Substituted carbazole dyes for efficient molecular photovoltaics: long electron lifetime and high open circuit voltage performance[†]

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We designed and synthesized new substituted carbazole dyes, **MK-14** and **-16**, for dye-sensitized solar cells (DSSCs) employing the I^-/I_3^- redox couple. By the addition of a hexyloxyphenyl substituent to previously reported carbazole dyes **MK-1** and **-2**, the electron lifetime and open circuit voltage of the DSSCs employing these dyes were increased, showing comparable values with those using a conventional Ru complex dye. This result was achieved by the retardation of the charge recombination, caused by more effective blocking of the I_3^- ion in the electrolyte than that in the cases of **MK-1** and **-2**. The result shows the importance of the position of alkyl chains attached to the main framework of dye molecules.

Introduction

Dye-sensitized solar cells (DSSCs) have become one of the promising molecular photovoltaics due to the high photo-tocurrent conversion efficiency as compared with amorphous silicon solar cells and the potential of low-cost production.^{1,2} Recently, organic dyes have been attracting much attention with respect to their application to molecular photovoltaics. While ruthenium complex dyes3 have kept the highest efficiency since the pioneering study,¹ a large number of organic dyes for use as molecular photovoltaics have been designed and synthesized because of the potential of organic dyes, such as the facile structural modification and high absorption coefficient.⁴ The highest energy conversion efficiency of DSSCs based on organic dyes (\sim 9%), however, is still lower than that based on ruthenium dyes ($\sim 11\%$). The reason for the lower efficiency is mostly faster charge recombination of the injected electron in the nanoporous TiO₂ electrode to a redox species in liquid electrolyte.⁵ Recent papers also show that DSSCs employing metal complex dyes such as porphyrin and phthalocyanine dyes, also suffer from fast recombination.6 Thus, to improve the efficiency of DSSCs, a design guide for sensitizing dyes to retard the recombination is essential.

In a previous report, we developed carbazole dyes with an alkyl-functionalized oligothiophene linker to a cyanoacetic acid moiety as an acceptor (MK-1 and -2, Fig. 1).7 In comparison to MK-3, which has no alkyl chain, we found that the alkyl chains on the thiophenes helped to form a blocking layer for I_3^- ions to be kept away from the TiO₂ electrode surface, hence increasing the electron lifetime and open circuit voltage (V_{OC}). To our knowledge, this is the first example of the addition of a function to organic dyes that retards charge recombination. Note that it is not evident that the addition of alkyl chain results in the retardation of charge recombination.8 It is important where the alkyl chains are attached and the packing density of the adsorbed dyes.^{8,9} In a series of coumarin dyes, we have observed that larger sized dye molecules tend to have a long electron lifetime.⁵ We have synthesized large molecules of carbazole dyes having up to six thiophenes with alkyl chains.⁹ Despite the expectation, $V_{\rm OC}$ was not improved. Even incident photon-to-current conversion efficiency (IPCE) tended to decrease with an increasing number



Fig. 1 Molecular structures of organic dyes, MK-1, -2, -14 and -16.

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of thiophenes. The problem with the larger dyes here seems to be undesired aggregation of the dyes on the TiO_2 surface,⁹ causing a larger space which allows I_3^- to penetrate into the dye layer.

To improve the photovoltaic performance of **MK** dyes, we designed and synthesized substituted carbazole dyes, **MK-14** and **MK-16**, which have a hexyloxyphenyl substituent¹⁰ on the carbazole moiety on the opposite side to an oligothiophene linker, shown in Fig. 1. Our strategy for the molecular design of these new dyes was based on two concepts: a further retardation of charge recombination without causing undesired aggregation by the addition of the substitute normal to the direction to the alkyl chains of **MK-1** and **-2**, and an extension of absorption wavelength by increasing the carbazole donor ability. Based on these dyes, comparable $V_{\rm OC}$ and electron lifetime of DSSCs with those for Ru dyes were achieved.

Results and discussion

Synthesis and UV spectra of dyes

Substituted carbazole dyes, **MK-14** and **-16** were prepared from 3-bromo-9-ethylcarbazole as described in Scheme 1 and 2.



Fig. 2 UV-vis spectra of dyes, **MK-14** (solid line) and **-16** (dotted line) in 20%THF-toluene.

Oligothiophene moieties were constructed by repeated Suzuki coupling and bromination. The purification of intermediates was performed by flash column chromatography and subsequent HPLC. The molecular structures of the compounds were fully



Scheme 1 Synthesis of organic dye MK-14; (a) (i) Mg, 4-*n*-hexyloxy-1-bromobenzene/THF, (ii) NiCl₂(dppp)/THF, (b) NBS/THF, (c) 5,5'-dimethyl-2-(4-*n*-hexylthiophen-2-yl)-1,3,2-dioxaborinane, Pd(PPh₃)₄, Na₂CO₃aq/DME, (d) POCl₃-DMF/DMF (e) cyanoacetic acid, piperidine/toluene-acetonitrile.



Scheme 2 Synthesis of organic dye MK-16; (a) NBS/THF, (b) 5,5'-dimethyl-2-(4-*n*-hexylthiophen-2-yl)-1,3,2-dioxaborinane, Pd(PPh₃)₄, Na₂CO₃aq/DME, (c) POCl₃-DMF/DMF, (d) cyanoacetic acid, piperidine/toluene-acetonitrile.

confirmed by ¹H NMR, ¹³C NMR and elemental analysis. Fig. 2 shows that the absorption maxima of the dyes were similar with those of **MK-1** and **-2** (480 nm, Fig. S1, ESI).⁹ The absorption edge of **MK-16** in the red region was observed to be slightly shifted to a longer wavelength than that of **MK-14** because of the larger number of thiophenes in the π -conjugated linker part. Due to the broad absorption band around 400 nm in the case of **MK-16**, however, an aggregation of dye molecules on the TiO₂ surface was considered to easily occur compared to **MK-14**.

Photovoltaic performances

Fig. 3 shows the action spectra of incident photon-to-current conversion efficiency (IPCE) for DSSCs with **MK-14** and **-16**. In comparison to **MK-1** and **-2** (Fig. S2, ESI), the onset wavelengths were shifted to longer wavelength.^{7,9} The onset wavelengths for **MK-16** were around 850 nm while that with **MK-2** was around 800 nm, suggesting the increased donor ability of **MK-16**. IPCE values more than 70% were observed in the range of 400 to 650 nm with a maximum value of 83% at 530 nm for the DSSC based on **MK-14**, while the maximum values for **MK-16** were slightly decreased.



Fig. 3 IPCE action spectra for solar cells based on MK-14 (solid line) and -16 (dotted line).

