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Synthesis of an All-in-One Molecule (for Organic Solar Cells)

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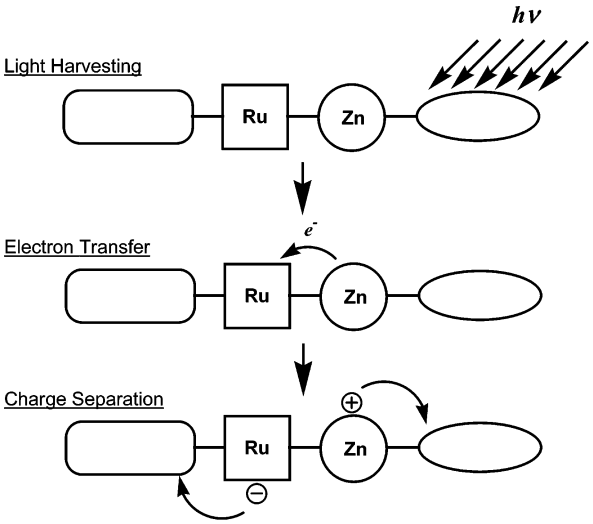

A multidomain compound with applications in the area of organic solar cells has been prepared. This all-in-one molecule compound integrates all the functionalities needed for solar cell action from light harvesting, carrier generation, and separation, to transport and contact to external electrodes. A convergent synthetic strategy with some 60 steps involving preparation of regioregular oligothiophenes, a zinc porphyrin, a bisterpyridine ruthenium(II) complex, a hetero oligo phenylenevinylene and functional end groups is described. Preliminary investigations of photovoltaic devices based on the target molecule gave values of 0.18 V, 0.0044 mA cm^{-2}, 29% and 0.000081% for the open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF), and efficiency (η). These poor values are compared to those obtained with an oligo-3-hexylthiophene which gave values of 0.7 V, 0.046 mA cm^{-2}, 24.6%, and 0.0081% for the open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF) and efficiency (η). This latter compound was also studied in a bulk heterojunction device with PCBM (1:1 blend) which gave values of 0.43 V, 0.45 mA cm^{-2}, 33.5%, and 0.063%.

Introduction

Dyadic molecules comprised of a terpyridine complex of ruthenium(II) and a porphyrin have long been studied as model systems for photosynthesis and recently also as candidates for active components in organic photovoltaic cells. These systems are attractive because of their photophysical properties such as very long-lived metal to ligand charge transfer (MLCT) excited states and high molar extinction coefficients in the visible range as shown by the groups of J.-P. Sauvage and J.-P. Collin.[1,2,3] In these dyads, the excited state that is produced on absorption of light leads to a charge separated state with high efficiency. Simpler ruthenium complexes have already been exploited in the so-called "dye-sensitized solar cells" introduced by M. Grätzel.[4] The key events that take place in a solar cell are absorption of light to produce an excited state followed by

(1) Sauvage, J.-P.; Collin, J.-P.; Chambron, J.-C.; Guillerez, S.; Coudret, C. *Chem. Rev.* **1994**, *94*, 993−1019.

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(4) (a) O'Reagan, B.; Grätzel, M. *Nature*, **1991**, *353*, 737−740 (b) Grätzel, M. *MRS Bull.* **2005**, *30*, 23−27.

10.1021/jo060491r CCC: $33.50
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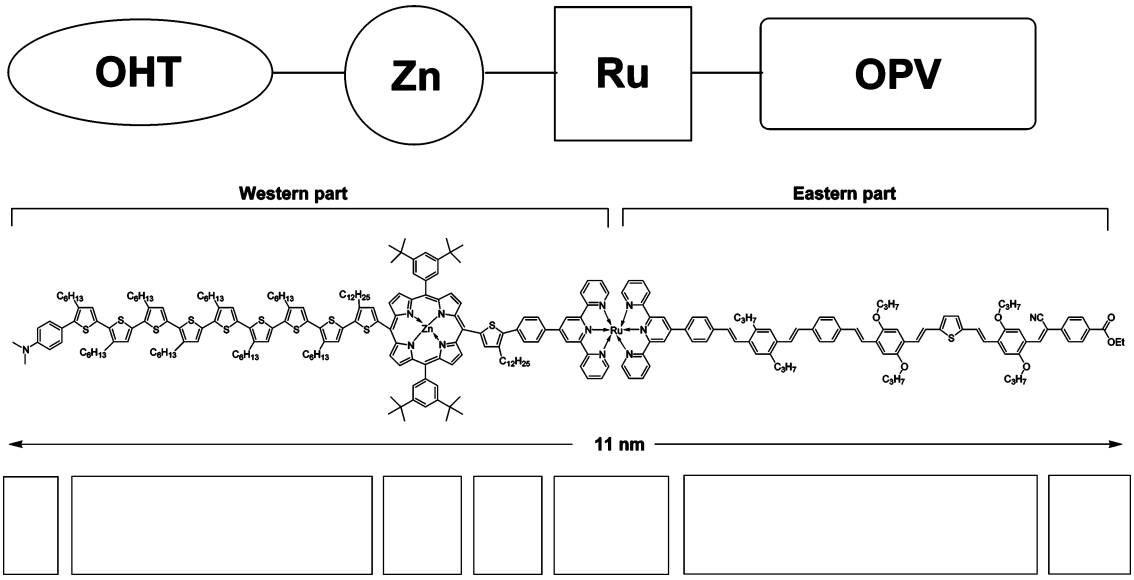
CHART 1. A Structural Drawing of the Dication of the Target Molecule 1[a]



[a] From the left is a donor dimethylaminophenyl moiety connected to an octamer of hexylthiophenes (OHT) linked by a dodecylthiophene group to an unsymmetrically substituted zinc porphyrin which in turn is joined to an unsymmetrically substituted ruthenium(II) terpyridine complex through another dodecylthiophene group. The last part of the molecule is made up by an oligophenylenevinylene (OPV) domain where each ring is differently substituted. Finally, the end of the molecule is terminated with an electron accepting cyanostilbene and a carboxylic acid group. Boxes below the molecule indicate individual domains.

charge separation. The positive and negative charges should then efficiently migrate to an anode and a cathode, respectively, where they are collected and can be used in an external circuit. Organic solar cells and the present status of this research area have been reviewed several times.[5,6,7]

In the present paper we wish to demonstrate the synthesis of a very large photochemically active multicomponent molecule that could act as the active component in a photovoltaic cell. The approach is based on the concept of domains where each of these is responsible for a certain functionality such as absorption of light, charge separation, and transport in the combined molecule. This concept also helps to make a convergent synthetic strategy of manageable units that can be built up and purified before the final assembly. Such a strategy is also more robust since variations of the individual domains can be readily made to investigate the effect on the solar cell function. The appeal of the all-in-one molecule solar cell concept is that all the critical components that are responsible for the photophysical transformation of light into charges can be arranged logically along the backbone of the molecule. Ideally such an optimized structure will be highly efficient. Whether this translates into an improved macroscopic device is another matter and depends among other things on the organization of the molecules. This aspect has not been addressed in the present paper, but could conceivably be achieved through monolayer film fabrication.[8] It is also in the anticipation of such methods that a carboxylic acid functionality and a dimethylamino group has been incorporated into the target molecule at the ends.

A schematic representation of such a conjugated multicomponent molecule is shown in Chart 1. The central part of the molecule is build up around a dyad consisting of a zinc porphyrin and a bisterpyridine ruthenium(II) complex. Pendant arms of an oligothiophene and an oligophenylenevinylene are meant to function both as antennae for light harvesting and as donor and acceptor groups for attraction of the photoinduced charges.

Several domains can be recognized in the target molecule depicted in Chart 1. Starting from the left or "western" side of the molecule it begins with an electron-donating dimethylaminophenyl group connected to a string of eight 3-hexylthiophene units joined in a regioregular fashion. This electron rich double domain is then connected through a a dodecylthiophene group to one side of the core of an unsymmetrical zinc porphyrin moiety. A small linker composed of a dodecylthiophene-phenyl group forms a bridge to an unsymmetrical bisterpyridine ruthenium(II) complex. The right side or "eastern" part of the molecule is a seven-mer hetero-oligophenylenevinylene structure terminated by a benzoic acid group. The detailed structure of the target molecule **1** was chosen from considerations of how each domain could contribute to the photophysical processes in a solar cell. The central porphyrin terpyridine ruthenium dyad was chosen for its well-known ability to perform tasks of energy/electron transfer and charge separation,[1−3] while the oligothiophene[9] and oligophenylenevinylene[10,11,12] arms were chosen as light harvesting and carrier transporting domains. Finally, end-groups were selected for possible anchoring to electrode surfaces or, in the case of the carboxylic acid group and the dimethylamino group, for possible amphiphilic behavior in Langmuir−Blodgett films.

Similar but less evolved examples of multicomponent molecules for solar cells have been reported. Examples are

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(6) Spanggaard, H.; Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2004**, *83*, 125−146
(7) Shaheen S. E.; Ginley, D. S.; Jabbour, G. E. *Org.-Based Photovoltaics, MRS Bull.* **2005**, *30*.
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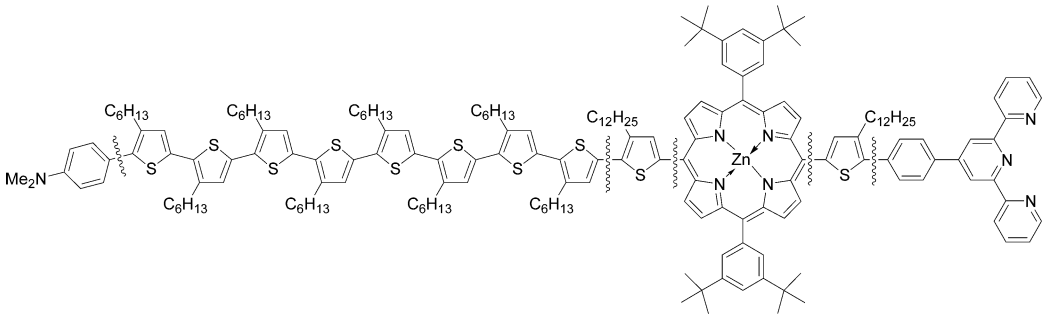
(11) Jørgensen, M.; Krebs, F. C. *J. Org. Chem.* **2004**, *69*, 6688−6696.
(12) Jørgensen, M.; Krebs, F. C. *J. Org. Chem.* **2005**, *70*, 6004−6017.

CHART 2. The Western Part 2.[a]



[a] The wavy lines indicate disconnections to possible domains. A *N,N*-dimethylaminophenyl group linked to a octa-hexylthiophene (OHT) can be recognized at one end, and a 4-phenyl-terpyridine can be recognized at the other. These groups are in turn connected to a zinc porphyrin through two dodecyl-thiophene residues.

oligomeric 3-hexylthiophenes terminated by zwitterionic ruthenium dyes[13] or porphyrin substituted by oligomeric 3-hexyl thiophenes[14] and 3-hexylthiophene oligomer domains and C_{60}.[15]

Retro Synthetic Analysis of the Target Molecule. One of the major goals of the present work is to show that even very complex and unsymmetrical conjugated molecules can be prepared using a convergent strategy where smaller domains are synthesized first and then connected through a few reactions to give the target molecule. Similar approaches have of course been used in other areas to prepare, for example, proteins *de novo*. The first logical disconnection of **1** is at the ruthenium complex. Reasonable methods have been developed to prepare unsymmetrically substituted bisterpyridine complexes of ruthenium(II). The target **1** can thus be split up in two unequal parts: the larger "west" composed of the oligothiophene connected to the zinc porphyrin substituted terpyridine, and the "east" terpyridine connected oligophenylenevinylene group. Until this final step, the intermediate molecules are neutral and soluble in standard organic solvents and therefore reasonably easy to purify by various chromatographic methods. An analysis of the chemistry needed for the construction of the eastern and western parts is described below.

The Western Part. Analysis of the more complicated western part indicated a logical set of disconnections into three domains as shown in Chart 2.

