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SYNTHESIS AND PROPERTIES OF UNSYMMETRICAL *N,N'*-DIALKYLTERRYLENEBIS(DICARBOXIMIDE) DERIVATIVES AND THEIR RELATED DERIVATIVES

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Abstract – Terrylene derivatives have optical absorptions in the longer wavelength region than the perylene dyes and an unsymmetrical terrylene derivatives are expected to have an improved orientation and solubility. Unsymmetrical terrylenebis(dicarboximide) derivatives and their related dicarboximide derivatives were prepared, and the absorption or emission of light in a solution or solid film and their semiconductor-character for Schottky devices or dye sensitized solar cell devices were investigated. In solution, unsymmetrical and symmetrical terrylene derivatives showed the same absorption or emission spectra and have absorption or emission peaks in the longer wavelength region than that of the perylenedicarboximide derivatives. In a solid, the terrylene derivatives showed broad absorption peaks in the wavelength region shorter than that in solution. The terrylene derivatives behaved as an n-type semiconductor for a Schottky device and their conversion efficiencies were equivalent value to that of the typical semiconductor phthalocyanine (H_2Pc). Perylenedicarboximide derivatives having a naphthalic anhydride moiety behave as a sensitizing dye for a dye sensitized solar cell.

INTRODUCTION

Visible absorption and luminescence spectra having broad peaks are shown for the solid film of the perylene and terrylene derivatives. They also show the characteristics for organic semiconductor substances. Therefore, they are expected to be used as a new material for organic solar cells or EL devices.

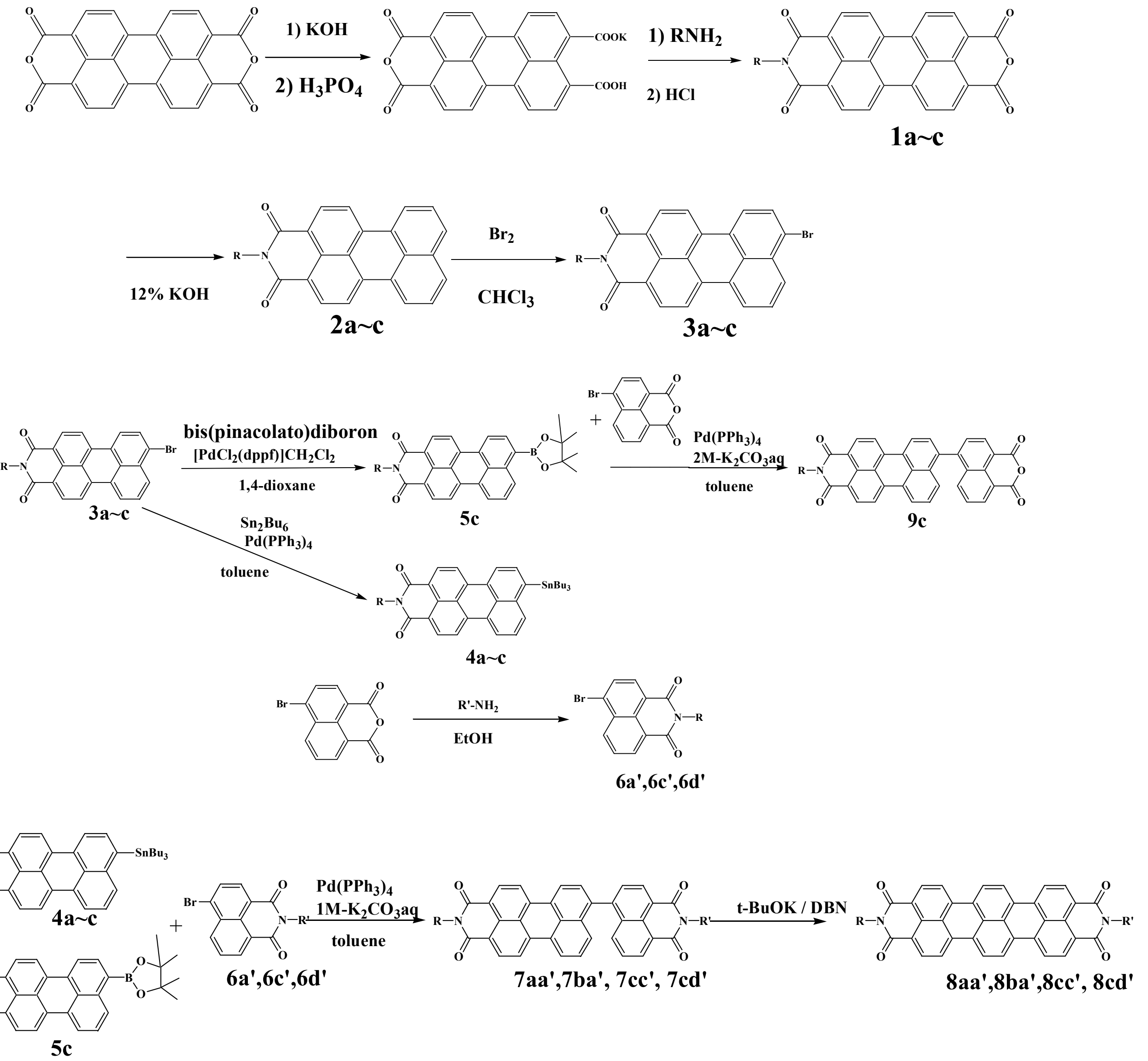
≠ Dedicated to Professor Albert Padwa on the occasion of his 75th birthday.

In an organic solar cell, 0.95%, a comparatively high photo conversion efficiency, is reported for an n-type semiconductor in the organic hetero-junction type cell which used copper phthalocyanine (CuPc) and a perylene derivative (PV).[1] Moreover, in recent research, the development of a new device showed that the p/n interface in this organic material is inserted by a co-deposition method. This device is called a p-i-n device and the conversion efficiency of the device is improved to 5% and its tandem device has been improved to 5.7%.[2,3] Previously, we reported the n-type semiconductor characteristics of the *N*-alkylperylenedicarboximide derivatives[4] and absorption spectra of the symmetrical terrylene derivatives.[5] In this study, we investigated the synthesis of unsymmetrical *N,N'*-dialkylterrylene derivatives **8ba'** and **8cd'** and their related perylene or terrylene dicarboximide derivatives which are expected to have absorptions in over a wide visible region. We then investigated the properties of these derivatives regarding their absorption spectra and semiconductor characteristics in a solid film or device.

