FULL PAPERS

Preparation and Acid-Responsive Photophysical Properties of T-Shaped π -Conjugated Molecules Containing a Benzimidazole Junction

Toshifumi Inouchi, Takuya Nakashima,* Masaya Toba, and Tsuyoshi Kawai*^[a]

Abstract: T-shaped π -conjugated molecules with an *N*-methyl-benzimidazole junction have been synthesized and their acid-responsive photophysical properties owing to the change in the π -conjugation system are discussed. Tshaped π -conjugated molecules consist of two orthogonal π -conjugated systems including a phenyl thiophene extended from the 2-position and alkyl phenylenes connected through various π -spacers from the 4,7-positions of the *N*-methyl-benzimidazole junction. The

Introduction

In the past two decades, π -conjugated molecules including polymers and oligomers have been widely studied for functional and practical applications. Recent advances in exploring π -conjugated molecules involve the development of nonlinear cross-conjugated molecules. Two-dimensional "Xshaped" conjugated molecules, so called cruciforms, have been attracting much interest in regard to the spatial separation of frontier molecular orbitals (FMOs) of the HOMO and LUMO. There have been a number of cruciforms with central scaffolds based on tetra-1,2,4,5-vinyl- or -ethynylsubstituted benzenes^[1] and bisoxazoles,^[2] demonstrated as fluorescent ion sensors,^[1,3] building units of π -conjugated^[4] and coordination polymers,^[5] and materials for molecular electronics on the electrode surface.^[2,6] Cross-conjugated benzodifuran (BDF) derivatives were also synthesized and

 [a] T. Inouchi, Dr. T. Nakashima, Dr. M. Toba, Prof. T. Kawai Graduate School of Materials Science
 Nara Institute of Science and Technology, NAIST
 8916-5 Takayama, Ikoma, Nara 630-0192 (Japan)
 Fax: (+81)743-72-6179
 E-mail: tkawai@ms.naist.jp
 ntaku@ms.naist.jp

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201100401.

 π -spacers, such as thiophene, ethyne, and ethane, have an effect on the acid response of photophysical properties in terms of changes in conformation, excited-state energy and charge-transfer (CT) characteristics. In particular, the π -conjugated molecule with ethynyl spacers exhibited a marked redshift in

Keywords: charge transfer • conjugation • fluorescence • heterocycles • photochemistry

the fluorescence spectrum with a large Stokes shift upon the addition of acid, whereas the other molecules showed substantial quenching. The redshift in emission was studied in detail by temperature-dependent fluorescence measurements, which indicated the transition to a CT state over the finite activation energy at the excited state. The change in the frontier molecular orbitals upon acid addition was further discussed by means of DFT calculations.

the effect of the π -spacers on the optical and electronic properties were discussed.^[7] Meanwhile, fused-N-aromatic groups including bisphenazine,^[8] carbazole,^[9] and benzimidazole^[10-12] were exploited as a central junction of T-shaped π conjugated molecules. In particular, benzimidazole has been considered to be an interesting building unit for π -conjugated molecular and polymer systems.^[10-12] For example, the self-assembling properties of T-shaped rod-coil molecules containing a benzimidazole unit were studied.^[10] A metalorganic framework was synthesized by using a benzimidazolium carbene-metal complex.^[11] The capability of the imidazole ring for the introduction of positive charge upon protonation or N,N'-dialkylation affords the modulation of π -conjugation systems including their expansion and pathway.^[12,13] Yamamoto et al. reported the change in the optical properties of π -conjugated polymers derived from a benzimidazole unit with phenyleneethynylene main chain on the addition of acid.[14]

X- and T-shaped cross-conjugated molecules possess twodimensional π -conjugation systems extended from π -cores, which are connected through various π -spacers, such as aromatic rings and double- and triple-bond linkages. The π spacers play a crucial role in the physicochemical properties of π -conjugated molecules, such as spectroscopic, electric, and crystallographic properties, in terms of molecular conformation and spread of FMOs and consequently in the applications of conjugated materials. In the present study, we investigated the photophysical properties of T-shaped π -conjugated molecules extended from a benzimidazole junction by three different π -spacers including thiophnene, ethyn, and ethene. Arylene-ethynylene derivatives are of particular interest in respect to their structure-property relationships, for example, the relationship between the rotation about the triple bond and optical properties. Okuyama et al. reported the barrier for the torsional motion of tolane was determined to be 202 cm⁻¹ in a supersonic free jet.^[15] Oligo- and poly(phenylene ethynylene)s have been investigated as electron-transport molecular wires, strong light emitters and nonlinear optical materials.^[16] Haley et al. investigated the structure-property relationships including ion sensing and two-photon absorption properties for tetrakis(arylethynyl)benzenes (TAEBs) by introducing various donor and acceptor substituents.^[17] Other π -spacers, thiophene and ethene units, are also of interest with regard to the effect of structural torsion on the π -conjugation system.^[12b]

To create a series of π -conjugated molecules capable of connecting functional units or molecular devices orthogonally, we designed T-shaped conjugated molecules with a benzimidazole junction, which can modulate the π -conjugation system by protonation and quaternization (Scheme 1). The



Scheme 1. Structures of T-shaped π -conjugated molecules and their acid responsivity.

 π -conjugation system partially communicates from Ar(L) to Ar(R) and Ar(V) to Ar(L), which is expected to fully expand by the protonation. We describe herein the synthesis of T-shaped π -conjugated molecules. The synthesized molecules are characterized in terms of electrochemical and photophysical properties. The acid-responsive optical properties are evaluated by means of spectroscopy and temperature-dependent fluorescent measurements. The effect of the protonation on the FMOs is also discussed by using time-dependent DFT (TD-DFT) calculations.

