Supporting Information

Electron-Donating Perylene-Tetracarboxylic Acids for Dye-Sensitized Solar Cells

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S1. Experimental Details.

General. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL AL300 (300 MHz for ^{1}H) and a JEOL ECX-400P (400 MHz for ^{1}H, 99.6 MHz for ^{13}C) spectrometer in $CDCl_3$ and acetic acid-d_4 and chemical shifts were noted in δ ppm with reference to internal tetramethylsilane peak for $CDCl_3$ and internal residual solvent peak (CHD_2COOD, 2.03 ppm) for acetic acid-d_4. Silica gel column chromatography was performed using UltraPure Silicagel (230-400 mesh, SiliCycle inc.). Alumina column chromatography was carried out using activated alumina (300 mesh, Wako). Reversed-phase column chromatography was performed using Cosmosil 76C_{18}-OPN (Nacalai). Thin layer chromatography (TLC) was carried out on aluminum plates coated with silica gel 60 F_{254} (Merck), aluminium oxide 60 F_{254} (Merck), or glass plates coated with functionalized silica gel (RP-18 F_{254}s, Merck). Infrared (IR) spectra were recorded in KBr pellet by using FT/IR-470Plus (JAS.CO). High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-HX110A spectrometer. All reactions were carried out under nitrogen. *N*,*N*'-bis(2,6-diisopropylphenyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxylic acid bisimide (**1**), [i] *N*-cyclohexyl-1,7-bis(pyrrolidin-1-yl)-3,4:9,10-tetracarboxylic acid-3,4-anhydride-9,10-imide (**Cy-PMI**), [ii] and *tert*-butyl 4-aminobenzoate [iii] were synthesized as described before.

Synthesis.

***N*,*N*'-bis(2,6-diisopropylphenyl)-1,7-bis(pyrrolidin-1-yl)perylene-3,4:9,10-tetracarb**

oxylic acid bisimide (2). A solution of **1** (1.00 g, 1.16 mmol) in pyrrolidine (30 mL) was heated at 50 °C (external temperature) with an oil bath for 14 h. After evaporation, the residue was subjected to the silica gel column chromatography (CH_2Cl_2/AcOEt = 30/1, R_f (CH_2Cl_2) = 0.44), followed by the subjection to the alumina column chromatography (hexane/$CHCl_3$ = 1/2, R_f (CH_2Cl_2)= 0.50) to give **2** (408 mg, 0.480 mmol, 41% yield) as green solids; IR (KBr); 2963, 2929, 2870, 1698, 1662, 1592, 1580, 1560, 1507, 1485, 1467, 1453, 1417, 1382, 1342, 1309, 1245, 1231, 1200, 1180, 1128, 1098, 1058, 972, 946, 894, 870, 842, 810, 791, 772, 755, 737, 719, 695, 665, 650, 680, 606, 580, 550, 532, 496, 483, 475, 458, 442, 425, 415; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (s, 2H), 8.52 (d, *J* = 8.1 Hz, 2H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.35 (d, *J* = 7.4 Hz, 4H), 3.92-3.72 (m, 4H), 3.00-2.75 (m, 4H), 2.80 (sept, *J* = 6.9 Hz, 4H), 2.20-1.90 (m, 8H), 1.19 (d, *J* = 6.9 Hz, 24H); ^{13}C NMR (99.6 MHz, $CDCl_3$) δ 164.24, 164.20, 146.77, 145.70, 134.83, 131.19, 130.51, 129.41, 127.26, 123.99, 122.95, 121.99, 121.30, 119.20, 118.41, 52.45, 29.13, 25.91, 24.09, 24.04; HRMS (FAB, positive mode) found 848.4329, $C_{56}H_{56}N_4O_4$ requires 848.4302.

***N*-(2,6-diisopropylphenyl)-1,7-bis(pyrrolidin-1-yl)-3,4:9,10-tetracarboxylic acid-3,4-anhydride-9,10-imide (*i*Pr-PMI).** A solution of **2** (163 mg, 0.192 mmol) and KOH (718 mg, 12.8 mmol) in *tert*-butyl alcohol (33 mL) was heated to reflux. After stirred for 1 h, the reaction mixture was poured into a mixture of acetic acid (41 mL) and 1N HCl aq (22 mL) and stirred for 5 h at room temperature. The resulting mixture was poured into a biphasic mixture of CH_2Cl_2 (100 mL) and H_2O (50 mL).

After separation, the organic layer was washed with brine (100 mL) and dried over $MgSO_4$. After filtration and evaporation, the residue was subjected to the silica gel column chromatography (CH_2Cl_2, then CH_2Cl_2/AcOEt = 100/1, then 50/1, R_f (CH_2Cl_2) = 0.30). The reprecipitation from CH_2Cl_2/MeOH gave ***i*Pr-PMI** (60.8 mg, 0.0881 mmol, 46% yield) as green solids. IR (KBr); 2963, 2929, 2868, 1764, 1730, 1700, 1664, 1592, 1579, 1559, 1543, 1507, 1456, 1419, 1345, 1311, 1244, 1228, 1201, 1145, 1128, 1101, 1009, 940, 867, 840, 804, 768, 739, 717, 692, 668, 649, 602, 578, 552, 531, 520, 509, 473, 440, 430, 413; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.50 (d, *J* = 7.8 Hz, 1H), 8.49 (s, 1H), 8.45 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 2H), 3.90-3.72 (m, 4H), 3.00-2.80 (m, 4H), 2.77 (sept, *J* = 6.9 Hz, 2H), 2.20-1.95 (m, 8H), 1.18 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (99.6 MHz, $CDCl_3$) δ 164.09, 164.03, 161.40, 160.84, 147.17, 146.42, 145.65, 136.02, 134.15, 131.03, 130.74, 130.41, 129.48, 128.80, 127.03, 124.76, 124.43, 124.01, 123.82, 122.79, 122.56, 122.51, 121.36, 119.83, 119.50, 117.46, 117.32, 114.52, 52.63, 52.48, 29.14, 25.89, 24.06, 24.01; HRMS (FAB, positive mode) found 689.2904, $C_{44}H_{39}N_3O_5$ requires 689.2890; UV-vis-NIR (λ_{max} (ε)) 708.0 nm (45600), 433.5 nm (17800).