RESULTS AND DISCUSSION

Synthesis of perylene and terrylene derivatives

Perylene and terrylene derivatives were prepared by the reaction in the Scheme. Naphthylperylenedicarboimide **7ba'** was prepared by the coupling reaction of tributylstannylperylenedicarboximide **4b** with bromonaphthalenedicarboximide **6a'** in the presence of the [$Pd(PPh_3)_4$] catalyst. Bororanylperylenedicarboximide **5c** was prepared by the reaction of bromoperylenedicarboximide **3c** with bis(pinacolato)diborane, and the reaction of **5c** with bromonaphthalenedicarboximide **6d'** in the presence of the [$Pd(PPh_3)_4$] catalyst produced the naphthylperylenedicarboximide **7cd'**. The cyclization of **7ba'** and **7cd'** with *t*-BuOK/DBN gave the unsymmetrical *N,N'*-dialkylterrylenebis(dicarboximide)s **8ba'** and **8cd'**, respectively. Müllen *et al.* synthesize soluble *N*-2,6-diisopropylphenyl substituted unsymmetrical terrylene derivatives by a similar method, but the dialkyl derivative is not tried.[6] Similarly, naphthylperylenedicarboximides **7aa'** and **7cc'** were prepared by the coupling reaction of the tributylstannylperylenedicarboximides **4a** and **4c** with bromonaphthalenedicarboximides **6a'** and **6c'** in the presence of the [$Pd(PPh_3)_4$] catalyst, respectively. The cyclization of **7aa'** and **7cc'** with *t*-BuOK/DBN gave the symmetrical *N,N'*-dialkylterrylenebis(dicarboximide)s **8aa'** and **8cc'**, respectively. Previously **8cc'** was obtained by the cyclizaion with KOH in ethanol, but the cyclization with *t*-BuOK/DBN gave **8cc'** in a high yield. The coupling reaction of **5c** with bromonaphthalic anhydride in the presence of the $Pd(PPh_3)_4$ catalyst gave naphthylperylenedicarboximide **9c**. The cyclization of **9c** with *t*-BuOK/DBN was no reaction.



a: R = Me, b: R = *n*-C_4H_9, c: R = *n*-C_5H_{11}, d: R = *n*-$C_{12}H_{25}$
a’: R’ = Me, b’: R’ = *n*-C_4H_9, c’: R’ = *n*-C_5H_{11}, d’: R’ = *n*-$C_{12}H_{25}$

Scheme

Photophysical Properties

Absorption and emission spectra of perylene and terrylene derivative

The absorption and emission spectra of the perylene derivatives **2c**, **3c**, **4c**, **5c**, **7cc’**, **9c**, and terrylene derivative **8cc’** in solution are shown in Figure 1 and Figure 2. The unsymmetrical terrylene derivatives **8ba’** and symmetrical terrylene derivatives **8aa’** and **8cc’** had the same absorption and fluorescence spectra as that of the symmetrical terrylene derivative **8cc’**. The terrylene derivatives had a higher absorption peak at a longer wavelength than that of the perylene derivatives. However the terrylene derivatives showed a lower fluorescence than that of the perylene derivstives. Based on this, it was suggested that the terrylene derivative **8cc'** underwent π stacking by its conjugated system, and energy transmission is easily occur between the molecules.

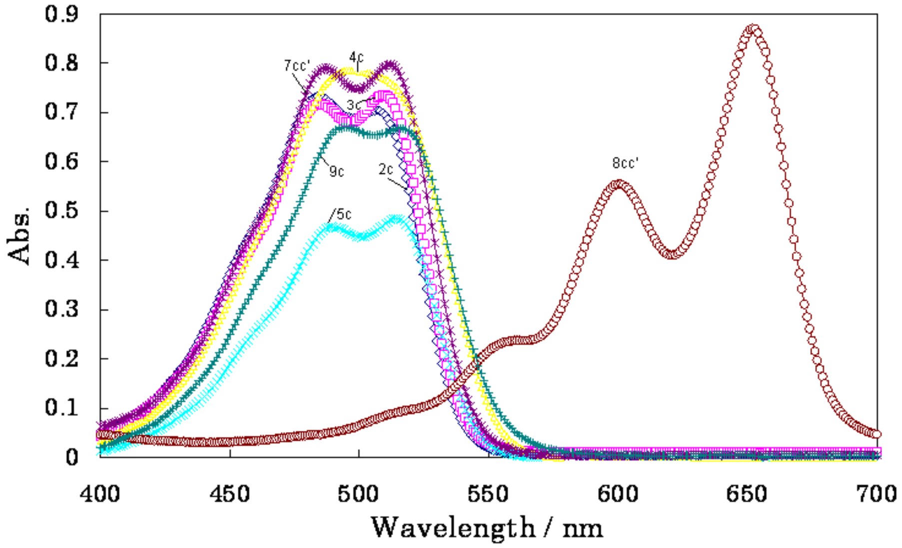


Figure 1. Absorption spectra of perylene derivatives (**2c**, **3c**, **4c**, **5c**, **7cc'**, **9c**) and terrylene derivative (**8cc'**) in chloroform (concentration: 2×10^{-5} M)

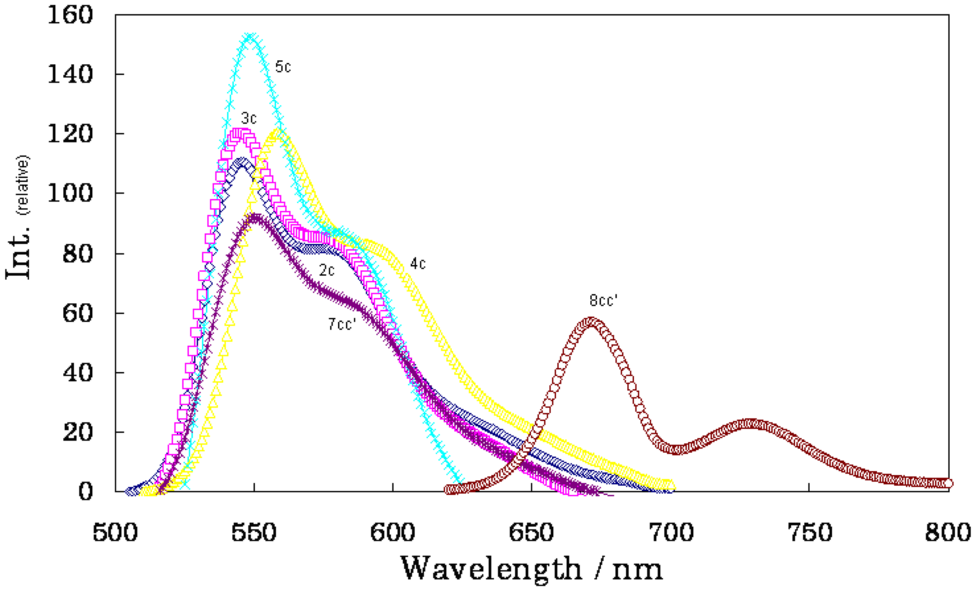


Figure 2. Emission spectra of perylene (**2c**, **3c**, **4c**, **5c**, **7cc'**) and terrylene (**8cc'**) derivatives in chloroform (concentration: 2×10^{-5} M)