Results and Discussion

Synthesis

A series of T-shaped conjugated molecules with an *N*-methylbenzimidazole junction were synthesized according to the reaction scheme depicted in Scheme 2. To evaluate the

effect of π -spacer on the response to protonation, thienylbenzene, ethynylbenzene, and vinylbenzene with an alkyl chain were extended from 4- and 7-positions of the central 2-phenylthiophenebenzimidazole, for TBIm, EBIm, and **VBIm**, respectively. The central 2-aryl-benzimidazole junction unit (7) was synthesized by the condensation of 5-phenylthiophene-2-carbaldehyde and 3,6-dibromobenzene-1,2diamine (5), which is reduced from 3,6-dibromobenzothiadiazole.^[10b,11] The central junction unit (7) was connected to side-chain π -units by palladium-catalyzed conventional cross-coupling reactions, Suzuki-Miyaura coupling for TBIm, Sonogashira-Hagihara coupling for EBIm, and Mizoroki-Heck coupling for VBIm. Each T-shaped molecule has a hexyl side chain at the both ends of Ar(L) and Ar(R)for improving the solubility in organic solvents. Synthesized molecules, compound 7, TBIm, EBIm, and VBIm were characterized by ¹H and ¹³C NMR spectroscopy, 2D ¹H NMR (COSY) spectroscopy, HRMS, and single-crystal X-ray crystallography.

X-ray Crystal Structures

Compound 7, TBIm, EBIm, and VBIm were readily recrystallized from the mixed solvent system of chloroform and nhexane, and their crystal structures were determined by Xray crystallographic analysis (Figure 1).^[18] Similar conformations were observed about the common structure, from benzimidazole to Ar(V), for all compounds. That is, the Ar(V)unit is almost coplanar with the central benzimidazole. The coplanarity was supposed to be harnessed by an S and N atomic contact between the thienyl sulfur in Ar(V) and the imidazolyl nitrogen atoms. The S-N distances in each crystal were estimated to be substantially shorter than the sum of van der Waals radii of S (0.185 nm) and N (0.155 nm); 0.303, 0.301, 0.296, and 0.314 nm for 7, TBIm, EBIm, and VBIm, respectively. In addition, another S-N interaction was found in TBIm between the central imidazolyl nitrogen and the thienyl sulfur in Ar(L) (S₂-N: 0.295 nm). Such S-N



Figure 1. ORTEP drawings of a) **TBIm**, b) **EBIm**, and c) **VBIm**. Hexyl group and hydrogen atoms are omitted for clarity.^[20]

Chem. Asian J. 2011, 6, 3020-3027

www.chemasianj.org 3021

FULL PAPERS



Scheme 2. Synthesis of T-shaped conjugated molecules: a) 2-(tributylstannyl)-thiophene, DMF, $[Pd(PPh_3)_4]$; b) **1**, *n*BuLi, 2,2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; c) CuI, triethylamine, PPh₃, $[PdCl_2(PPh_3)_2]$, trimethylsilylacetylene; d) tributylvinyltin, $[Pd(PPh_3)_4]$; e) NaBH₄; f) 5-phenylthiophene-2-carbaldehyde, *p*TsOH; g) K₂CO₃, methyliodide; h) **2**, Na₂CO₃ aq.(2M), $[Pd(PPh_3)_4]$; i) **3**, CuI, triethylamine, PPh₃, $[PdCl_2(PPh_3)_2]$, TBAF; j) **4**, triethylamine, Pd(OAc)₂, P(*o*Tol)₃.

heteroatom interactions are also considered to be responsible for the planarity of conjugated polymers composed of, for example, co-thiophene-banzo[c]1,2,5-thiadiazole structures.^[19] Meanwhile, the Ar(R) units for **TBIm** and **VBIm**

Optical and Electrochemical Properties

The UV/Vis absorption and fluorescence spectra of Tshaped conjugated molecules and compound **7** were measured in dichloromethane (Figure 2), and results are sum-

were twisted from the central benzimidazole by about 40° due to the steric repulsion between the *N*-methyl group and Ar(R) unit, whereas the aryl unit at the other side, Ar(L), lies on almost the same plane with benzimidazole. In contrast, the relative rotations of Ar(L) and Ar(R) about the central benzimidazole unit were not affected by the substitutent on the imidazolyl ring owing to its linear and rodlike structural nature for **EBIm** (Figure 1b).



Figure 2. Absorption (left) and fluorescence (right) spectra and those after the addition of TFA (0.01 mL;): a) Compound 7, b) **TBIm**, c) **EBIm**, d) **VBIm** in CH_2Cl_2 (1.0×10^{-6} M, 3 mL).

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 1. Photophysical properties of compounds in $\rm CH_2Cl_2$ solution in the presence and absence of TFA.

Compd	λ_{abs} [nm]	λ _{onset} [nm]	$\lambda_{ m em}$ [nm]	$ u_{ m ST} $ [cm ⁻¹]	$arPsi_{ m F}$
7	339	390	422	5845	0.05
7+H ⁺	357	413	441	5375	0.14
TBIm	353	443	509	8722	0.22
TBIm+H ⁺	359	445	600	11188	> 0.03
EBIm	365	411	449	5163	0.86
EBIm+H ⁺	373	427	517	7503	0.33
VBIm	369	440	504	7296	0.56
VBIm+H ⁺	357	447	452, 543	9595	0.05

marized in Table 1. The absorption maxima of the π - π^* transition, λ_{abs} , were found at 339, 353, 365, and 369 nm and the emission peaks, λ_{em} , were observed at 422, 509, 449, and 504 nm for **7**, **TBIm**, **EBIm**, and **VBIm**, respectively. T-shaped conjugated molecules exhibited a substantial redshift both in absorption and emission bands in comparison with compound **7**, which clearly suggests the expansion of the π -system by the extension of π -conjugation from Ar(L) to Ar(R). The fluorescence quantum yields, Φ_{f} , were measured to be 0.05, 0.22, 0.86, and 0.56 for **7**, **TBIm**, **EBIm**, and **VBIm**, respectively. **EBIm** thus showed the highest value of Φ_{f} and the smallest Stokes shift, ν_{ST} =5163 cm⁻¹, reflecting the photophysical nature of the aryleneethynylene spacer.

