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Efficient Synthesis of a Regioregular Oligothiophene Photovoltaic Dye Molecule, MK-2, and Related Compounds: A Cooperative Hypervalent Iodine and Metal-Catalyzed Synthetic Route

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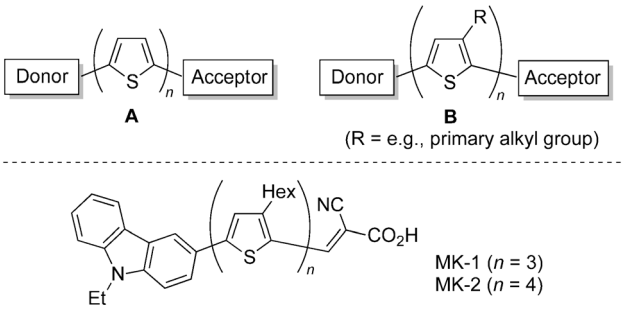
Abstract: We have successfully established an efficient route to the core structure of donor–acceptor head-to-tail (H–T)-linked regioregular oligothiophenes, which includes the following key synthetic steps, that is, hypervalent iodine induced direct and regioselective coupling of thiophenes and the use of the obtained bithiophenes as excellent coupling substrates for the Suzuki and Stille couplings. The versatility of this new approach is highlighted in the dramatic improvement of the yield (ca. 59% overall yield) of MK-2, a high-performance organic dye, for photovoltaic applications.

Keywords: C–C coupling · donor–acceptor systems · dyes/sensitizers · iodine · sulfur heterocycles

Introduction

The dye-sensitizing solar cells (DSSCs), which were first developed by the Grätzel group's pioneering research in the early 1990s,[1] meet a consensus of mankind in demanding the clean production of renewable energy from sunlight for global environmental conservation. Originally, the DSSCs typically used ruthenium-based hybrid metal–organic dyes to achieve high levels of solar-energy-to-electricity conversion efficiency (η).[2] During the development of more efficient DSSCs, optimizing the properties and cost of the dye photosensitizers has been further required. Thus, systematic molecular engineering that contributes to the multidisciplinary fields of the photovoltaic material development has been presented to date based on a wide variety of artificial organic compounds with their successful use as dye sensitizers.[3]

One of the impressive research studies on such dye developments for solar cells has been made in this century by the group of Hara and Koumura, who developed the oligothiophene-based MK dyes with the donor–acceptor moieties as nonmetal sensitizers with a promising efficient photovoltaic performance close to the ruthenium-based dyes for the DSSCs.[4] For the molecular design, the regioregular long alkyl chains at the oligothiophenes are very important to suppress aggregation of the dye molecules and to increase the molar extinction coefficient.[5] Alkyl substituents prevent



the approach of electron carriers to the TiO_2 surface, which decreases the reorganization energy of the dye. Therefore, dyes with unsubstituted oligothiophene donor–acceptor linkages (type **A**) showed poorer η values than those with substituted oligothiophene linkages (type **B**) in photovoltaic applications.[6] The screening of the MK-type compounds has proved that MK-2 containing the tetrameric oligothiophene spacer showed the highest η value of 8.3%. The nonmetal organic dyes have several advantages in view of the material cost and green chemistry and the characteristics of the extinction coefficients and their structural variations. Since the discovery of MK-2, an exhaustive number of artificial donor–acceptor-type compounds tethered by the π-thiophene spacers have been investigated for understanding the structure–activity relationship on the photovoltaic function of the organic dye sensitizers with the challenge of achieving a higher η value for the purpose of developing a more efficient solar cell.[7,8]

The MK dyes are comprised of the donor and acceptor units at the edges of the regioregular oligothiophene centers. Despite the elegant molecular design of the MK dyes and related compounds as photovoltaic materials, the regioselective construction of the oligothiophene structures and ex-

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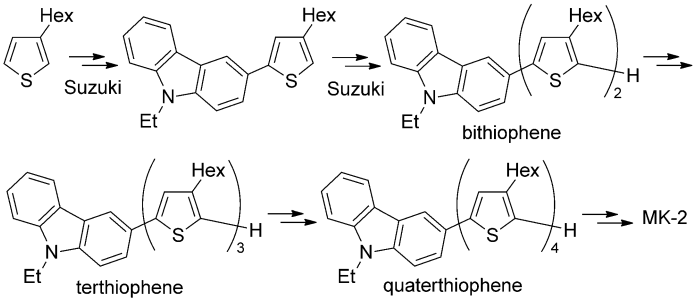
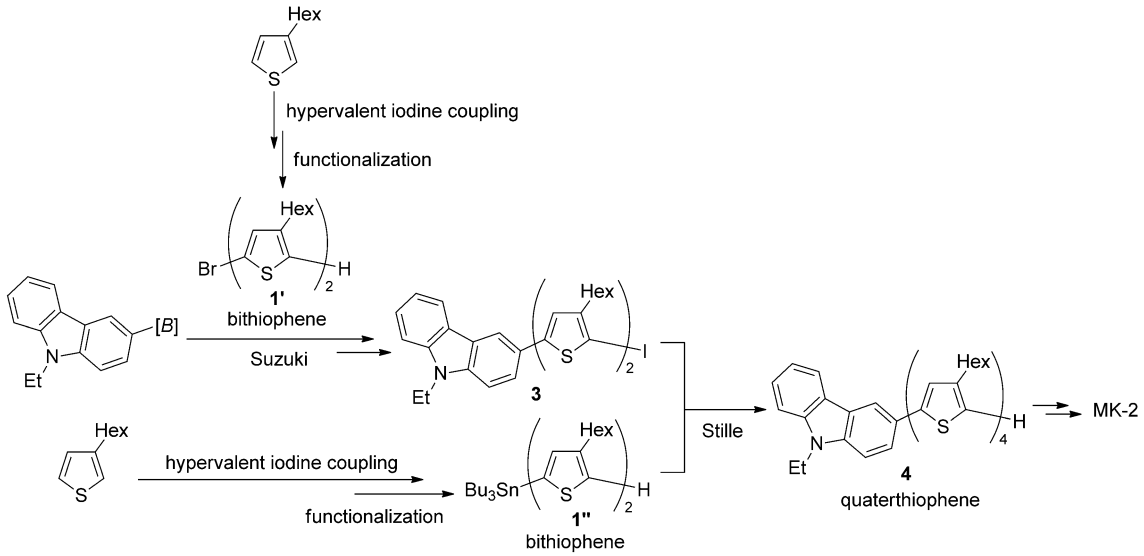
pansion of the π-moieties by the conventional cross-coupling methods, such as the Suzuki and Stille reactions, usually required multiple steps,[9] thus making the preparation of these dyes quite cumbersome. Hence, the synthesis of MK-2 in the original report consists of a total of 10 steps with an overall 13% yield by starting from the commercially available 3-hexylthiophene, in which the head-to-tail (H–T) thiophene linkage and donor carbazole were embedded stepwise by repetition of the conventional Suzuki coupling.[4] The MK-2 synthesis is illustrated in Scheme 1. During the synthesis, all the aryl–aryl bonds in MK-2 were connected by the Suzuki coupling, and the oligothiophene structure was repeatedly elongated by introducing the thiophene monomer employing the corresponding thienyl boronate as the main component (linear synthesis). This scheme must deal with a number of coupling precursors derived from the thiophene monomer, dimer, and trimer as intermediates, which causes the large number of synthetic steps and would thus restrict the production of MK-2 to between 6–27% overall yields. To reduce the number of linear steps of the synthesis, Mori et al. has recently proposed new coupling strategies for the construction of the oligothiophenes that involve selective recognition of the thiophene C–H bonds in the presence of a halogen functional group for further diversification,[10] which has realized the concise synthesis of MK-2 in a similar yield to that of the original report.[10b]