The absorption spectra in a solid are shown in Figure3. In a absorption of the perylene derivatives, the spectra of the vapor deposit film had absorption peaks at 450~550 nm, and in the terrylene derivatives, its absorption spectra had absorption peaks at 550~600 nm that is a shorter wavelength area than that in solution. All absorptions peaks were also broader than in solution. The absorption cover almost all visible area. All the terrylene derivatives showed different absorption spectra in the solid form. In order to investigate the orientation of the vapor deposition film of **8cd'**, X-ray diffraction of the vapor deposited film was then measured. However, the film of **8cd'** did not show diffraction peaks and did not show an clear orientation. Therefore, it was suggested that it is a regularly aggregated film instead of a completely amorphous film.

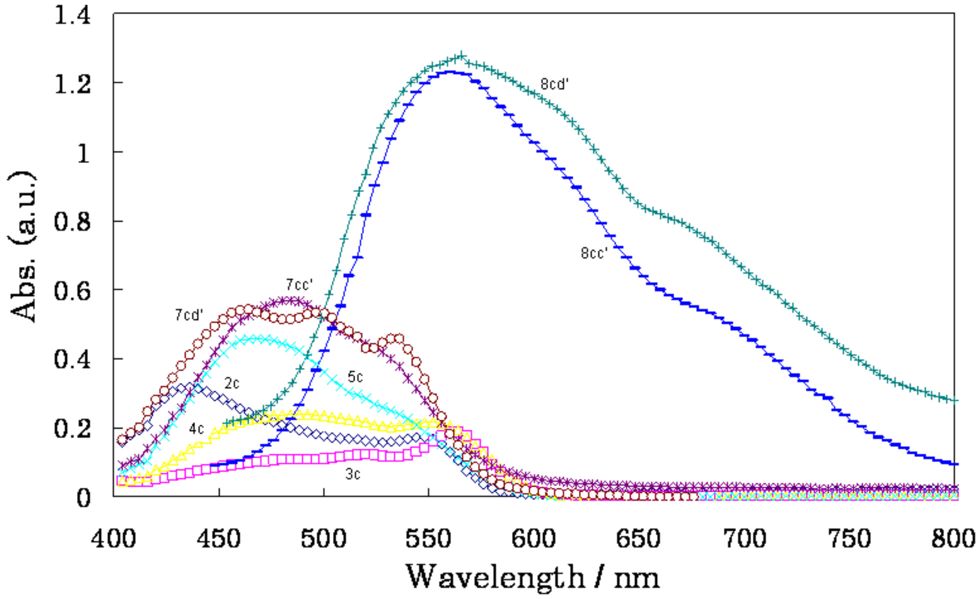


Figure 3. Absorption spectra of deposited film (film thickness: 100 nm) for perylene derivatives (**2c**, **3c**, **4c**, **5c**, **7cc'**, **7cd'**) and terrylene derivatives (**8cc'**, **8cd'**)

Photovoltaic properties

The action spectrum of the schottky device using **8cd'** between Au and Al electrodes and the absorption spectrum of **8cd'** are shown in Figure 4. High photo current occurs on during irradiation from the Au side, but no photo current occurs on the Al side irradiation. From this, it turned out that **8cd'** behaved as an n-type semiconductor because Au has a higher work function than that of Al. The photoelectric transfer characteristics of the terrylene derivatives **8aa', 8cc', 8cd'** were investigated, and **2c** and H_2Pc were used for the comparison (Table 1). The conversion efficiency of the terrylene derivatives was equivalent to the comparison substances. Moreover, the conversion efficiency of the symmetrical **8cc'** and unsymmetrical **8cd'** were almost the same. From this, it turned out that there was no influence on the photoelectric transfer characteristic of the asymmetrical structure.

The photoelectric transfer characteristic of dye sensitized devices for perylene derivative **9c** are shown in Table 2. TiO_2 electrodes in a device were dye-coated by immersing them in dye solutions at room temperature. 1,2-Tetrachloroethane (TCE), dichloromethane (DCM), and chloroform (TCM) were used

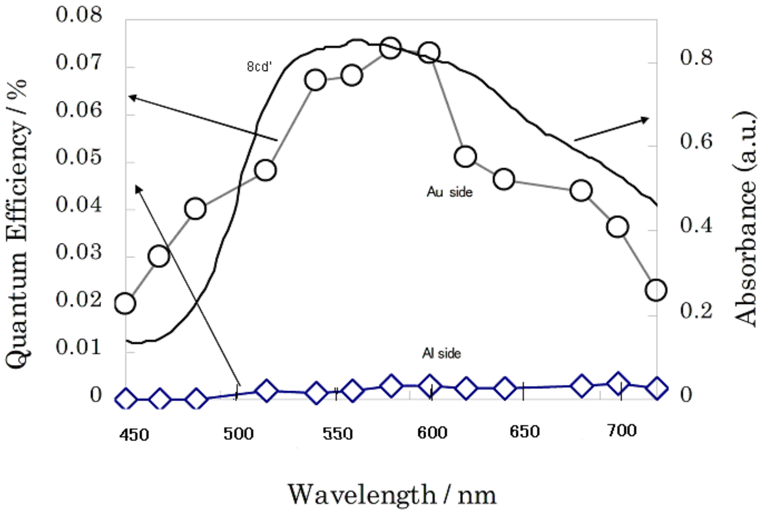


Figure 4. Photocurrent action spectra of Schottky device consisting of terrylene derivative (**8cd'**) and absoption spectrum of **8cd'**

Table 1. The conversion characteristic of Schottky device for terrylene derivatives (**8aa'**, **8cc'**, **8cd'**)