Electrochemical properties of **7**, **TBIm**, **EBIm**, and **VBIm** were determined by the cyclic voltammetry (CV) measurements in THF. The reduction potentials, E_{onset} of **7** and T-shaped compounds were found at -2.02, -2.09, -2.01, and -2.10 V versus Ag/Ag⁺ (Table 2). The LUMO energy

Table 2. Electrochemical properties and band gap energies of compounds in THF.

Compd.	$E_{ m red}{}^{[a]}$ [V]	λ _{onset} ^[b] [nm]	LUMO [eV] ^[c]	HOMO [eV] ^[d]	$E_{ m g} [m eV]^{[m d]}$
7	-2.02	390	-2.58	-5.76	3.18
TBIm	-2.09	447	-2.51	-5.29	2.78
EBIm	-2.01	419	-2.59	-5.55	2.96
VBIm	-2.10	444	-2.50	-5.29	2.80

[a] Onset of reduction curve. [b] In THF $(1.0 \times 10^{-6} \text{ M})$. [c] LUMO = $[-(E_{\text{onsetred}}-0.20)-4.8]$ eV, in which 0.20 V is the value for the half-wave potential of ferrocene/ferrocenium versus Ag/Ag⁺ in THF and 4.8 eV is the energy level of ferrocene below the vacuum. [d] Estimated from optical energy gap.

levels, which are the degree of electron affinity, were estimated from the reference energy level of half-wave potential of the ferrocene/ferrocenium redox couple (4.8 eV below the vacuum level). Since those compounds possess a similar value of LUMO level including compound 7, the central benzimidazole unit is dominant for the electron affinity nature. The HOMO levels were also calculated relative to the corresponding LUMO levels by using optical band gaps approximated by λ_{onset} in absorption spectra.

Optical Properties after the Addition of TFA

To study changes in the π -conjugation system in response to protonation, an excess amount of trifluoroacetic acid (TFA, 0.5 mL) was added to the dichloromethane solutions $(1.0 \times$ 10⁻⁶м, 3 mL). As shown in Figure 2 and Table 1, slight redshifts in λ_{onset} were observed by the addition of TFA, which indicated the extension of the π -conjugation system. More obviously, marked quenching in fluorescence accompanied by the increase of $v_{\rm ST}$ were found for T-shaped conjugated molecules. The increases in Stokes shift, Δv_{ST} , upon protonation were 2466, 2340, and 2299 cm⁻¹ for TBIm, EBIm, and **VBIm**, respectively, in which the effect of π -spacer was not as prominent as $v_{\rm ST}$ of neutral compounds (8722, 5163, and 7296 cm^{-1} for **TBIm**, **EBIm**, and **VBIm**, respectively, Table 1). These results indicate a change in the emission mechanism upon the protonation of the imidazole junction unit. Since only EBIm was still emissive at room temperature even after the protonation and showed a significant fluorescent color change from green to blue upon protonation, emission lifetime and low-temperature fluorescence were measured for EBIm.

Lifetime and Temperature-Dependent Fluorescence Measurements

The emission decay profile of **EBIm** was numerically fitted by single exponential kinetics with a time constant of τ = 2.89 ns. From the values of emission lifetime and quantum yield, the apparent radiative and nonradiative rate constants were calculated to be $k_r = 2.8 \times 10^8$ and $k_{nr} = 6.8 \times 10^7 \text{ s}^{-1}$, respectively. When TFA, as a proton source, was added the emission lifetime was extended to 3.74 ns, which gave the values $k_r = 8.8 \times 10^7$ and $k_{nr} = 1.8 \times 10^8 \text{ s}^{-1}$. The extension of emission lifetime despite the decrease in emission quantum yield upon protonation implies that the emission process might involve the excited-state relaxation from a locally excited (LE) state to another state, that is, an intramolecular charge-transfer (ICT) state.

We then investigated the temperature-dependent emission profile of EBIm in 2-methyltetrahydrofuran (2-MeTHF) as a glass matrix in the presence of TFA. The protonation of EBIm under the same conditions was confirmed by the upfield shift of the chemical shift of N-methyl protons by ¹H NMR spectroscopic measurements.^[20] As shown in Figure 3, the emission peak exhibited a continuous redshift with a rise in temperature from 77 to 180 K, whereas no obvious change was found in the emission profile in the absence of TFA.^[20] The emission peak position at 77 K was at 446 nm for **EBIm** with TFA, which is almost corresponding to that of EBIm without TFA. The blueshift of the emission peak at low temperature indicated the presence of a potential barrier from the Franck-Condon state to the ICT state. Figure 4 depicted the simplified energy diagram of the photophysical pathway of $\mathbf{EBIm} + \mathbf{H}^+$. The activation energy to the ICT state was sufficiently larger than the thermal energy at low temperature (below 120 K) and consequently the



Figure 3. Fluorescence spectral change of **EBIm+H⁺** in 2-MeTHF/TFA $(3.0/0.5 \text{ mL}, 1.0 \times 10^{-6} \text{ M})$ at low temperature.