Scheme 1. Original linear synthesis of MK-2.

We have also been engaged in developing the oxidative biaryl coupling reactions of thiophenes and another series of heteroaromatic compounds for synthesizing the oligomers in our continuous studies of hypervalent iodine chemistry.[11,12] Thus, the coupling of electron-rich thiophenes would be induced by the combination of a hypervalent iodine reagent with a suitable Lewis acid.[11] After having been inspired by the importance of the oligothiophene structures in many organic materials,[13] we have recently extended the strategy to 3-alkylthiophenes in a highly regioselective manner. As a result, a novel direct route to the H–T bithiophenes from 3-alkylthiophenes has been realized for the first time with regioselectivity control by activation of the oxidant with bromotrimethylsilane.[14] Our direct approach from the monomers has significant advantages as it can avoid the stoichiometric metalation or halogenation steps of the aromatics that increases the synthetic steps,[15] which has stimulated our regiocontrolled bithiophene synthesis by reducing the difficulty in the synthesis of the oligothiophene-based dyes. At this point, we have commenced the synthesis of MK-2 and now suggest a more practical convergent synthetic route to MK-2 in Scheme 2 based on the progressive use of the bithiophene molecules directly obtained by the reaction of the thiophene monomer with hypervalent iodine reagents.

We now report an efficient coupling route to the core structure of the donor–acceptor regioregular oligothiophenes for photovoltaic applications by utilizing the unsymmetrical bithiophenes, which can be effectively obtained by our regioselective hypervalent iodine coupling technology, as a crucial intermediate. Based on the cooperative use of the hypervalent iodine and conventional metal-catalyzed

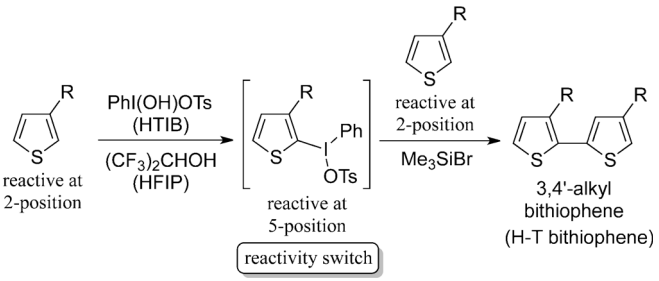


Scheme 2. Convergent synthesis of MK-2 utilizing bithiophene units.

couplings, the significance of this approach is highlighted by the dramatic improvement in the yield of the MK-2 dye. The highly efficient Suzuki coupling procedures utilizing the bithiophene as the electrophile for the middle-stage introduction of the donor carbazole moiety and a series of potentially useful electron-donors have also been documented.

Results and Discussion

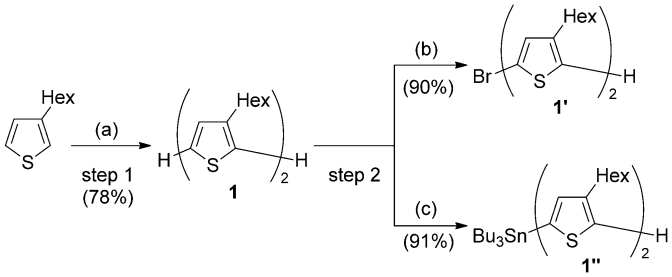
Efficient approach to the regioregular bithiophene units by using the hypervalent iodine reagent: The unsymmetric bithiophene structure, the focus of this study, is readily accessible by using the hypervalent iodine oxidative coupling of 3-alkylthiophene.[16] The exclusive formation of the H–T dimers of 3-alkylthiophene can be well explained by the reaction mechanism shown in Scheme 3. To the hypervalent



Scheme 3. Straightforward approach toward H–T bithophenes by hypervalent iodine induced regioselective coupling. R = electron-rich groups, such as alkyl.

iodine reagent, the alkyl thiophenes are inherently reactive at the most electron-rich 2-position of the thiophene ring, rapidly yielding the corresponding thienyliodonium(III) salts as the sole product by the dehydrative condensation with [hydroxy(tosyloxy)iodo]benzene (HTIB, Koser's reagent).[17] Interestingly, the formed iodonium salts, on the other hand, can exclusively react at the other remote α-position of the thiophene ring with external aromatic nucleophiles by suitable activations.[18] The fluoroalcohols, that is, hexafluoroisopropanol (HFIP), can promote both the reaction processes as the highly polar and non-nuleophilic protic solvent. The two-reaction sequence formally enables the arylation at the less reactive 5-position of the 3-alkylthiophenes. Based on this unique reactivity by switching to a concept through the iodonium salts for modulating the reactivity of the heteroaromatic compounds, the H–T-linked bithiophenes can be directly obtained in one pot from the 3-alkylthiophenes when using the thiophenes themselves as the aromatic nucleophiles. The two-thiophene connection can selectively occur at the 5-position of the thiophene ring of the iodonium salts and the 2-position of the 3-alkylthiophenes, resulting in the formation of the unsymmetrical bithiophene without producing other possible regioisomers. This type of oxidative coupling is quite unique for hypervalent iodine reagents, as other oxidative coupling methods that use metal-based oxidants would typically produce symmetric homodimers as the major product.[19]

Accordingly, we performed a gram-scale preparation of the required H–T bithiophene unit **1** by the hypervalent iodine oxidative coupling as the first step of the MK-2 synthesis from the commercial 3-hexylthiophene (Scheme 4).