Dye	V_{oc} (V)	J_{sc} (mA/cm^2)	f.f.	η (%)
8aa'	0.11	6.4×10^{-3}	0.24	7.5×10^{-4} a)
8cc'	0.13	8.4×10^{-6}	0.20	1.0×10^{-4} a)
	0.96	3.7×10^{-3}	0.12	4.4×10^{-4} b)
8cd'	0.84	3.4×10^{-3}	0.13	3.8×10^{-4} b)
2c	0.96	8.9×10^{-6}	0.25	1.2×10^{-4} a)
	0.56	2.3×10^{-3}	0.28	3.6×10^{-4} b)
H_2Pc	0.69	4.2×10^{-4}	0.22	1.9×10^{-3} a)
	0.66	5.5×10^{-3}	0.23	8.3×10^{-4} b)

a) Al: 10 nm, Au: 15 nm, Dye: 200 nm, Irradiance: 2.14 mW / cm^2
b) Al: 15 nm, Au: 10 nm, Dye: 100 nm, Irradiance: 100 mW / cm^2

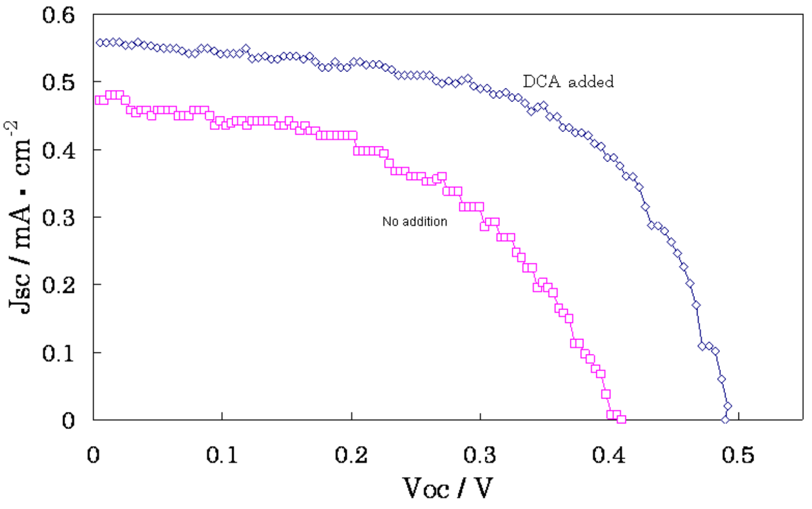


Figure 5. Current density voltage characteristics of dye sensitized device for perylene derivative (**9c**) (solvent: $CHCl_3$, immersion time: 24 h)

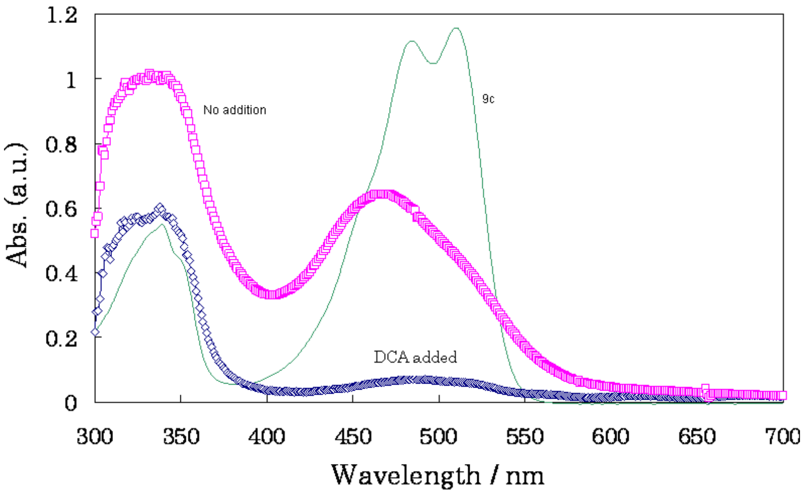


Figure 6. Absorption spectra of solution and dye-sensitized device for perylene derivative (**9c**) added DCA (solvent: $CHCl_3$, immersion time: 24 h)

for a solvent and the electrode immersed for 12 h in the TCM solution had the highest conversion. The conversion efficiency was improved by the solvent selection and immersion time. The conversion characteric of the device using a dye solution containing deoxycholic acid (DCA) was improved. The effect to prevent aggregation of the dye was reported.[7] The different behavior in each solvent was then shown. The TCM solvent had the most improved conversion efficiency and the current density voltage characteristics are shown in Figure 5. The absorption spectra of the solution nand the device at this time is shown in Figure 6. Since the absorption spectra became broad than the solution, it was suggested that dye was aggregating. For this case, the effect of the DCA addition was a little high in the TCM solvent and prevented aggregation of the dye was suggested. The conversion efficiency of η= 0.17% is a higher efficiency in perylene derivatives, and naphthalic anhydride moiety was shown to be effective anchor for the TiO_2 electrode in dye sensitized devices.

Table 2. Influence of solvent and added DCA on the conversion characteristic of dye sensitized device for perylene derivative (**9c**)

Solvent[a)b)]	V_{oc} (V)	J_{sc} (mA/cm^2)	f.f.	η (%)
DCM	0.47	0.38	0.50	0.089
TCM	0.49	0.57	0.59	0.17
TCE	0.45	0.46	0.62	0.13

a) Dye: **9c** was used with DCA (deoxycholic acid)
b) Immersion time: DCM (dichloromethane) 24 h, TCM (chloroform) 24 h, TCE (1,2-tetrachloroethane) 24 h

CONCLUSION

Unsymmetrical terrylenebis(dicarboximide) derivatives and their related dicarboximide derivatives were prepared, and their absorption or emission of light in a solution or solid film and the semiconductor-characteristics for Schottky devices or dye sensitized solar cell devices were investigated. In solution, the unsymmetrical and symmetrical terrylene derivatives showed the same absorption or emission spectra and had absorption or emission peaks in the longer wavelength region than that of the perylenedicarboximide derivatives. In a solid, the terrylene derivatives showed broad absorption peaks in the shorter wavelength region than that in solution. The terrylene derivatives **8cc’** and **8cd’** behaved as an n-type semiconductor in Schottky devices, and the conversion efficiencies of the terrylene derivatives were equivalent to that of the usual semiconductor substance H_2Pc. Perylene derivative **9c** having the naphthalic anhydride anchoring moiety behaved as a sensitizing dye for the DSSC and conversion efficiency showed 0.10%. Moreover, when DCA was added, the conversion efficiency improved to 0.17%. It was suggested that the DCA addition effectively prevented aggregation in high conjugated system molecules.