Figure 4. Schematic energy diagram of EBIm+H⁺.

emission took place from the LE state. Since the thermal energy between 130 and 160 K was almost comparable with the activation energy E_a , the emission from the ICT state was also observable and superimposed with the LE state emission to some extent depending on the temperature. Finally, the emission peak appeared at around 510 nm above 170 K, in which the thermal energy was sufficiently larger than E_a and the ICT emission became dominant. Thus the protonation of the benzimidazole junction switches the emission state from LE to ICT and the extension of π -conjugation through 4- to 7-positions increases the shift in emission peak relative to compound 7 without an orthogonal π conjugation system, which indicates the ICT between orthogonally oriented π -conjugation systems. Furthermore, the emission spectrum of $\mathbf{EBIm} + \mathbf{H}^+$ in a polymer matrix (PMMA) gave the emission peak at 450 nm,^[20] which is almost identical to that in a solution without TFA. These results indicate that the ICT state would involve molecular twisting (TICT).

Theoretical Study

The FMOs of T-shaped π -conjugated molecules were then calculated by using the DFT method,^[21] based on the Becke 3LYP basis set.^[22] For the calculation, the Gaussian $03^{[23]}$ suite of programs was used. The most stable geometries were optimized at the RB3LYP/6-31G* level and then the one-electron transition energies were estimated by the TD-

DFT^[24] method at the RB3LYP/6-311+G^{**} level. Both FMOs of HOMO and LUMO for **7** spread almost thorough the molecule, which clearly indicates the π -conjugation connection between benzimidazole and Ar(V) due to the coplanarity between the benzimidazole and the phenyl thiophene. TD-DFT calculations indicated the π - π * transition corresponding to the S₀-S₁ transition involves the electronic transition mainly from HOMO-1 and HOMO to LUMO and LUMO+1. Figure 5 shows these FMOs for **EBIm** before



Figure 5. FMOs of **EBIm** and **EBIm**+ H^+ (HOMO-1 to LUMO+1) together with their relative energies.

and after the protonation. The electronic transition with the lowest energy (HOMO-LUMO) was calculated to be at 425.2 nm with the oscillator strength f=0.73, which corresponds to the electronic transition from the orbital expanded through Ar(L) to Ar(R) with slight infiltration to the Ar(V) direction to the FMO spread thorough the molecule including Ar(V). The most intense transition with f=1.02corresponding to the HOMO to LUMO+1 transition appeared at 364.9 nm in accordance with the experimental result (Figure 2). The electron distribution around Ar(L) was weakened relative to that around Ar(R) in the FMO of LUMO+1. Upon protonation, a marked redshift in HOMO to LUMO transition (522.7 nm, f=0.25) was observed. The calculation indicated that this transition is partly forbidden probably due to the perpendicular configuration of HOMO

www.chemasianj.org

and LUMO. Likewise, the FMOs of HOMO and LUMO were orthogonally situated to each other for $TBIm + H^+$ and $VBIm + H^+$, resulting in the forbidden nature of transitions.^[20] Meanwhile, the HOMO to LUMO+1 (373.7 nm, f=1.47) was simulated to be the most intense band for $EBIm + H^+$ and other T-shaped molecules, which also exhibited a redshift from 364.9 to 373.7 nm after the protonation. The FMO of HOMO for $EBIm + H^+$ was rather locallized in the Ar(L)–Ar(R) π -conjugation unit, whereas that of LUMO+1 was delocalized in the whole molecule. It might be also noted that the most prominent change in the FMOs was observed in the HOMO-1 level after the protonation. The HOMO-1 state, which also contributed to the S_0-S_1 transition, was delocalized in the "L"-shape between Ar(V) and Ar(R) for **EBIm**, whereas the delocalization expanded to the whole molecule after the protonation. The protonation thus perturbed the FMOs of T-shaped conjugated molecules and the resulting separated and orthogonally oriented FMOs of HOMO and LUMO might be responsible for the ITC characteristic of **EBIm**+**H**⁺.

Conclusions

We have synthesized T-shaped π -conjugated molecules with a benzimidazole junction that connects the orthogonally-oriented π -systems, and their photosysical properties and acid responsivity were studied. Thienyl-, ethynyl-, and vinyl-benzenes were introduced as a π -expander to lateral direction, which effectively extended the π -conjugation system to show a redshift both in absorption and emission spectra in comparison with the linear conjugated molecule 7. The absorption and emission peaks further shifted to longer wavelengths upon protonation for T-shaped π -conjugated molecules. The time-resolved and low-temperature emission measurements of EBIm indicated the excited state relaxation from the LE state to ICT state through a potential barrier with an activation energy smaller than the thermal energy at room temperature. The TD-DFT calculation reveals the proton-responsive FMOs, which may be responsible for the change in the emission mechanism from LE state emission to ICT emission. The T-shaped π -conjugated molecules should play an important role as a responsive junction unit that orthogonally connects functional units in molecular devices. Moreover, a bis(benzimidazole) unit would serve as a junction for unprecedented cruciforms.

Experimental Section

General

¹H (300 MHz) and ¹³C NMR (75 MHz) spectra were recorded on a JEOL JNM-AL300 spectrometer. ¹H NMR (500 MHz) spectra were recorded on a JEOL JNM-ECP500 spectrometer. Recycling preparative GPC and normal-phase HPLC were performed on a LC-9110NEXT (Japan Analytical Industry) and a Hitachi LaChrom Elite HPLC system, respectively. HRMS were measured by a JEOL JMS-700 MStation spectrometer. X-ray crystal structures were obtained with a Rigaku R-AXIS

RAPID/S. UV/Vis absorption and fluorescence spectra were obtained on a JASCO V-670 spectrophotometer and a JASCO FP-6500 fluorescence spectrophotometer, respectively. For the temperature-dependent fluorescence study, the temperature of samples was controlled by an Oxford Instruments variable-temperature liquid nitrogen cryostat OptistatDN in the range from 77 K to room temperature. Absolute fluorescence quantum yields of compounds were measured by using a Hamamatsu C9920-02. Cyclic voltammetry was performed on a µ-AUTOLAB III potentiostat/galvanostat equipped with an Electrochemical Analysis System software in an argon-filled glove box. A platinum wire was used as a counter electrode, an Ag/Ag+ electrode was used as a reference electrode, and a platinum disk electrode was used as a working electrode. The measurements were conducted in a solution of 0.1 M tetrabuthylammonium hexafluorophosphate (TBAPF₆) in THF at a scan rate of 100 mV s⁻¹ at room temperature in an argon-filled glove box. Fluorescence lifetime measurements were performed by using a picosecond fluorescence measurement system (Hamamatsu C4780) with a streak scope (Hamamatsu C4334). The excitation source was generated by Nd:YVO4 laser (Coherent, Verdi) pumped Ti:Sapphire laser system (Coherent, Mira-900) equipped with a cavity dumper (Coherent, PulseSwitch).