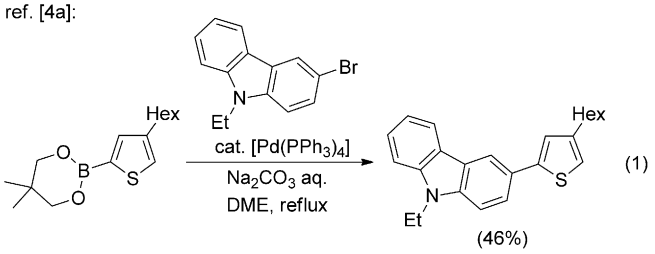
Scheme 4. Synthesis of 3-hexylthiophene H–T-type dimer **1** and its functionalized compounds **1′** and **1″**: a) 3-hexylthiophene, PhI(OH)OTs (HTIB, 1 equiv), TMSBr (2 equiv) in HFIP, RT, 3 h; b) bithiophene **1**, *n*-butyllithium (1 equiv) in tetrahydrofuran (THF), −78 °C, 2 h; then molecular bromine (1.05 equiv), 35 min; c) bithiophene **1**, LDA (1 equiv) in THF, −40 °C, 10 min.; then tri-*n*-butyltin chloride (1.05 equiv), −78 °C to RT, 3 h.

With the standard procedure that uses HTIB and bromotrimethylsilane, the desired H–T-linked coupling product **1** was formed in a perfect regioselective manner (over 99%) in preference to other regioisomers. After chromatography or distillation, the pure bithiophene **1** was obtained in 78% yield, which was then converted to the halogen electrophile **1′** and organometallic nucleophile **1″** in yields of 90 and 91% by selective lithiation[20] followed by quenching with molecular bromine (for halide **1′**) and tri-*n*-butyltin chloride (for **1″**), respectively, for the later-stage metal-catalyzed cross-couplings. These bithiophenes **1**, **1′**, and **1″** are stable in a refrigerator for at least several months without special storage conditions.

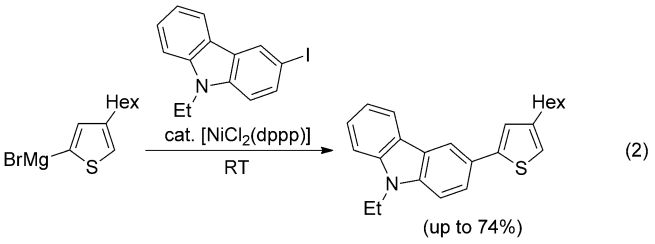
Bithiophenes as the efficient coupling partner for donor molecules: In previous reports,[4,10] the efficiency of the installation of the donor carbazole moiety to the thiophene core of MK-2 has remained unsatisfactory, leading to the decreasing overall yields during the syntheses. In fact, the reaction of the thiophene boronate with the bromocarbazole during the early stage was reported in the original report[4a] to only allow the Suzuki coupling in 46% yield for the incorporation of the donor aromatic to the thiophene monomer [Eq. (1)]. Thereafter, the same research group modified the coupling substrates for a better production yield of the target compound, which afforded the same MK-2 intermediate in a moderate yield (74%) by the Kumada coupling [Eq. (2)]. Later, Mori and co-workers applied their elegant oxidative C–H arylation strategy of thiophenes to aryl iodides for introducing the carbazole group to the thiophene [Eq. (3)] during a shorter synthetic route to MK-2 (nine steps from 3-hexylthiophene), despite the lower overall

yield (<6%).[10a] They have also further improved the synthetic steps to be more attractive by utilizing the controlled metalation of thiophene C–H bonds by using the Knochel–Hauser base (TMPMgCl·LiCl, TMPH = 2,2,6,6-tetramethylpiperidine) or the combination of a Grignard reagent and a catalytic amount of a secondary amine, followed by alternative cross-coupling with iodocarbazole, but the aryl–aryl bond-forming step of the thiophene and carbazole [Eq. (4)] is the most problematic in terms of the yield during the entire process.[10b] All these reported cases have the synthetic hurdle of introducing the donor moiety.

ref. [4a]:

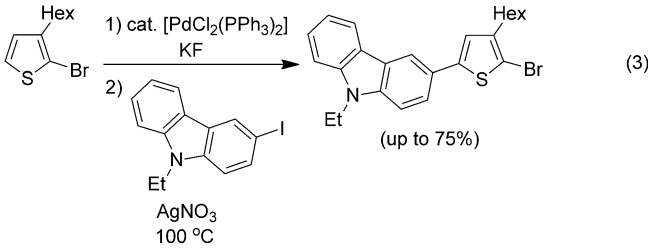


(1)



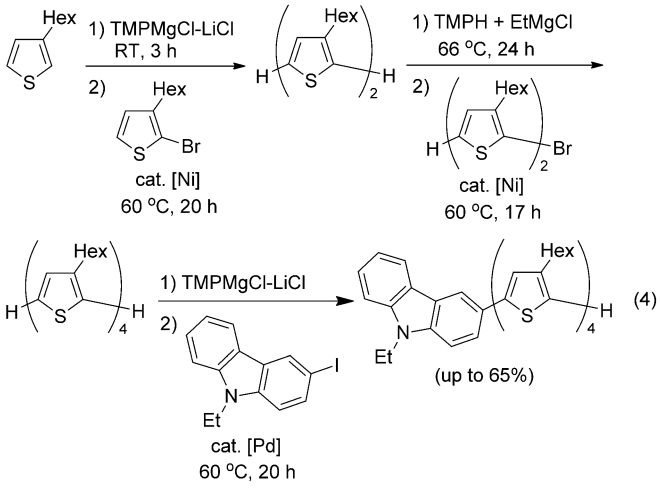
(2)

ref. [10a]:



(3)

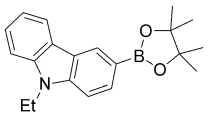
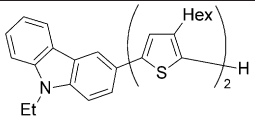
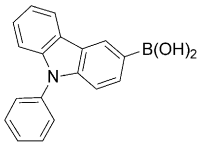
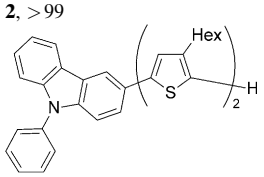
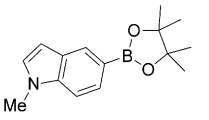
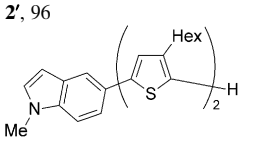
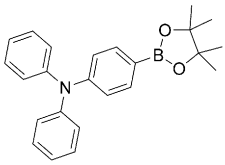
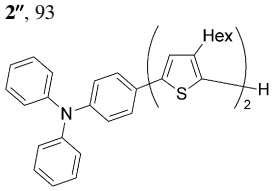
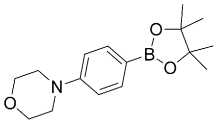
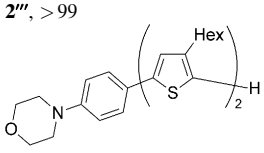
ref. [10b]:



(4)

Thus, the usability of the bithiophene **1′** as an electrophile in cross-coupling was first investigated before carrying out the synthesis of MK-2. We tested the Suzuki couplings for the extensive range of organoboronic compounds in Table 1 derived from the different types of electron-rich aromatic amines for the purpose of validating the reactivity of the bithiophene halide **1′** as a universal module for the installation of the donor moieties to the oligothiophene-based dyes. Thus, the reaction of the bithiophene **1′** was examined by using a 4 mol% loading of the palladium catalyst with only a slight excess of the boronic acid in toluene at reflux in the presence of the phase-transfer catalyst (Aliquat 336) and a weak base (Table 1). Surprisingly, a series of electron-rich carbazole[21] (Table 1, entries 1 and 2), indole[22] (Table 1, entry 3), aromatic,[23] and aliphatic aryl amines[24] (Table 1, entries 4 and 5) could be readily introduced to the bithiophene backbone in unbelievably high yields by the Suzuki couplings by using the bithiophene halide **1** without any optimization of the reaction conditions. Even in these cases, only a slight excess of the organoboron compounds

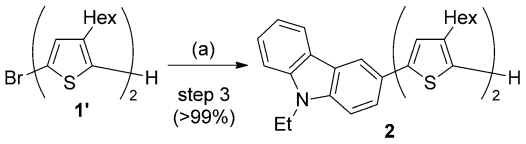
Table 1. Suzuki coupling of the bithiophene halide **1′** with carbazole compounds and extended series of donor aromatics.[a]

Entry	Organoboron Compound	Product, Yield [%][b]
1		 **2**, >99
2		 **2′**, 96
3		 **2″**, 93
4		 **2‴**, >99
5		 **2⁗**, >99

[a] Reactions were carried out by using 1.1 equivalents of the organoboron compound in the presence of 4 mol% palladium catalyst at reflux in degassed toluene overnight. See details in the Experimental Section. [b] Isolated yield after purification.

(1.1 equiv) was required to completely convert the bithiophene molecule **1′**.

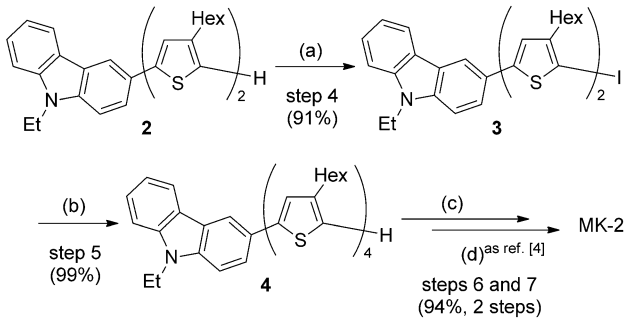
Accordingly, the Suzuki coupling reaction of the bithiophene halide **1′** with the carbazole boronic acid derivative was subsequently conducted to furnish the aryl–aryl bond between the oligothiophene part and carbazole donor of MK-2 (Scheme 5). We were very pleased to confirm the remarkably high-yielding incorporation of the donor carbazole under the stated reaction conditions. The use of 4 mol% of the palladium catalyst was sufficient to maintain the reaction rate with efficiencies similar to that in Table 1. It should be noted that one of the important steps in the reported MK-2 syntheses produces an unsatisfactory yield of the carbazole coupling.[4,10] The bithiophene **1′** thus seems to significantly facilitate the metal-catalyzed coupling efficiency for installing the donor carbazole moiety. On the other hand, the use of a coupling combination of bithiophene boronic acid and a carbazole halide would give rise to the same product **2** in poorer yield under the same catalytic conditions.[25,26]



Scheme 5. High-yielding installation of donor carbazole by utilizing the bithiophene halide **1′** as the electrophile for a Suzuki coupling reaction: a) bithiophene halide **1**, 9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)carbazole (1.1 equiv), catalytic amount of tetrakis(triphenylphosphine)palladium (4 mol%), a few drops of Aliquat 336, and 2M aq. sodium carbonate in degassed toluene, reflux, 12 h.

Based on the significant observations, we consider that the present coupling route to the regioregular oligothiophene compounds involving the bithiophenes as key intermediates has significant merits as a guideline of being valuable not only to provide the efficient preparation of the known high-performance synthetic dyes, for example, MK-2, but also to influence future synthetic design of a wide array of the related oligothiophene-based dyes.[27]

Completion of the MK-2 synthesis: In clear contrast to the previous reports, our synthetic approach based on the coupling of the bithiophene **1′** has, unexpectedly, realized the smooth and perfect introduction of the carbazole group. For the donor-installed thiophene dimer **2**, iodination by selective α-lithiation of the terminal thiophene ring was then carried out to produce the coupling precursor **3** for elongation of the thiophene core (Scheme 6, step 4). The functionalized dimer **3** obtained in 91% yield was successively subjected to the standard Stille coupling conditions with the discretely prepared bithiophene nucleophile **1″** in Scheme 4, giving the corresponding regioregular thiophene tetramer **4** in an almost quantitative yield after heating at reflux for 12 h. The use of the bromide instead of the iodide **3** decreased the product yield and reaction efficiencies because it forces the oxidative addition to be markedly slower during the Stille coupling. The spectra of the obtained tetramer **4** are in perfect agreement with an authentic sample from a previous study.[4,10]



Scheme 6. Completion of the synthesis of MK-2: a) carbazole–bithiophene coupling product **2**, *n*-butyllithium (1.2 equiv) in THF, −78°C, 30 min; then elemental iodine (2 equiv), 30 min; b) iodobithiophene **3**, stannyl bithiophene **1″** (see Scheme 4, 1.5 equiv), cat. tetrakis(triphenylphosphine)palladium (4 mol%) in degassed toluene, reflux, 12 h; c) quarterthiophene **4**, phosphorus oxychloride in DMF, 0°C, 30 min; then 70°C for 7 h; d) quaterthiophene aldehyde **5**, cyanoacetic acid (2 equiv) in a mixed solvent of acetonitrile, toluene, and piperidine, reflux, 4 h.

Finally, the synthesis of MK-2 through this synthetic route has been completed by attaching the end-capping acceptor, that is, the vinyl cyanoacetic acid moiety, to the donor-carrying tetramer **4** according to the original reports[4] by modified two-step procedures (steps 6 and 7, see the Experimental Section). Our short synthetic route to MK-2 involves a total of seven steps and can provide the target compound in a shorter reaction time and in a markedly higher yield (over 59% overall yield) than that of the original (13–26%)[4] and later-reported approaches (ca. 27%)[10] when using the same commercial material. The notable features of the present strategy are characterized by the high yields of all the synthetic steps, the benefits of which should come from the smart preparation of the regioregular bithiophene **1** and successful use of the coupling precursors **1′** and **1″** during the synthesis.