***N*-(4-*tert*-butoxycarbonylphenyl)-*N'*-(2,6-diisopropylphenyl)-1,7-bis(pyrrolidin-1-yl)perylene-3,4:9,10-tetracarboxylic acid bisimide (3).** A mixture of ***i*Pr-PMI** (32.4 mg, 0.0470 mmol), *tert*-butyl 4-aminobenzoate (25.5 mg, 0.132 mmol), zinc acetate dihydrate (6.0 mg, 0.027 mmol), and imidazole (500 mg) was heated at 140 °C in a

sealed Schlenk tube. After stirred for 2 h, the reaction mixture was cooled to room temperature. The resulting solids were dispersed in 1N HCl aq (6 mL) and sonicated for 30 min. The resulting mixture was poured into a biphasic mixture of 1N HCl aq (14 mL) and $CHCl_3$ (20 mL). After separation, the aqueous layer was extracted with $CHCl_3$ (20 mL). The combined organic layer was washed with brine (20 mL) and dried over $MgSO_4$. After filtration and evaporation, the residue was subjected to the silica gel column chromatography (CH_2Cl_2, then CH_2Cl_2/AcOEt = 100/1, then 50/1, then 40/1, R_f (CH_2Cl_2/AcOEt = 50/1) = 0.43). The reprecipitation from CH_2Cl_2/MeOH gave **3** (29.0 mg, 0.0335 mmol, 71% yield) as green solids. IR (KBr); 2963, 2927, 2868, 1698, 1665, 1592, 1579, 1560, 1508, 1455, 1443, 1342, 1307, 1290, 1246, 1231, 1198, 1180, 1166, 1117, 1057, 1020, 972, 946, 893, 860, 840, 828, 807, 772, 753, 740, 715, 688, 662, 642, 633, 622, 594, 550, 530, 521, 513, 500; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.56 (s, 1H), 8.53-8.50 (m, 2H), 8.20 (d, *J* = 7.5 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 2H), 3.95-3.70 (m, 4H), 3.00-2.80 (m, 4H), 2.79 (sept, *J* = 6.6 Hz, 2H), 2.20-1.95 (m, 8H), 1.64 (s, 9H), 1.19 (d, *J* = 6.6 Hz, 12H); ^{13}C NMR; (99.6 MHz, $CDCl_3$) δ 165.12, 164.21, 164.10, 146.84, 146.63, 145.69, 139.58, 135.09, 134.65, 132.25, 131.16, 130.57, 130.47, 129.43, 128.78, 127.24, 124.21, 123.99, 122.92, 122.75, 122.15, 121.71, 121.26, 119.38, 118.95, 118.64, 118.16, 81.28, 52.43, 29.14, 28.23, 25.90, 24.08, 24.03; HRMS (FAB, positive mode) found 864.3875, $C_{55}H_{52}N_4O_6$ requires 864.3887.

***N*-(4-carboxylphenyl)-*N'*-(2,6-diisopropylphenyl)-1,7-bis(pyrrolidin-1-yl)perylene-3,4:9,10-tetracarboxylic acid bisimide (*i*Pr-PBI).** A mixture of **3** (29.0 mg, 0.0335 mmol), trifluoroacetic acid (10 mL), 5wt% H_2SO_4 aq (7.5 mL), and $CHCl_3$ (10 mL) was heated to reflux. After stirred for 24 h, the reaction mixture was cooled to room temperature. The resulting biphasic mixture was separated and the aqueous layer was extracted with $CHCl_3$ (20 mL). The combined organic layer was washed with saturated $NaHCO_3$ aq (20 mL), saturated NH_4Cl aq (20 mL), and brine (50 mL) and dried over $MgSO_4$. After filtration and evaporation, the residue was subjected to the silica gel column chromatography (AcOEt/MeOH = 10/1, R_f = 0.40), followed by the subjection to the reversed-phase column chromatography (AcOEt/MeOH = 1/4, R_f = 0.53). The reprecipitation from CH_2Cl_2/hexane gave ***i*Pr-PBI** (22.3 mg, 0.0276 mmol, 82% yield) as green solids. IR (KBr); 3440, 2963, 2930, 2869, 1697, 1664, 1592, 1578, 1559, 1507, 1455, 1415, 1384, 1343, 1309, 1246, 1231, 1200, 1128, 1100, 1057, 1021, 972, 946, 843, 825, 807, 775, 752, 739, 718, 693, 669, 657, 611, 600, 582, 567, 557, 545, 534, 519, 512; ^{1}H NMR (300 MHz, acetic acid-d_4) δ 8.64 (s, 1H), 8.59 (d, *J* = 8.4 Hz, 1H), 8.54 (s, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 2H), 7.83-7.80 (m, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 3.95-3.75 (m, 4H), 2.95-3.75 (m, 4H), 2.83 (sept, *J* = 6.9 Hz, 1H), 2.20-1.90 (m, 8H), 1.14 (d, *J* = 6.9 Hz, 12H); HRMS (FAB, positive mode) found 808.3221, $C_{51}H_{44}N_4O_6$ requires 808.3261; UV-vis-NIR (λ_{max} (ε)) 709.0 nm (42000), 435.5 nm (16800). ^{13}C NMR spectrum could not be measured because of the low solubility.