EXPERIMENTAL

General The IR spectra were recorded by a JASCO FT IR 410 using a potassium bromide pellet. The ^{1}H and ^{13}C NMR spectra were recorded by a JOEL JNM AL-300 in $CDCl_3$. The electron impact (EI) mass spectra were recorded by a JOEL JMS-SX102A, and the fast atom bombardment (FAB) mass spectra were recorded by a JOEL MS-700. The UV/Vis spectra were recorded using a JASCO V-570. The Fluorescence spectra were recorded using a JASCO FP-6200. The thicknesses of the films were measured using an ALVAC CRT-5000.

Preparation of dicarboximide derivatives of terrylene and perylene

Perylene derivatives **1a~c** and **2a~c** were prepared as described in the literature.[5,8] 3,4:9,10-Perylenetetracarboxilic dianhydride, all the alkylamines and 4-bromo-1,8- naphthalic anhydride were commercially obtained.

N-Alkyl-9-bromoperylene-3,4-dicarboximides(3a~c) (a: alkyl = methyl, b: alkyl = butyl, c: alkyl = pentyl)

3a and **3b** were prepared as described in the literature.[9]

3c: Compound **2c** (1.0 g, 2.5 mmol) was dissolved in 500 mL of $CHCl_3$ with slight warming. After cooling to 55 ℃, bromine (1.6 g, 4 mol. equiv.) was dropwise added and the mixture was stirred at 55 ℃ for 5.5 h. The $CHCl_3$ and residual bromine were removed *in vacuo,* and the residue, after recrystallization from benzene, gave **3c** (1.2 g, 96%). mp > 300 ℃. ^{1}H NMR (300MHz, $CDCl_3$): δ = 8.48 (d, 2H, *J*=7.8Hz, Ar. H), 8.37~8.20 (m, 4H, Ar. H), 8.11 (d, 1H, *J*=8.1Hz, Ar. H), 7.80 (d, 1H, *J*=8.1Hz, Ar. H), 7.63 (t, 1H, *J*=8.1Hz, Ar. H), 4.12 (t, 2H, *J*=4.2Hz, CH_2), 1.69~0.78 ppm (m, 9H, CH_2, CH_3). ^{13}C NMR (125MHz, $CDCl_3$): δ =163.5, 136.4, 130.8, 130.5, 128.6 126.7, 123.2, 120.5, 119.6, 40.4, 30.9, 29.3, 22.5, 14.0 ppm. UV/Vis ($CHCl_3$) λ_{max} (ε): 510 (37000), 485 nm (36000). Fluorescence ($CHCl_3$) λ_{max}: 581, 545 nm. MS (FAB) m/z: 469 [M-1], 471 [M+1]. IR (KBr, cm^{-1}): 1685, 1640 ($\nu_{c=o}$).

N-Alkyl-9-tributylstannylperylene-3,4-dicarboximide(4a~c) (a: alkyl = methyl, b: alkyl = buyl. c: alkyl = pentyl) and *N*-pentyl-9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-perylene-3,4-dicarboximide (5c)

A mixture of 0.50 g each of the *N*-alkyl-9-bromoperylene-3,4-dicarboximide(**3a~c**) (**3a**: 1.21×10^{-3} mol, **3b**: 1.10×10^{-3} mol, **3c**: 1.06×10^{-3} mol), 1.5 mol ratio hexabutyltin, and 1.7 mol% tetrakis(triphenylphosphine)palladium(0) was dissolved in toluene (30 mL) under a nitrogen atmosphere and refluxed for 72 h with stirring. After cooling, the toluene was removed in vacuo and the product was separated from the residue by silica gel column chromatography using CH_2Cl_2 as the eluent and the recrystallization from EtOH gave each **4a~c**, **4a**: 0.46 g (64.0%), **4b**: 0.64 g (88.9%), **4c**: 0.54 g (75.2%).

4a: UV-Vis. (H_2SO_4) 613 nm; MS(FAB) (m/z) 626 $[M+1]^+$; ^{1}H-NMR ($CDCl_3$) δ(ppm)= 0.8-1.6 (m, 27H, Bu_3), 3.41 (s, 3H, CH_3), 7.49 (t, *J*=8 Hz, 1H, Arom.H), 7.65 (d, *J*=8 Hz, 1H, Arom.H), 7.71 (d, *J*=8 Hz, 1H, Arom.H), 8.05 (m, *J*=8 Hz, 4H, Arom.H), 8.24 (d, *J*=8 Hz, 2H, Arom.H).

Anal. Calcd for $C_{35}H_{39}O_2NSn$ (%): C, 67.32; H, 6.30; N, 2.24, Found: C, 67.50; H, 6.33; N, 2.49.

4b: UV-Vis. (H_2SO_4) 613 nm; MS(FAB) (m/z) 667 $[M+1]^+$; ^{1}H-NMR ($CDCl_3$) δ(ppm)= 0.77-2.10 (m, 34H, Bu_3, C_3H_7), 4.17 (t, *J*=8 Hz, 2H, CH_2), 7.63 (d, *J*=8 Hz, 1H, Arom.H), 7.66 (t, *J*=8 Hz, 1H, Arom.H), 8.24 (d, *J*=8 Hz, 1H, Arom.H), 8.27 (d, *J*=8 Hz, 1H, Arom.H), 8.29 (d, *J*=8 Hz, 1H, Arom.H), 8.35 (d, *J*=8 Hz, 1H, Arom.H), 8.41 (d, *J*=8 Hz, 1H, Arom.H), 8.50 (d, *J*=8 Hz, 1H, Arom.H), 8.53 (d, *J*=8 Hz, 1H, Arom.H).

Anal. Calcd for $C_{38}H_{45}O_2NSn$ (%): C, 68.48; H, 6.81; N, 2.10, Found: C, 68.37; H, 7.02; N, 2.37.

4c: mp 109~111 ℃ (110~111 ℃),[5] UV-Vis. (H_2SO_4) 613 nm; MS(FAB) (m/z) 682 $[M+1]^+$; ^{1}H-NMR ($CDCl_3$) δ(ppm)= 0.82-0.88 (m, 12H, CH_3), 1.16-1.55 (m, $(CH_2)_3$, $(CH_2)_2$), 1.69 (m, 2H, CH_2), 4.13 (t, *J*=8 Hz, 2H, CH_2), 7.58 (d, *J*=8 Hz, 1H, Arom.H), 7.73 (t, *J*=8 Hz, 1H, Arom.H), 7.77 (d, *J*=8 Hz, 1H, Arom.H), 8.30 (d, *J*=8 Hz, 1H, Arom.H), 8.36 (dd, *J*=8 Hz, 1H, Arom.H), 8.40 (d, *J*=8 Hz, 1H, Arom.H), 8.53 (dd, *J*=8 Hz, 1H, Arom.H).