 Table 1
 Solar-cell performance for DSSCs^a

Dye	w/μm	${\rm TiO_2}^b$	$J_{\rm SC}/{ m mA~cm^{-2}}$	$V_{\rm OC}/{\rm V}$	FF	Eff./%
MK-14 ^c	4.8	a	11	0.72	0.64	4.8
MK-14 ^{c,d}	4.8	a	1.1	0.64	0.67	4.6
MK-16 ^c	4.7	a	11	0.72	0.60	4.7
MK-16 ^{c,d}	4.7	a	1.2	0.65	0.66	5.0
N719 ^c	4.8	a	9.5	0.74	0.70	4.9
N719 ^{c,d}	4.8	a	0.97	0.63	0.69	4.3
$MK-2^c$	5.1	a	11	0.69	0.64	5.0
MK-14 ^c	6.0	b	13.1	0.77	0.62	6.3
N719 ^c	6.0	b	10.3	0.79	0.77	6.3
MK-14 ^e	12.0	b	14.5	0.76	0.71	7.8
MK-16 ^e	12.0	b	14.5	0.73	0.69	7.3
MK-14	16.5	b	16.0	0.71	0.71	8.1

^{*a*} Incident light: AM 1.5G (100 mW cm⁻²) with a mask and without an anti-reflection film. ^{*b*} TiO₂, a: HPW-18NR, cell area, c.a. 0.16 cm² with a mask (0.17 cm²), b: home made TiO₆ with a scattering layer, cell area c.a. 0.25 cm² with a mask (0.2354 cm²). ^{*c*} Electrolyte: 0.6 M DMPImI + 0.1 M LiI + 0.05 M I₂ + 0.5 M TBP in acetonitrile. ^{*d*} Under a ND10 filter. ^{*e*} 0.6 M DMPImI + 0.1 M LiI + 0.1 M I₂ + 0.5 M TBP in acetonitrile. ^{*f*} 0.6 M DMPImI + 0.1 M LiI + 0.2 M I₂ + 0.5 M TBP in acetonitrile.

The photovoltaic performances of the DSSCs employing MK-14 and -16 with a thin-film TiO₂ electrode (4.8 μ m) are summarized in Table 1, including the data of MK-2 and N719 (a Ru complex dye). The $V_{\rm OC}$ values for the DSSCs based on MK-14 and -16 were slightly lower and higher than those with N719 under one sun and one tenth sun conditions, respectively. Fill factor (FF) of DSSCs with MK-14 and -16 were low under one sun conditions, but increased under one tenth sun conditions. After one day storage of the cells, FF was also increased (Table S2, ESI). Fill factor is mainly influenced by series resistance and shunt resistance of solar cells. Since the change of recombination rate is little during one day storage (Fig. S3, ESI), the increase of FF is mainly related to the decrease of series resistance. The molecular size of MK dyes is larger than that of N719, and thus, its influence on the diffusion of the redox couple would be expected. In order to fabricate highly efficient DSSCs, we prepared the DSSCs from home-made TiO₂ particles, denoted as b in Table 1. With thicker TiO₂ films to absorb more light and with an electrolyte containing a higher concentration of I_3^- to increase the conductivity of the electrolytes, increases of J_{sc} and FF were obtained. At this moment, the maximum η value of 8.1% for MK-14 was obtained under AM 1.5 G irradiation (100 mW cm⁻²) with the electrolyte: 0.6 M DMPImI + 0.1 M LiI + 0.2 M I_2 + 0.5 M TBP in acetonitrile, and with an aperture mask and without antireflection film.

Electron lifetime measurements

Fig. 4 shows the electron lifetime and open circuit voltage of the DSSCs. The electron lifetime in the DSSCs with MK-14 and -16 were improved from those of with MK-2 and they were the longest among the all organic dyes we have measured.^{5b} Note that the difference between the lifetimes in the DSSCs/N719 and those in the DSSCs/MK-2 were smaller than that in the previously published paper.5b This is probably due to the higher packing density of MK-2 on the TiO₂ by employing toluene for the dye solution instead of mixed solvents of AN/tBuOH/ toluene. The effect of solvent and packing density in detail will be addressed elsewhere. Here, under the conditions of low light intensity, the effect of the additional alkyl chain was more prominent, that is, a longer lifetime is seen than that of DSSCs using N719 (Fig. 4(a) and Fig. S4, ESI). This is consistent with the higher V_{OC} of DSSCs under low light intensity (Table 1). The $V_{\rm OC}$ is influenced not only by the charge recombination rate but also by the shift of the conduction band edge potential (E_{CB}) of TiO_2 . Fig. 4(b) shows that the V_{OC} values of the DSSCs were the same at the matched electron density, regardless of the dyes examined here, suggesting comparable E_{cb} among the DSSCs.

The retardation of the charge recombination could be caused by more efficient blocking of I_3^- and/or the decreased $I_3^$ concentrations due to the negatively charged oxygen atom in the substituent. We measured the electron lifetime in DSSCs with a decreased amount of adsorbed dyes, where the physical blocking effect was not expected, and observed large decreases of the lifetime in the DSSCs using **MK-14**, and **-16** (Fig. S5, ESI), suggesting the physical block is more significant.

The cause of the longer electron lifetime with the new dyes than that with **N719** under low light intensity is not clear yet. The drawback of the new dyes was the low fill factor. This might be





Fig. 4 Electron lifetimes in the DSSCs employing MK (metal free organic) and N719 (Ru complex) dyes (a), and open circuit voltage (b) as a function of electron density in the DSSCs.

caused by the decreased ion mobility in the electrolytes, where the additional alkyl chain would prevent not only the approach of I₃⁻ to the TiO₂ surface but also the diffusion of electrolytes in the pore of the TiO₂ electrodes. The different light intensity dependence between the new dyes and the others might be related to different redox couple concentration profiles under steady light intensity, that is, I_3^- ions could not diffuse back to Pt electrodes effectively, increasing the concentrations of I_3^- in the pore of the electrode. The increased FF with the electrolyte containing high $[I_3^-]$ on Table 1 is consistent with this hypothesis. The higher $[I_3^-]$ is also favorable in view of the I^-/I_3^- redox potential, that is, it increases the potential difference between the conduction band edge of the TiO₂ and the I^{-}/I_{3}^{-} . On the other hand, the high $[I_3^-]$ increases the charge recombination rate and the absorption of light by the electrolyte. Thus, fine tuning of the concentration is needed. The optimization would be more effective when the optimization of the size and distribution of pore in the TiO₂ electrode occur simultaneously. In addition, the

new alkyl chain of MK-14 and MK-16 normal to the adsorption site would be more effective to block larger molecule redox couples¹¹ and/or polymer hole conductors.