***N*-(4-*tert*-butoxycarbonylphenyl)-*N'*-cyclohexyl-1,7-bis(pyrrolidin-1-yl)perylene-3,4:9,10-tetracarboxylic acid bisimide (4).** A mixture of **Cy-PMI** (33.8 mg, 0.0553 mmol), *tert*-butyl 4-aminobenzoate (26.0 mg, 0.135 mmol), zinc acetate dihydrate (5.0 mg, 0.023 mmol), and imidazole (400 mg) was heated at 140 °C in a sealed Schlenk tube. After stirred for 2 h, the reaction mixture was cooled to room temperature. The resulting solids were dispersed in 1N HCl aq (6 mL) and sonicated for 30 min. The resulting mixture was poured into a biphasic mixture of 1N HCl aq (14 mL) and $CHCl_3$ (20 mL). After separation, the aqueous layer was extracted with $CHCl_3$ (20 mL). The combined organic layer was washed with brine (40 mL) and dried over $MgSO_4$. After filtration and evaporation, the residue was subjected to the silica gel column chromatography (CH_2Cl_2, then CH_2Cl_2/AcOEt = 100/1, then 50/1, then 40/1, then 30/1, R_f (CH_2Cl_2/AcOEt = 40/1) = 0.40). The reprecipitation from CH_2Cl_2/MeOH gave **4** (37.4 mg, 0.0475 mmol, 86% yield) as green solids. IR (KBr); 2970, 2929, 2853, 1693, 1654, 1593, 1578, 1560, 1507, 1483, 1453, 1415, 1339, 1306, 1291, 1257, 1245, 1230, 1213, 1190, 1164, 1120, 1020, 981, 949, 927, 895, 867, 839, 828, 806, 739, 767, 754, 716, 702, 679, 654, 633, 617, 585, 558, 530, 521, 511; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.48 (s, 1H), 8.44 (d, *J* = 7.6 Hz, 1H), 8.42 (d, *J* = 7.6 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 5.13-5.05 (m, 1H), 3.85-3.65 (m, 4H), 2.95-2.70 (m, 4H), 2.65-2.55 (m, 2H), 2.15-1.87 (m, 10H), 1.80-1.70 (m, 3H), 1.63 (s, 9H), 1.55-1.33 (m, 3H); ^{13}C NMR (99.6 MHz, $CDCl_3$) δ 165.15, 164.52, 164.11, 146.78, 146.38, 139.61, 134.92, 133.94, 132.20, 130.55, 130.24, 129.97, 128.79, 127.16, 126.58, 124.19, 123.68, 122.67, 122.63, 122.20,

121.41, 121.11, 120.80, 119.91, 118.78, 118.68, 117.62, 81.25, 53.80, 52.27, 29.20, 28.23, 26.63, 25.83, 25.55; HRMS (FAB, positive mode) found 786.3421, $C_{49}H_{46}N_4O_6$ requires 786.3417.

***N*-(4-carboxylphenyl)-*N'*-cyclohexyl-1,7-bis(pyrrolidin-1-yl)perylene-3,4:9,10-tetra carboxylic acid bisimide (Cy-PBI).** A mixture of **4** (10.3 mg, 0.0131 mmol), trifluoroacetic acid (10 mL), 5wt% H_2SO_4 aq (7.5 mL), and $CHCl_3$ (10 mL) was heated to reflux. After stirred for 43 h, the reaction mixture was cooled to room temperature. The resulting biphasic mixture was separated and the aqueous layer was extracted with $CHCl_3$ (20 mL). The combined organic layer was washed with saturated $NaHCO_3$ aq (20 mL), saturated NH_4Cl aq (20 mL), and brine (50 mL) and dried over $MgSO_4$. After filtration and evaporation, the residue was subjected to the silica gel column chromatography (AcOEt/MeOH = 10/1, then 5/1, then 1/1, R_f (AcOEt/MeOH = 10/1) = 0.30), followed by the subjection to the reversed-phase column chromatography (AcOEt/MeOH = 1/4, R_f = 0.44). The reprecipitation from CH_2Cl_2/hexane gave **Cy-PBI** (6.1 mg, 0.0083 mmol, 64% yield) as green solids. IR (KBr); 3450, 2929, 2853, 1692, 1651, 1592, 1579, 1560, 1507, 1483, 1453, 1416, 1339, 1309, 1245, 1230, 1214, 1198, 1124, 1021, 980, 948, 927, 881, 860, 907, 770, 715, 660, 626, 617, 605, 592, 556, 532, 509, 499; ^{1}H NMR (400 MHz, acetic acid-d_4) δ 8.51-8.32 (m, 4H), 8.30 (d, *J* = 8.6 Hz, 2H), 7.68-7.45 (m, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 5.12-5.03 (m, 1H), 3.80-3.60 (m, 4H), 2.90-2.60 (m, 6H), 2.20-1.70 (m, 13H), 1.55-1.25 (m, 3H); HRMS (FAB, positive mode) found 730.2784, $C_{45}H_{38}N_4O_6$ requires 730.2791; UV-vis-NIR (λ_{max} (ε))

704.5 nm (42300), 434.0 nm (16700). ^{13}C NMR spectrum could be measured because of the low solubility.

Spectral measurements. Steady-state absorption spectra were measured with a Lambda 900 (PerkinElmer) UV/VIS/NIR spectrometer with a data interval of 0.5 nm. These spectra were taken with about 10^{-4}-10^{-6} M solutions in a quartz cell with pathlength of 1 cm and 1 mm. Steady-state fluorescence spectra were acquired on a SPEX FluoroMax-3 spectrometer with a data interval of 1 nm. These spectra were taken with about 10^{-6} M solutions in a quartz cell with pathlength of 1 cm. The solution was degassed by bubbling with Ar for 30 min before measurements. Spectral grade CH_2Cl_2 (Wako) was used without further purification for these measurements.

Electrochemical measurements. Differential pulse voltammetry measurements were performed on an ALS660A electrochemical analyzer in deaerated CH_2Cl_2 containing 0.1 M $TBAPF_6$ as a supporting electrolyte. A conventional three-electrode cell was used with a grassy carbon working electrode and a platinum wire as a counter electrode. The measured potentials were recorded with respect to the $Ag/AgNO_3$ reference electrode (Fc/Fc^+, 0.20 V vs $Ag/AgNO_3$). Ferrocene/ferrocenium (Fc/Fc^+, 0.64 V vs NHE) was used as an internal standard for all measurements.

	***i*Pr-PMI**	**Cy-PMI**	***i*Pr-PBI**	**Cy-PBI**
E_{ox} (V)[a]	0.26	0.27	0.21	0.24

[a] First oxidation potential (E_{ox}) vs Fc/Fc^+.

