them in the final stage, our method of constructing A-D-A is not limited to the presented structure but enables the synthesis of various related compounds for photophysical purposes. Investigation of basic photophysical behavior of the dyad presented herein gives proof for the identity of the product. The negligible emission from PDI in the recorded fluorescence spectra suggests highly efficient energy transfer between donor and acceptor, which can be explained by the close proximity of the chromophores within a rigid scaffold. Comparison of absorption and emission spectra of dyad 1 and dyad 26 displays the equivalence of both structures for the given purposes, thus justifying the change from bisphenylethyne to a terphenylene spacer in design for reasons of synthetic feasibility.

In future experiments, a multistep sequence of energy transfer events can be induced in **26** by selective excitation of the PDI chromophore. In this scenario, the excited PDI first transfers efficiently the excitation energy to any of both TDI acceptors. This process can be studied in great detail by single-molecule spectroscopy at liquid helium temperatures, which not only allows one to deduce the energy transfer rate constant from PDI to TDI from the zero-phonon line width of the PDI donor,¹⁸ but also will reveal to which extent both TDI

acceptors are involved in the energy transfer process and how they communicate after collecting energy from PDI. A very promising surplus of the low temperature experiments relates to the fact that the sharp zero-phonon transitions of the TDIs in excitation and emission can be spectrally separated. Consequently, because of the reduced spectral overlaps compared to room temperature,¹⁹ it might be possible to modify the energy flow from PDI to one of the TDIs by selective saturation of the optical transition of this particular TDI.

EXPERIMENTAL SECTION

Perylenetetracaboxylic tetrabutylester,¹⁶ 1,4-dibromo-2,5-dioctylbenzene,²⁰ and N-(4-bromo-2,6-di*iso*propylphenyl)-N'-(2,6di*iso*propylphenyl)terrylene-3,4:11,12-tetracarboxdiimide¹⁷ were prepared as described in the literature.

N,N'-Bis(4-bromo-2,6-diisopropylphenyl)perylene-3,4:9,10tetracarboxylic bisimide (9). Perylenetetracaboxylic tetrabutylester (34) (5.0 g, 7.66 mmol), ZnCl₂ (2.09 g, 15.32 mmol), and 4-bromo-2,6-diisopropylaniline (29.43 g, 114.89 mmol) were stirred in molten imidazole (150 g) at 180 °C under argon atmosphere overnight. After the mixture was cooled down to 100 °C, the slurry was poured into 150 mL of methanol. The precipitate was collected by filtration and dried under vacuum. Purification by column chromatography on silicagel (dichloromethane) yielded compound 9 as a dark red solid (5.46 g, 82%). HR MALDI-TOF MS (dithranol): m/z = 866.1371, calc. for $C_{48}H_{41}Br_2N_2O_4$: 866.1355. ¹H NMR (300 MHz, CD_2Cl_2) $\delta = 8.79$ (m, 8H), 7.49 (s, 4H), 2.74 (p, J = 6.8 Hz, 4H), 1.16 (s, 12H), 1.13 (s, 12H). ¹³C NMR (75 MHz, CD_2Cl_2) δ = 149.2, 135.8, 132.6, 130.83, 130.76, 128.1, 127.4, 124.3, 124.2, 123.8, 29.9, 24.1. MP: > 400 °C. FT-IR: $\tilde{\nu} = 748, 812, 841, 862, 957, 970, 1176, 1198, 1250, 1344, 1356,$ 1404, 1452, 1459, 1468, 1577, 1593, 1662, 1674, 1705, 2850, 2868, 2924, 2956 cm⁻

2',5'-Dioctyl-4,4"-bis(trimethylsilane)-1,1':4',1"-terphenylene (27). The 1,4-dibromo-2,5-dioctylbenzene (2.32 g, 5.03 mmol), 4-trimethylsilylphenylboronic acid (2.15 g, 11.08 mmol), and K₂CO₃ (13.92 g, 100.69 mmol) were dissolved in a mixture of solvents of toluene (50 mL), water (10 mL), and ethanol (2 mL). The mixture was degassed by argon bubbling for 30 min before $Pd(PPh_3)_4$ (582) mg, 0.50 mmol) was added. The reaction was run at 95 °C under argon atmosphere overnight. The aqueous phase was extracted with toluene twice, and the combined organic solutions were dried over $Mg_2SO_4.$ The solution was concentrated under reduced pressure and then filtered over a pad of silica. The solvent was removed by rotary evaporation to give a yellow oil, which was treated with cold ethanol. After shaking of the two phases, a precipitate formed, which was filtered from the remaining solvent. The solid was washed with cold methanol to give the title compound as a colorless solid (2.80 g, 93%). ¹H NMR (300 MHz, CD_2Cl_2) δ = 7.59 (d, J = 8.1 Hz, 4H), 7.35 (d, J = 8.1 Hz, 4H), 7.12 (s, 2H), 2.62-2.52 (m, 4H), 1.55-1.43 (m, 4H), 1.32–1.11 (m, 20H), 0.86 (t, J = 6.9 Hz, 6H), 0.32 (s, 18H). ¹³C NMR (75 MHz, CD_2Cl_2) δ = 143.7, 142.1, 139.9, 138.8, 134.4, 132.3, 130.0, 33.8, 33.2, 32.9, 30.8, 30.61, 30.5, 24.0, 15.3, 0.00. HRMS (ESI +): calc. for $C_{40}H_{63}Si_2 [M + H]^+$ 599.4461, found: 599.4468. MP: 78 °C. FT-IR: $\tilde{\nu}=627,\,690,\,725,\,754,\,825,\,837,\,1113,\,1248,\,1261,\,1379,$ 1458, 1483, 1599, 2854, 2923, 2954 cm⁻¹