Conclusions

We newly synthesized hexyloxyphenyl substituted carbazole dyes for DSSCs and demonstrated that a hexyloxyphenyl substituent increased the electron lifetime, and consequently gave a higher open circuit voltage. The result was achieved by having the blocking effect not only on the lateral direction with respect to the TiO₂ surface as for MK-1 and -2 but also on the normal direction as for MK-14 and -16. Our approach shows that two functions: sensitization of TiO2 and retardation of charge recombination, can be added separately, and such separated design would provide a wide selection of molecular design for the functionalization. In comparison to the case of N719, these dyes still need to be improved in view of electron lifetime. We consider the shape of the dyes; spherical for N719 and cylindrical for the MK series, has an important role on the recombination rate.

Experimental section

General methods

¹H NMR spectra were recorded on a Bruker Avance400 (400 MHz). ¹³C NMR spectra were recorded on a Bruker Avance400 (100 MHz). Chemical shifts are denoted in δ -unit (ppm) relative to CDCl₃, THF-d₈. The splitting patterns are designated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet) and br (broad). Elemental analyses were measured by a CE Instruments EA1110 automatic elemental analyzer. Column chromatography was performed on silica gel (Kanto, Silica Gel 60N, spherical, 40-50 mm). Most of the organic compounds were finally purified by preparative HPLC (YRU-880 detector from SHIMAMURA Tec.) on silica gel (pre-packed column, CPS-HS-221-05 or CPS-223L-1 from KUSANO KAGAKU) The solvents were distilled and dried, if necessary, by standard methods. Reagents and starting materials were used as obtained from Aldrich, Wako, Kanto Chemical, TCI, Merck. Absorption spectra were measured with a SHIMADZU UV-3101PC.

Synthesis

9-Ethyl-3-(4-(n-hexyloxy)phenyl)-9H-carbazole 2. A Grignard reagent was prepared from 4-n-hexyloxy-1-bromobenzene (1.69 g, 6.57 mmol) and magnesium turnings (176 mg, 7.22 mmol) in anhydrous THF (30 mL). The resulting mixture was refluxed for 1 h. After cooling, the solution of the Grignard reagent was added dropwise to an ice-cooled suspension of 9-ethyl-3-bromo-9H-carbazole (900 mg, 3.28 mmol) and Ni(dppp)Cl₂ (18 mg, 0.033 mmol) in THF (30 mL). The reaction mixture was refluxed overnight. The mixture was carefully quenched with sat. NH₄Cl aqueous solution, and extracted with several portions of EtOAc. The combined organic layer was washed with H₂O and brine, dried over MgSO₄, and evaporated under reduced pressure. The crude product was purified by flash column chromatography (hexane/EtOAc = 100/1) and subsequent purification by HPLC (silica gel, hexane/EtOAc = 25/1) to afford 932 mg (2.40 mmol,

73%) of 9-ethyl-3-(4-(*n*-hexyloxy)phenyl)-9*H*-carbazole **2** as a white solid, ¹H NMR (400 MHz, CDCl₃) δ 8.26 (1H, dd, *J* = 1.8, 0.6 Hz), 8.16 (1H, ddd, *J* = 7.8, 1.2, 0.8 Hz), 7.69 (1H, dd, *J* = 8.5, 1.5 Hz), 7.65 (2H, d, *J* = 8.9 Hz), 7.50 (1H, ddd, *J* = 8.2, 7.0, 1.2 Hz), 7.47–7.42 (2H, m), 7.26 (1H, ddd, *J* = 7.8, 6.9, 1.0 Hz), 7.03 (2H, d, *J* = 8.9 Hz), 4.39 (2H, q, *J* = 7.2 Hz), 4.04 (2H, t, *J* = 6.6 Hz), 1.88–1.81 (2H, m), 1.56–1.50 (2H, m), 1.47 (3H, t, *J* = 7.2 Hz), 1.42–1.36 (4H, m), 0.95 (3H, t, *J* = 7.1 Hz), ¹³C NMR (100 MHz, CDCl₃) δ 158.0, 140.2, 138.9, 134.4, 131.9, 128.0, 125.6, 124.8, 123.3, 123.0, 120.3, 118.7, 118.2, 114.7, 108.5, 108.4, 67.9, 37.3, 31.6, 29.3, 25.7, 22.6, 14.0, 13.6. Anal. Calcd for C₂₆H₂₉NO: C, 84.06; H, 7.87; N, 3.77. Found. C, 84.11; H, 7.75; N, 3.67.

3-Bromo-9-ethyl-6-(4-(n-hexyloxy)phenyl)-9H-carbazole 3. To a solution of 9-ethyl-3-(4-(n-hexyloxy)phenyl)-9H-carbazole 2 (903 mg, 2.33 mmol) in THF (20 mL) was added N-bromosuccinimide (435 mg, 2.45 mmol). The reaction mixture was stirred at room temperature for 1 h, and quenched with 10% aqueous solution of Na₂CO₃ and extracted with EtOAc three times. The combined organic layer was washed with H2O and brine, dried over MgSO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 10/1) and successive HPLC on silica gel (hexane/EtOAc = 25/1) to obtain bromide 3 (882 mg, 1.98 mml, 84%) as a white solid, ¹H NMR (400 MHz, CDCl₃) δ 8.25 (1H, d, J = 1.8 Hz), 8.20 (1H, d, J = 1.8 Hz), 7.69 (1H, dd, J = 8.5, 1.8 Hz), 7.61 (2H, d, J = 8.8 Hz), 7.55 (1H, dd, J = 8.7, 1.8 Hz), 7.43 (1H, dd, J = 8.5 Hz), 7.28 (1H, d, J = 8.7 Hz), 7.02 (2H, d, J = 8.8 Hz), 4.34 (2H, q, J = 7.2 Hz), 4.03 (2H, t, J = 6.6 Hz), 1.87–1.80 (2H, m), 1.55–1.47 (2H, m), 1.43 (3H, t, J = 7.2 Hz), 1.40–1.36 $(4H, m), 0.94 (3H, t, J = 7.0 Hz), {}^{13}C NMR (100 MHz, CDCl_3)$ δ 158.2, 139.3, 138.9, 134.2, 128.3, 128.1, 125.6, 124.8, 123.2, 122.4, 118.5, 114.8, 111.6, 109.9, 108.8, 68.1, 37.7, 31.6, 29.3, 25.8, 22.6, 14.1, 13.8. Anal. Calcd for C₂₆H₂₈BrNO: C, 69.33; H, 6.27; N, 3.11. Found. C, 69.49; H, 6.17; N, 3.04.