5c: A mixture of **3c** (1.5 g, 3.0 mmol), bis(pinacolato)diboron (1.3 g, 5.1 mmol), and potassium acetate (1.5 g, 15 mmol) was dissolved in dioxane (150 mL) under a nitrogen atmosphere. The $[PdCl_2(dppf)]\cdot CH_2Cl_2$ catalyst (0.27 g, 0.3 mmol) was added to the mixture. The resulting mixture was stirred for 16 h at 80 ℃. The product mixture was then washed with distilled water and CH_2Cl_2. The organic layer was separated, dried over $MgSO_4$, and the crude product was purified by column chromatography on silica with CH_2Cl_2 to afford **5c** (1.3 g, 81%). mp > 250 ℃. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.61 (d, 1H, *J*=8.4 Hz, Ar. H), 8.13 (d, 1H, *J*=8.1 Hz, Ar. H), 7.94~7.81 (m, 5H, Ar. H), 7.38 (t, 1H, *J*=8.1 Hz, Ar. H), 7.16 (d, 1H, *J*=9.0 Hz, Ar. H), 4.05 (t, 2H, *J*=7.5 Hz, CH_2), 2.10 (br, 2H, CH_2), 1.43~1.36 (m, 12H, CH_2), 1.18 (br, 4H, CH_2), 0.81 ppm (br, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 163.7, 137.7, 136.9, 136.0, 131.5, 131.2, 130.9, 129.1, 128.5, 127.2, 126.9, 123.2, 122.2, 120.9, 120.4, 119.8, 113.0, 40.4, 29.7, 29.3, 27.8, 25.0, 22.7, 22.5, 21.1, 14.1 ppm. UV/Vis ($CHCl_3$) λ_{max} (ε): 515 (24000), 490 nm (23000). Fluorescence ($CHCl_3$) λ_{max}: 580, 548 nm. MS (FAB) m/z: 518 [M+H]. IR (KBr, cm^{-1}): 1687, 1648 ($\nu_{c=o}$).

***N*-Alkyl-4-bromonaphthalene-1,8-dicarboximide (6a'~c') (a': alkyl = methyl, c': alkyl = pentyl, d': alkyl = dodecyl).**

6a'~c' were prepared by the condensation of 4-bromo-1,8-naphthalic anhydride with each alkylamine in

EtOH.[5,10]

6a': Yield 81.0%, mp 195.0~196.0 ℃ (185~186 ℃),[10] MS(EI) 289, 291 (M^+), ^{1}H-NMR ($CDCl_3$) δ= 3.50 (s, 3H, CH_3), 7.77 (t, 1H, Arom.H), 7.97 (d, 1H, Arom.H), 8.33 (d, 1H, Arom.H), 8.50 (d, 1H, Arom.H), 8.59 (d, 1H, Arom.H).

6c': Yield 71%, mp 92.0~92.5 ℃, MS(FAB) 346, 348 $(M+1)^+$, ^{1}H-NMR ($CDCl_3$) δ= 0.84 (t, *J*=4.5 Hz, 3H, CH_3), 1.18~1.53 (m, 6H, CH_2), 4.09 (t, *J*=4.5 Hz, 2H, CH_2), 7.78 (t, *J*=7.2 Hz, 1H, Arom.H), 7.96 (d, *J*=8.1 Hz, 1H, Arom.H), 8.49 (d, *J*=7.2 Hz, 1H, Arom.H), 8.53 (d, *J*=7.2 Hz, 1H, Arom.H), 8.60 (d, *J*=7.2 Hz, 1H, Arom.H).

6d': Yield 97%, mp 69.5~70.0 ℃, MS (FAB) 444, 446 $(M+1)^+$, ^{1}H-NMR ($CDCl_3$) δ= 0.80 (t, *J*=4.5 Hz, 3H, CH_3), 1.13~1.38 (m, 18H, CH_2), 1.65 (q, *J*=4.8 Hz, 2H, CH_2), 4.08 (t, *J*=4.5 Hz, 2H, CH_2), 7.77 (t, *J*=7.2 Hz, 1H, Arom.H), 7.97 (d, *J*=8.1 Hz, 1H, Arom.H), 8.34 (d, *J*=7.2 Hz, 1H, Arom.H), 8.48 (d, *J*=7.2 Hz, 1H, Arom.H), 8.59 (d, *J*=7.2 Hz, 1H, Arom.H).

_N_-Alkyl-9-(_N_-alkylnaphthalene-1,8-dicarboimide)perylene-3,4-dicarboimide(7aa',ba',cc',cd') (aa': alkyl = _N_-methyl, _N_-methyl, ba': alkyl = _N_-butyl, _N_-methyl, cc': alkyl = _N_-pentyl, _N_-pentyl, cd': alkyl = _N_-pentyl, _N_-dodecyl)

A mixture of 0.50 g each of **4a~c** (**4a**: 8.01×10^{-4} mol, **4b**: 7.50×10^{-4} mol, **4c**: 7.34×10^{-4} mol) and 0.25 g each of **6a',c'** (**6a'**: 8.62×10^{-4} mol, **6c'**: 7.34×10^{-4} mol) was dissolved in toluene (50 mL). A 10 mL solution of 1M-K_2CO_3 in water was added to the mixture and then flushed with nitrogen, 8% mol [$Pd(PPh_3)_4$] was added and the reaction mixture was stirred for 16 h at 80 ℃ under a nitrogen atmoshere. After cooling, the mixture was filtered and toluene was removed in vacuo. The residue was separated by column chromatography using CH_2Cl_2:THF:hexane(4:1:1) as the eluent, and rcrystallization from EtOH gave each **7aa'**: 0.33 g (81.4%), **7ba'**: 0.37 g (84.0%), **7cc'**: 0.38 g (76.4%).