Preparation of dye-modified TiO_2 electrode.[iv] Nanoporous TiO_2 films were prepared from colloidal suspension of TiO_2 nanoparticles (P25, Nippon Aerogel) dispersed in deionized water and Triton X-100. The suspension was deposited on a transparent conducting glass (Asahi Glass, SnO_2: F, 9.4 ohm/sq) by using doctor blade technique. The films were annealed at 723 K for 1 h, followed by similar deposition and annealing (723 K, 1 h) for the 13-μm-thick TiO_2 films. The thickness of the films was determined using surface roughness/profile measuring instrument (SURFCOM 130A, ACCRETECH). The TiO_2 electrodes were immersed into each of the 0.15 mM solution of dyes at room temperature. After dye adsorption, the dye-coated electrodes were copiously rinsed with the same solvent used for the adsorption.

Photovoltaic measurements. The photovoltaic measurements were performed in a sandwich cell consisting of the dye-sensitized TiO_2 electrode as the working electrode and a platinum-coated conducting glass as the counter electrode. The two electrodes were placed on top of each other using a thin transparent film of Surlyn polymer (Dupont) as a spacer to form the electrolyte space. A thin layer of electrolyte (0.1 M LiI, 0.05 M I_2, 0.6 M 2,3-dimethyl-1-propylimidazolium iodide, and 0.5 M 4-*t*-butylpyridine in acetonitrile) was introduced into the interelectrode space. The IPCE values and photocurrent-voltage characteristics were determined by using a potentiostat (Bunko–Keiki Co., Ltd., Model HCSSP-25) irradiated with simulated AM 1.5 solar light (100 mW cm^{-2}, Bunko–Keiki Co., Ltd., Model CEP-2000). All the experimental values were given as an average from three independent measurements.

(i) Chao, C.-C.; Leung, M.-k.; Su, Y. O.; Chiu, K.-Y.; Lin, T.-H.; Shieh, S.-J.; Lin, S.-C. *J. Org. Chem.* **2005**, *70*, 4323.

(ii) Würthner, F.; Stepanenko, V.; Chen, Z.; Saha-Möller, C. R.; Kocher, N.; Stalke, D. *J. Org. Chem.* **2004**, *69*, 7933.

(iii) Tayler, E. C.; Fletcher, S. R.; Sabb, A. L. *Synth. Commun.* **1984**, *14*, 921.

(iv) (a) Imahori, H.; Hayashi, S.; Umeyama, T.; Eu, S.; Oguro, A.; Kang, S.; Matano, Y.; Shishido, T.; Ngamsinlapasathian, S.; Yoshikawa, S. *Langmuir* **2006**, *22*, 11405.
(b) Eu, S.; Hayashi, S.; Umeyama, T.; Oguro, A.; Kawasaki, M.; Kadota, N.; Matano, Y.; Imahori, H. *J. Phys. Chem. C* **2007**, *111*, 3528.

S2. NMR Spectra.

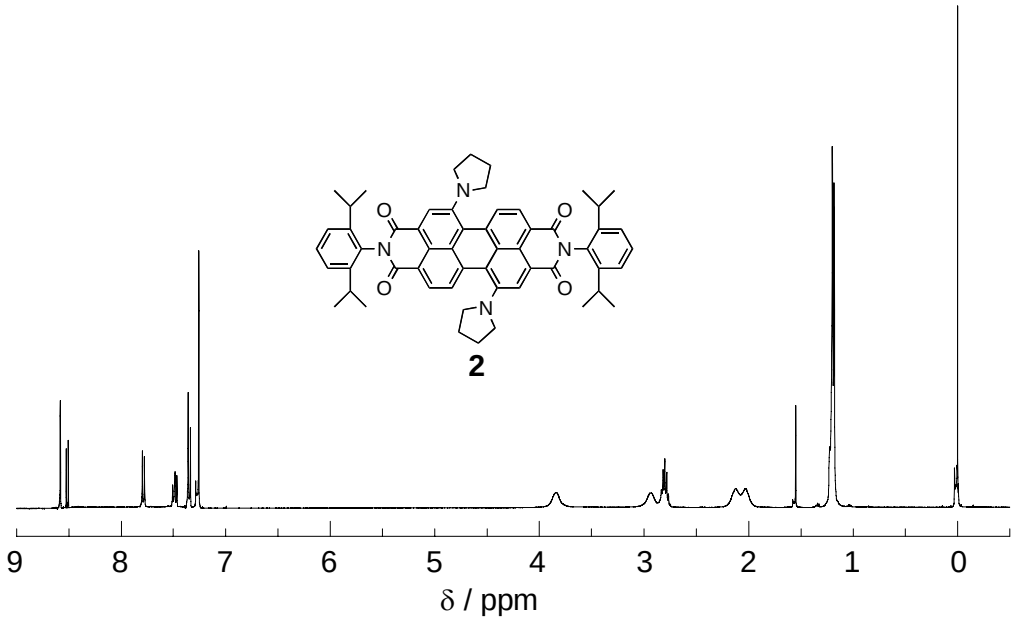

Figure S2-1. ^{1}H NMR spectrum of **2** in $CDCl_3$.

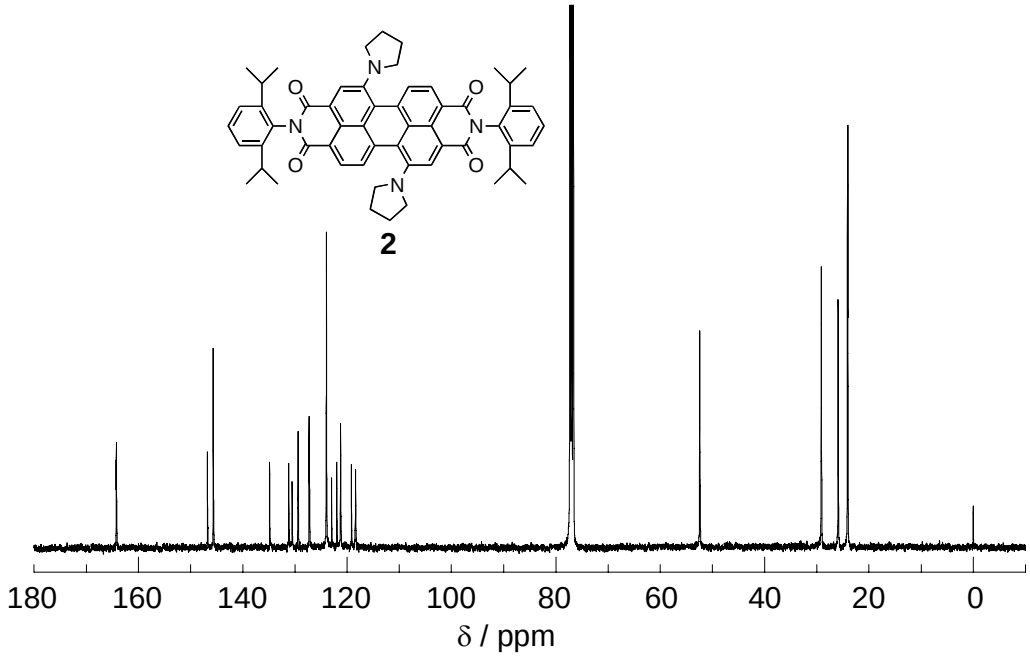

Figure S2-2. ^{13}C NMR spectrum of **2** in $CDCl_3$.