9-Ethyl-3-(4-(n-hexyloxy)phenyl)-6-(4-n-hexylthiophen-2-yl)-9H-carbazole 4. The mixture of 3-bromo-9-ethyl-6-(4-(nhexyloxy)phenyl)-9H-carbazole 3 (328 mg, 0.73 mmol), 4-n-hexylthiophene-2-boronic acid ester (306 mg, 1.09 mmol), tetrakis(triphenylphosphine)palladium (84 mg, 0.073 mmol) and 0.5 mL of 10% aqueous solution of Na_2CO_3 in dimethoxyethane (10 mL) was refluxed for 24 h. After cooling, H₂O was added and the reaction mixture was extracted with EtOAc three times. The combined organic layer was washed with H₂O and brine, dried over MgSO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 25/1) and successive HPLC on silica gel (hexane/EtOAc = 25/1) to obtain a monothiophene adduct 4 (255 mg, 0.47 mmol, 65%) as a white solid, ¹H NMR (400 MHz, CDCl₃) δ 8.35 (1H, d, J = 1.8Hz), 8.30 (1H, d, J = 1.8 Hz), 7.72 (1H, dd, J = 8.5, 1.8 Hz), 7.68 (1H, dd, J = 8.5, 1.8 Hz), 7.64 (2H, d, J = 8.6 Hz), 7.43 (1H, d, J = 8.5 Hz), 7.38 (1H, d, J = 8.5 Hz), 7.21 (1H, d, J = 1.3 Hz), 7.02 (2H, J = 8.6 Hz), 6.85 (1H, d, J = 1.3 Hz), 4.37 (2H, q, J = 7.2 Hz), 4.04 (2H, t, J = 6.6 Hz), 2.66 (2H, br t, J = 7.8 Hz), 1.88-1.80 (2H, t, J = 7.8 Hz), 1.88m), 1.74-1.66 (2H, m), 1.55-1.48 (2H, m), 1.46 (3H, t, J = 7.2 Hz), 1.43–1.35 (10H, m), 0.94 (3H, t, J = 7.0 Hz), 0.93 (3H, t, J = 7.0 Hz), ¹³C NMR (100 MHz, CDCl₃) δ 158.1, 145.2, 144.1, 139.6,

139.3, 134.2, 132.1, 127.9, 125.9, 125.0, 124.0, 123.35, 123.27, 123.2, 118.2, 118.0, 117.4, 114.7, 108.65, 108.61, 67.9, 37.4, 31.7, 31.6, 30.7, 30.4, 29.3, 29.1, 25.7, 22.60, 22.57, 14.1, 14.0, 13.6. Anal. Calcd for $C_{36}H_{43}NOS$: C, 80.40; H, 8.06; N, 2.60, S, 5.96. Found. C, 80.19; H, 8.44; N, 2.65, S, 5.84.

9-Ethyl-3-(4-(n-hexyloxy)phenyl)-6-(5-bromo-4-n-hexylthiophen-2vl)-9H-carbazole 5. The bromination of 9-ethyl-3-(4-(n-hexyloxy)phenyl)-6-(4-n-hexylthiophen-2-yl)-9H-carbazole 4 (239 mg, 0.44 mmol) with N-bromosuccinimide (87 mg, 0.49 mmol) in THF (5 mL) was carried out in a similar manner to that of 3. The crude product was purified by column chromatography (hexane/ EtOAc = 25/1) and successive HPLC on silica gel (hexane/EtOAc = 50/1) to obtain bromide 5 (271 mg, 0.44 mml, 99%) as a white solid, ¹H NMR (400 MHz, CDCl₃) δ 8.28 (1H, d, J = 1.8 Hz), 8.26 (1H, d, J = 1.8 Hz), 7.69 (1H, dd, J = 8.5, 1.8 Hz), 7.64 (2H, d, J = 8.8 Hz), 7.62 (1H, dd, J = 8.5, 1.8 Hz), 7.43 (1H, d, J = 8.5 Hz), 7.37 (1H, d, J = 8.5 Hz), 7.06 (1H, s), 7.02 (2H, J = 8.8 Hz), 4.36 (2H, q, J = 7.2 Hz), 4.03 (2H, t, J = 6.6 Hz), 2.61 (2H, br t, J = 7.8 Hz), 1.87–1.80 (2H, m), 1.71–1.63 (2H, m), 1.55–1.50 (2H, m), 1.46 (3H, t, J = 7.2 Hz), 1.42–1.33 (10H, m), 0.94 (3H, t, J = 7.0 Hz), 0.93 (3H, t, J = 7.0 Hz), ¹³C NMR (100 MHz, CDCl₃) δ 158.2, 145.0, 143.0, 139.9, 139.5, 134.3, 132.4, 128.1, 125.3, 125.1, 123.8, 123.5, 123.3, 122.8, 118.5, 117.4, 114.8, 108.84, 108.81, 106.5, 68.1, 37.7, 31.7, 31.6, 29.8, 29.7, 29.3, 29.0, 25.8, 22.6, 22.6, 14.11, 14.05, 13.8. Anal. Calcd for C₃₆H₄₂BrNOS: C, 70.11; H, 6.86; N, 2.27, S, 5.20. Found. C, 70.16; H, 7.14; N, 2.27, S. 5.16.

9-Ethyl-3-(4-(n-hexyloxy)phenyl)-6-(3,4'-di-n-hexyl-[2,2']bithiophen-5-yl)-9H-carbazole 6. The Suzuki-coupling reaction of bromide 5 (467 mg, 0.76 mmol) with 4-n-hexylthiophene-2boronic acid ester (318 mg, 1.14 mmol) using Pd(PPh₃)₄ (87 mg, 0.078 mmol) as a catalyst in DME (10 mL) was carried out in a similar manner to that for 4. The crude product was purified by column chromatography (hexane/EtOAc = 25/1) and successive HPLC on silica gel (hexane/EtOAc = 25/1) to obtain bithiophene 6 (457 mg, 0.65 mmol, 86%) as a slightly yellow oil, ¹H NMR (400 MHz, CDCl₃) δ 8.34 (1H, d, J = 1.8 Hz), 8.30 (1H, d, J = 1.8 Hz), 7.72 (1H, dd, J = 8.5, 1.8 Hz), 7.69 (1H, dd, J = 8.5, 1.8 Hz), 7.64 (2H, d, J = 8.8 Hz), 7.44 (1H, d, J = 8.5 Hz), 7.39 (1H, d, J = 8.5 Hz), 7.20 (1H, s), 7.04–7.00 (3H, m), 6.89 (1H, d, J = 1.2 Hz), 4.39 (2H, q, J = 7.2 Hz), 4.03 (2H, t, J = 6.6 Hz), 2.80 (2H, br t, J = 7.8 Hz), 2.63 (2H, br t, J = 7.8 Hz), 1.87–1.79 (2H, m), 1.77– 1.62 (4H, m), 1.47 (3H, t, J = 7.2 Hz), 1.53–1.28 (18H, m), 0.95– 0.89 (9H, m), ¹³C NMR (100 MHz, CDCl₃) δ 158.1, 143.5, 142.9, 140.1, 139.7, 139.4, 136.2, 134.2, 132.2, 129.2, 128.0, 126.6, 125.3, 125.1, 124.7, 123.7, 123.4, 123.3, 119.4, 118.3, 117.3, 114.7, 108.72, 108.71, 68.0, 37.5, 31.7, 31.7, 31.6, 30.9, 30.6, 30.5, 30.3, 29.6, 29.33, 29.30, 29.0, 25.7, 22.64, 22.60, 22.60, 14.1, 14.1, 14.0, 13.7. Anal. Calcd for C₄₆H₅₇NOS₂: C, 78.47; H, 8.16; N, 1.99, S, 9.11. Found. C, 78.71; H, 8.62; N, 2.01, S, 8.72.