Conclusion

We have described an efficient synthetic route to donor–acceptor-linked regioregular oligothiophenes, specifically, the high-performance MK-2 dye, for photovoltaic applications based on the cooperative use of the hypervalent iodine and metal-catalyzed coupling technologies for the construction of the π-expanded oligoarene architectures. All the steps to the target molecules can proceed in high yields and the overall yield for the MK-2 synthesis is dramatically improved to approximately 59% in comparison to the known reported sequences. The unsymmetrical bithiophene **1**, which is directly obtainable in good yield from 3-alkylthiophene by hypervalent iodine coupling with complete regiochemical control, serves as the key and excellent intermediate in this method. During the synthesis, we also noted that

the bithiophene unit **1′** clearly facilitated the metal-catalyzed couplings for installing the donor moiety to the π-linked oligothiophene systems, and thus the highly efficient Suzuki coupling procedure utilizing the bithiophene electrophile **1′** toward a series of potentially useful electron donors was demonstrated to contribute to the future study of the design and access to the related regiocontrolled thiophene molecules.

Experimental Section

General: Melting point (m.p.) was measured by Stuart melting-point apparatus SMP3 AC input 100V. ^{1}H NMR (and ^{13}C NMR) spectra were recorded by a JEOL JMN-400 spectrometer operating at 400 or 300 MHz (100 or 75 MHz for ^{13}C NMR spectra) in $CDCl_3$ at 25 °C with tetra methylsilane as an the internal standard. The data are reported as follows: chemical shift in ppm (δ), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant (Hz). The IR spectra were obtained by using a Hitachi 270–50 spectrometer. The HRMS were performed by the Elemental Analysis Section of Osaka University.

Analytical TLC was performed on MERCK silica gel, grade 60 F_{254}. The spots and bands were detected by UV irradiation (254, 365 nm). Column chromatography for isolation of the products was carried out on Merk Sillica Gel 60 (230–400 mesh). Unless otherwise noted, all the chemicals for the reactions and column chromatography in this study were obtained from several commercial suppliers and used as received without further purification.

MK-2 synthesis

Step 1: Direct synthesis of H–T-linked bithiophene 1 by the hypervalent iodine induced regioselective coupling (Scheme 4): A gram-scale preparation: In an open flask, HTIB (7.7 g, 20 mmol) and then bromotrimethylsilane (5.4 mL, 40 mmol) were added to a stirred solution of 3-hexylthiophene (6.7 g, 40 mmol) in hexafluoroisopropanol (100 mL) at room temperature; the color of the solution immediately changed to brown. After stirring for 3 h, dichloromethane (300 mL) and saturated aq. sodium carbonate (200 mL) were successively added to the reaction mixture. The organic layer was then separated and the solvents were evaporated to dryness. The residue was evaporated and subjected to column chromatography on silica gel (eluent/hexanes) or bulb-to-bulb distillation under reduced pressure to give the regioselectively coupled H–T bithiophene **1** (5.3 g, 15.6 mmol) in 78% yield. The regiochemistry of the obtained bithophene product **1** was confirmed by comparing it with an authentic sample.

3,4′-Dihexyl-2,2′-bithiophene (***1***):[14] Pale-yellow oil; b.p. 165 °C (0.02 mmHg); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84–0.92 (m, 6H), 1.20–1.35 (m, 12H), 1.52–1.70 (m, 4H), 2.63 (t, 2H, J = 8.4 Hz), 2.74 (t, 2H, J = 8.4 Hz), 6.89–6.92 (m, 2H), 7.03 (s, 1H), 7.12 ppm (d, 1H, J = 5.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.6, 29.0, 29.1, 29.2, 29.7, 30.4, 30.5, 30.7, 31.6, 31.7, 119.9, 123.4, 124.8, 127.3, 129.9, 130.9, 135.8, 139.3, 143.5 ppm.

Step 2a: Selective bromination of the H–T bithiophene 1 (Scheme 4): The H–T bithiophene **1** (3.34 g, 10.0 mmol) was added in a flame-dried flask under a nitrogen atmosphere. After lowering the temperature to −78 °C, *n*-butyllithium (2.5 M solution in hexanes, 4.4 mL, 11.0 mmol) was added dropwise over 1.5 h to the stirred solution, and then the resulting solution was stirred for an additional 1 h. At the same temperature, a solution of bromine (1.68 g, 10.5 mmol) in dry tetrahydrofuran (THF, 5 mL) was slowly added for about 15 min. The mixture was stirred for a further 20 min and a few drops of an aqueous methanolic solution of sodium thiosulfate were added at that temperature. The reaction mixture was warmed to room temperature, poured into ice-cold water and extracted with diethyl ether. The organic phase was washed successively with 3% aq. sodium thiosulfate (30 mL), water (20 mL), and 10% aq. sodium chloride (50 mL), and was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel by using hexanes as the eluent to give the regioselectively brominated H–T bithiophene **1′** (3.7 g, 9.0 mmol) in 90% yield.

5-Bromo-3,4′-dihexyl-2,2′-bithiophene (***1′***):[20a] Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84–0.89 (m, 6H), 1.27–1.30 (m, 12H), 1.54–1.62 (m, 4H), 2.57 (t, 2H, J = 8.4 Hz), 2.64 (t, 2H, J = 8.4 Hz), 6.85 (s, 2H), 6.87 ppm (s, 1H).

Step 2b: Preparation of organostannyl bithiophene compound 1″ as a Stille coupling precursor (Scheme 4): A solution of bithiophene **1** (2.47 g, 6.0 mmol) in anhydrous THF was cooled to −40 °C under a nitrogen atmosphere and treated with an equimolar amount of lithium diisopropylamide (LDA) in THF, which was freshly prepared from distilled diisopropylamine and *n*-butyllithium (in hexanes). The lithiation was conducted for 10 min, and the solution was then treated at −78 °C with tri-*n*-butyltin chloride (2.05 g, 6.3 mmol). The reaction mixture was allowed to warm to room temperature over a 3 h period, then the solvent was evaporated to dryness. The resulting oily residue was dissolved in hexanes and filtered to remove solid lithium chloride byproduct to obtain compound **1″** in approximately 91% yield. The organotin compound was used without further purification for the synthetic step 5 in the synthesis of MK-2.