2-(4-Hexylphenyl)thiophene (1)

A mixture of 1-bromo-4-hexylbenzene (3.0 g, 12 mmol), 2-(tributylstannyl)thiophene (4.8 g, 13 mmol), and anhydrous DMF (72 mL) was degassed by bubbling with N₂ for 30 min and then [Pd(PPh₃)₄] (0.76 g, 0.66 mmol) was added to the mixture. The resulting mixture was stirred overnight at 90 °C, and then quenched by the addition of NH₄Cl solution. The crude product was extracted with *n*-hexane and the combined organic layer was dried over MgSO₄ and filtered. Potassium fluoride was added to the filtrate and the mixture was stirred for 5 h. After the solvent had been removed, the residue was purified by silica gel column chromatography by using *n*-hexane as the eluent to yield **1** as a clear oil. Compound **1** was used in the next reaction without further purification. R_f = 0.4 (*n*-hexane); ¹H NMR (300 MHz, CD₂Cl₂, TMS): δ =7.52–7.49 (m, 2H), 7.30–7.15 (m, 4H), 7.05–7.02 (m, 1H), 2.59 (t, 2H), 1.60 (m, 2H), 1.30 (m, 6H), 0.88 ppm (m, 3H).

2-[5-(4-Hexylphenyl)thiophen-2-yl]-4,4,5,5-tetramethyl-1,3,2dioxaborolane (2)

Compound 1 (2.5 g, 10 mmol) and anhydrous THF (60 mL) were added to a dried four-neck flask and the resulting mixture was stirred at -78 °C under a N₂ atmosphere. *n*BuLi (6.6 mL, 1.6 m in *n*-hexane, 11 mmol) was added dropwise to a well-stirred solution and further stirred at -78 °C for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2- dioxaborolane (2.5 mL, 12 mmol) was then added and the mixture was allowed to warm up to room temperature over 7 h. Water was added to the reaction mixture, which was extracted with chloroform. The combined organic fraction was washed with saturated brine, dried over MgSO₄, filtered, and concentrated. The crude product was purified by alumina column chromatography by using chloroform as the eluent to yield **2** (1.1 g, 29%) as a yellow crystal. ¹H NMR (300 MHz, CD₂Cl₂, TMS): δ =7.57–7.53 (m, 3H), 7.35 (d, 1H), 7.21–7.19(m, 2H), 2.61 (t, 2H), 1.58 (m, 2H), 1.33 (m, 18H), 0.88 ppm (m, 3H).

[(4-Hexylphenyl)ethynyl]trimethylsilane (3)

A mixture of 1-bromo-4-hexylbenzene (3.3 g, 14 mmol), CuI (0.14 g, 0.71 mmol), PPh₃ (0.38 g, 1.5 mmol), triethylamine (60 mL), and anhydrous THF (20 mL) were degassed with N₂ for 30 min. Then, [Pd-(PPh₃)₂Cl₂] (0.48 g, 0.68 mmol) and trimethylsilylacetylene (3.8 g, 38 mmol) were added to the mixture. The resulting mixture was stirred overnight at 70 °C and then quenched by the addition of water. The reaction mixture was extracted with ethyl acetate, and the combined organic layer was dried over MgSO₄, filtered, and concentrated. The crude product was purified with alumina column chromatography by using *n*-hexane as the eluent to yield **3** as a yellow oil. It was used in the next reaction without further purification. R_f =0.5 (*n*-hexane); ¹H NMR (300 MHz, CD₂Cl₂, TMS): δ =7.41–7.35 (m, 2H), 7.15–7.06 (m, 2H), 2.57 (t, 2H), 1.59 (m, 2H), 1.31 (m, 6H), 0.88 (m, 3H), 0.26–0.22 ppm (m, 9H).

FULL PAPERS

1-Hexyl-4-vinylbenzene (4)

A mixture of 1-bromo-4-hexylbenzene (1.3 g, 5.3 mmol), tributylvinyltin (1.7 g, 5.5 mmol), and anhydrous DMF (60 mL) was degassed with N₂ for 30 min. Then, [Pd(PPh₃)₄] (0.32 g, 0.27 mmol) was added to the reaction mixture and it was stirred for 3.5 h at 90 °C. After the mixture had been quenched by the addition of NH₄Cl solution, it was extracted with *n*-hexane and the combined organic layer was dried over MgSO₄ and filtered. Potassium fluoride was added to the filtrate and the mixture stirred for 5 h. After the solvent had been removed, the crude product was purified by silica gel column chromatography by using *n*-hexane as the eluent to yield **4** (0.56 g, 56%) as a clear oil. R_f =0.5 (*n*-hexane); ¹H NMR (300 MHz, CD₂Cl₂, TMS): δ =7.33–7.31 (m, 2H), 7.15–7.13 (m, 2H), 6.68 (t, 1H), 5.70 (d, 1H), 5.18 (d, 1H), 2.59 (t, 2H), 1.54 (m, 2H), 1.30 (m, 6H), 0.88 ppm (m, 3H).