The most challenging domain in the western part was the zinc porphyrin moiety both because reasonably large amounts were needed and also because we wanted a porphyrin substituted differently and specifically in the 5 and 15 positions. Several options were investigated since many unsymmetrical porphyrins have been reported in the literature. Unfortunately, yields are usually rather low and in most cases the acid catalyzed porphyrin ring formation is also reversible until the oxidation step, resulting in an impure distribution of isomers and homologues.[16] A special case seems to be dibromo-bis(3,5-di(*tert*-butyl)phenyl)-porphyrin **4** previously prepared by Plater et al. that was reported to yield unsymmetrical porphyrins through sequential reactions at the two brominated positions.[17] This relatively insoluble compound is obtained from pyrrole via dipyrryl methane and 3,5-di(*tert*-butyl)benzaldehyde. Later it was found necessary to introduce two dodecylthiophene groups instead of the bromine atoms. These groups then became linkers to the octahexylthiophene and terpyridine domains. Regioregular octahexylthiophene has been prepared previously using either solid-phase techniques or solution chemistry.[18] We chose a modification of the solution strategy that relies on the different regioselectivity of bromination versus lithiation of 3-hexylthiophene. Bromination with NBS occurs preferably in the 2-position adjacent to the electron releasing alkyl group, whereas lithiation is directed to the 5-position. The lithio-thiophene can then react with an electrophile such as trimethyl tin chloride creating a 5-stannyl-thiophene that can be used in a Stille coupling with the 2-bromothiophene derivative. The result is a regioregular head-to-tail coupling of two thiophene moieties. Fortunately, this reaction scheme can be extended beyond the dimer to the higher oligomers. Other groups can be incorporated via the brominated or the trimethyltin thiophene species. In the present case, the dimethylaminophenyl group could be introduced in one end while the rest of the western part was attached in the other end using these handles. Finally, the terpyridine domain present in the western part could be prepared in a Kröhnke type reaction starting from a substituted benzaldehyde and 2-acetylpyridine.

The Eastern Part. We have previously developed a stepwise unidirectional synthesis of oligo-phenylene-vinylene type compounds,[11,12] and it was therefore reasonably straightforward to construct the eastern part (**3**) of **1** shown in Chart 3. This stepwise synthesis is based on stilbene type monomers with a methyl-phoshonate ester at one end and an acetal protected aldehyde functionality at the other. Each step begins with a Horner-Wadsworth-Emmons reaction between a terminal aldehyde of the oligomer and the phosphonate ester of the monomer. During acidic workup, the acetal is removed to expose a new aldehyde group ready for another step. As described earlier we have synthesized a number of different monomers and a slightly more evolved oligomer was therefore planned for the eastern part with most of the aromatic rings differently substituted to show the potential of this methodology. Finally, an electron accepting group was added at the terminal end of the molecule. For this purpose a cyano-methyl-benzoic ester was constructed that could be condensed with the terminal aldehyde of the oligomer in a Knoevenagel reaction.

(13) Krebs, F. C.; Biancardo, M. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 142−165.
(14) Krebs, F. C.; Spanggaard, H. *Sol. Energy Mater. Sol. Cells* **2005**, *88*, 363−375
(15) Narutaki, M.; Takimiya, K.; Otzubo, T.; Harima, Y.; Zhang, H.; Araki, Y.; Ito, O. *J. Org. Chem.* **2006**, *71*, 1761−1768.
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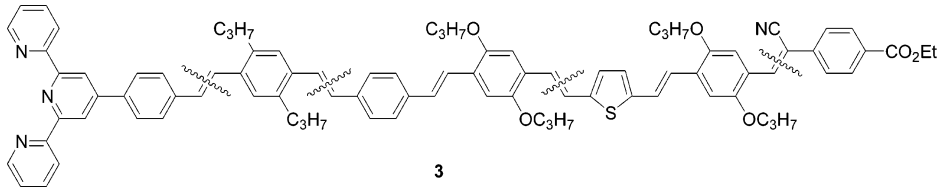
(17) Plater, M. J.; Aiken, S.; Bourhill, G. *Tetrahedron* **2002**, *58*, 2405−2413.
(18) Kirschbaum, T.; Bäuerle, P. *Synth. Met.* **2001**, *119*, 127−128.

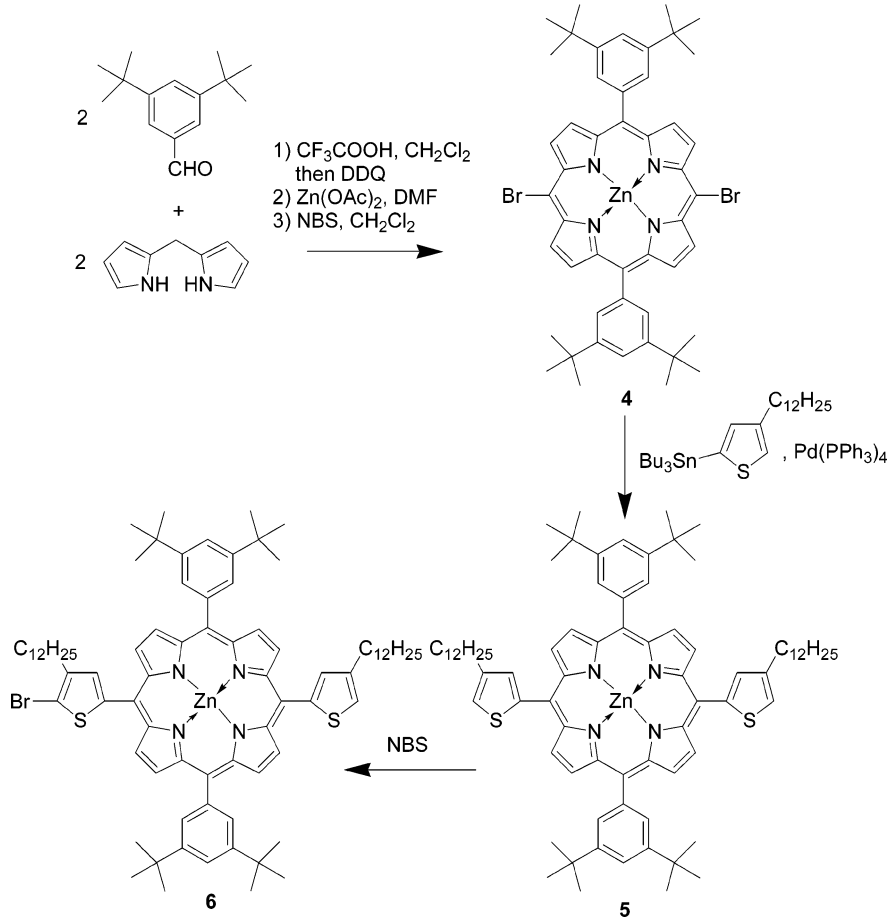
CHART 3. The Eastern Part (3)[a]



3

[a] The eastern part (**3**) of the target molecule **1** is an oligophenylenevinylene with each aromatic ring differently substituted and end-capped with a terpyridine ligand and a benzoic acid residue. Disconnections to smaller units are indicated with wavy lines.

SCHEME 1. Synthesis of the Unsymmetrical [5-(3-Dodecyl-5-bromo-thiophenyl),15-(3-dodecylthiophenyl)-10,20-bis-(3,5-bis-*tert*-butylphenyl)porphinato]zinc(II) 6



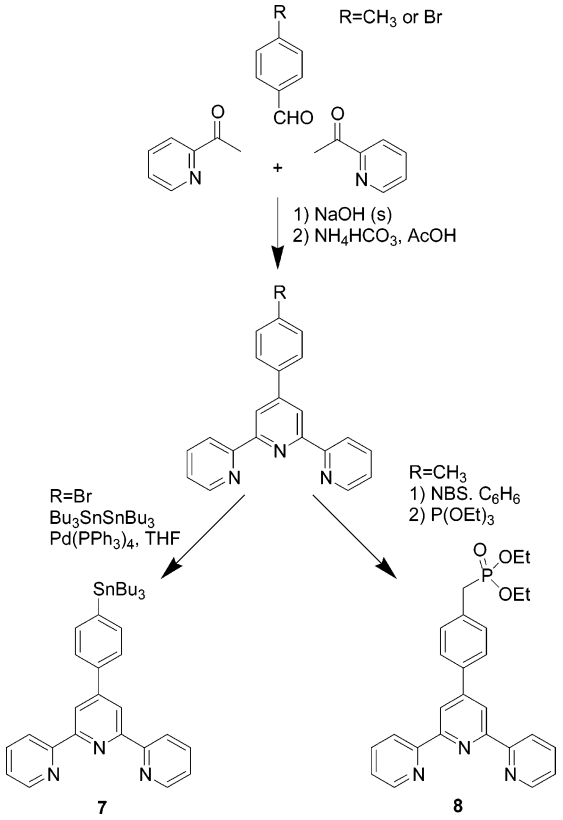
Results and Discussion

Synthesis of the Western Part 2. The key porphyrin [5,15-bis-bromo-10,20-bis-(3,5-bis-*tert*-butylphenyl)porphinato]-zinc-(II) (**4**) was prepared in nine steps, using the synthesis described by Plater et al., in a 100 g scale.[17]

The main reason for success in this case is probably because of the low solubility of the product compared to all the impurities. On the other hand, reactions involving the two bromine atoms in **4** were very sluggish. Several attempts of Suzuki type couplings with arylboronic acids and even Stille type reactions with trialkyl arylstannanes failed. The original article describes the palladium(0) and copper(I) catalyzed Sonogashira reaction with trimethylsilyacetylene which gave the bisacetylene porphyrin in excellent yield over 16 h. The low reactivity seen here can perhaps be ascribed to sterical hindrance, though this is not immediately obvious from the structure. Finally a solution to the problem was found. Stille type coupling with 4-alkyl-2-trimethylstannyl-thiophenes gave bis(4-alkyl-thienyl)-porphyrins, like **5**, where the 5-positions on the thiophene moieties adjacent to the alkyl groups were sufficiently reactive for further functionalizations. Three different alkyl thiophene tin reagents were tested with the hexyl and octyl variants still being too insoluble to allow chromatographic cleanup. Ultimately, dodecylthiophene groups were found to impart enough solubility for this purpose. The next step was to find a practical way of obtaining an unsymmetrical halogenated derivative that could be coupled to the terpyridine ligand on one side and to the octahexylthiophene on the other in a Stille reaction. Bromination, using 1 equiv of NBS, at 5-positions of the two pendant thiophenes proceeded to give a mixture of the starting material **5** and the monobrominated product **6** (Scheme 1) (70%) that was used directly in the next step.

Synthesis of the terpyridine ligands needed in both the eastern and western parts were carried out using the method of Cave

SCHEME 2. Synthesis of 4-Tributyltinphenyl-terpyridine 7 and (4-[2,2′;6′,2″]Terpyridin-4′-yl-benzyl)-phosphonic Acid Diethyl Ester 8



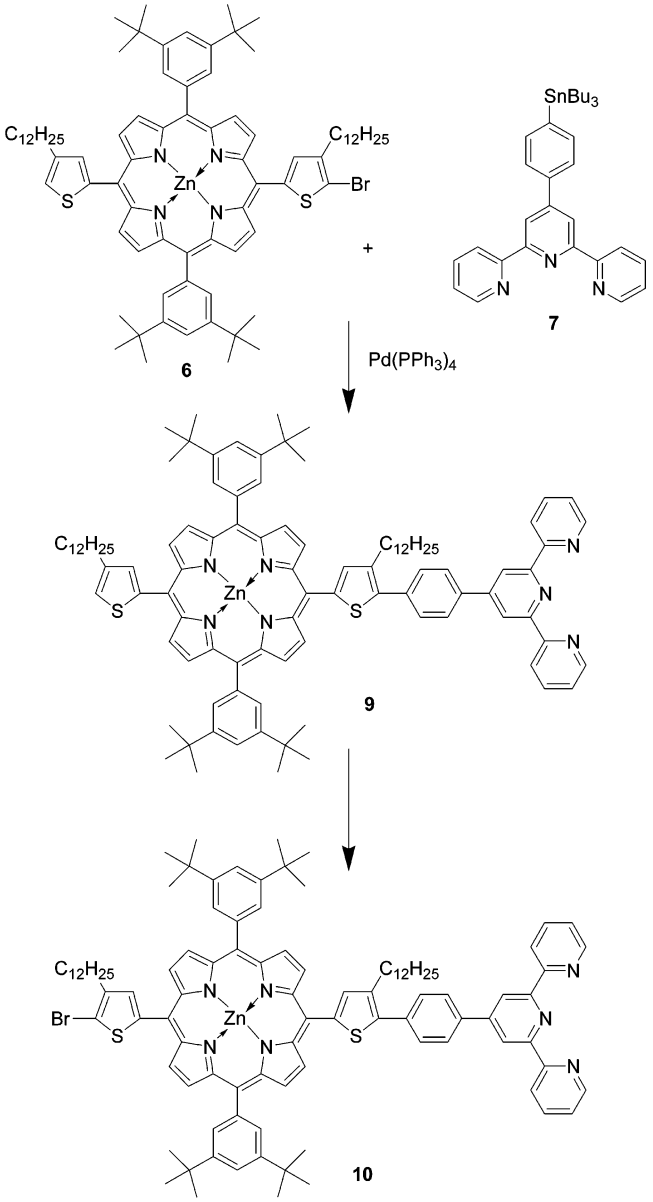
and Raston[19] where 1 equiv of a substituted benzaldehyde and 2 equiv of 2-acetyl-pyridine were ground together with sodium hydroxide in a mortar. The intermediate was reacted with an ammonium salt in hot acetic acid to form the 4-aryl-terpyridines as shown in Scheme 2.