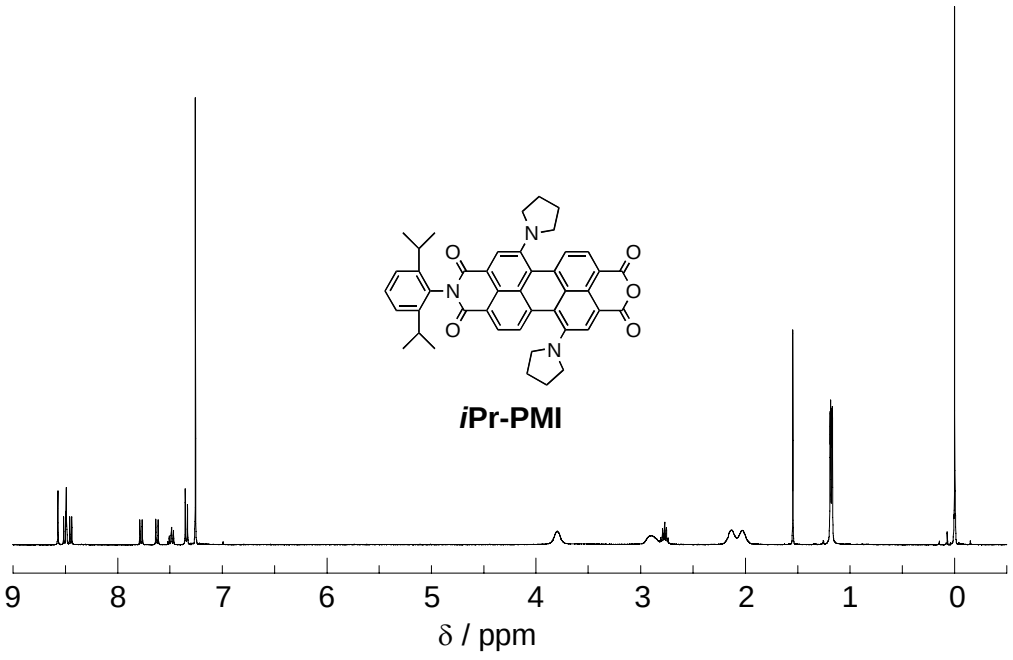

Figure S2-3. ^{1}H NMR spectrum of ***i*Pr-PMI** in $CDCl_3$.

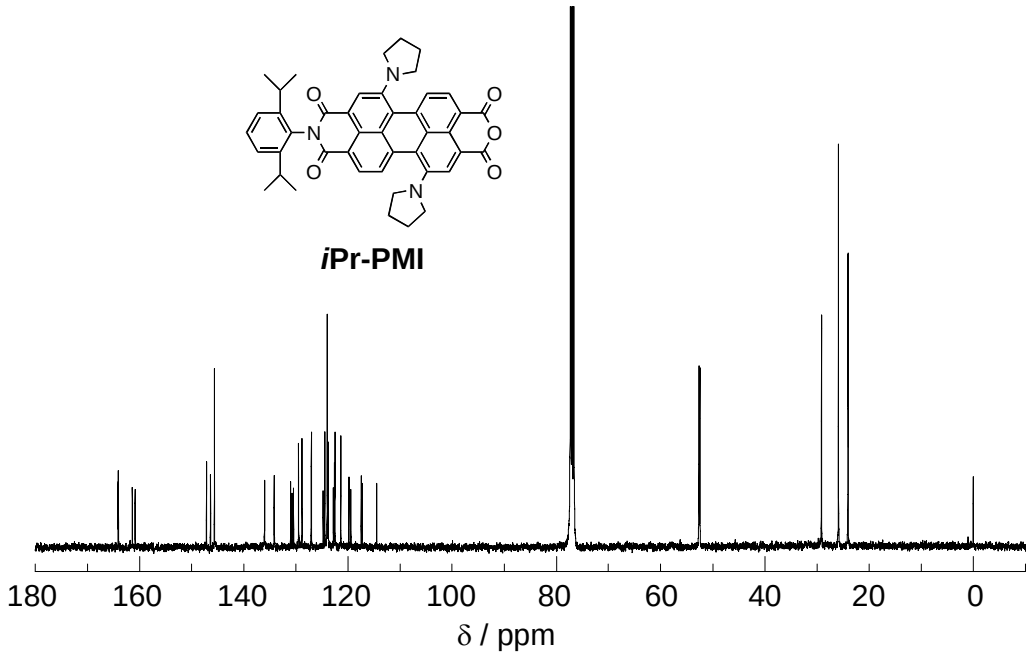

Figure S2-4. ^{13}C NMR spectrum of ***i*Pr-PMI** in $CDCl_3$.