3,6-Dibromobenzene-1,2-diamine (5)

NaBH₄ (3.4 g, 90 mmol) was added portionwise to a dried four-neck round-bottomed flask charged with 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (3.0 g, 10 mmol) in anhydrous ethanol (100 mL) under a N₂ atmosphere at 0 °C. The mixture was stirred at room temperature for 13 h. After the consumption of reactant was confirmed by TLC analysis, the solvent was removed. Water was added to the residue, which was extracted with ethyl acetate. The combined organic layer was dried over MgSO₄ to yield **5** (2.5 g, 93%) as a white solid. R_f =0.5 (ethyl acetate/*n*-hexane 1:3); ¹H NMR (300 MHz, CD₂Cl₂, TMS): δ =6.83 (s, 2H), 3.89 ppm (brs, 4H).

4,7-Dibromo-2-(5-phenylthiophen-2-yl)-1H-benzo[d]imidazole (6)

A mixture of **5** (2.5 g, 9.2 mmol), 5-phenylthiophene-2-carbaldehyde (2.0 g, 11 mmol), *p*-toluenesulfonic acid monohydrate (0.17 g, 0.99 mmol) and anhydrous ethanol (50 mL) was refluxed for 24 h under a N₂ atmosphere. The reaction was quenched by the addition of water and ethyl acetate. The organic layer was separated and dried over MgSO₄. After removal of the solvent, the product was washed with diethyl ether several times to yield **6** (1.8 g, 46%) as a brown powder. R_f =0.5 (ethylacetate/*n*-hexane 1:3); ¹H NMR (300 MHz, [D₆]DMSO, TMS): δ =13.48 (brs, 1H), 8.15 (d, *J*=4.2 Hz, 1H), 7.79–7.76 (m, 2H), 7.65 (d, *J*=3.9 Hz, 1H), 7.46 (t, 1H), 7.39–7.32 ppm (m, 4H).

4,7-*Dibromo-1-methyl-2-(5-phenylthiophen-2-yl)-1H*-benzo[*d*]imidazole (7)

Compound **6** (1.8 g, 4.0 mmol), K_2CO_3 (1.7 g, 12 mmol), methyliodide (0.50 mL, 8.0 mmol), and anhydrous ethanol (30 mL) were added to a dried four-neck round-bottomed flask. After the reaction mixture had been stirred for 1 h, the solvent was evaporated and the resulting residue was washed with water, *n*-hexane, and diethyl ether several times to yield **7** (1.6 g, 89%) as a brown powder. R_f =0.8 (chloroform); ¹H NMR (300 MHz, [D₆]DMSO, TMS): δ =7.83 (m, 3H), 7.74 (m, 1H), 7.49 (m, 2H), 7.42 (m, 3H), 4.29 ppm (s, 3H); ¹³C NMR (75 MHz, [D₆]DMSO, TMS): δ =149.8, 147.2, 142.6, 133.6, 132.8, 131.4, 129.4, 128.7, 128.4, 126.4, 125.8, 124.9, 111.8, 102.3, 34.72 ppm; HRMS (ESI): *mlz*: calcd for C₁₈H₁₂Br₂N₂S: 448.9146 [*M*+H]⁺; found: 448.9131.

4,7-Bis[5-(4-hexylphenyl)thiophen-2-yl]-1-methyl-2-(5-phenylthiophen-2-yl)-1H-benzo[d]imidazole (**TBIm**)

A mixture of **7** (0.29 g, 0.64 mmol), **2** (1.0 g, 2.7 mmol), 2 M Na₂CO₃ solution (30 mL), and THF (40 mL) was degassed with N₂ for 30 min. Then, $[Pd(PPh_3)_4]$ (0.080 g, 0.069 mmol) was added to the mixture. The resulting mixture was stirred overnight at 90 °C. The reaction mixture was extracted with ethyl acetate and the combined organic layer was dried over MgSO₄, filtered, and concentrated. The crude product was purified with alumina column chromatography by using ethyl acetate/*n*-hexane (1:5) as the eluent. The separated product was further purified by preparative GPC (chloroform) and normal-phase HPLC (chloroform/*n*-hexane) to yield **TBIm** (0.22 g, 44%) as a yellow powder. ¹H NMR (500 MHz, CD₂Cl₂, TMS): δ = 8.22 (d, 1H), 7.75–7.74 (m, 2H), 7.66–7.64 (m, 2H), 7.63 (m, 1H), 7.61–7.59 (m, 2H), 7.58 (m, 1H), 7.47 (m, 2H), 7.45 (m, 2H), 7.41 (d, 1H), 7.34 (m, 1H), 7.32–7.31 (m, 1H), 7.26–7.24(m, 4H), 7.14 (m, 1H), 3.82 (s, 3H), 2.64–2.63 (m, 4H), 1.64 (m, 4H), 1.33 (m,

12 H), 0.90 ppm (m, 6H); 13 C NMR (75 MHz, CD₂Cl₂, TMS): δ =149.7, 147.9, 145.5, 144.8, 143.4, 143.1, 140.5, 139.7, 138.3, 135.8, 134.0, 132.3, 132.2, 131.8, 129.8, 129.5, 129.4, 128.7, 128.5, 128.4, 127.1, 126.3, 125.9, 125.6, 124.3, 124.3, 123.8, 123.7, 122.9, 119.3, 118.0, 36.0, 36.0, 35.3, 35.3, 32.2, 31.9, 29.4, 23.1, 14.3 ppm; HRMS (ESI): m/z: calcd for $C_{50}H_{50}N_2S_3$: 775.3214 $[M+H]^+$; found: 775.3231.