9-Ethyl-3-(4(*n*-hexyloxy)phenyl)-6-(5'-bromo-3,4'-di-*n*-hexyl-[2,2']bithiophen-5-yl)-9*H*-carbazole 7. The bromination of bithiophene 6 (457 mg, 0.65 mmol) with *N*-bromosuccinimide (121 mg, 0.68 mmol) in THF (5 mL) was carried out in a similar manner to that of 3. The crude product was purified by column chromatography (hexane/EtOAc = 25/1) and successive HPLC on silica gel

(hexane/EtOAc = 25/1) to obtain bromide 7 (497 mg, 0.64 mml, 98%) as a yellow oil, ¹H NMR (400 MHz, CDCl₃) δ 8.33 (1H, d, J = 1.8 Hz), 8.29 (1H, d, J = 1.8 Hz), 7.71 (1H, dd, J = 8.5, 1.8 Hz), 7.69 (1H, dd, J = 8.5, 1.8 Hz), 7.64 (2H, d, J = 8.8 Hz), 7.44 (1H, d, J = 8.5 Hz, 7.39 (1H, d, J = 8.5 Hz), 7.19 (1H, s), 7.02 (2H, d, J = 8.8 Hz), 6.86 (1H, s), 4.38 (2H, q, J = 7.2 Hz), 4.03 (2H, t, J =6.6 Hz), 2.76 (2H, br t, J = 7.8 Hz), 2.58 (2H, br t, J = 7.8 Hz), 1.87-1.79 (2H, m), 1.75-1.59 (4H, m), 1.46 (3H, t, J = 7.2 Hz), 1.53-1.30 (18H, m), 0.96-0.89 (9H, m), ¹³C NMR (100 MHz, CDCl₃) & 158.1, 143.4, 142.3, 140.6, 139.8, 139.3, 136.1, 134.1, 132.2, 128.1, 127.9, 125.9, 125.1, 125.0, 124.6, 123.7, 123.4, 123.2, 118.2, 117.2, 114.7, 108.70, 108.68, 107.9, 67.9, 37.5, 31.7, 31.6, 31.6, 30.6, 29.6, 29.54, 29.50, 29.3, 29.3, 28.9, 25.7, 22.62, 22.60, 22.58, 14.1, 14.1, 14.0, 13.7. Anal. Calcd for C₄₆H₅₆BrNOS₂: C, 70.56; H, 7.21; N, 1.79, S, 8.19. Found. C, 70.19; H, 7.30; N, 1.78, S, 8.31.

9-Ethyl-3-(4-(n-hexyloxy)phenyl)-6-(3,4',4"-tri-n-hexyl-[2,2',5', 2"|terthiophen-5-yl)-9H-carbazole 8. The Suzuki-coupling reaction of bromide 7 (417 mg, 0.53 mmol) with 4-n-hexylthiophene-2-boronic acid ester (224 mg, 0.80 mmol) using Pd(PPh₃)₄ (62 mg, 0.053 mmol) as a catalyst in DME (10 mL) was carried out in a similar manner to that of 4. The crude product was purified by column chromatography (hexane/EtOAc = 25/1) and successive HPLC on silica gel (hexane/EtOAc = 25/1) to obtain terthiophene 8 (394 mg, 0.45 mmol, 85%) as a yellow oil, ¹H NMR (400 MHz, CDCl₃) δ 8.35 (1H, d, J = 1.8 Hz), 8.31 (1H, d, J = 1.8 Hz), 7.73 (1H, dd, J = 8.5, 1.8 Hz), 7.69 (1H, dd, J = 8.5, 1.8 Hz), 7.65 (2H, d, J = 8.8 Hz), 7.44 (1H, d, J = 8.5 Hz), 7.39 (1H, d, J = 8.5 Hz)Hz), 7.22 (1H, s), 7.03 (2H, J = 8.8 Hz), 7.02 (1H, s), 7.00 (1H, d, J = 1.2 Hz), 6.91 (1H, d, J = 1.2 Hz), 4.37 (2H, q, J = 7.2 Hz), 4.04 (2H, t, J = 6.6 Hz), 2.84 (2H, br t, J = 7.8 Hz), 2.79 (2H, br t, JJ = 7.8 Hz), 2.64 (2H, br t, J = 7.8 Hz), 1.88–1.80 (2H, m), 1.80– 1.63 (6H, m), 1.47 (3H, t, J = 7.2 Hz), 1.54–1.29 (24H, m), 0.97– 0.88 (12H, m), ¹³C NMR (100 MHz, CDCl₃) δ 158.1, 143.5, 143.0, 140.3, 139.8, 139.41, 139.39, 135.7, 134.2, 134.2, 132.2, 130.4, 128.8, 128.0, 127.9, 126.9, 125.2, 125.1, 124.9, 123.7, 123.5, 123.3, 119.7, 118.3, 117.3, 114.7, 108.7, 108.7, 68.0, 37.5, 31.71, 31.67, 31.67, 31.62, 30.54, 30.52, 30.45, 30.34, 29.7, 29.4, 29.31, 29.31, 29.26, 29.0, 25.8, 22.65, 22.61, 22.61, 22.61, 14.11, 14.08, 14.08, 14.04, 13.8. Anal. Calcd for C₅₆H₇₁NOS₃: C, 77.28; H, 8.22; N, 1.61, S, 11.05. Found. C, 77.36; H, 8.64; N, 1.61, S, 11.07.