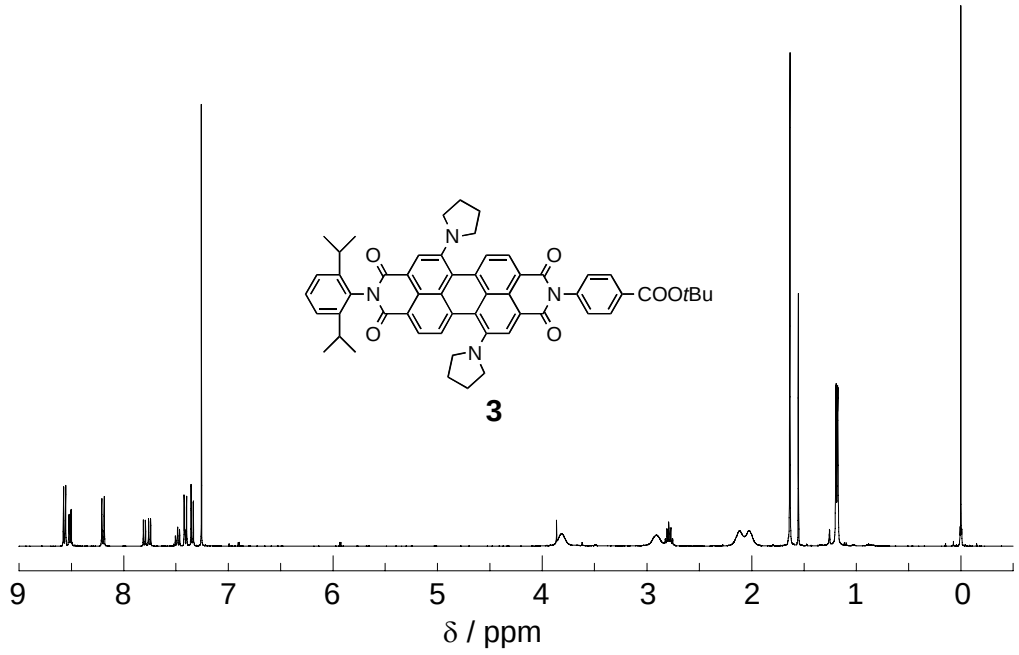

Figure S2-5. ^{1}H NMR spectrum of **3** in $CDCl_3$.

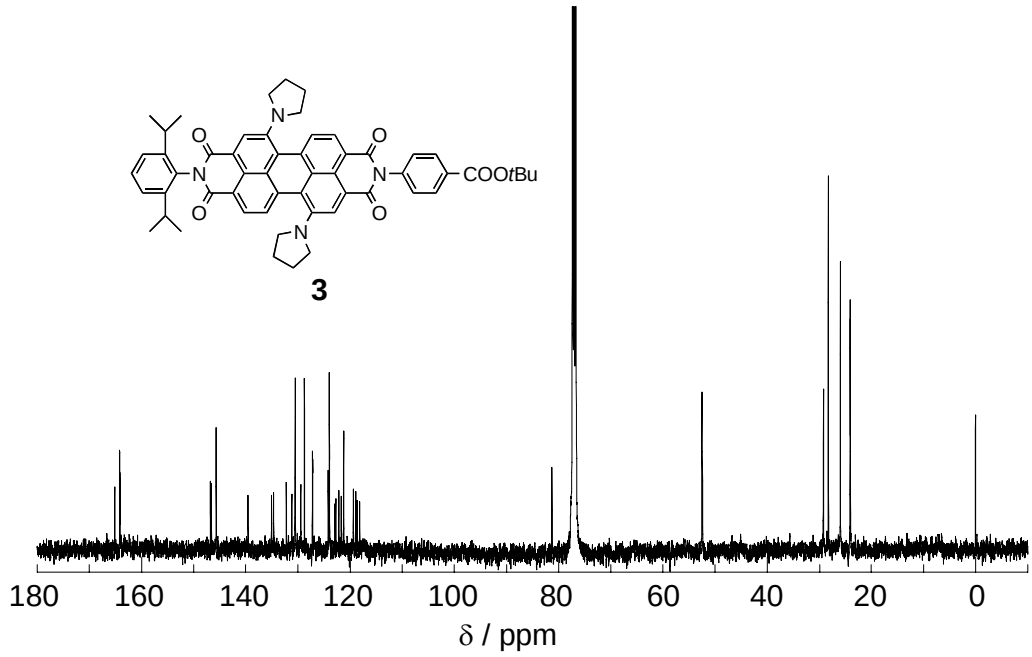

Figure S2-6. ^{13}C NMR spectrum of **3** in $CDCl_3$.

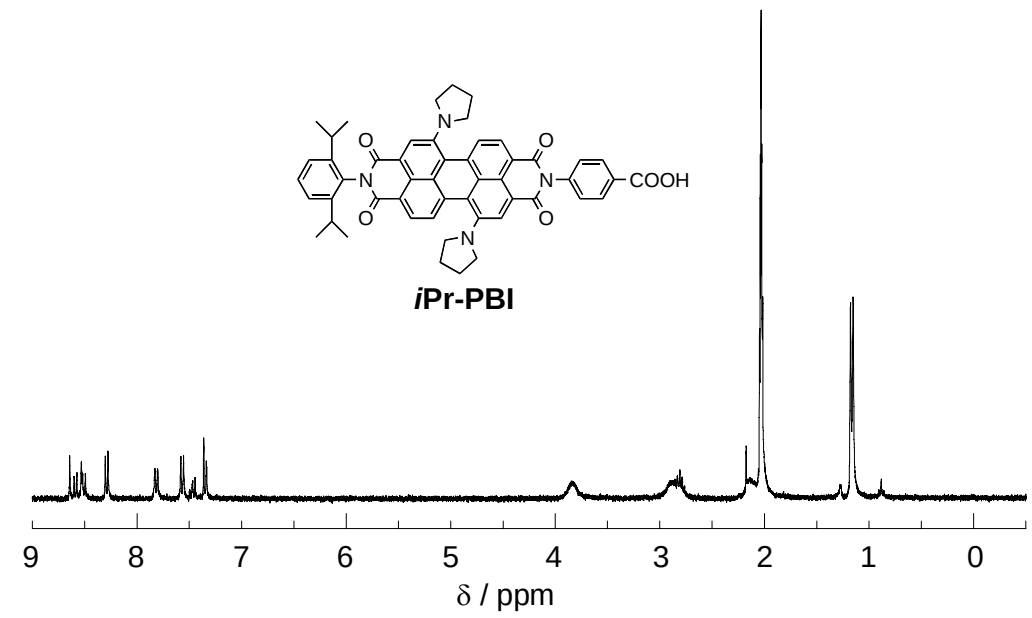

Figure S2-7. ^{1}H NMR spectrum of ***i*Pr-PBI** in acetic acid-d_4.