4,7-Bis[(4-hexylphenyl)ethynyl]-1-methyl-2-(5-phenylthiophen-2-yl)-1Hbenzo[d]imidazole (EBIm)

A mixture of 7 (0.45 g, 1.0 mmol), CuI (0.012 g, 0.063 mmol), PPh₃ (0.031 g, 0.12 mmol), triethylamine (9 mL), and anhydrous THF (3 mL) was degassed with N₂ for 30 min. Then, [PdCl₂(PPh₃)₂] (0.059 g, 0.084 mmol), 3 (0.67 g, 2.6 mmol) and tetrabutylammonium fluoride (TBAF) (in THF 1M, 2mL) were added to the mixture. The resulting mixture was stirred overnight at 70 °C and then quenched by the addition of water. The reaction mixture was extracted with dichloromethane and the combined organic solution was washed with saturated brine, dried over MgSO₄, filtered, and concentrated. The crude product was purified with alumina column chromatography by using ethyl acetate/n-hexane (1:5) as the eluent. The separated product was further purified by recycling preparative GPC (chloroform) and normal-phase HPLC (chloroform/n-hexane) to yield EBIm (0.41 g, 61%) as a yellow powder. ¹H NMR (500 MHz, CD₂Cl₂, TMS): $\delta = 7.74-7.73$ (m, 2H), 7.63 (d, 1H), 7.58-7.56 (m, 2H), 7.51-7.50 (m, 2H), 7.47-7.46 (m, 1H), 7.45-7.43 (m, 2H), 7.42 (s, 2H), 7.38-7.35 (m, 1H), 7.25-7.23 (m, 4H), 4.48 (s, 3H), 2.67-2.64 (m, 4H), 1.64 (m, 4H), 1.33 (m, 12H), 0.90 ppm (m, 6H); ¹³C NMR (75 MHz, CD₂Cl₂, TMS): $\delta = 149.6$, 148.1, 144.8, 144.4, 144.3, 135.8, 133.9, 132.0, 131.6, 131.5, 130.0, 129.5, 129.1, 129.0, 128.8, 128.1, 126.6, 126.4, 124.3, 120.7, 120.3, 115.1, 107.4, 96.0, 95.7, 86.5, 85.6, 36.3, 34.0, 32.1, 31.7, 31.7, 29.4, 29.4, 23.0, 14. 3 ppm; HRMS (ESI): m/z: calcd for C₄₆H₄₆N₂S: 659.3460 [*M*+H]⁺; found: 659.3427.

4,7-*Bis*(4-hexylstyryl)-1-methyl-2-(5-phenylthiophen-2-yl)-1H-benzo[*d*]imidazole (**VBIm**)

A mixture of 7 (0.56 g, 1.2 mmol), 4 (0.53 g, 2.8 mmol), triethylamine (0.5 mL), and anhydrous DMF (10 mL) was degassed with N_2 for 30 min. Then, $Pd(OAc)_2$ (0.11 g, 0.49 mmol) and $P(oTol)_3$ (0.20 g, 0.66 mmol) were added to the solution. The resulting mixture was stirred overnight at 120°C and then quenched by the addition of water. The reaction mixture was extracted with chloroform and the combined organic layer was washed with saturated brine, dried over MgSO4, filtered, and concentrated. The crude product was purified with alumina column chromatography by using ethyl acetate/n-hexane (1:5) as an eluent. The separated product was further purified by recycling preparative GPC (chloroform) and normal-phase HPLC (chloroform/n-hexane) to yield VBIm (0.13 g, 16%) as a yellow powder. ¹H NMR (500 MHz, CD₂Cl₂, TMS): $\delta = 7.88-7.84$ (d, 1H), 7.77-7.75 (m, 1H), 7.74-7.73 (m, 2H), 7.71-7.68 (m, 1H), 7.59-7.57 (d, 2H), 7.55-7.54 (m, 1H), 7.50-7.49 (d, 2H), 7.47 (m, 2H), 7.46 (s, 2H), 7.44 (m, 1H), 7.38-7.35 (m, 1H), 7.24-7.21 (m, 4H), 7.10-7.07(d, 1H), 4.24 (s, 3H), 2.65-2.62 (m, 4H), 1.63 (m, 4H), 1.33 (m, 12H), 0.90 ppm (m, 6H); 13 C NMR (75 MHz, CD₂Cl₂, TMS): $\delta = 149.0$, 147.6, 143.5, 143.1, 142.0, 135.9, 135.2, 135.1, 134.0, 132.2, 131.5, 131.1, 129.7, 129.5, 129.2, 129.1, 128.6, 128.3, 127.0, 126.8, 126.3, 124.2, 124.2, 123.3, 123.1, 122.1, 120.7, 36.1, 36.1, 35.7, 32.2, 31.9, 30.1, 29.5, 29.4, 23.1, 14.3 ppm; HRMS (ESI): m/z: calcd for C₄₆H₅₀N₂S: 663.3773 [*M*+H]⁺; found: 663.3765.

Acknowledgements

The authors thank S. Katao, Y. Nishiyama, and Y. Kajiki for their assistance in X-ray crystallography, mass spectrometry, and CV measurements, respectively.