The tributyltin group was introduced by a palladium(0) catalyzed reaction of 4-bromophenyl-terpyridine with excess bis-(tributyltin).[13] Bromination of 4-tolyl-terpyridine with NBS in benzene followed by reaction with triethyl phosphite to give the terpyridine phosphonate ester reagent has already been described.[12,20,3]

Stille coupling of **6** and **7** proceeded to give the porphyrin-terpyridine adduct **9**. Bromination on the remaining thiophene unit on the other side of the molecule gave compound **10** as shown in Scheme 3.

The final domain in the western part **2** was the dimethylaminophenyl end-capped octahexylthiophene which was constructed from 3-hexyl-thiophene in fourteen steps. Controlled lithiation of 3-hexylthiophene with LDA followed by reaction with trimethyltin chloride gave 2-trimethylstannyl-4-hexyl-thiophene (**11**),[21] while bromination of 3-hexylthiophene with NBS gave 2-bromo-3-hexyl-thiophene (**12**).[22] Stille coupling of these two compounds yielded dihexyl-dithiophene (**13**)[23] mainly as the

SCHEME 3. Synthesis of the Bromothiophenyl and Terpyridine Substituted Porphyrin 10



head-to-tail isomer. Some homo coupling of the stannane **11** occurs resulting in contamination with the head-to-head dimer. The regioregularity of all the subsequent compounds in this domain depended on the purity of **13**, and it was therefore carefully redistilled a number of times using a jacketed and silvered column packed with Teflon Raschig rings. Very careful and slow distillation taking a conservatively cut middle fraction gave a sufficiently pure product. This was divided in two portions and subjected to stannylation and bromination to give the mono-trimethylstannyl-dithiophene **14** and the monobromo-dithiophene **15**. Part of the monobromo compound **15** was combined with **14** in a Stille reaction to obtain the tetrahexyl-tetrathiophene **16**.[14] Another part monobromo-dithiophene **15** was coupled together with 4-dimethylaminophenyl boronic acid in a Suzuki reaction to give the end-capped dithiophene **17**. Lithiation of **17** followed by reaction with trimethyltin chloride

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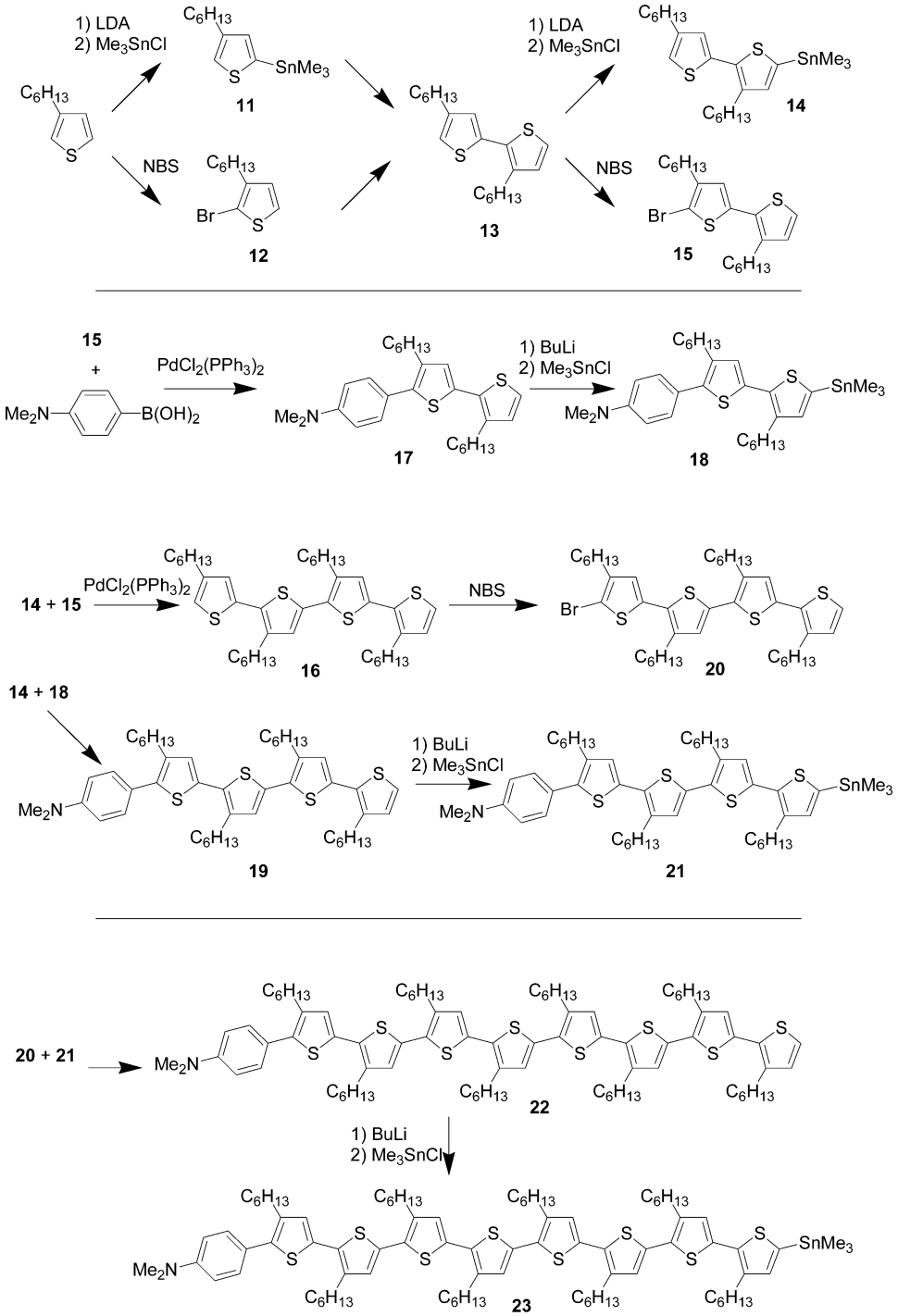
(21) Malenefent, P. R. L.; Groenendaal, L.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1998**, *120*, 10990−10991.

(22) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904−912.

(23) Kirschbaum, T.; Briehn, C. A.; Bäuerle, P. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1211−1216.

SCHEME 4. Synthesis of the Dimethylaminophenyl End-Capped Octahexyl-octathiophene Trimethylstannane 23



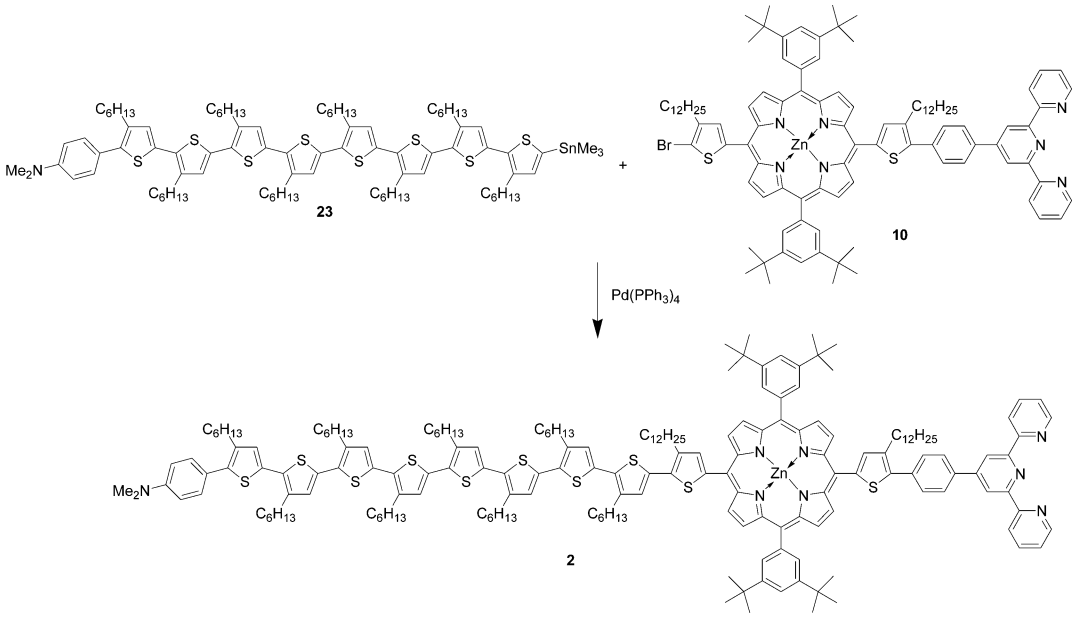
gave the end-capped dithienylstannane **18** needed for a Stille coupling with **15** to give the end-capped quaterthiophene **19**. Quarterthiophene **16** was selectively monobrominated to the bromo-quaterthiophene **20**. The end-capped quaterthiophene **19** was stannylated to give compound **21** and finally condensed with **20** in a Stille reaction to form the dimethylaminophenyl end-capped octameric thiophene **22**. Compound **22** was lithiated and reacted with trimethyltin chloride to give the stannylated derivative **23** as shown in Scheme 4.

Compound **22** is analogous to regioregular poly-3-hexylthiophene which is one of the most commonly used materials used as the active compound in organic solar cells.[24] Stille coupling of compound **23** with the bromothiophene part of the porphyrin **10** afforded the western part (**2**) of **1** as shown in Scheme 5. In all, construction of the western part **2** required thirty steps from commercially available materials.

Synthesis of the Eastern Part 3. The preparation of the eastern part **3** (shown in Scheme 6) was based on the stepwise unidirectional synthesis developed earlier.[11,12] That approach depends on the availability of different monomer units of substituted stilbenes with a protected aldehyde functionality and

(24) Loewe, R. S.; McCullough, R. D. *Chem. Mater.* **2000**, *12*, 3214−3221.

SCHEME 5. Final Assembly of the Western Part 2



a benzylic phosphonate ester group. In the first step, (4-[2,2′;6′,2″]terpyridin-4′-yl-benzyl)-phosphonic acid diethyl ester **8** was coupled with 4-(5,5-dimethyl-[1,3]dioxan-2-yl)-2,5-dipropyl-benzaldehyde **24**[12] in a HWE reaction followed by deprotection of the acetal function to give the stilbene terpyridine derivative **25**. Two more stilbene units were added using monomers **26** and **27** previously prepared in the same methodology to give the hetero oligophenylenevinylenes **28** and **29** with a terpyridine in one end and an aldehyde function in the other. This terminal aldehyde was utilized in a Knoevenagel condensation with 4-cyanomethyl-benzoic acid ethyl ester[25] **30**. This end group was added both because of its electron accepting ability and also because the ester function might be hydrolyzed at a later stage. A carboxylic acid placed at the end might serve as an anchoring point to an electrode surface or even as a hydrophilic group enabling film formation.

In all, twenty-six synthetic steps were carried out for this part of the target molecule from commercially available starting materials. Many of these went into the construction of the monomeric stilbenes and have been described previously and are therefore not shown in Scheme 6. It also illustrates how complicated conjugated systems can be constructed fairly easily in a modular and convergent strategy once the building blocks have been acquired.