5"-[9-Ethyl-3-(4-(*n*-hexyloxy)phenyl)-9*H*-carbazol-6-yl]-3',3",4tri-*n*-hexyl-[2,2',5',2"]terthiophene-5-carbaldehyde 9. To a cold solution of terthiophene 8 (155 mg, 0.18 mmol) in dry DMF (2 mL) at 0 °C was added a Vilsmeier reagent, which was prepared with 0.05 mL of POCl₃ in DMF (0.2 mL). The mixture was stirred at 70 °C for 7 h, and quenched with 10% aqueous solution of NaOAc (10 mL) after cooling, and extracted with EtOAc three times. The combined organic layer was washed with H₂O and brine, dried over MgSO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 10/1) and successive HPLC on silica gel (hexane/EtOAc = 10/1) to obtain aldehyde 9 (103 mg, 0.12 mml, 64%) as an orange oil, ¹H NMR (400 MHz, CDCl₃) δ 10.02 (1H, s), 8.34 (1H, d, *J* = 1.8 Hz), 8.30 (1H, d, *J* = 1.8 Hz), 7.72 (1H, dd, *J* = 8.5, 1.8 Hz), 7.69 (1H, dd, *J* = 8.5, 1.8 Hz), 7.64 (1H, d, *J* = 8.8 Hz), 7.44 (1H, d, J = 8.5 Hz), 7.40 (1H, d, J = 8.5 Hz), 7.22 (1H, s), 7.05 (1H, s), 7.04 (1H, s), 7.02 (1H, d, J = 8.8 Hz), 4.38 (2H, q, J = 7.2 Hz), 4.03 (2H, t, J = 6.6 Hz), 2.95 (2H, br t, J = 7.8 Hz), 2.84 (4H, br t, J = 7.8 Hz), 1.87–1.80 (2H, m), 1.78–1.68 (6H, m), 1.47 (3H, t, J = 7.1 Hz), 1.53–1.31 (24H, m), 0.95–0.89 (12H, m), ¹³C NMR (100 MHz, CDCl₃) δ 181.5, 158.2, 153.4, 145.3, 143.9, 142.5, 141.2, 140.0, 139.5, 136.6, 135.9, 134.3, 132.4, 128.9, 128.4, 128.12, 128.08, 127.8, 125.2, 125.1, 125.0, 123.8, 123.5, 123.3, 118.5, 117.5, 114.8, 108.8, 108.8, 68.1, 37.7, 31.68, 31.65, 31.6, 31.5, 31.4, 30.4, 30.1, 29.83, 29.81, 29.33, 29.29, 29.26, 29.0, 28.4, 25.7, 22.63, 22.60, 22.60, 22.5, 14.10, 14.06, 14.0, 14.0, 13.8. Anal. Calcd for C₅₇H₇₁NO₂S₃: C, 76.21; H, 7.97; N, 1.56, S, 10.71. Found. C, 76.30; H, 8.17; N, 1.58, S, 10.84.

2-Cyano-3-[5"-[9-ethyl-3-(4-(n-hexyloxy)phenyl)-9H-carbazol-6-yl]-3',3",4-tri-*n*-hexyl-[2,2',5',2"]terthiophen-5-yl]acrylic acid, MK-14. A mixture of aldehyde 9 (70 mg, 0.078 mmol) with cyanoacetic acid (13 mg, 0.16 mmol) in dry acetonitrile (2 mL) and dry toluene (2 mL) was refluxed in the presence of piperidine (0.5 mL) for 15 h. After cooling the mixture was diluted with chloroform, and the organic layer was washed with aqueous HCl (1 N), H₂O and brine, dried over Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (CHCl₃ \rightarrow CHCl₃/EtOH = 10/1) to obtain a dye MK-14 (61 mg, 0.063 mmol, 81%) as dark-red solids, ¹H NMR (400 MHz, THF-d₈) δ 8.47 (1H, br s), 8.41 (1H, s), 8.40 (1H, br s), 7.74 (1H, br d, J = 8.5 Hz), 7.70 (1H, dd, J = 8.5, 1.1 Hz), 7.65 (2H, d, J = 8.8 Hz), 7.53 (1H, d, J = 8.5 Hz), 7.52 (1H, d, J = 8.5 Hz), 7.36 (1H, s), 7.23 (1H, s), 7.13 (1H, s), 6.99 (2H, d, J = 8.8 Hz), 4.45 (2H, q, J = 7.0 Hz), 4.01 (2H, t, J = 6.5 Hz), 2.94-2.83 (6H, m), 1.84-1.65 (8H, m), 1.54-1.29 (27H, m), 0.95-0.90 (12H, m), ¹³C NMR (100 MHz, CDCl₃) δ 168.4, 158.2, 156.3, 146.7, 144.4, 144.1, 143.8, 141.6, 140.0, 139.5, 137.7, 134.3, 132.4, 129.3, 128.6, 128.5, 128.2, 128.1, 126.8, 125.3, 125.2, 124.9, 123.8, 123.5, 123.3, 118.5, 117.4, 116.2, 114.8, 108.9, 108.9, 93.3, 68.1, 37.8, 31.75, 31.73, 31.63, 31.55, 31.2, 30.34, 30.31, 30.1, 30.0, 29.4, 29.32, 29.27, 29.1, 29.0, 25.8, 22.7, 22.63, 22.63, 22.57, 14.15, 14.13, 14.06, 14.06, 13.9. Anal. Calcd for C₆₀H₇₂N₂O₃S₃: C, 74.65; H, 7.52; N, 2.90, S, 9.96. Found. C, 72.68; H, 7.29; N, 2.78, S, 9.64.

9-Ethyl-3-(4-(n-hexyloxy)phenyl)-6-(5"-bromo-3,4',4"-tri-n-hexyl-[2,2',5',2"]terthiophen-5-yl)-9H-carbazole 10. The bromination of terthiophene 8 (250 mg, 0.29 mmol) with N-bromosuccinimide (56 mg, 0.32 mmol) in THF (5 mL) was carried out in a similar manner to that of 3. The crude product was purified by column chromatography (hexane/EtOAc = 25/1) and successive HPLC on silica gel (hexane/EtOAc = 25/1) to obtain bromide 10 (251 mg, 0.26 mml, 92%) as a yellow oil, ¹H NMR (400 MHz, CDCl₃) δ 8.35 (1H, br s), 8.31 (1H, d, *J* = 1.8 Hz), 7.73 (1H, dd, *J* = 8.4, 1.5 Hz), 7.69 (1H, dd, J = 8.5, 1.8 Hz), 7.65 (2H, d, J = 8.7 Hz), 7.43 (1H, d, J = 8.4 Hz), 7.39 (1H, d, J = 8.5 Hz), 7.22 (1H, s), 7.03 (2H, J = 8.7 Hz), 7.02 (1H, s), 6.86 (1H, s), 4.37 (2H, q, J =7.1 Hz), 4.04 (2H, t, J = 6.6 Hz), 2.83 (2H, br t, J = 7.8 Hz), 2.74 (2H, br t, *J* = 7.8 Hz), 2.59 (2H, br t, *J* = 7.8 Hz), 1.88–1.80 (2H, m), 1.78–1.60 (6H, m), 1.47 (3H, t, J = 7.1 Hz), 1.54–1.30 (24H, m), 0.97–0.90 (12H, m), ¹³C NMR (100 MHz, CDCl₃) δ 158.1, 143.2, 142.4, 140.6, 140.0, 139.9, 139.4, 135.5, 134.8, 134.3, 132.3, 128.1, 127.9, 126.4, 125.20, 125.17, 124.9, 123.8, 123.5, 123.3,

118.4, 117.4, 114.8, 108.8, 108.8, 108.4, 68.0, 37.6, 31.71, 31.65, 31.62, 31.61, 30.53, 30.53, 29.7, 29.6, 29.5, 29.34, 29.31, 29.31, 29.23, 28.9, 25.8, 22.65, 22.62, 22.62, 22.59, 14.12, 14.08, 14.08, 14.05, 13.8. Anal. Calcd for $C_{56}H_{70}BrNOS_3$: C, 70.86; H, 7.43; N, 1.48, S, 10.13. Found. C, 70.34; H, 7.73; N, 1.50, S, 9.51.