A. J. Zucchero, P. L. Mcgrier, U. H. F. Bunz, Acc. Chem. Res. 2010, 43, 397–408.

- [2] J. E. Klare, G. S. Tulevski, K. Sugo, A. de Picciotto, K. A. White, C. Nuckolls, J. Am. Chem. Soc. 2003, 125, 6030–6031.
- [3] P. L. McGrier, K. M. Solntsev, A. J. Zucchero, O. R. Miranda, V. M. Rotello, L. M. Tolbert, U. H. F. Bunz, *Chem. Eur. J.* **2011**, *17*, 3112– 3119.
- [4] a) K. Osowska, O. Š. Miljanić, *Chem. Commun.* 2010, 46, 4276–4278; b) Y. Ie, T. Kawabata, T. Kaneda, Y. Aso, *Chem. Lett.* 2006, 35, 1366–1367.
- [5] W. W. Gerhardt, A. J. Zucchero, C. R. South, U. H. F. Bunz, M. Weck, *Chem. Eur. J.* 2007, 13, 4467–4474.
- [6] S. Grunder, R. Huber, V. Horhoiu, M. T. González, C. Schönenberger, M. Calame, M. Mayor, J. Org. Chem. 2007, 72, 8337–8344.
- [7] C. Yi, C. Blum, M. Lehmann, S. Keller, S.-X. Liu, G. Frei, A. Neels, J. Hauser, S. Schürch, S. Decurtins, J. Org. Chem. 2010, 75, 3350– 3357.
- [8] a) D.-C. Lee, K. Jang, K. K. McGrath, R. Uy, K. A. Robins, D. W. Hatchett, *Chem. Mater.* 2008, *20*, 3688–3695; b) K. Jang, J. M. Kinyanjui, D. W. Hatchett, D.-C. Lee, *Chem. Mater.* 2009, *21*, 2070–2076; c) K. Jang, A. D. Ranasinghe, C. Heske, D.-C. Lee, *Langmuir* 2010, *26*, 13630–13636.
- [9] K.-S. Moon, H.-J. Kim, E. Lee, M. Lee, Angew. Chem. 2007, 119, 6931–6934; Angew. Chem. Int. Ed. 2007, 46, 6807–6810.
- [10] a) D.-J. Hong, E. Lee, H. Jeong, J.-k. Lee, W.-C. Zin, T. D. Nguyen,
 S. C. Glotzer, M. Lee, Angew. Chem. 2009, 121, 1692–1696; Angew.
 Chem. Int. Ed. 2009, 48, 1664–1668; b) L. Liu, D.-J. Hong, M. Lee,
 Langmuir 2009, 25, 5061–5067.
- [11] K. Oisaki, Q. Li, H. Furukawa, A. U. Czaja, O. M. Yaghi, J. Am. Chem. Soc. 2010, 132, 9262–9264.
- [12] a) M. Toba, T. Nakashima, T. Kawai, *Macromolecules* **2009**, *42*, 8068–8075; b) M. Toba, T. Nakashima, T. Kawai, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 1895–1906; c) T. Terashima, T. Nakashima, T. Kawai, *Org. Lett.* **2007**, *9*, 4195–4198.
- [13] A. J. Boydston, P. D. Vu, O. L. Dykhno, V. Chang, A. R. Wyatt II, A. S. Stockett, E. T. Ritschdorff, J. B. Shear, C. W. Bielawski, J. Am. Chem. Soc. 2008, 130, 3143–3156.
- [14] a) H. Hayashi, T. Yamamoto, *Macromolecules* 1998, *31*, 6063–6070;
 b) T. Yamamoto, T. Uemura, A. Tanimoto, S. Sasaki, *Macromolecules* 2003, *36*, 1047–1053.
- [15] a) K. Okuyama, T. Hasegawa, M. Ito, N. Mikami, J. Phys. Chem. 1984, 88, 1711–1716; b) K. Okuyama, M. C. R. Cockett, K. Kimura, J. Phys. Chem. 1992, 97, 1649–1654.
- [16] a) Z.-F. Shi, L.-J. Wang, H. Wang, X.-P. Cao, H.-L. Zhang, *Org. Lett.* 2007, *9*, 595–598; b) Y. Tang, Z. Zhou, K. Ogawa, G. P. Lopez, K. S. Schanze, D. G. Whitten, *Langmuir* 2009, *25*, 21–25; c) G. T. Dalton, M. P. Cifuentes, L. A. Watson, S. Petrie, R. Stranger, M. Samoc, M. G. Humphrey, *Inorg. Chem.* 2009, *48*, 6534–6547.
- [17] a) J. A. Marsden, J. J. Miller, L. D. Shirtcliff, M. M. Haley, J. Am. Chem. Soc. 2005, 127, 2464–2476; b) E. L. Spitler, L. D. Shirtcliff,

M. M. Haley, J. Org. Chem. 2007, 72, 86–96; c) S. Samori, S. Tojo,
M. Fujitsuka, E. L. Spitler, M. M. Haley, T. Majima, J. Org. Chem.
2008, 73, 3551–3558; d) K. Ohta, S. Yamada, K. Kamada, A. D. Slepkov, F. A. Hegmann, R. R. Tykwinski, L. D. Shirtcliff, M. M. Haley, P. Sałek, F. Gel'mukhanov, H. Ågren, J. Phys. Chem. A 2011, 115, 105–117.

- [18] CCDC-822135 (TBIm), -822134 (EBIm), and 822136 (VBIm) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [19] a) M. Karikomi, C. Kitamura, S. Tanaka, Y. Yamashita, J. Am. Chem. Soc. 1995, 117, 6791-6792; b) A. S. Özen, C. Atilgan, G. Sonmez, J. Phys. Chem. C 2007, 111, 16362-16371.
- [20] See the Supporting Information.
- [21] a) P. Hohenberg, W. Kohn, *Phys. Rev.* **1964**, *136*, 864–871; b) W. Kohn, L. J. Sham, *Phys. Rev.* **1965**, *140*, 1133–1138.
- [22] a) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200–1211; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; c) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200–206; d) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- [23] Gaussian 03 (Revision D.01), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Ivengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanavakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- [24] a) R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.* **1996**, 256, 454–464; b) M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahub, *J. Chem. Phys.* **1998**, 108, 4439–4449; c) R. E. Stratmann, G. E. Scuseria, M. J. Frisch, *J. Chem. Phys.* **1998**, 109, 8218–8224.

Received: April 22, 2011 Published online: August 3, 2011