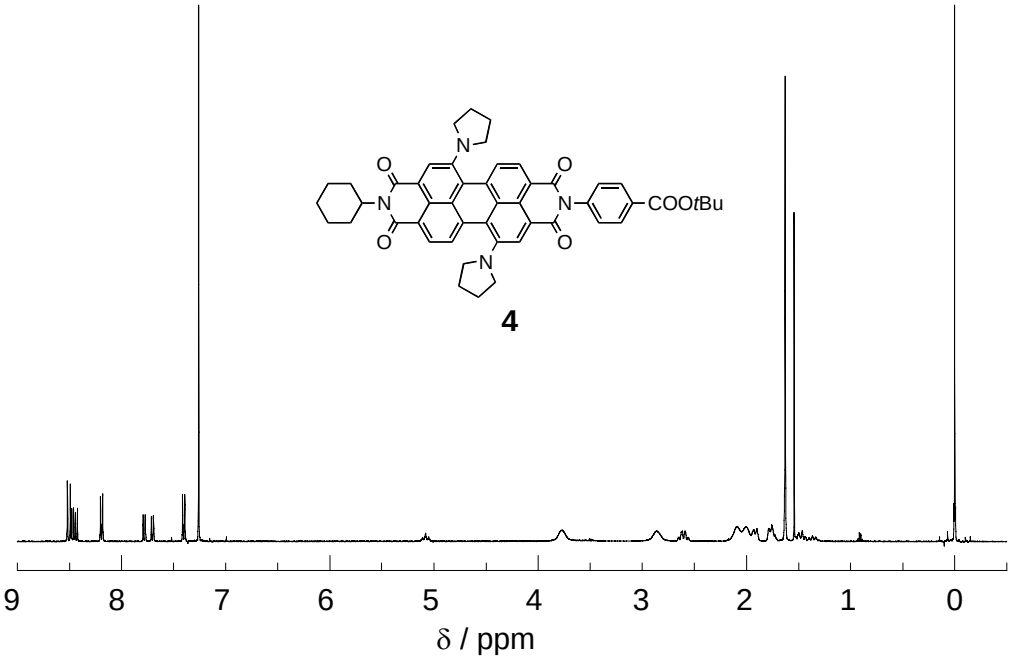

Figure S2-8. ^{1}H NMR spectrum of **4** in $CDCl_3$.

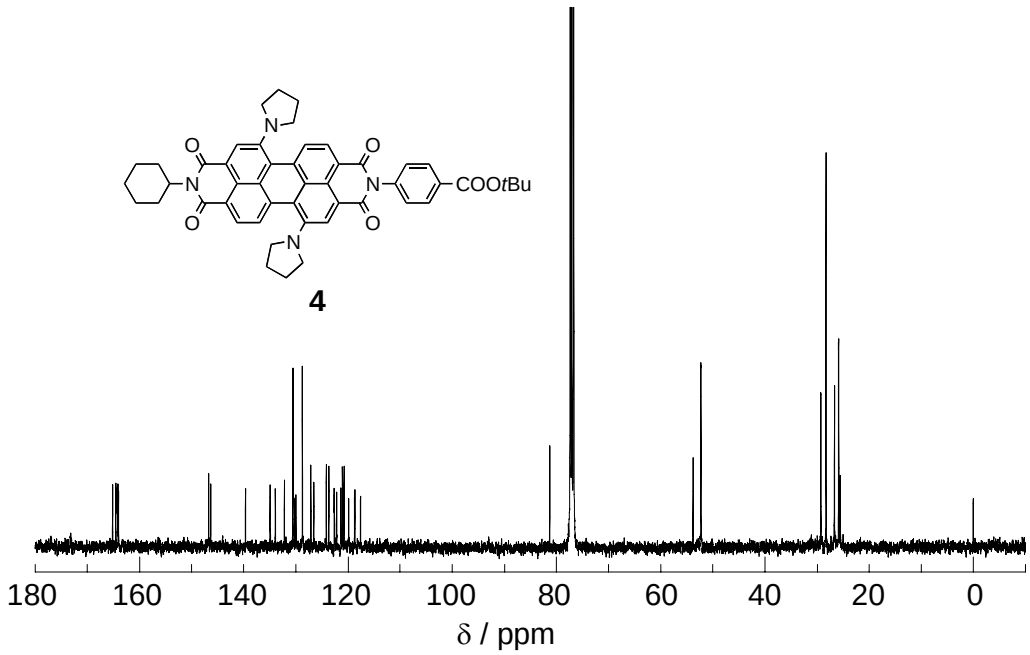

Figure S2-9. ^{13}C NMR spectrum of **4** in $CDCl_3$.

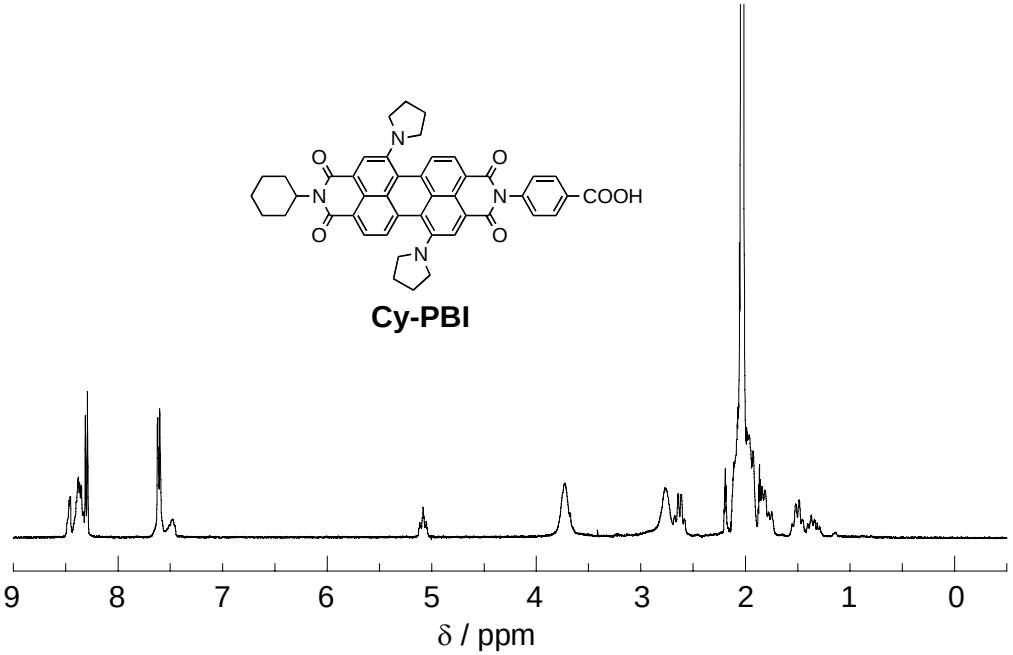

Figure S2-10. ^{1}H NMR spectrum of **Cy-PBI** in acetic acid-d_4.