5-Tributylstannyl-3,4′-dihexyl-2,2′-bithiophene (***1″***): Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86–0.92 (m, 15H), 1.06–1.11 (m, 6H), 1.28–1.35 (m, 18H), 1.52–1.59 (m, 4H), 2.57 (t, 2H, J = 8.4 Hz), 2.74 (t, 2H, J = 8.4 Hz), 6.83 (s, 1H), 6.90 (s, 1H), 6.92 ppm (s, 1H); IR (KBr): $\tilde{\nu}$ = 2954, 2923, 2854, 1522, 1463, 1415, 1375, 1291, 1184, 1071, 1045, 1020, 962, 935, 913, 878, 835, 763, 747, 724, 686, 674, 649, 638, 619, 612, 601 cm^{-1}.

Step 3: High-yielding Suzuki coupling utilizing the bithiophene halide 1′ (Scheme 5): Commercially available 9-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)carbazole (185 mg, 0.58 mmol) and tetrakis(triphenylphosphine)palladium (23 mg, 0.02 mmol) in degassed toluene (2 mL), including a few drops of Aliquat 336 and 2 M aq. sodium carbonate solution (0.33 mL), were added to a stirred mixture of the bithiophene halide **1′** (206 mg, 0.50 mmol). The solution was heated at reflux with vigorous stirring for 12 h under a nitrogen atmosphere. The mixture was poured into water (5 mL) and extracted with ethyl acetate. The organic extract was successively washed with water (5 mL) and brine (5 mL). After drying with anhydrous sodium sulfate, the solvent was evaporated and the residue was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate 50:1) to give the pure coupling product (264 mg, 0.50 mmol) quantitatively.

9-Ethyl-3-[3,4′-dihexyl(2,2′-bithiophene)-5-yl]carbazole (***2***):[4] Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, 3H, J = 6.6 Hz), 0.91 (t, 3H, J = 6.6 Hz), 1.24–1.40 (m, 12H), 1.48 (t, 3H, J = 7.1 Hz), 1.60–1.73 (m, 4H), 2.60 (t, 2H, J = 7.8 Hz), 2.70 (t, 2H, J = 7.8 Hz), 4.40 (q, 2H, J = 7.1 Hz), 6.80 (s, 1H), 7.04 (d, 1H, J = 1.3 Hz), 7.09 (s, 1H), 7.29–7.23 (m, 1H), 7.53–7.42 (m, 3H), 7.56 (dd, 1H, J = 8.4, 1.8 Hz), 8.12 (d, 1H, J = 7.7 Hz), 8.17 ppm (d, 1H, J = 1.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 14.0, 14.1, 22.6 (×2), 28.8, 29.0, 29.2, 30.3, 30.5, 31.0, 31.6, 31.7, 37.6, 108.3, 108.6, 118.4, 119.0, 120.5, 121.1, 122.8, 123.0, 124.5, 125.0, 125.8, 125.9, 127.1, 135.0, 137.5, 137.9, 138.7, 139.2, 140.3, 144.0 ppm.

Step 4: α-Iodination of the thiophene ring of carbazole–bithiophene coupling product 2 (Scheme 6): A solution of *n*-butyllithium (1.57 M in hexanes, 1.0 mL) was added dropwise at −78 °C under a nitrogen atmosphere to a stirred solution of carbazole–bithiophene coupling product **2** (686, 1.3 mmol) in THF (10 mL). After stirring for 30 min, elemental iodine (660 mg, 2.6 mmol) was added in one portion and stirring was continued for a further 30 min. The reaction mixture was poured into water (5 mL) and the organic phase was separated. The aqueous phase was extracted with diethyl ether (30 mL) twice. The combined organic layers were dried over anhydrous sodium sulfate and concentrated in vacuo. Purification of the residue by column chromatography on silica gel by using hexanes/ethyl acetate (50:1) as the eluent afforded the desired α-iodinated product **3** (771 mg, 1.18 mmol) in 91% yield.

9-Ethyl-3-[3,4′-dihexyl-5′-iodo(2,2′-bithiophene)-5-yl]carbazole (***3***):[10a] Yellow sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94–0.85 (m, 6H), 1.43–1.23 (m, 12H), 1.45 (t, 3H, J = 7.1 Hz), 1.74–1.60 (m, 4H), 2.56 (t,

2H, $J=7.8$ Hz), 2.75 (t, 2H, $J=7.9$ Hz), 4.38 (q, 2H, $J=7.2$ Hz), 6.82 (s, 1H), 7.17 (s, 1H), 7.27–7.25 (m, 1H), 7.40 (d, 1H, $J=8.7$ Hz), 7.42 (d, 1H, $J=8.6$ Hz), 7.49 (ddd, 1H, $J=8.1$, 7.0, 0.9 Hz), 7.70 (dd, 1H, $J=8.4$, 1.5 Hz), 8.14 (d, 1H, $J=7.6$ Hz), 8.29 ppm (d, 1H, $J=1.5$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.9$, 14.3, 22.7, 22.8, 29.1, 29.4, 29.7, 30.1, 30.8, 31.8, 31.9, 32.5, 37.7, 73.5, 108.7, 108.8, 117.6, 119.2, 120.7, 123.0, 123.5, 124.0, 124.9, 125.3, 126.0, 126.1, 128.5, 139.7, 140.5, 141.0, 141.4, 143.8, 147.6 ppm.

Step 5: Stille-type cross-coupling of the two bithiophene units 3 and 1″, leading to the tetrameric core of MK-2 (Scheme 6): A mixture of 5-tributylstannyl-3,4′-dihexyl-2,2′-bithiophene **1″** (372 mg, 0.60 mmol), 9-ethyl-3-[3,4′-dihexyl-5′-iodo(2,2′-bithiophene)-5-yl]carbazole **3** (260 mg, 0.40 mmol), and tetrakis(triphenylphosphine)palladium (18.6 mg, 0.016 mmol) in degassed toluene (4 mL) was heated at reflux for 12 h. After cooling, a solution of tetrabutylammonium chloride in THF (1 M, 0.4 mL) was added and the solvents were evaporated under reduced pressure. The crude coupling product was purified by column chromatography on silica gel (hexanes/ethyl acetate 50:1) to give the quaterthiophene **4** (339 mg, 0.399 mmol) in 99% yield.