9-Ethyl-3-(4-(n-hexyloxy)phenyl)-6-(3,4',4",4"' -tetra-n-hexyl-[2,2'5', 2".5".2" louaterthiophen-5-vl)-9H-carbazole 11. The Suzukicoupling reaction of bromide 10 (251 mg, 0.26 mmol) with 4-nhexylthiophene-2-boronic acid ester (148 mg, 0.53 mmol) using Pd(PPh₃)₄ (31 mg, 0.026 mmol) as a catalyst in DME (10 mL) was carried out in a similar manner to that of 4. The crude product was purified by column chromatography (hexane/ EtOAc = 25/1) and successive HPLC on silica gel (hexane/EtOAc = 25/1) to obtain quaterthiophene 11 (253 mg, 0.24 mmol, 92%) as an orange oil, ¹H NMR (400 MHz, CDCl₃) δ 8.35 (1H, d, J = 1.8 Hz), 8.30 (1H, d, J = 1.8 Hz), 7.73 (1H, dd, J = 8.5, 1.8 Hz), 7.69 (1H, dd, J = 8.5, 1.8 Hz), 7.65 (2H, d, J = 8.8 Hz), 7.44 (1H, d, J = 8.5 Hz), 7.40 (1H, d, J = 8.5 Hz), 7.21 (1H, s), 7.02 (2H, J = 8.8 Hz), 7.01–6.96 (3H, m), 6.90 (1H, br s), 4.39 (2H, q, J = 7.1Hz), 4.03 (2H, t, J = 6.6 Hz), 2.86–2.74 (6H, m), 2.62 (2H, br t, J = 7.8 Hz), 1.87–1.79 (2H, m), 1.78–1.61 (8H, m), 1.47 (3H, t, J = 7.1 Hz), 1.53–1.32 (30H, m), 0.97–0.88 (15H, m), ¹³C NMR (100 MHz, CDCl₃) δ 158.1, 143.6, 143.1, 140.4, 139.8, 139.6 139.5, 139.4, 135.6, 134.3, 134.2, 133.6, 132.3, 130.8, 129.9, 128.8, 128.2, 128.0, 128.0, 127.0, 125.2, 125.1, 124.9, 123.7, 123.5, 123.3, 119.9, 118.4, 117.3, 114.7, 108.8, 108.8, 68.0, 37.6, 31.72, 31.69, 31.67, 31.66, 31.63, 30.55, 30.52, 30.48, 30.46, 30.4, 29.8, 29.5, 29.4, 29.32, 29.28, 29.28, 29.2, 29.0, 25.8, 22.7, 22.64, 22.61, 22.61, 21.61, 14.13, 14.10, 14.08, 14.08, 14.04, 13.8. Anal. Calcd for C₆₆H₈₅NOS₄: C, 76.47; H, 8.26; N, 1.35, S, 12.37. Found. C, 76.00; H, 8.49; N, 1.38, S, 11.54.

5^{"//}-[9-Ethyl-3-(4-(*n*-hexyloxy)phenyl)-9*H*-carbazol-6-yl]-3['],3^{"/},3^{"/}4tetra-n-hexyl-[2,2',5',2",5",2"']quaterthiophene-5-carbaldehyde 12. To a cold solution of quaterthiophene 11 (253 mg, 0.27 mmol) in dry DMF (5 mL) at 0 °C was added a Vilsmeier reagent, which was prepared with 0.1 mL of POCl₃ in DMF (0.5 mL). The mixture was stirred at 70 °C for 7 h, and quenched with 10% aqueous solution of NaOAc (30 mL) after cooling, and extracted with dichloromethane three times. The combined organic layer was washed with H₂O and brine, dried over MgSO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (hexane/EtOAc = 10/1) and successive HPLC on silica gel (hexane/EtOAc = 10/1) to obtain aldehyde 12 (208 mg, 0.20 mml, 80%) as a dark-orange oil, ¹H NMR (400 MHz, CDCl₃) δ 10.02 (1H, s), 8.35 (1H, d, J = 1.8Hz), 8.30 (1H, d, J = 1.8 Hz), 7.72 (1H, dd, J = 8.5, 1.8 Hz), 7.69 (1H, dd, J = 8.5, 1.8 Hz), 7.64 (1H, d, J = 8.8 Hz), 7.43 (1H, d, J)= 8.5 Hz), 7.39 (1H, d, J = 8.5 Hz), 7.22 (1H, s), 7.05 (1H, s), 7.03–7.01 (4H, m), 4.38 (2H, q, J = 7.2 Hz), 4.03 (2H, t, J = 6.6 Hz), 2.95 (2H, br t, J = 7.8 Hz), 2.86–2.80 (6H, m), 1.87–1.80 (2H, m), 1.79–1.67 (8H, m), 1.47 (3H, t, J = 7.2 Hz), 1.53–1.30 (30H, m), 0.97–0.88 (15H, m), ¹³C NMR (100 MHz, CDCl₃) δ 181.4, 158.1, 153.2, 145.1, 143.3, 142.4, 140.6, 140.4, 139.8, 139.4, 136.0, 135.9, 135.1, 134.2, 132.3, 129.2, 129.1, 128.4, 128.4, 128.0, 127.7, 125.09, 125.07, 124.9, 123.6, 123.4, 123.2, 118.3, 117.3, 114.7, 108.7, 108.7, 68.0, 37.6, 31.7, 31.64, 31.60, 31.58, 31.5, 31.3, 30.4, 30.3, 30.1, 29.8, 29.8, 29.6, 29.3, 29.27, 29.26,

29.2, 28.9, 28.3, 25.7, 22.62, 22.59, 22.57, 22.57, 22.5, 14.09, 14.06, 14.02, 13.99, 13.99, 13.8. Anal. Calcd for $C_{67}H_{85}NO_2S_4$: C, 75.58; H, 8.05; N, 1.32, S, 12.05. Found. C, 75.10; H, 8.16; N, 1.34, S, 11.56.