Final Assembly of the Target Molecule 1 at the Ruthenium Complex. The assembly of the target molecule **1** at the bisterpyridine ruthenium(II) complex was first attempted using the method developed by Collin et al.[3] A terpyridine ruthenium-(III) trichloride complex is formed rapidly by mixing hydrated ruthenium trichloride with the eastern part **3** in a 1:1 molar ratio to give the **3**−Ru(III) trichloride complex as a very insoluble black compound. Characterization was limited to mass spectroscopy (MALDI-TOF) with **3**−Ru(III) dichloride as the dominant peak in the spectrum. An excess of this intermediate had to be used in the following reaction with **2**, but even then the reaction was incomplete. Analysis by MALDI-TOF also indicated that some scrambling occurred with the formation of symmetrical complexes of **3**−Ru−**3** and of **2**−Ru−**2**. Several variations of the reaction conditions were studied with different choice of solvents and temperatures. Intractable mixtures that could not be separated by chromatography were invariably produced and another approach was sought. One alternative procedure that has not received much attention is to use the well characterized cymene−ruthenium(II) dichloride complex, $[\{(\eta^6\text{-cymene})\text{Ru}(\mu\text{Cl})\}_2\text{Cl}_2]$.[26] This complex is readily soluble in organic solvents and the weakly bound cymene ligand is easily substituted. Furthermore, since it is already a Ru(II) complex it does not require a reduction step limiting the number of possible products. It was found that the overnight reaction of cymene−ruthenium(II) dichloride and terpyridine **3** in 1,2-dichlorobenzene gave the complex **3**−Ru(II) dichloride as shown by MALDI-TOF.

Addition of 1 equiv of **2** and heating the mixture to reflux for 3 h gave a mixture of products, but with the **2**−Ru(II)−**3** (**1**) as the major component. Much work was then invested in purifying the product. Thin-layer chromatography (TLC) using silica plates pretreated with potassium hexafluorophosphate initially seemed quite promising as shown in Figure S3 (Supporting Information). A mixed eluent system with a solution of potassium hexafluorophosphate in methanol−THF was found to separate the mixture and the individual spots were cut out, extracted and analyzed with MALDI-TOF to prove the identity of the compounds. Preparative TLC was investigated as a means of obtaining larger amounts for characterization by NMR, but it was not feasible to separate more than a few milligrams that were further contaminated by the eluent containing potassium hexafluorophosphate. Similar difficulties were encountered using both flash chromatography and HPLC where many eluent systems were tried. Small samples in the range of a few milligrams were obtained and analyzed by MALDI-TOF MS. The isotope distribution in the molecular ion ($C_{278}H_{326}N_{12}O_6$-

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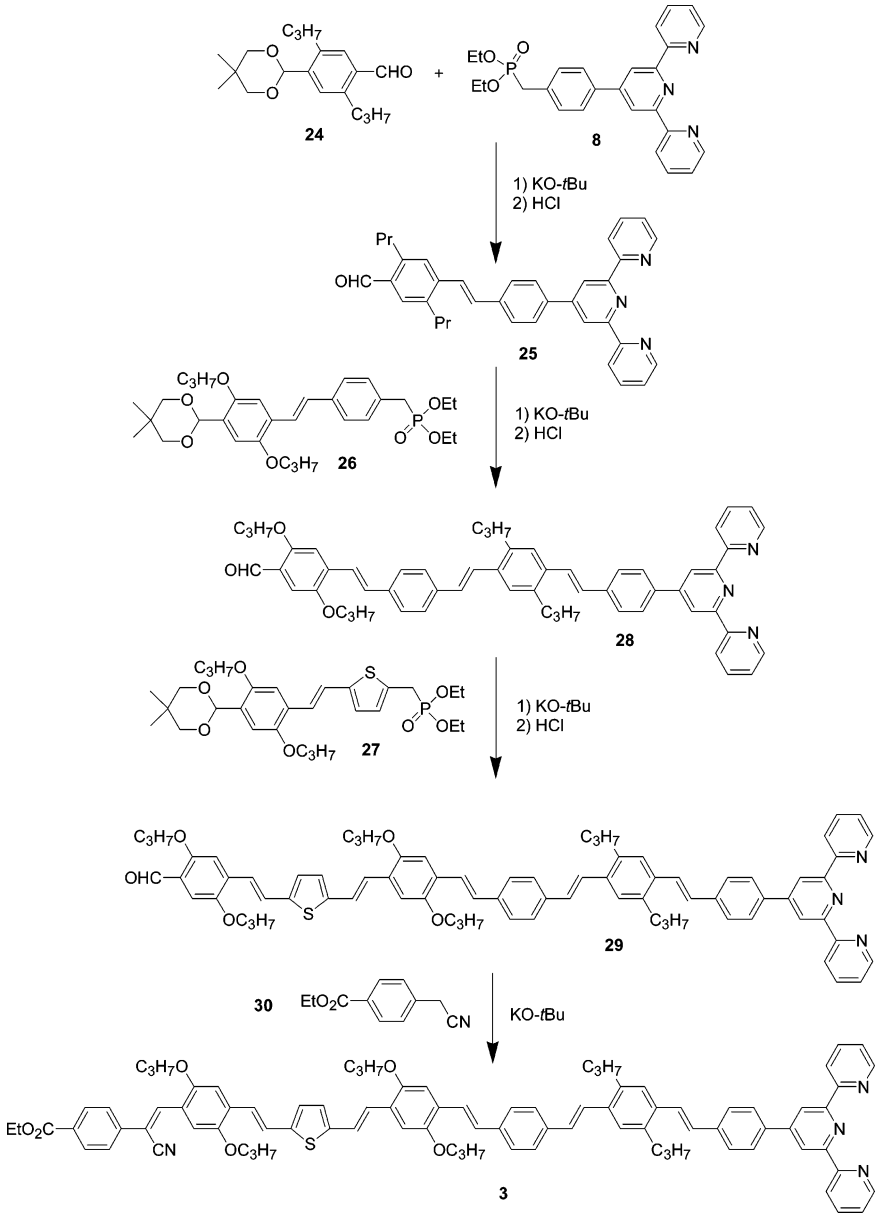
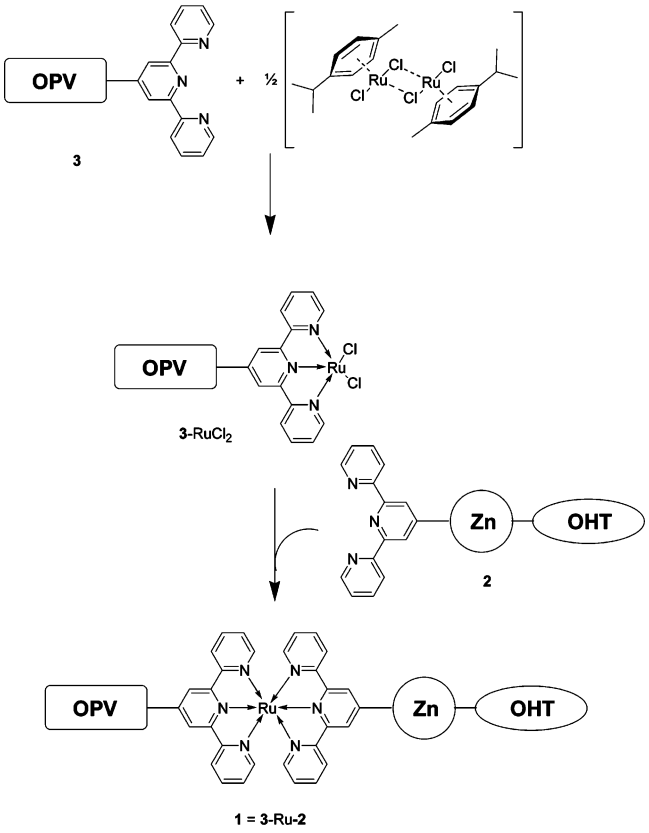
SCHEME 6. Synthesis of the Terpyridine Substituted Hetero Oligo Phenylenevinylene Eastern Part 3



$RuS_{11}Zn$) without counterions is centered around 4450 *m*/*z* as shown in figure S4 (Supporting Information).

Characterization of the Eastern and Western Parts with NMR. The proton NMR spectra of the final building blocks **2** and **3** are complicated by many overlapping signals, but some significant features are clearly seen. In the spectrum of the western part (**2**) (Figure 1 top) two sets of AB signals occur at 9.1 and 9.4 ppm that are due to the porphyrin ring protons. The C_{2v} symmetry of the porphyrin is broken by the two different substituents in the 5 and 15- positions, and this is clearly seen in the splitting of the signal at 9.4 ppm. A characteristic group of signals with a singlet at 8.9 ppm and two doublets at 8.70−8.76 ppm originates from the terpyridine group. The singlet at 8.9 ppm is due to the two protons on the central pyridine ring, while the doublets are part of the AA′XX′ systems on the other two pyridine rings. The protons on the thiophenes of the regioregular octahexylthiophene group fall in the multiplet centered at 7 ppm. Signals at 8.1 ppm and a multiplet at 7.9 ppm originate from the meta coupled aromatic protons on the two *tert*-butyl phenyl groups. It is not as easy to correlate the spectrum of the eastern part (**3**) with specific groups because of a more extensive overlap of signals. A group consisting of a singlet at 8.79 ppm and two doublets at 8.69 and 8.76 ppm stands out and is due to the terpyridine moiety. In the aliphatic part of the spectrum of **3** (not shown) a triplet at 1.42 ppm and a quartet at 4.42 ppm are attributed to the terminal ethyl ester group. A multiplet centered at 4.1 ppm is due to the oxymethylene groups in the four propoxy groups and the multiplet at 2.8 ppm is due to the aryl-methylene groups of the two propyl groups. While it is not possible to make a rigorous assignment of all NMR signals because of many overlapping regions, distinct signals from all the domains in each of the molecules could be identified. It was much more difficult to obtain a proton NMR of the target molecule **1** partly because only very limited amounts could be produced and also because the final proton spectrum, accumulated over 50 h, showed rather broad signals. This may be due to several factors. The large size and molecular weight together with increased viscosity of the solution decrease

SCHEME 7. Assembly of the Target Molecule through the Ruthenium(II) Complex in a Sequential Reaction between 3 and [Cymene-$RuCl_2$]$_2$ Followed by 2[a]



[a] All in *o*-dichlorobenzene.

the tumbling rate. A small impurity of paramagnetic ruthenium(III) species cannot be excluded either. Little information could therefore be obtained from the NMR spectrum, though broad signals at 9.5 and 9 ppm originating from the porphyrin structure could be discerned.

UV−Visible Spectroscopy. Electronic spectra of some of the domains as well as of the final target molecule in tetrahydrofurane were obtained and are shown in Figure 2 The dimethylaminophenyl terminated octa(3-hexylthiophene) **22** has a broad maximum at 429 nm which is typical of oligothiophenes in solution. The eastern part **3** consisting of an oligo phenylenevinylene terminated with a terpyridine at one end and a cyanovinylenebenzoic ester residue at the other have three maxima at 386, 430, and 481 nm. Complexation with ruthenium(II) dichloride broadened the spectrum slightly so that only the highest maximum at ca. 480 nm is retained. The spectrum of the terpyridine terminated zinc porphyrin **10** is dominated by the typical intense and narrow Soret band at 430 nm with two smaller Q-bands at 561 and 608 nm. When these chromophores are combined in the target molecule **1**, a spectrum with all these features is obtained. It is still dominated by the Soret band shifted slightly to 432 nm and broadened because of an underlying absorption band of the octathiophene moiety. A shoulder at ~480 nm is obviously due to the eastern part, and two smaller peaks from the Q-bands of the porphyrin can be recognized.