7aa': UV-Vis. (H_2SO_4) 625 nm; MS(FD) (m/z) 545 $[M]^+$; ^{1}H-NMR ($CDCl_3$) δ(ppm)= 3.48 (s, 3H, CH_3), 3.49 (s, 3H, CH_3), 7.40 (d, *J*=8 Hz, 1H, Arom.H), 7.56 (t, *J*=8 Hz, 1H, Arom.H), 7.71 (d, *J*=8 Hz, 1H, Arom.H), 7.76 (dd, *J*=8 Hz, 2H, Arom.H), 7.95 (d, *J*=8 Hz, 1H, Arom.H), 8.24 (t, *J*=8 Hz, 2H, Arom.H), 8.32 (dd, *J*=8 Hz, 2H, Arom.H), 8.44 (dd, *J*=8Hz, 2H, Arom.H), 8.48 (d, *J*=8 Hz, 1H, Arom.H), 8.58 (d, *J*=8 Hz, 1H, Arom.H).

7ba': UV-Vis. (H_2SO_4) 625 nm; MS(FD) (m/z) 587 $[M]^+$; ^{1}H-NMR ($CDCl_3$) δ(ppm)= 0.94 (t, 3H, CH_3), 1.19 (m, 2H, CH_2), 1.70 (m, 2H, CH_2), 3.57 (s, 3H, CH_3), 4.16 (t, 2H, CH_2), 7.32 (d, *J*=8 Hz, 1H, Arom.H), 7.42 (d, *J*=8 Hz, 1H, Arom.H), 7.56 (t, *J*=8 Hz, 1H, Arom.H), 7.60 (d, *J*=8 Hz, 1H, Atom.H), 7.78 (dd, *J*=8 Hz, 2H, Arom.H), 8.42 (dd, *J*=8 Hz, 2H, Arom.H).

7cc': UV-Vis. (H_2SO_4) 625 nm; MS(MS) (m/z) 656 $[M]^+$; ^{1}H-NMR ($CDCl_3$) δ(ppm)= 0.86-0.89 (m, 6H, CH_3), 1.37-1.38 (m, 8H, $((CH_2)_2)$), 1.71 (m, 4H, CH_2), 4.16 (tt, 4H, CH_2), 7.33 (d, *J*=8 Hz, 1H, Arom.H), 7.40 (t, *J*=8 Hz, 1H, Arom.H), 7.53 (d, *J*=8 Hz, 1H, Arom.H), 7.58 (t, *J*=8 Hz, 1H, Arom.H), 7.77 (dd, *J*=8 Hz, 2H, Arom.H), 8.39-8.60 (m, 7H, Arom.H), 8.69 (d, *J*=8 Hz, 1H, Arom.H).

7cd’: Compounds **5c** (0.7 g, 1.4 mmol) and **6d’** (0.8 g, 1.8 mmol) were dissolved in toluene (100 mL). A solution of K_2CO_3 in water (10 mL, 1 M) and EtOH were added, and the mixture flushed with nitrogen. A [$Pd(PPh_3)_4$] catalyst (0.16 g, 0.14 mmol) was added, and the reaction mixture stirred under nitrogen for 16 h at 80 ℃. The reaction mixture was purified by column chromatography on silica with CH_2Cl_2 to give **7cd’** (0.9 g, 85%): mp > 300 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.68~8.38 (m, 5H, Ar. H), 7.76 (d, 1H, *J*=7.8 Hz, Ar. H), 7.57~7.33 (m, 6H, Ar. H), 4.15~4.13 (m, 4H, CH_2), 1.60~1.18 (m, 8H, CH_2), 0.85~0.78 ppm (m, 10H, CH_2, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 164.1, 163.4, 139.1, 136.5, 136.2, 131.4, 131.2, 131.1, 130.7, 129.7, 129.4, 129.0, 128.5, 127.4, 127.2, 123.7, 123.1, 122.8, 121.1, 120.4, 120.3, 40.6, 40.4, 31.9, 29.6, 29.4, 29.3, 28.2, 27.8, 27.2, 22.7, 22.4, 14.1, 14.0 ppm. UV/Vis ($CHCl_3$) λ_{max} (ε): 512 (40000), 488 nm (40000). Fluorescence ($CHCl_3$) λ_{max}: 588, 552 nm. MS (FAB) m/z: 755 [M+H]. IR (KBr, cm^{-1}): 1689, 1654 ($\nu_{c=o}$).

_N_-Alkyl, _N’_-Alkylterrylene-3,4:11,12-tetracarbox-diimide(8aa’,ba’,cc’,cd’) (aa’: alkyl = _N,N’_-dimethyl, ba’: _N_-butyl, _N’_-methyl, cc’: alkyl = _N,N’_-’dipentyl, cd’: alkyl = _N_-pentyl, _N’_-dodecyl)

A mixture of 1,5-diazabicyclo[4.3.0]non-5ene (DBN) 9.1 g (7.3×10^{-2} mol) and *t*-BuOK 1.6 g (7.2×10^{-2} mol) was stirred for 1 h at 190 ℃ under a nitrogen atmosphere. To the mixture was added 0.5 g each of **7aa’**, **7ba’**, **7cc’** (**7aa’**: 9.18×10^{-4} mol, **7ba’**: 8.52×10^{-4} mol, **7cc’**: 7.62×10^{-4} mol), and the mixture was stirred for 7 h at 190 ℃. After cooling, water was added to the mixture and the mixture was filtered. The residue was washed with MeOH and extracted with $CHCl_3$. Removing $CHCl_3$ in vacuo each gave each **8aa’** (60.5%), **8ab’** (55.2%), and **8cc’** (93.0%).

8aa’: mp > 300 ℃, UV-Vis. (H_2SO_4) 807 nm; MS(FD) (m/z) 543[M]$^+$.

8ba’: mp > 300 ℃, UV-Vis. (H_2SO_4) 807 nm; MS(FD) (m/z) 585[M]$^+$; ^{1}H-NMR ($CDCl_3$) δ (ppm) = 0.87 (t, 3H, CH_3), 1.18 (m, 2H, CH_2), 1.61 (m, 2H, CH_2), 3.58 (s, 3H, CH_3), 4.15 (t, 2H, CH_2), 7.24-7.65 (m, 12H, Arom.H).

8cc’: mp > 300 ℃ (> 300 ℃),[5] UV-Vis.(H_2SO_4) 807 nm; MS(EI) (m/z) 654 [M]$^+$, HRMS(EI) calcd for $C_{44}H_{34}N_2O_4$ 654.2519, found 654.2516.