4,4"-**Diiodo-2**',5'-**dioctyl-1,1**':**4**',**1**"-**terphenylene (28).** Compound 27 (2.80 g, 4.67 mmol) was dissolved in dry dichloromethane (80 mL). While being stirred in an ice bath, iodine monochloride (1 molar solution in CH_2Cl_2 , 9.79 mL, 9.79 mmol) was added dropwise under exclusion of light. After 2 h at 0 °C, the excess of iodine monochloride was quenched by addition of saturated sodium sulfite solution. The aqueous phase was extracted with dichloromethane, the combined organic extracts dried over $MgSO_4$, and finally the solvent was removed under reduced pressure. The obtained dark colored oil was dissolved in hot ethanol before the same amount of *n*-hexane was added. Upon slowly cooling the mixture in a refrigerator, the product precipitated as a fine colorless powder, which was collected by suction

filtration and dried under vacuum. The final product was obtained as a colorless solid (2.73 g, 83%). FD-MS: 706.20 (100%). HR MALDI-TOF MS (dithranol): m/z = 706.1536, calc. for C₃₄H₄₄I₂: 706.1532. ¹H NMR (300 MHz, CD₂Cl₂) δ = 7.76 (d, *J* = 8.3 Hz, 4H), 7.10 (d, *J* = 8.3 Hz, 4H), 7.07 (s, 2H), 2.57–2.49 (m, 4H), 1.50–1.36 (m, 4H), 1.34–1.09 (m, 20H), 0.86 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (75 MHz, CD₂Cl₂) δ = 142.0, 140.5, 138.1, 137.7, 131.9, 131.3, 92.8, 33.0, 32.4, 32.0, 30.0, 29.8, 29.7, 23.2, 14.5. MP: 70 °C. FT-IR: $\tilde{\nu}$ = 513, 534, 719, 741, 825, 1005, 1065, 1379, 1473, 2852, 2922, 2952 cm⁻¹.

2',5'-Dioctyl-4,4"-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-1,1':4',1"-terphenylene (24). The 4,4"-diiodo-2',5'-dioctyl-1,1':4',1"-terphenyl (1.41 g; 2.00 mmol), KOAc (1.41 g, 14.37 mmol), and bis(pinacolato)diboron (1.52 g, 6.00 mmol) were suspended in 100 mL of dry DMF. After 30 min of argon bubbling, Pd(dppf)Cl₂ (158 mg, 0.20 mmol) was added, and the mixture was stirred under argon atmosphere at 85 °C for 2 h. After completion, the solvent was removed under reduced pressure, and the black residue was purified by column chromatography on silica-gel (petroleum ether/dichloromethane, 1:1) yielding 1.02 g (73%) of the title compound as a colorless solid. HRMS (ESI+): calc. for $C_{46}H_{69}B_2O_4$ [M + H]⁺ 707.5382, found: 707.5378. ¹H NMR (300 MHz, CD_2Cl_2) $\delta = 7.82$ (d, J = 8.1 Hz, 4H), 7.37 (d, J = 8.0 Hz, 4H), 7.12 (s, 2H), 2.67–2.44 (m, 4H), 1.54–1.41 (m, 4H), 1.37 (s, 24H), 1.32–1.11 (m, 20H), 0.86 (t, I = 6.8 Hz, 6H). ¹³C NMR (75 MHz, CD₂Cl₂) $\delta = 145.5$, 141.4, 138.1, 135.0, 131.4, 129.3, 84.4, 33.2, 32.4, 32.1, 30.1, 29.8, 29.7, 25.3, 23.3, 14.5. MP: 141 °C. FT-IR: $\tilde{\nu}=511,\,660,\,741,\,845,\,860,\,962,\,1018,$ 1093, 1144, 1269, 1323, 1360, 1398, 1608, 2853, 2924, 2956, 2976 cm^{-1} .