Photovoltaic Studies. The ultimate test of the all-in-one molecule was the action as a photovoltaic material in a device. Such a test is by nature comparative since the photovoltaic

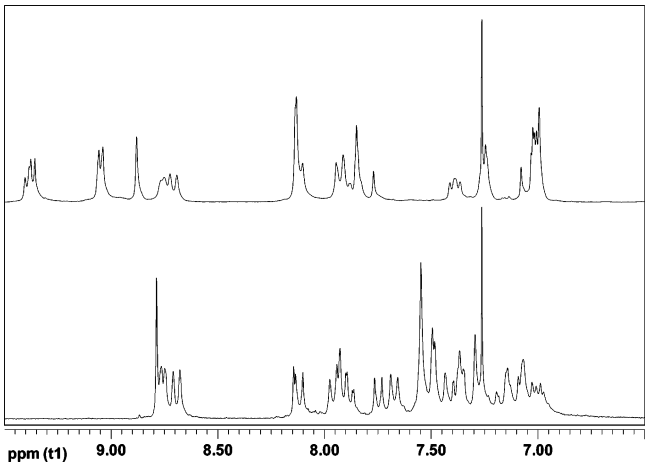


FIGURE 1. The aromatic region of the 1H NMR spectra of the western part (**2**) (top) and of the eastern part (**3**) (bottom).

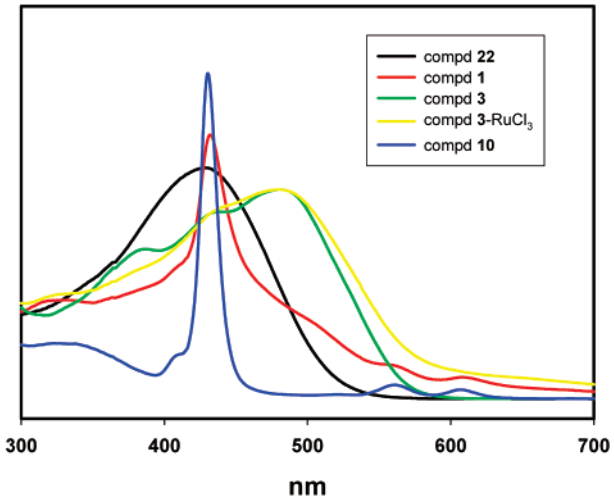


FIGURE 2. Absorption spectra of some of the domains in THF solution together with the target molecule **1**. The vertical scale is in arbitrary units.

measurement is a bulk measurement and therefore molecular organization and morphology become determining factors for the efficiency with which the system converts sunlight into electrical energy. The success of polymer photovoltaics in the current state of the art relies on the concept of a bulk heterojunction where two materials are mixed and provide separate conduction paths for holes and electrons through an interpenetrating network morphology. The success for this system is granted by the spontaneous (and fortuitous) phase separation during solution processing of the mixture into solid films. In the context of this work, the organization of an all-in-one molecule is a challenge beyond the scope of this work while the molecular structure has been designed to accommodate different conduction paths and end groups allowing for molecular organization using, for example, the Langmuir−Blodgett technique or layer-by-layer deposition. The photovoltaic studies reported amount to a bulk measurement of spin-coated films. The active area of the devices was 3 cm^2 giving a realistic picture of large area device performance. As a comparative measure, we chose to prepare devices with a byproduct from the synthesis of compound **1** as depicted in chart **2**.

Photovoltaic studies on a reference oligo-3-hexylthiophene employing a simple geometry where a thin film was sandwiched

between ITO/PEDOT:PSS and aluminum electrodes gave photovoltaic parameters expected for a homopolymer device. Values of 0.7 V, 0.046 mA cm^{-2}, 24.6%, and 0.0081% were obtained for the open circuit voltage, V_{oc}, short circuit current, I_{sc}, fill factor, FF, and efficiency, η. The device exhibited weak dark rectification with a rectification ratio of 7 @ |±1 V|. The absorption spectrum of the solid film exhibited vibronic fine structure, and the optical absorption extended up to above 600 nm giving an optical band gap of ~2 eV. The material is from this point of view similar to poly-3-hexylthiophene as expected. The action spectrum[27] was symbatic with the absorption spectrum. A bulk heterojunction device formed between the oligomeric 3-hexylthiophene and PCBM 1:1 (w/w) gave expected improvements in the photovoltaic performance with a decrease in the open circuit voltage. Values of 0.43 V, 0.45 mA cm^{-2}, 33.5%, and 0.063% were obtained for the open circuit voltage, V_{oc}, short circuit current, I_{sc}, fill factor, FF, and efficiency, η. Good dark rectification of 121 @ |±1 V| was obtained, and an action spectrum that was symbatic with the absorption spectrum was also observed (see Supporting Information).

In contrast to the traditional properties observed for oligomeric 3-hexylthiophene, the photovoltaic responses for compound **1** were much poorer. Values of 0.18 V, 0.0044 mA cm^{-2}, 29%, and 0.000081% were obtained for the open circuit voltage, V_{oc}, short circuit current, I_{sc}, fill factor, FF, and efficiency, η. No dark rectification was observed. The action spectrum was symbatic with the absorption spectrum (see Supporting Information). These values are much poorer than the pure homopolymer device, and there are many possible explanations for this. We assume that the poorer performance is linked to the properties of the molecule and thus neglect experimental error connected to the device geometry, device preparation, and impurities in the material. It has been observed earlier that the incorporation of porphyrin systems on their own into the backbone of an oligothiophene[14] leads to poorer photovoltaic performance because of efficient energy transfer to the porphyrin moiety and internal conversion.[27] When the performance of compound **1** is compared to that of the reference oligomer, it is clear that the energy is not converted into charge carriers in an external circuit while the device geometry is the same. The conclusion from the present experiments is thus that compound **1** efficiently converts the energy internally and is inefficient at generating and separating charge carriers. While charge carrier generation could be successful with the absence of efficient carrier transport channels, the earlier data[14,28] and the present experiments with the reference oligomer of 3-hexylthiophene are against this argument.

A possible modification of the target molecule **1,** which was suggested by a referee, would be to omit the porphyrin moiety. Charge separation could in principle arise through the MLCT transition followed by migration of the electron and hole into different pendant oligomers. Such a system has already been prepared and evaluated as an active material in solar cells.[29] Efficient energy transfer from the conjugated polymers to the terpyridine ruthenium complex was observed and a higher efficiency of about 0.1% for the solar cell was found. This is clearly better than in the present case, but still far from optimal and in the same range as that of a simple poly-phenylenevinylene based solar cell.

Conclusion

Most active materials for organic solar cells today are based on simple polymers such as the poly phenylenevinylenes (PPVs), poly 3-hexylthiophene (P3HT) and used in bulk heterojunction devices with the good electron acceptor PCBM. Many of the important functions such as the carrier generation and separation rely on the polymer/PCBM interface, while the electron and hole transport depends on the ordering of the material into a bicontinuous network type structure. Another approach that we have tried here is to pack all the photophysical and electronic functionalities necessary for a solar cell into one molecule. As described earlier much inspiration came from the large amount of work done by the groups of J.-P. Sauvage and J.-P. Collin on dyadic molecules with a zinc porphyrin and a bisterpyridine ruthenium(II) complex linked together. This unit is very efficient at transforming the excited state to a charge separated one. A logical step forward in creating an all-in-one molecule for organic solar cells presented here was to add conjugated oligomers suited for transport of the electron and the hole. This was realized with a dimethylaminophenyl terminated octahexylthiophene domain linked to the zinc porphyrin via a dodecylthiophene unit and a cyanovinyl benzoic ester terminated hetero oligophenylenevinylene linked to one of the terpyridine moieties of the ruthenium(II) complex. One of the deficiencies of the molecule **1** is that it lacks a good electron transporting domain. In our view, convincing candidates for organic electron transporting oligomers or polymers have not been presented in the literature, except for C_{60}. The electron−hole pair generated is therefore not automatically separated onto the different pendant arms of the molecule. Most of the driving force for this separation normally arises at the heterojunction and electrode interfaces.

Photovoltaic devices were constructed from the target molecule **1** and compared with devices made from oligomeric 3-hexylthiophene. The performance in terms of converting light into electricity is very poor with a short circuit current (I_{sc}) of 4.4 μA cm^{-2} and efficiency (η) of 0.000081%. This is 100 times less efficient than the device based on the reference 3-hexylthiophene oligomer and more than a 1000 times worse than that of the bulk heterojunction of reference oligomer and PCBM. There could be several reasons for this failure. First of all, if efficient charge separation occurs in **1** then the subsequent charge transport between molecules may depend heavily on their orientation with respect to each other. This issue could be tested by preparing devices with the molecules of **1** in an ordered monolayer. The dimethylamino and carboxylic acid end groups have already been included in **1** that could be used to make Langmuir−Blodgett films. Further work along this route is however a study in itself. Another even more serious deficiency of the target molecule may lie with the choice of the zinc porphyrin moiety. Several photovoltaic studies with compounds including this group have now shown very low light-to-electricity efficiency. In one case the efficiency versus wavelength plot was antibatic in the region of the porphyrin absorption. One explanation may be that the zinc porphyrin moiety is very efficient in nonradiative conversion of the excited (or charge separated) state competing with the charge transport. So while the well studied porphyrin−ruthenium(II) complex

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dyad is very efficient at transforming the excitation into a long-lived MLCT mediated charge separated state, it may not be possible to utilize this in a practical device.