8cd’: Compound **7cd’** (0.1 g, 0.1 mmol), *t*-BuOK (1.6 g, 14 mmol), and 1,5-Diazabicyclo[4,3,0]non-5-ene (DBN) (1.8 g, 15 mmol) were injected into the flask under nitrogen atmosphere. The mixture was stirred for 7 h at 190 ℃. After cooling to room temperature, the solution was poured into water to give a precipitate. The dark crude product was washed with MeOH. A blue solid was obtained by reprecipitation of the product from $CHCl_3$/hexane to give **8cd’** (75 mg, 75%). mp > 300 ℃. ^{1}H NMR (300 MHz, $CDCl_3$), δ =7.65~7.19 (m, 12H, Ar. H), 4.17~4.13 (m, 4H, CH_2), 1.61~1.18 (m, 8H, CH_2), 0.87~0.82 ppm (m, 24H, CH_2, CH_3). UV/Vis ($CHCl_3$) λ_{max} (ε): 653 (44000), 601 nm (28000). Fluorescence ($CHCl_3$) λ_{max}: 728, 671 nm. MS (EI) m/z: 752 [M]. HRMS (EI) calcd for $C_{51}H_{48}O_4N_2$ 752.3614 found 752.3616. IR (KBr, cm^{-1}): 1689, 1643 ($\nu_{c=o}$).

***N*-Penty-9-(1,8-naphthalic anhydride)perylene-3,4-dicarboximide (9c)**

A mixture of compounde **5c** (0.4 g, 0.8 mmol) and 4-bromo-1,8-naphthalic anhydride (0.45 g, 1.6 mmol) were dissolved in toluene (100 mL). A solution of K_2CO_3 in water (10 mL, 1 M) and EtOH (5 mL) was added to the mixture, and the mixture was flushed with nitrogen. The [$Pd(PPh_3)_4$] catalyst (90 mg, 0.08 mmol) was added, and the reaction mixture was stirred under a nitrogen atmosphere for 16 h at 90 ℃. The reaction mixture was cooled to room temperature and the resulting salt was collected by filtration. The salt was poured into concentrated HCl. The crude product was purified by column chromatography on silica with the eluate of $CHCl_3$: EtOAc 9 : 1 to give **9c** (4 g, 78%). mp > 300 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.79 (d, 1H, *J*=7.4 Hz, Ar. H), 8.69~8.57 (m, 4H, Ar. H), 8.52~8.44 (m, 3H, Ar. H), 7.99~7.92 (m, 2H, Ar. H), 7.71~7.64 (m, 2H, Ar. H), 7.51 (t, 1H, *J*=8.1 Hz, Ar. H), 7.34 (d, 1H, *J*=8.2 Hz, Ar. H), 4.19 (t, 2H, *J*=7.5 Hz, CH_2), 1.77 (br, 2H, CH_2), 1.52 (br, 2H, CH_2), 1.43 (br, 4H, CH_2), 0.93 ppm (br, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 163.8, 160.5, 160.4, 146.1, 138.1, 136.6, 136.3, 134.0, 133.68, 133.2, 133.0, 131.6, 131.5, 131.4, 130.7, 130.4, 129.8, 129.7, 129.5, 129. 0, 128.4, 128.2, 127.8, 126.6, 124.0, 122.9, 121.7, 121.5, 120.8, 120.7, 119.3, 118.9, 40.5, 29.3, 27.8, 22.5, 14.0 ppm. UV/Vis ($CHCl_3$) λ_{max} (ε): 510 (58000), 484 nm (56000). Fluorescence ($CHCl_3$) λ_{max}: 546 nm. MS (FAB) m/z: 587 [M+H]. IR (KBr, cm^{-1}): 1778, 1737 ($\nu_{c=o}$), 1691, 1651 ($\nu_{c=o}$). Anal. Calcd for $C_{39}H_{25}NO_5$(%): C 79.70 H 4.29 N 2.38. Found: C 79.31 H 4.43 N 2.32.

Photovoltaic effects

Organic Thin Film Solar Cells

Glass plates were cleaned in acetone, ultrasonically washed twice for 10 min, and then dried. First, a semitransparent Al electrode (15 nm) was deposited by high-vacuum (10^{-3} Pa) thermal evaporation onto the glass plates, the dye layers (100 or 200 nm) were then deposited on the Al electrode. Finally, Au electrode (5 or 10 nm) was deposited on the dye layers. These devices were made using Bell Jar type organic vapor deposition equipment (KITANO SEIKI). We chosen the terrylene derivatives **8**, perylene derivative **2c** and phthalocyanine dye (H_2Pc) as the semiconductor.

Dye Sensitized Solar Cells (DSSC)

Fluorine doped tin oxide (FTO) glass plates were cleaned in a 10%-aq.sodium hydroxide solution, and ultrasonically washed for 1 min, then two times with water for 1 min in an ultrasonic bath. Finally, it was rinsed in 2-propanol for 5 and 10 min in an ultrasonic bath, and dried.

A paste for the transparent nanocrystalline-TiO_2 layer (7.3 μm) was coated on the FTO glass plates by the spincast method using a K-359SD-1 SPINNER (KYOWA RIKEN). The electrodes coated with TiO_2 pastes were gradually heated under an air flow at 450 ℃ for 60 min. Thickness of the film was determined by Dektek3ST (ULVAC). After sintering at 220 ℃ and cooling to 150 ℃, the nanostructured TiO_2 electrodes were dye-coated by immersing them in dye solutions (2×10^{-4} M) at room temperature for 12 h or 24 h. Dye solutions that contained saturated deoxycholic acid (DCA) and neat were used. Three kinds of solvents; i.e. CH_2Cl_2 (DCM), $CHCl_3$ (TCM), and 1,2-tetrachloroethane (TCE) were used. Moreover, acetic acid processing was performed as a surface treatment. The electrolyte consisted of 0.5 M LiI, 0.3 M 1-hexyl-3-propylimidazolium iodide (HeMeImI), 0.58 M t-butylpyridine (TBP), and 30 mM I_2 in MeCN.

Measurement of Photovoltaic effect.

The current-voltage (I-V) characteristics under illumination were measured in air at room temperature using an electrometer (ADVANTEST-TR8652, ADVANTEST-TR 6142). A 750 W halogen light source (RIKAGAKU SEIKI) was then used to provide radiation of 2.14 or 100 mW cm^{-2} at the surface of the solar cell. Since the irradiation energy of a light source in a long wavelength region was strong, it was intercepted by using an IR cut-off filter, and the light of the domain was considered to be similar to sunlight. The action spectra were measured the photo current when it was irradiated with 440 nm ~ 720 nm monochromatic light at the solar cells, and the photoelectric current measured at that time.

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