2-Cyano-3-[5^{"'}-(9-ethyl-3-(4-(n-hexyloxy)phenyl)-9H-carbazol-6-yl]-3',3"',3"'',4-tetra-*n*-hexyl-[2,2',5',2",5",2"']quaterthiophenyl-5vllacrvlic acid. MK-16. A mixture of aldehvde 12 (208 mg, 0.20 mmol) with cyanoacetic acid (33 mg, 0.39 mmol) in a mixed solvent of dry acetonitrile (2 mL) and dry toluene (2 mL) was refluxed in the presence of piperidine (0.5 mL) for 20 h. After cooling the mixture was diluted with chloroform, and the organic layer was washed with aqueous HCl (1 N), H₂O and brine, dried over Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (CHCl₃ \rightarrow $CHCl_3/ethanol = 10/1$) to obtain a dye MK-16 (209 mg, 0.19) mmol, 95%) as a dark-red solid, ¹H NMR (400 MHz, THF-d₈) δ 8.46 (1H, br s), 8.41 (1H, s), 8.40 (1H, br s), 7.74 (1H, br d, J =8.5 Hz), 7.69 (1H, dd, J = 8.5, 1.1 Hz), 7.65 (2H, d, J = 8.8 Hz), 7.51 (1H, d, J = 8.5 Hz), 7.50 (1H, d, J = 8.5 Hz), 7.34 (1H, s), 7.24 (1H, s), 7.12 (1H, s), 7.10 (1H, s), 6.99 (2H, d, J = 8.8 Hz), 4.44 (2H, q, J = 7.2 Hz), 4.00 (2H, t, J = 6.5 Hz), 2.93–2.82 (8H, m), 1.84–1.63 (10H, m), 1.55–1.28 (33H, m), 0.95–0.89 (15H, m), ¹³C NMR (100 MHz, THF-*d*₈) δ 164.6, 159.3, 155.4, 144.7, 144.6, 143.9, 143.5, 141.7, 141.6, 141.1, 140.6, 137.1, 136.3, 135.1, 133.3, 130.8, 130.3, 130.1, 130.0, 129.1, 129.0, 128.6, 128.3, 126.1, 125.9, 125.8, 124.7, 124.42, 124.39, 119.1, 118.1, 116.9, 115.4, 109.9, 109.8, 98.2, 68.6, 38.3, 32.74, 32.69, 32.69, 32.6, 32.5, 32.2, 31.5, 31.4, 31.3, 30.8, 30.6, 30.34, 30.34, 30.30, 30.2, 30.2, 29.9, 29.5, 26.8, 23.58, 23.56, 23.56, 23.54, 23.47, 14.53, 14.50, 14.49, 14.4, 14.4, 14.1. Anal. Calcd for C₇₀H₈₆N₂O₃S₄: C, 74.29; H, 7.66; N, 2.48, S, 11.33. Found. C, 74.42; H, 7.91; N, 2.42, S, 11.56.

Preparation of dye-sensitized TiO₂ electrodes

Nanocrystalline TiO_2 photoelectrodes were prepared from a solution containing TiO_2 nano-particles (HPW-18NR, Catalysts & Chemicals Ind. Co., Ltd.). The paste was applied on to transparent conducting oxide (SnO₂:F) by doctor-blading techniques and annealed at 550 °C for 30 min in air.

To fabricate highly efficiency DSSCs, nanocrystalline TiO₂ photoelectrodes were prepared by a screen printing using TiO₂ nanoparticles and an organic TiO₂ paste prepared by methods reported in a previous paper.¹² The TiO₂ paste consisted of TiO₂ nanoparticles (ca. 20 nm), ethyl cellulose as a binder, and α terpineol as a solvent. The TiO₂ paste was printed on a glass substrate coated with transparent conducting oxide and subsequently sintered at 500 °C in air for 1 h. The thickness of the TiO₂ thin films, was measured with an Alpha-Step 300 profiler (TENCOR INSTRUMENTS). The TiO₂ film electrode consists a transparent layer (8 or 12.5 μ m) and a scattering layer (4 μ m), which contains large TiO₂ particles (av. 100 nm) and small particles (av. 20 nm) at a molar ratio of 4:6. The MK dyes were dissolved at a concentration of 0.3 mM in toluene (KANTO CHEMICAL). A Ru complex dye (N719) was obtained from Peccell Technology and dissolved in a mixed solvents of AN and tBuOH. The TiO₂ films were immersed in the dye solutions and then kept at 25 °C for more than 12 h to allow the dye to adsorb to the TiO₂ surface, and rinsed with the same solvents. The electrolyte was 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPImI) + 0.1 M LiI + 0.05 M I_2 + 0.5 M 4-*tert*butylpyridine (TBP) in AN. Reagent-grade LiI (WAKO CHEMICAL) and I_2 (WAKO) were used for the electrolyte. DMPImI was purchased from TOMIYAMA PURE CHEM-ICAL INDUSTRIES Ltd. A Pt counter electrode were prepared by sputtering (*ca.* 200 nm) onto TCO-coated glass substrate.

Photovoltaic measurements of the solar cells

The photovoltaic performance of the solar cells was measured with a source meter (ADVANTEST, R6246). We employed an AM 1.5G solar simulator (WACOM, WXS-80C-3) as the light source. The incident light intensity was calibrated by using a standard solar cell composed of a crystalline silicon solar cell and an IR-cut off filter (SCHOTT, KG-5), giving the photoresponse range of amorphous silicon solar cell (produced and calibrated by Japan Quality Assurance Organization). For highly efficient DSSCs, we used an aperture mask (0.2354 cm²) attached onto the top of the cells in the photovoltaic measurements. Action spectra of the monochromatic incident photon-to-current conversion efficiency (IPCE) of the solar cell were measured with a CEP-99W system (BUNKOH-KEIKI Co., Ltd.).

Transient photovoltage measurements

Electron lifetimes in the DSSCs were obtained by stepped lightinduced transient measurements of photovoltage. The experimental procedure for the measurements is described in detail elsewhere.13 In short, DSSCs were irradiated by a diode laser (Coherent, Lablaser, $\lambda = 635$ nm) and the decay of open circuit voltage, caused by step-wise decrease of a small fraction of the laser intensity, was measured. The measurement was repeated with various initial laser intensities, giving different electron density in the DSSCs. Electron lifetime (τ) was obtained by fitting an exponential function, $\exp(-t/\tau)$, to the voltage decay. The electron density was estimated by the charge extraction method introduced by Peter and co-workers.14 Our experimental setup is described in a previous paper.¹⁵ In short, irradiated laser light was turned off simultaneously with the switch from open circuit to short circuit conditions. Then, the induced transient current was recorded, and then the amount of the charges in the DSSC at open circuit conditions was obtained by numerical integration of the current transient. The control of the laser intensity and circuit conditions was performed by LabVIEW with a DAQ card (National Instruments).

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