Experimental Section

General. 2-Trimethylstannyl-4-hexylthiophene (**11**) was prepared as described in ref 14, 2-bromo-3-hexylthiophene (**12**) was prepared as described in ref 22, 3,4′-dihexyl-[2,2′]bithiophene (**13**) was prepared as described in ref 14, 5′-bromo-3,4′-dihexyl-[2,2′]-bithiophene (**15**), 5-trimethylstannyl-3,4′-dihexyl-[2,2′]bithiophene (**14**), 3,4′,4″,4‴-tetrahexyl-[2,2′;5′,2″;5″,2‴]quarterthiophene (**16**), and 5‴-bromo-3,4′,4″,4‴-tetrahexyl-[2,2′;5′,2″;5″,2‴]quarterthiophene (**20**) were prepared as described in ref 14. The regioselective lithiation of [4-(4,3′-dihexyl-[2,2′]bithiophenyl-5-yl)-phenyl]-dimethyl-amine (**17**), dimethyl-[4-(4,3′,3″,3‴-tetrahexyl-[2,2′;5′,2″;5″,2‴]quaterthiophen-5-yl)-phenyl]-amine (**19**), and dimethyl-[4-(4,3′,3″,3‴,3⁗,3⁗′,3⁗″,3⁗‴,3⁗⁗′-octahexyl-[2,2′;5′,2″;5″,2‴;5⁗,2⁗′;5⁗″,2⁗‴;5⁗⁗,2⁗⁗′;5⁗⁗″,2⁗⁗‴]- octithiophen-5-yl)-phenyl]-amine (**22**) and subsequent reaction with trimethylstannyl chloride to give respectively [4-(4,3′-dihexyl-5′-trimethylstannanyl-[2,2′]bithiophenyl-5-yl)-phenyl]-dimethyl-amine (**18**), dimethyl-[4-(4,3′,3″,3‴-tetrahexyl-5‴-trimethylstannanyl-[2,2′;5′,2″;5″,2‴]quaterthiophen-5-yl)-phenyl]-amine (**21**), and dimethyl-[4-(4,3′,3″,3‴,3⁗,3⁗′,3⁗″,3⁗‴,3⁗⁗′-octahexyl-5⁗⁗⁗-trimethylstannanyl-[2,2′;5′,2″;5″,2‴;5⁗,2⁗′;5⁗″,2⁗‴;5⁗‴,2⁗⁗′;5⁗⁗,2⁗⁗″]-octithiophen-5-yl)-phenyl]-amine (**23**) was performed by a method similar to the one described in ref 14, and the freshly prepared tin reagent solutions were used directly to prepare compounds dimethyl-[4-(4,3′,3″,3‴-tetrahexyl-[2,2′;5′,2″;5″,2‴]quaterthiophen-5-yl)-phenyl]-amine (**19**), dimethyl-[4-(4,3′,3″,3‴,3⁗,3⁗′,3⁗″,3⁗‴,3⁗⁗′-octahexyl-[2,2′;5′,2″;5″,2‴;5⁗,2⁗′;5⁗″,2⁗‴;5⁗‴,2⁗⁗′;5⁗⁗,2⁗⁗″]-octithiophen-5-yl)-phenyl]-amine (**22**), and 5-(5-{dimethyl-[4-(4,3′,3″,3‴,3⁗,3⁗′,3⁗″,3⁗‴,3⁗⁗′-octahexyl-[2,2′;5′,2″;5″,2‴;5⁗,2⁗′;5⁗″,2⁗‴;5⁗‴,2⁗⁗′;5⁗⁗,2⁗⁗″]-octithiophen-5-yl)-phenyl]-amine-5⁗⁗⁗-yl}-4-dodecyl-thiophen-2-yl)-10,20-bis-(3,5-di-*tert*-butyl-phenyl)-15-[4-dodecyl-5-(4-[2,2′;6′,2″]terpyridin-4′-yl-phenyl)-thiophen-2-yl]porphinato-zinc(II) (**2**). 1,4-Dipropylbenzene, 2,5-dipropyl-1,4-dibromobenzene, 2,5-dipropyl-4-formyl-1-bromobenzene, 2,5-dipropyl-4-(5,5-dimethyl-1,3-dioxan-2-yl)-1-bromobenzene, 2,5-dipropyl-4-(5,5-dimethyl-1,3-dioxan-2-yl)benzaldehyde, 4-diethylphosphonomethylstyrene, 1,4-dipropoxybenzene, 2,5-dipropoxy-1,4-dibromobenzene, 2,5-dipropoxy-4-formyl-1-bromobenzene, 2,5-dipropoxy-4-(5,5-dimethyl-1,3-dioxan-2-yl)-1-bromobenzene, 2,5-dipropoxy-4-(5,5-dimethyl-1,3-dioxan-2-yl)benzaldehyde, 2-[2,5-dipropoxy-4-(2-thiophen-2-yl-vinyl)-phenyl]-5,5-dimethyl-[1,3]dioxane, 5-{2-[4-(5,5-dimethyl-[1,3]dioxan-2-yl)-2,5-dipropoxy-phenyl]-vinyl}-thiophene-2-carbaldehyde, thiophen-2-ylmethyl-phosphonic acid diethyl ester, {4-[2-(4-formyl-2,5-dipropoxy-phenyl)-vinyl]-benzyl}-phosphonic acid diethyl ester, (4-{2-[4-(5,5-dimethyl-[1,3]dioxan-2-yl)-2,5-dipropoxy-phenyl]-vinyl}-benzyl)-phosphonic acid diethylester (**26**), and (5-{2-[4-(5,5-dimethyl-[1,3]dioxan-2-yl)-2,5-dipropoxy-phenyl]-vinyl}-thiophen-2-ylmethyl)-phosphonic acid diethyl ester (**27**) were prepared as described in ref 11 and ref 12. 4′-Tolyl-[2,2′;6′,2″]terpyridine, 4′-(4-bromomethyl-phenyl)-[2,2′;6′,2″]terpyridine, and (4-[2,2′;6′,2″]-terpyridin-4′-yl-benzyl)-phosphonic acid diethyl ester (**8**) were described in ref 12. 4-Bromomethylbenzoic acid ethylester and 4-cyanomethylbenzoic acid ethylester (**30**) were prepared as described in ref 25. 3,5-Ditertbutyltoluene, 3,5-ditertbutylbenzylbromide, 3,5-ditertbutylbenzaldehyde, 2,2′-dipyrrylthione, 2,2′-dipyrryl ketone, 2,2′-dipyrrylmethane, 5,15-bis-(3,5-ditertbutylphenyl)-porphyrin, 5,15-bis-(3,5-ditertbutylphenyl)porphinato-zinc(II) and 5,15-dibromo-10,20-bis-(3,5-ditertbutylphenyl)porphinato-zinc-(II) (**4**) were prepared as described in ref 17. 3-Dodecylthiophene was prepared as described in ref 30, 2-trimethylstannyl-4-dodecylthiophene was prepared as described in ref 31, 5-(5-Bromo-4-dodecyl-thiophen-2-yl)-10,20-bis-(3,5-di-*tert*-butyl-phenyl)-15-(4-dodecyl-thiophen-2-yl)porphinato-zinc(II) (**5**) was prepared in-situ and 4′-(4-bromophenyl)-[2,2′:6′,2″]terpyridine (**7**) was prepared as described in ref 32.

[4-(4,3′-Dihexyl-[2,2′]bithiophenyl-5-yl)-phenyl]-dimethyl-amine (17). Compound **15** (50 mmol), dimethylaminophenylboronic acid (9 g, excess), $(PPh_3)_2PdCl_2$ (300 mg, catalyst), K_2CO_3 (30 g, excess), toluene (100 mL), and water (200 mL) were mixed and degassed with argon. The mixture was heated to reflux for 16 h and then poured into water and extracted with toluene. The toluene phase was washed with water, dried, and evaporated. The product was dissolved in hexane and passed through a column (6 cm × 10 cm Ø), washing with hexane (5 L) to remove unreacted **15**, and finally the yellow product was liberated with ether. The crude product was mixed with HCl(aq) concentrated, and the aqueous phase was washed with petrol. The aqueous phase was then made basic and extracted with ether. Drying and evaporation gave a mixture of the product and 4-dimethylaminophenol. The mixture was distilled on a Kugelrohr apparatus at 150 °C/2 × 10^{-3} mBar to remove the phenol. The remaining oil was pure compound **17**. Yield: 4.5 g (20%). ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 0.85−0.92 (m, 6H), 1.20−1.42 (m, 12H), 1.62−1.78 (m, 4H), 2.64 (t, 2H, J = 8 Hz), 2.76 (t, 2H, J = 8 Hz), 3.01 (s, 6H), 6.78 (d, 2H, J = 9 Hz), 6.91 (d, 1H, J = 5 Hz), 6.97 (s, 1H), 7.13 (d, 1H, J = 5 Hz), 7.35 (d, 2H, J = 9 Hz). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 14.0, 22.6, 28.8, 29.2, 29.3, 30.7, 30.9, 31.7, 40.5, 112.2, 122.9, 128.2, 129.9, 130.0, 131.2, 132.9, 137.7, 138.5, 138.9, 149.7. MS: m/z 453.25184; calcd for $C_{28}H_{39}NS_2$ (M+), 453.2500 (deviation 3.97 ppm). Anal. Calcd for $C_{28}H_{39}NS_2$: C, 74.12; H, 8.66; N, 3.09. Found: C, 74.51; H, 8.81; N, 3.25.

Dimethyl-[4-(4,3′,3″,3‴-tetrahexyl-[2,2′;5′,2″;5″,2‴]quaterthiophen-5-yl)-phenyl]-amine (19). Compound **17** (4.1 g, 9 mmol) was added to a solution of diisopropylamine (0.9 g, 9 mmol) in dry THF (200 mL) containing *n*-BuLi (10 mL, 0.88M, 9 mmol) at −78 °C. The mixture was left to heat up to −10 °C for 1 h and then cooled to −78 °C. Trimethylstannyl chloride (1.9 g, excess) was added, and the mixture was allowed to reach room temperature. The solution of **18** thus obtained was mixed directly with a solution of **15** (9 mmol in DMF, argon degassed) and $(PPh_3)_2PdCl_2$ (300 mg, catalyst) and heated to gentle reflux for 48 h. The mixture was evaporated, and the oil was mixed with water and hexane. The organic phase was washed with water once, dried, and loaded onto a column of silica (5 cm × 12 cm Ø). The silica was washed with hexane (2 L) and then with hexane containing ether (5%). A yellow band was collected and gave an orange oil on evaporation. Washing the column with ether gave the symmetrical homocoupled compound as a red oil that crystallized (1 g); it could be recrystallized from ethanol. The orange oil was evaporated on a Kugelrohr apparatus at 150 °C/2 × 10^{-3} mBar to remove traces of solvent to give **19**. Yield: 4.7 g (66%). ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 0.90−0.98 (m, 12H), 1.25−1.47 (m, 24H), 1.64−1.80 (m, 8H), 2.61 (t, 2H, J = 8 Hz), 2.84 (t, 6H, J = 8 Hz), 3.03 (s, 6H), 6.81 (d, 2H, J = 9 Hz), 6.94 (d, 1H, J = 5 Hz), 6.99 (s, 1H), 7.01 (s, 1H), 7.05 (s, 1H), 7.18 (d, 1H, J = 5 Hz), 7.39 (d, 2H, J = 9 Hz). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 14.1, 22.6; 28.8, 29.3, 29.5, 30.4, 30.5, 30.6, 30.7, 31.0, 31.7, 40.5, 112.9, 123.0, 123.5, 128.1, 128.5, 128.7, 130.0, 130.1, 130.6, 130.7, 131.3, 132.6, 133.2, 133.9, 137.6, 138.7, 139.2, 139.5, 139.6, 149.8. MS: m/z 785.41509; calcd for $C_{48}H_{67}NS_4$ (M+), 785.4121.

Dimethyl-[4-(4,3′,3″,3‴,3⁗,3⁗′,3⁗″,3⁗‴,3⁗⁗′-octahexyl-[2,2′;5′,2″;5″,2‴;5⁗,2⁗′;5⁗″,2⁗‴;5⁗‴,2⁗⁗′;5⁗⁗,2⁗⁗″]-octithiophen-5-yl)-phenyl]-amine (22). Compound **19** (2 g, 2.54 mmol) was dissolved in dry THF (50 mL) and placed in a dry flask (250 mL)

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under argon. The mixture was cooled to −78 °C. *n*-BuLi (2 mL, 1.49 M, slight excess) was added. The color instantly changed from light yellow to dark orange, and the mixture was stirred for 30 min. Trimethyl tin chloride (0.52 g, slight excess) was added. The mixture was allowed to reach room temperature. The color became light orange (compound **21**). The solution was mixed directly with compound **20** (2.53 mmol) in dry DMF (50 mL) and degassed with argon. $(PPh_3)_4Pd(0)$ (250 mg, catalyst) was added, and the mixture was heated to reflux under argon. The reaction was stopped after 87 h, and the mixture was evaporated and dissolved in hexane and washed with water. The hexane phase was dried and evaporated to give a bright red oil (4.1 g) of compound **22**. The oil was purified by preparative SEC in $CHCl_3$ (0.5% Et_3N) on a column system comprising a precolumn and a 100 Å column (25 mm Ø × 600 mm) in succession with a 1000 Å column (25 mm Ø × 600 mm). Yield: 1.5 g (41%). ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 0.91−0.97 (m, 24H), 1.40−1.48 (m, 48H), 1.63−1.76 (m, 16H), 2.71 (t, 2H, J = 8 Hz), 2.75 (t, 14H, J = 8 Hz), 3.03 (s, 6H), 6.81 (d, 2H, J = 9 Hz), 6.96 (d, 1H, J = 5 Hz), 6.98−7.06 (m, 7H), 7.17 (d, 1H, J = 5 Hz), 7.40 (d, 2H, J = 9 Hz). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 14.1, 22.7, 28.8, 28.9, 29.0, 29.3, 29.5, 29.6, 30.4, 30.5, 30.6, 30.7, 31.0, 31.7, 40.4, 112.3, 122.3, 123.6, 126.5, 126.6, 128.1, 128.6, 130.0, 130.1, 130.4, 130.5, 130.6, 130.7, 130.8, 131.4, 132.6, 133.1, 133.5, 133.7, 133.8, 133.9, 134.1, 134.7, 137.8, 138.8, 139.2, 139.62, 139.67, 139.79, 139.81, 139.86, 140.26, 142.5, 142.7, 143.6, 149.8. MS: *m*/*z* 1449.74157; calcd for $C_{88}H_{123}NS_8$ (M+), 1449.7347.