*9-Ethyl-3-[3,4′,4″,4‴-tetrahexyl(2,2′:5′,2″:5″,2‴-quaterthiophene)-5-yl]carbazole (**4**)*:[4] Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.89$–0.95 (m, 12H), 1.30–1.44 (m, 24H), 1.46 (t, 3H, $J=7.2$ Hz), 1.62–1.80 (m, 8H), 2.63 (t, 2H, $J=7.8$ Hz), 2.75–2.87 (m, 6H), 4.38 (q, 2H, $J=7.2$ Hz), 6.91 (d, 1H, $J=1.3$ Hz), 6.99 (s, 1H), 7.00 (d, 1H, $J=1.3$ Hz), 7.02 (s, 1H), 7.21 (s, 1H), 7.27 (ddd, 1H, $J=7.5$, 7.0, 1.0 Hz), 7.43–7.39 (m, 2H), 7.50 (ddd, 1H, $J=8.2$, 7.0, 1.2 Hz), 7.73 (dd, 1H, $J=8.5$, 1.8 Hz), 8.15 (d, 1H, $J=7.5$ Hz), 8.32 ppm (d, 1H, $J=1.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.8$, 14.1 (×3), 14.1 (×2), 22.6 (×3), 22.7, 29.0, 29.2, 29.3, 29.4, 29.5, 29.7, 30.4, 30.5 (×3), 30.6, 31.7 (×5), 37.5, 108.6, 108.7 (×2), 119.0, 119.9, 120.5, 122.8, 123.3, 123.7, 125.0, 125.2, 125.9, 127.0, 128.1, 128.2, 128.8, 129.9, 130.8, 133.6, 134.3, 135.5, 139.4, 139.5, 139.6, 140.3, 140.4, 143.1, 143.6 ppm.

Step 6: Improved procedure for the α-formylation of the thiophene ring of tetramer 4 (Scheme 6): The Vilsmeier reagent was added to an ice-cold solution of quaterthiophene **4** (270 mg, 0.31 mmol) in dry DMF (2 mL), which was prepared in situ with phosphorus oxychloride (0.12 mL) in DMF (0.6 mL) at 0°C for 30 min. Then, the mixture was stirred at 70°C for 7 h. After cooling, the reaction mixture was quenched with 10% aq. sodium acetate (35 mL) and extracted with ethyl acetate (20 mL) three times. The combined organic layers were washed with water (20 mL) and brine (20 mL), dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes/ethyl acetate 15:1) to give the aldehyde **5** (272 mg, 0.31 mmol) in 99% yield.

*5‴-(9-Ethyl-9H-carbazol-3-yl)-3′,3″,3‴,4-tetrahexyl(2,2′:5′,2″:5″,2‴-quaterthiophene)-5-carboxaldehyde (**5**)*:[4] Dark-orange oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.95$–0.88 (m, 12H), 1.29–1.42 (m, 24H), 1.46 (t, 3H, $J=7.2$ Hz), 1.68–1.80 (m, 8H), 2.79–2.86 (m, 6H), 2.95 (t, 2H, $J=7.8$ Hz), 4.38 (q, 2H, $J=7.2$ Hz), 7.01 (s, 1H), 7.02 (s, 1H), 7.06 (s, 1H), 7.21 (s, 1H), 7.27 (ddd, 1H, $J=7.9$, 7.1, 0.9 Hz), 7.39–7.43 (m, 2H), 7.50 (ddd, 1H, $J=8.2$, 7.1, 1.1 Hz), 7.72 (dd, 1H, $J=8.5$, 1.8 Hz), 8.14 (d, 1H, $J=7.9$ Hz), 8.31 (d, 1H, $J=1.8$ Hz), 10.02 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=13.7$, 14.0 (×2), 14.1 (×2), 22.5, 22.6 (×3), 28.3, 28.9, 29.2 (×2), 29.3, 29.5, 29.7, 29.8, 30.1, 30.3, 30.4, 31.3, 31.5, 31.6 (×2), 31.7, 37.5, 108.5, 108.6, 117.3, 119.0, 120.4, 122.7, 123.2, 123.6, 124.9, 125.0, 125.9, 127.7, 128.0, 128.4 (×2), 129.1, 129.2, 135.1, 135.9, 136.0, 139.4, 140.3, 140.4, 140.6, 142.4, 143.3, 145.1, 153.2, 181.4 ppm.

Step 7:[4] Completion of the synthesis of MK-2 (Scheme 6): A mixture of aldehyde **5** (211 mg, 0.24 mmol) with cyanoacetic acid (40 mg, 0.48 mmol) in a mixed solvent of dry acetonitrile (5 mL) and toluene (2 mL) was heated at reflux in the presence of piperidine (1 mL) for 4 h. After cooling, the reaction mixture was diluted with dichloromethane (30 mL), and the organic layer was washed with water (10 mL) and brine (10 mL), dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (chloroform/ethanol) to give the dye, MK-2 (216 mg, 0.23 mmol), in 95% yield.

2-Cyano-3-[5‴-(9-ethyl-9H-carbazol-3-yl)-3′,3″,3‴,4-tetrahexyl(2,2′:5′,2″:5″,2‴-quaterthiophene]-5-yl]-2-propenoic acid (MK-2):[4] Dark-red solid; ^{1}H NMR (400 MHz, [D$_8$]THF): $\delta=0.90$–0.94 (m, 12H), 1.41 (t, 3H, J = 7.2 Hz), 1.28–1.51 (m, 24H), 1.63–1.81 (m, 8H), 2.82–2.93 (m, 8H), 4.43 (q, 2H, J = 7.2 Hz), 7.09 (s, 1H), 7.13 (s, 1H, s), 7.17 (t, 1H, J = 7.2 Hz), 7.24 (s, 1H), 7.32 (s, 1H), 7.43 (ddd, 1H, J = 8.0, 7.2, 0.8 Hz), 7.48–7.52 (m, 2H), 7.73 (d, 1H, J = 8.5 Hz), 8.15 (d, 1H, J = 7.7 Hz), 8.40 (s, 1H), 8.41 ppm (s, 1H); ^{13}C NMR (100 MHz, [D$_8$]THF): $\delta=14.1$, 14.4, 14.5 (×3), 23.5 (×2), 23.6 (×2), 29.1, 29.5, 29.9, 30.1, 30.2 (×2), 30.3, 30.4, 30.6, 30.8, 31.3, 31.4, 31.5, 32.2, 32.5, 32.7 (×2), 38.2, 98.1, 109.6, 109.8, 117.0, 117.9, 119.8, 121.2, 123.9, 124.4 (×2), 125.9, 126.0, 126.8, 128.2, 129.0, 129.1, 130.0, 130.1, 130.3, 130.7, 136.3, 137.1, 140.6, 141.5 (×2), 141.6, 143.4, 143.8, 144.6, 144.7, 155.3, 164.6 ppm.

The overall yield of the MK-2 synthesis is over 59% when starting from commercially available 3-hexylthiophene.

Efficient Suzuki coupling of the bithophene halide 1′ with an extended series of organoboron compounds (Table 1): The Suzuki-coupling was examined by using the bithiophene halide **1′** (0.25 mmol) with 1.1 equivalents of organoboron compounds (0.275 mmol) in the same procedure to that described in the Experimental Section, step 3. The pure products (**2′**: 138 mg, 0.24 mmol, 96%; **2″**: 108 mg, 0.23 mmol, 93%; **2‴**: 145 mg, 0.25 mmol, >99%; **2⁗**: 124 mg, 0.25 mmol, >99%) were obtained by column chromatography on silica gel (**2′**: hexanes/ethyl acetate 50:1; **2″**: hexanes/ethyl acetate 50:1; **2‴**: hexanes/ethyl acetate 50:1; **2⁗**: hexanes/ethyl acetate 10:1).