Terphenylene-PDI-Terphenylene (25). PDI 9 (410 mg, 0.471 mmol) and terphenylene 24 (1.00 g, 1.42 mmol) were dissolved in toluene (350 mL) before a solution of K₂CO₃ (1.96 g, 14.15 mmol) in water, and some drops of ethanol were added. The mixture was degassed by argon bubbling for 30 min before Pd(PPh₃)₄ (55 mg, 0.047 mmol) was added, and then the mixture was stirred at 85 °C overnight. After consumption of the starting compound 9, the two phases were separated, the organic solvent removed by rotary evaporation, and the crude mixture purified by column chromatography on silica with CH₂Cl₂ as eluent. Final purification was done by GPC in toluene, and the title compound was isolated as orange-red solid (480 mg, 54%). FD-MS: 1867.35 (100%). ¹H NMR (300 MHz, CD_2Cl_2) $\delta = 8.83$ (s, 8H), 7.84 (d, J = 8.0 Hz, 4H), 7.80 (d, J = 8.2 Hz, 4H), 7.65 (s, 4H), 7.52 (d, J = 8.2 Hz, 4H), 7.40 (d, J = 8.0 Hz, 4H), 7.22 (s, 2H), 7.16 (s, 2H), 2.86 (p, J = 6.8 Hz, 4H), 2.72-2.54 (m, 8H), 1.62-1.41 (m, 8H), 1.37 (s, 24H), 1.32-1.17 (m, 64H), 0.91-0.81 (m, 12H). ¹³C NMR (75 MHz, CD_2Cl_2) δ = 164.3, 147.1, 145.5, 142.8, 141.9, 141.4, 141.1, 140.2, 138.2, 138.1, 135.8, 135.0, 132.6, 131.6, 131.4, 131.1, 130.8, 130.4, 129.3, 127.7, 127.5, 124.2, 124.0, 123.7, 84.4, 33.19, 32.4, 32.13, 32.08, 30.3, 30.10, 30.08, 29.88, 29.85, 29.76, 29.74, 25.3, 24.4, 23.3, 14.5. EA calc. for C₁₂₈H₁₅₂B₂N₂O₈, C: 82.29; H: 8.20; N: 1.50; found C: 82.13; H: 8.22; N: 1.50. MP: 278 °C. FT-IR: $\tilde{\nu} = 513, 521, 660, 748, 804, 812, 841, 858, 960, 1016,$ 1090, 1144, 1176, 1196, 1254, 1269, 1321, 1344, 1356, 1404, 1468, 1579, 1595, 1668, 1707, 2854, 2869, 2924, 2958 cm⁻¹.

TDI-PDI-TDI Dyad (26). Compound 25 (20 mg, 0.011 mmol) and monobromo-TDI 11 (39 mg, 0.043 mmol) were dissolved in oxylene (7.5 mL), a solution of K₂CO₃ (59 mg, 0.428 mmol) in water (2 mL), and ethanol (1.5 mL) was added. After degassing for 15 min by argon bubbling, $Pd(PPh_3)_4$ (1 mg) was added, and the reaction mixture was stirred at 95 °C under argon atmosphere overnight. After completion, the organic phase was separated from the aqueous phase, and the solvent was removed under reduced pressure. The crude mixture was subjected to size-exclusion chromatography with toluene as eluent. The product was obtained as a dark blue solid (11 mg, 32%). HR MALDI-TOF MS (dithranol): m/z = 3279.6709, calc. for $C_{232}H_{218}N_6O_{12}$: 3279.6633. ¹H NMR (300 MHz, $CD_2Cl_2 + CS_2$ 7:1) δ = 8.88–8.68 (m, 32H), 7.77 (d, J = 7.9 Hz, 8H), 7.61 (d, J = 2.2 Hz, 8H), 7.51 (d, J = 7.7 Hz, 8H), 7.35 (d, J = 7.7 Hz, 4H), 7.23 (s 4H), 2.91-2.66 (m, 20H), 1.65-1.48 (m, 8H, superimposed with H_2O), 1.38–1.25 (m, 90H), 1.19 (d, J = 6.8 Hz, 24H), 0.91 (m, 12H). ¹³C NMR: because of low solubility, no carbon NMR could be

recorded. MP: > 400 °C. FT-IR: $\tilde{\nu}$ = 501, 740, 806, 841, 1014, 1039, 1072, 1095, 1120, 1261, 1358, 1379, 1462, 1585, 1666, 1705, 1727, 2848, 2870, 2916, 2957 cm^{-1}.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.5b04602.

All NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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