5,15-Bis-(3,5-di-*tert*-butyl-phenyl)-10,20-bis-(4-dodecyl-thiophen-2-yl)porphinato-zinc(II) (5). 3-Dodecyl-2-tributyltin-thiophene (2.75 g, 6.62 mmol) dissolved in dry THF (80 mL) was added dropwise to a stirred solution of compound **4** (3.00 g, 3.31 mmol) in dry THF (300 mL). After the addition, the solution was degassed with argon and stirred for an additional 10 min when $(PPh_3)_4Pd(0)$ (150 mg, 0.13 mmol) was added in one portion. The mixture was refluxed under argon and monitored by MALDI-TOF. After 5 h an additional amount of $(PPh_3)_4Pd(0)$ (50 mg, 0.04 mmol) was added, and the mixture was refluxed overnight. The reaction mixture was evaporated to dryness, dissolved in heptane, and filtered through silica (4 × 8 cm Ø). The product was eluted with 4% ethyl acetate in heptane to give 3.15 g of crude purple solid **5**. The product was purified by preparative SEC in $CHCl_3$ (0.5% Et_3N) on a column system composed of a precolumn and a 100 Å column (25 mm Ø × 600 mm) in succession with a 1000 Å column (25 mm Ø × 600 mm). This gave a purple solid (2.23 g, 54%). ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): δ = 0.87 (t, *J*1 = 6.6 Hz, 6H), 1.28−1.47 (m, 36H), 1.55 (s, 36H), 1.92 (p, 4H), 2.95 (t, J = 7.6 Hz, 4H), 7.42 (s, 2H, ArH), 7.77 (d, J = 1.4 Hz, 2H, ArH), 7.82 (t, J = 1.8 Hz, 2H, ArH), 8.09 (d, J = 1,8 Hz, 4H, ArH), 9.00 (d, J = 4.7 Hz, 4H, ArH), 9.22 (d, J = 4.7 Hz, 4H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): δ = 14.78, 23.4, 30.1, 30.2, 30.3, 30.4, 30.4, 31.5, 31.5, 32.4, 32.6, 35.8, 113.7, 121.6, 122.6, 123.8, 130.4, 132.5, 133.1, 135.82, 142.4, 142.7, 144.1, 149.3, 151.5, 151.7. MS: *m*/*z* 1248.69884; calcd for $C_{80}H_{104}N_4S_2Zn$ (M+), 1248.6999.

4′-(4-Tributylstannylphenyl)-[2,2′:6′,2″]terpyridine (7). 4′-(4-Bromophenyl)-[2,2′:6′,2″]terpyridine (2.00 g, 5,17 mmol) was stirred in toluene (5 mL) when bis(tributyltin) (6.5 mL, 12.22 mmol, 2.5 equiv) was added in one portion, and the mixture was degassed with argon. $(PPh_3)_4Pd(0)$ (200 mg, 0.17 mmol) was added, and the mixture was refluxed overnight. The reaction mixture was monitored by MALDI-TOF, and after being cooled to ambient temperature, the product was purified on a short column, silica (5 × 8 cm Ø), using toluene to remove impurities. The product was eluted with toluene/ THF 20:1, giving a slightly yellowish oil, (1.56 g, 50,4%). ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): δ = 0.92 (t, J = 7.3 Hz, 9H), 1.09−1.15 (m, 6H), 1.30−1.44 (m, 6H), 1.53−1.63 (m, 6H), 7.34 (dd, J = 1.1 Hz, J = 6.0 Hz, 1H, ArH), 7.37 (dd, J = 1.1 Hz, J = 6.0 Hz, 1H, ArH), 7.62 (d, J = 7.9 Hz, 2H, ArH), 7.84−7.92 (m, 4H, ArH), 8.69 (d, J = 7.9 Hz, 2H, ArH), 8.73−8.76 (m, 2H, ArH), 8.77 (s, 2H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): δ = 10.4, 14.4, 28.0, 29.8, 119.6, 122.0, 124.4, 127.3, 137.5, 137.7, 138.7, 144.2, 149.8, 151.23, 156.6, 157.1. MS: *m*/*z* 600.24005; calcd for $C_{33}H_{41}N_3Sn$ (MH+), 600.2395.

5,15-Bis-(3,5-di-*tert*-butyl-phenyl)-10-[4-dodecyl-5-(4-[2,2′;6′,2″]-terpyridin-4′-yl-phenyl)-thiophene-2-yl]-20-(4-dodecyl-thiophen-2-yl)porphinato-zinc(II) (9). NBS (320 mg, 1.80 mmol) dissolved in DMF (30 mL) was added dropwise to a stirred solution of compound **5** (2.23 g, 1.78 mmol) dissolved in dry THF (150 mL) and DMF (250 mL). The reaction mixture was monitored by MALDI-TOF. Additional NBS (100 mg, 0.56 mmol), dissolved in DMF (10 mL), was added after 4 h of stirring at room temperature. The mixture was left stirring overnight at room temperature. NMR showed approximately 70% conversion to compound **6** with no formation of dibrominated material. It was found desirable to use this mixture without further purification. To the stirred solution of **6** thus prepared (approximately 2.36 g, 1.78 mmol, NMR showing a purity of approx 70%), a solution of compound **7** (1.07 g, 1.78 mmol, excess) dissolved in DMF (40 mL) was added dropwise while degassing with argon. After the addition, $(PPh_3)_4Pd(0)$ (150 mg, 0.13 mmol) was added, and the solution was refluxed over the weekend. The reaction was monitored by MALDI-TOF and stopped when the starting material was no longer detectable. The mixture was evaporated to dryness. The crude product was purified by flash column chromatography on silica washing with hexane followed by chloroform to remove impurities. The product was eluted using 2% THF in chloroform. This gave a purple solid 950 mg (50%). ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): δ = 0.85−0.94 (m, 6H), 1.26−1.48 (m, 36H), 1.61 (s, 36H), 1.93−2.01 (m, 4H), 2.99 (t, J = 7.7 Hz, 2H), 3.13 (t, J = 7.7 Hz, 2H), 7.36 (dd, J = 1.1 Hz, J = 6.0 Hz, 1H, ArH), 7.39 (dd, J = 1.1 Hz, J = 6.0 Hz, 1H, ArH), 7.45 (s, 1H, ArH), 7.81 (d, J = 1.4 Hz, 1H, ArH), 7.86−7.93 (m, 5H, ArH), 7.97 (d, J = 8.4 Hz, 2H, ArH), 8.12−8.17 (m, 6H, ArH), 8.68 (d, J = 7.9 Hz, 2H, ArH), 8.75 (d, J = 4.7 Hz, 2H, ArH), 8.88 (s, 2H, ArH), 9.04 (d, J = 4,7 Hz, 2H, ArH), 9.08 (d, J = 4,7 Hz, 2H, ArH), 9.25 (d, J = 4,7 Hz, 2H, ArH), 9.43 (d, J = 4,7 Hz, 2H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): δ = 14.7, 14.8, 23.4, 23.5, 30.0, 30.1, 30.3, 30.4, 30.4, 30.4, 30.4, 31.5, 31.6, 32.0, 32.5, 32.6, 32.6, 35.8, 46.1, 112.9, 113.4, 119.4, 121.5, 122.0, 122.5, 123.7, 124.5, 128.3, 130.5, 130.6, 132.4, 133.0, 133.1, 135.7, 136.5, 137.1, 137.5, 138.0, 138.8, 140.0, 142.6, 142.7, 143.5, 144.6, 149.2 (broad 2 signals), 149.9, 150.4, 151.5 (broad 2 signals), 151.5, 151.6, 156.7, 157.0. MS: *m*/*z* 1555.8098; calcd for $C_{101}H_{117}N_7S_2Zn$ (M+), 1555.

5-(5-Bromo-4-dodecyl-thiophen-2-yl)-10,20-bis-(3,5-di-*tert*-butyl-phenyl)-15-[4-dodecyl-5-(4-[2,2′;6′,2″]terpyridin-4′-yl-phenyl)-thiophen-2-yl]porphinato-zinc(II) (10). NBS (70.0 mg, 0.39 mmol) dissolved in DMF (15 mL) is added dropwise to a stirred solution of compound **9** (550 mg, 0.35 mmol) dissolved in DMF (200 mL) and dry THF (100 mL). The reaction mixture was monitored by MALDI-TOF. An additional amount of NBS (25.0 mg, 0.14 mmol) dissolved in DMF (10 mL) was added after 4 h. The mixture is stirred over the weekend at room temperature, evaporated, dissolved in chloroform, and washed with water to give a purple solid. Yield: 490 mg (86%). ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): δ = 0.84−0.87 (m, 6H), 1.27−1.36 (m, 36H), 1.57 (s, 36H), 1.87−1.97 (m, 4H), 2.93 (t, J = 7.7 Hz, 2H), 3.10 (t, J = 7.7 Hz, 2H), 7.36 (dd, J = 1.1 Hz, J = 6.0 Hz, 1H, ArH), 7.39 (dd, J = 1.1 Hz, J = 6.0 Hz, 1H, ArH), 7.62 (s, 1H, ArH), 7.83−7.85 (m, 3H, ArH), 7.87−7.95 (m, 4H, ArH), 8.10−8.13 (m, 6H, ArH), 8.70 (d, J = 7.9 Hz, 2H, ArH), 8.76 (d, J = 4.7 Hz, 2H, ArH), 8.87 (s, 2H, ArH), 9.00 (t, J = 5.0 Hz, 4H, ArH), 9.21 (d, J = 4.7 Hz, 2H, ArH), 9.36 (d, J = 4.7 Hz, 2H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$, 300 K, TMS): δ = 14.8 (broad 2 signals), 21.3, 23.3, 23.3, 30.0, 30,1, 30.2, 30.3, 30.3, 30.4, 30.5, 30.7, 32.0, 32.5, 32.6, 32.7, 35.7, 46.3, 110.8, 111.7, 113.1, 119.4, 121.4. 122.1, 123.7, 124.5, 128.3, 130.6, 132.0, 132.4, 133.1, 133.2, 134.8, 136.5, 137.1, 137.5, 138.0, 138.8, 140.0, 141.8, 142.7, 143.4, 144.7, 149.2 (broad, 2 signals), 149.9, 150.4, 151.3, 151.4, 151.4, 151.5, 156.8, 157.0; MS: *m*/*z* 1656.7100; calcd for $C_{101}H_{116}N_7BrS_2Zn$ (MNa+), 1656.7032.

2,5-Dipropyl-4-[2-(4-[2,2′;6′,2″]terpyridin-4′-yl-phenyl)-vinyl]-benzaldehyde (25). Compound **24**[12] (4.7 g, ca. 15 mmol) and compound **8** (6.2 g, 13 mmol) in THF (150 mL) were stirred while potassium *tert*-butoxide (4 g 35 mmol) was added. The dark red mixture was heated to reflux for 30 min and then poured into water. Solvents were removed in a vacuum, and the beige solid was filtered off and washed successively with water (2 × 100 mL) and methanol (2 × 50 mL). Finally the product was dried in a vacuum. Yield: 7.85 g, 99%. Mp: 193−4 °C. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.02 (t, 3H, J = 7 Hz), 1.04 (t, 3H, J = 7 Hz), 1.62−1.78 (m, 4H), 2.80 (t, 2H, J = 8 Hz), 3.02 (t, 2H, J = 8 Hz), 7.18 (d, 1H, J = 16 Hz), 7.36 (ddd, 1H, J = 1 Hz, J = 5 Hz, J = 7 Hz), 7.44 (d, 1H, J = 16 Hz), 7.53 (s, 1H), 7.66 (s, 1H), 7.68 (d, 2H, J = 8 Hz), 7.88 (dd, 1H, J = 1 Hz, J = 7 Hz), 7.96 (d, 2H, J = 8 Hz), 8.68 (d, 2H, J = 8 Hz), 8.75 (d, 2H, J = 5 Hz), 8.78 (s, 2H), 10.26 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ: 14.0, 24.1, 25.5, 34.2, 34.9, 118.6, 121.4, 123.8, 126.1, 127.3, 127.7, 128.1, 131.9, 136.8, 137.9, 138.2, 138.6, 141.1, 143.1, 149.1, 149.5, 156.0, 156.3, 191.7. MS: *m*/*z* 524.2678; calcd for $C_{36}H_{33}N_3O$ (MH+), 524.2696.