*3-[3,4′-Dihexyl(2,2′-bithiophene)-5-yl]-9-phenylcarbazole (**2′**)*: Yellow sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.88$–0.91 (m, 6H), 1.32–1.40 (m, 12H), 1.60–1.73 (m, 4H), 2.62 (t, 2H, $J=8.4$ Hz), 2.79 (t, 2H, $J=8.4$ Hz), 6.88 (s, 1H), 7.00 (d, 1H, $J=1.2$ Hz), 7.19 (s, 1H), 7.30–7.39 (m, 1H), 7.40–7.47 (m, 4H), 7.55–7.65 (m, 5H), 8.17 (d, 1H, $J=8.0$ Hz), 8.33 ppm (d, 1H, $J=1.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 22.6 (×2), 29.0, 29.3, 29.5, 30.4, 30.5, 30.7, 31.7, 109.9, 110.1, 117.3, 119.6, 120.2, 120.4, 123.3, 123.8, 124.1, 125.1, 126.3, 126.5, 126.9, 127.0, 127.6, 129.5, 129.9, 136.1, 137.5, 140.3, 140.4, 141.4, 142.7, 143.6 ppm; IR (KBr): $\tilde{\nu}=3050$, 2924, 2854, 1599, 1501, 1454, 1362, 1330, 1233, 1175, 1027, 912, 836, 806, 744, 696, 682, 667, 659, 640, 622 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{38}H_{41}NS_2$: 575.2860 $[M]^+$; found: 575.2689.

*3-[3,4′-Dihexyl(2,2′-bithiophene)-5-yl]-N-methylindole (**2″**)*: Light-yellow sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.88$–0.91 (m, 6H), 1.32–1.41 (m, 12H), 1.62–1.69 (m, 4H), 2.61 (t, 2H, $J=8.4$ Hz), 2.76 (t, 2H, $J=8.4$ Hz), 3.78 (s, 3H), 6.49 (d, 1H, $J=2.4$ Hz), 6.86 (s, 1H), 6.97 (d, 1H, $J=1.6$ Hz), 7.04 (d, 1H, $J=3.2$ Hz), 7.11 (s, 1H), 7.29 (d, 1H, $J=8.4$ Hz), 7.47 (dd, 1H, $J=8.4$, 1.6 Hz), 7.85 ppm (d, 2H, $J=1.2$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 22.6 (×2), 29.0, 29.3, 29.5, 30.4, 30.5, 30.6, 31.7, 32.9, 11.3, 109.5, 118.0, 119.4, 120.1, 124.8, 125.9, 126.7, 128.8, 129.1, 129.6, 136.3, 136.4, 140.1, 143.5 ppm (×2); IR (KBr): $\tilde{\nu}=3100$, 2925, 2854, 1616, 1537, 1467, 1420, 1377, 1332, 1297, 1247, 1155, 1106, 1080, 1010, 913, 832, 796, 740, 718, 682, 675, 641, 629, 611 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{29}H_{37}NS_2$: 463.2367 $[M]^+$; found: 463.2386.

*4-[3,4′-Dihexyl(2,2′-bithiophene)-5-yl]-N,N-diphenylbenzenamine (**2‴**)*: Yellow sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.85$–0.89 (m, 6H), 1.28–1.36 (m, 12H), 1.59–1.65 (m, 4H), 2.58 (t, 2H, $J=8.4$ Hz), 2.72 (t, 2H, $J=8.4$ Hz), 6.85 (s, 1H), 6.94 (d, 1H, $J=1.2$ Hz), 6.99–7.10 (m, 8H), 7.22–7.26 (m, 5H), 7.41 ppm (d, 2H, $J=8.4$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 22.6, 29.0, 29.2, 29.4, 30.4, 30.5, 30.6, 31.7, 119.7, 123.0, 123.7, 124.5, 125.1, 126.3, 126.9, 128.3, 129.3, 129.8, 136.0, 140.2, 141.4, 143.6, 147.2, 147.5 ppm; IR (KBr): $\tilde{\nu}=3031$, 2926, 2855, 1591, 1507, 1493, 1327, 1280, 1219, 1177, 853, 822, 775, 739, 696, 675, 663, 647, 625 cm^{-1}; HRMS (EI): *m/z*: calcd for $C_{38}H_{43}NS_2$ [FAB]$^+$: 577.2837; found: 577.2851.

*4-[3,4′-Dihexyl(2,2′-bithiophene)-5-yl]phenylmorpholine (**2⁗**)*: Light-yellow sticky oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.87$–0.90 (m, 6H), 1.27–1.39 (m, 12H), 1.61–1.66 (m, 4H), 2.59 (t, 2H, $J=8.4$ Hz), 2.72 (t, 2H, $J=8.4$ Hz), 3.17 (t, 4H, $J=4.8$ Hz), 3.85 (t, 4H, $J=4.8$ Hz), 6.85 (d, 1H, $J=1.2$ Hz), 6.88 (d, 2H, $J=8.4$ Hz), 6.94 (d, 1H, $J=1.2$ Hz), 7.01 (s, 1H), 7.48 ppm (d, 2H, $J=8.4$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 14.2, 22.6, 29.0, 29.3, 29.4, 30.4, 30.5, 30.6, 31.7, 49.0, 66.8, 115.6, 119.6, 124.6, 125.9, 126.4, 126.8, 129.2, 136.1, 140.2, 141.7, 143.5, 150.5 ppm; IR

(KBr): $\tilde{\nu}$ = 3029, 2926, 2854, 1607, 1514, 1448, 1378, 1335, 1228, 1123, 1070, 1051, 930, 857, 821, 740, 648, 626, 610 cm^{-1}; HRMS (FAB): *m/z*: calcd for $C_{30}H_{41}ONS_2$: 495.2630 $[M]^+$; found: 495.2647.

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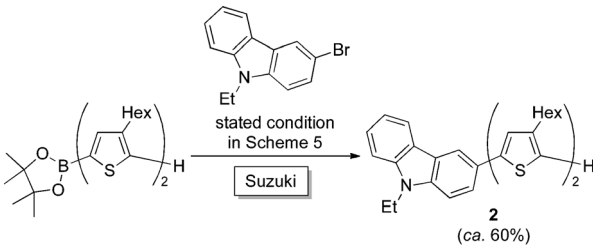

2
(*ca.* 60%)

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