4-{2-[4-(2-{2,5-Dipropyl-4-[2-(4-[2,2′;6′,2″]terpyridin-4′-yl-phenyl)-vinyl]-phenyl}-vinyl)-phenyl]-vinyl}-2,5-dipropoxy-benzaldehyde (28). Compound **26** (3.5 g, ca. 6.2 mmol) and compound **25** (3.0 g, 5.7 mmol) was dissolved in THF (150 mL), and potassium *tert*-butoxide (3.5 g, excess) was added. The reaction mixture was heated to reflux for 30 min. It was then poured into water (400 mL), which precipitated the acetal protected product as a bright yellow powder. This material was washed on the filter with water (3 × 100 mL), ethanol (2 × 100 mL), and petrol (2 × 100 mL) to remove salts and excess reagents. The slightly moist product (ca. 5.3 g, ca. 100%) was taken up in THF (400 mL) and treated with concentrated hydrochloric acid (25 mL) to hydrolyze the acetal. A dark red gel formed that thickened considerably on heating. The mixture was allowed to stand for 1 h to complete the reaction. The mixture was poured into a large beaker containing a solution of sodium carbonate in water (500 mL) and stirred vigorously to break up the gel. Slowly the dark red gel disappeared, and a two-phase system with an orange THF phase appeared. The solvents were removed in a vacuum, and the brownish residue was filtered off. The raw product was washed with water (3 × 200 mL), ethanol (3 × 100 mL), and petrol (2 × 100 mL).Yield: 4.67 g, 97%. Mp: 280 (dec) °C. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.03−1.14 (m, 12H), 1.72 (pentet, 4H, J = 7 Hz), 1.90 (pentet, 4H, J = 7 Hz), 2.73−2.84 (m, 4H), 4.02 (t, 2H, J = 7 Hz), 4.10 (t, 2H, J = 7 Hz), 7.06 (d, 1H, J = 16 Hz), 7.11 (d, 1H, J = 16 Hz), 7.2−7.5 (m, 10H), 7.56 (s, 4H), 7.67 (d, 2H, J = 8 Hz), 7.85−7.96 (m, 4H), 8.69 (d, 2H, J = Hz), 8.75 (d, 2H, J = 4 Hz), 8.79 (s, 2H), 10.47 (s, 1H). MS: *m*/*z* 844.4457; calcd for $C_{58}H_{57}N_3O_3$ (MH+), 844.4473.

4-(2-{5-[2-(4-{2-[4-(2-{2,5-Dipropyl-4-[2-(4-[2,2′;6′,2″]terpyridin-4′-yl-phenyl)-vinyl]-phenyl}-vinyl)-phenyl]-vinyl}-2,5-dipropoxy-phenyl)-vinyl]-thiophen-2-yl}-vinyl)-2,5-dipropoxy-benzaldehyde (29). Compound **28** (3.0 g, 3.6 mmol) and compound **27** (2.5 g, 4.4 mmol) were dissolved in THF (150 mL) and treated with potassium *tert*-butoxide (2.5 g, excess) at reflux for 30 min. The reaction mixture was then poured into water (250 mL) precipitating the raw acetal protected product as red solid. The THF was removed in a vacuum, and the residue was filtered off. This material was washed with water (3 × 200 mL), ethanol (2 × 100 mL), and diethyl ether (2 × 100 mL). The remaining solid was taken up in THF (300 mL) and heated to reflux. Concentrated hydrochloric acid (15 mL) was added, precipitating a red solid. Stirring became easier after a short while, and the mixture was allowed to stand for 30 min to complete the deprotection of the acetal. Water (300 mL) was added, and the stirred mixture was treated with sodium carbonate in portions until basic. The THF was removed in a vacuum, and the red product was filtered and washed with water (200 mL), ethanol (2 × 100 mL), and diethyl ether (2 × 100 mL). The product was dried in a vacuum to give a brick red powder. Yield: 3.22 g, 76%. ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.02−1.19 (m, 18H), 1.74 (q, 4H, J = 8 Hz), 1.82−1.98 (m, 8H), 2.75−2.85 (m, 4H), 4.0−4.1 (m, 8H), 6.97−7.5 (m, 18H), 7.55 (s, 4H), 7.68 (d, 2H, J = 8 Hz), 7.86−7.98 (M, 4H), 8.69 (d, 2H, J = 8 Hz), 8.76 (d, 2H, J = 4 Hz), 8.79 (s, 2H), 10.45 (s, 1H). MS: *m*/*z* 1170.5864; calcd for $C_{78}H_{79}N_3O_5S$ (MH+), 1170.5813.

4-{1-Cyano-2-[4-(2-{5-[2-(4-{2-[4-(2-{2,5-dipropyl-4-[2-(4-[2,2′;6′,2″]terpyridin-4′-yl-phenyl)-vinyl]-phenyl}-vinyl)-phenyl]-vinyl}-2,5-dipropoxy-phenyl)-vinyl]-thiophen-2-yl}-vinyl)-2,5-dipropoxy-phenyl]-vinyl}-benzoic acid ethyl ester (3). Compound **29** (500 mg, 0.43 mmol) and compound **30** (250 mg, excess) were mixed in THF (50 mL) and treated with potassium *tert*-butoxide at reflux for 10 min. Stirring at room temperature was continued for another 30 min to complete the reaction. Acetic acid (ca. 0.5 mL) was added, and the solvent was removed in a vacuum. The dark residue was triturated with hot ethanol (2 × 50 mL) and with diethyl ether and dried in a vacuum. Yield 495 mg (86%). ^{1}H NMR ($CDCl_3$, 250.1 MHz) δ: 1.03−1.2 (m, 18H), 1.42 (t, 3H, J = 7 Hz), 1.71 (q, 4H, J = 7 Hz), 1.83−1.99 (m, 8H), 2.75−2.8 (m, 4H), 4.04−4.14 (m, 8H), 4.42 (q, 2H, J = 7 Hz), 7.0−7.49 (m, 18H), 7.55 (s, 4H), 7.66 (d, 2H, J = 8 Hz), 7.74 (d, 2H, J = 8 Hz), 7.86−7.97 (m, 6H), 8.12 (d, 2H, J = 8 Hz), 8.14 (s, 1H), 8.69 (d, 2H, J = 8 Hz), 8.76 (d, 2H, J = 5 Hz), 8.79 (s, 2H). MS: *m*/*z* 1341.6480; calcd for $C_{89}H_{88}N_4O_6S$ (MH+), 1341.6497.

5-(5-{Dimethyl-[4-(4,3′,3″,3‴,3⁗,3⁗′,3⁗″,3⁗‴-octahexyl-[2,2′;5′,2″;5″,2‴;5‴,2⁗;5⁗,2⁗′;5⁗′,2⁗″;5⁗″,2⁗‴]-octithiophen-5-yl)-phenyl]-amine-5⁗‴-yl}-4-dodecyl-thiophen-2-yl)-10,20-bis-(3,5-di-*tert*-butyl-phenyl)-15-[4-dodecyl-5-(4-[2,2′;6′,2″]terpyridin-4′-yl-phenyl)-thiophen-2-yl]porphinato-zinc(II) (2). Compound 22 (0.6 g, 0.41 mmol) was placed in a 100 mL flask that had been dried in an oven at 300 °C for 1 h. The flask was cooled in dry argon. THF (40 mL) was added, and the mixture was cooled to −78 °C using dry ice/acetone. *n*-BuLi (0.5 mL, 1 M, excess) was added, and the color changed from bright orange to deep red. It was stirred for 15 min. Solid trimethyltin chloride (150 mg, excess) was added, and the mixture was allowed to reach room temperature. The color gradually became light orange. The solution of compound 23 thus prepared (0.41 mmol) was mixed with compound 10 (0.6 g, 0.37 mmol) dissolved in dry THF (20 mL). $(PPh_3)_4Pd(0)$ (100 mg) was added, and the dark brown/green mixture was heated to reflux. The reaction was conveniently followed using TLC. After 36 h the reaction was stopped, and the product was purified using preparative SEC in $CHCl_3$ (0.5% Et_3N) on a column system compposed of a precolumn and a 100 Å column (25 mm Ø × 600 mm) in succession with a 1000 Å column (25 mm Ø × 600 mm). Yield: 375 mg (30%). ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): δ: 0.8−0.94 (m, 30H), 1.1−1.8 (m, 136H), 1.9−2.03 (m, 4H), 2.65 (t, 4H, J = 8 Hz), 2.75−2.95 (m, 18H), 3.09 (t, 2H, J = 8 Hz), 3.17 (t, 2H, J = 8 Hz), 7.0−7.1 (m, 9H), 7.2−7.3 (m, 4H), 7.39 (t, 2H, J = 7 Hz), 7.77 (s, 1H), 7.85 (broad s, 4H), 7.85−7.95 (m, 4H), 8.1 (s+s, 7H), 8.70 (d, 2Hm J = 8 Hz), 8.76 (d, 2H, J = 4 Hz), 8.88 (s, 2H), 9.05 (d, 4H, J = 5 Hz), 9.37 (d, 2H, J = 5 Hz), 9.39 (d, 2H, J = 5 Hz). MS: *m*/*z* 3003.5384; calcd for $C_{189}H_{238}N_8S_{10}$-Zn (M+), 3003.53625.

Synthesis of the Target Compound 1. To a solution of compound **3** (24 mg, 0.018 mmol) dissolved in 1,2-dichlorbenzene (5 mL), the ruthenium complex $[\{(\eta^6\text{-cymene})Ru(\mu Cl)\}_2Cl_2]$[24] (5.57 mg, 0.009 mmol) dissolved in 3 mL of 1,2-dichlorbenzene was added through a septum. The mixture was stirred overnight under argon at room temperature. Compound **2** (55 mg, 0.018 mmol) dissolved in 1,2-dichlorbenzene (5 mL) was added via syringe, and the mixture was refluxed under argon for 3 h. MALDI-TOF showed a variety of side products, starting materials, and the desired compound. Several different methods were tried to isolate the desired product.

1. Preparative Thin Layer Chromatography. Two different types of plates were used, C-18-silica on glass (250 μm, 20 cm × 20 cm) and neutral alumina on glass (250 μm, 20 cm × 20 cm). Both types were coated with a saturated solution of potassium

hexafluorophosphate in water using an airbrush. The plates were then dried in an oven at 80 °C overnight.

A mixed eluent consisting of a saturated solution of potassium hexafluorophosphate in THF and chloroform (1:1) was used to separate the product from unreacted starting materials and byproducts. Regions containing the product according to MALDI-TOF were scraped of the plates and collected. Unfortunately, it was impossible to extract the product using various solvents. Apparently it binds very effectively to the stationary phase (alumina or C-18 silica).

2. Flash Chromatography. The reaction mixture was evaporated to dryness, dissolved in minimum $CHCl_3$, and applied to a column (5 cm × 2.5 cm Ø) of silica gel (0.015−0.040 mm) and washed with $CHCl_3$ to remove traces of starting materials. A small amount of product could be eluted with a mixture of THF and $CHCl_3$ (1:10) saturated with tetrabutylammonium hexaflourophosphate. It contained some byproducts and salts.

3. HPLC. Merck HITACHI, L 2130, PLRP−S 300 Å, 5 μm, 250 mm × 4.6 mm polymeric reversed phase column was used. The mixture was separated in two steps using gradients of methanol and THF with 5 mM of tetrabutylammonium hexafluorophosphate. Evaporation of the eluent in a vacuum gave a dark semisolid containing the target compound **1** together with a small amount of salts.

4. MALDI-TOF MS. MALDI-TOF MS with dihydroxy-benzoic acid (DHB) matrix gave a distribution of peaks around the molecular ion at 4450 in accordance with the calculated spectrum (Figure S4, Supporting Information). Independent verification was obtained from an external mass spectral service (Chemistry Department, University of Copenhagen).

Photovoltaic Device Preparation. Devices were prepared by spin-coating a chlorobenzene solution of **1** (20 mg mL^{-1}) at 1500 rpm onto PEDOT:PSS covered Indium Tin Oxide (ITO) substrates. The ITO substrates had a sheet resistance of 5−15 ohms $square^{-1}$ and were cleaned by ultrasonication in 2-propanol and dried in a stream of argon prior to spin coating a layer of PEDOT:PSS (Baytron at 2800 rpm). The PEDOT:PSS layer was dried at 180 °C for 1 h. Aluminum electrodes were evaporated thermally at a pressure $< 1 \times 10^{-6}$ mBar to a thickness of 100 nm. Electrical contacts were prepared using conducting silver epoxy that was hardened at 65 °C for 10 min prior to measurements using a Keithley 2400 sourcemeter. All measurements were carried out in air. Photovoltaic data were recorded using a Solarkonstant KHS 575 sun simulator that delivered white light with AM1.5 spectral distribution. The spectrum was monitored using an optical spectrometer (Avaspec 2048). The incident light intensity was determined using a certified bolometric pyranometer from Eppley laboratories prior to measurements. Action spectra were recorded using a setup described earlier with a longer source to grating distance and cylindrical lenses for improved incident light intensity and bandwith.[27]

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Supporting Information Available: Photovoltaic experimental details, overview of all synthetic steps, mass spectral and NMR characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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