S3.

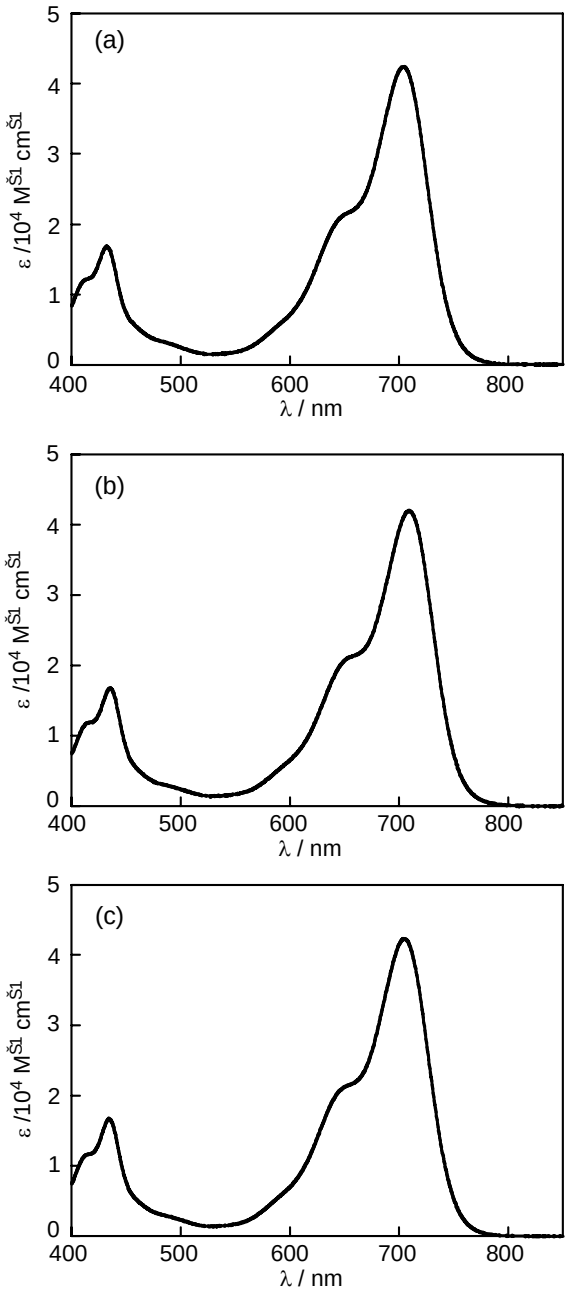

Figure S3. Absorption spectra of (a) **Cy-PMI**, (b) ***i*Pr-PBI**, and (c) **Cy-PBI** in CH_2Cl_2.

S4.

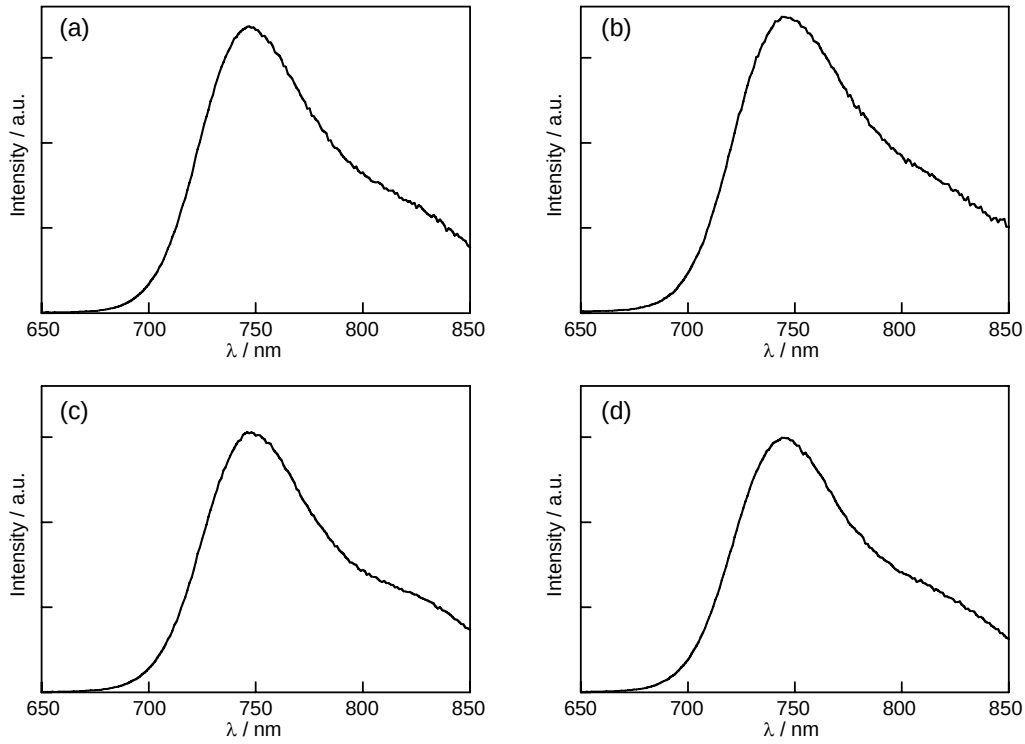

Figure S4. Fluorescence spectra of (a) ***i*Pr-PMI**, (b) **Cy-PMI**, (c) ***i*Pr-PBI**, and (d) **Cy-PBI** in CH_2Cl_2 with an excitation wavelength of 430 nm where the absorbances of the compounds are identical.

S5.

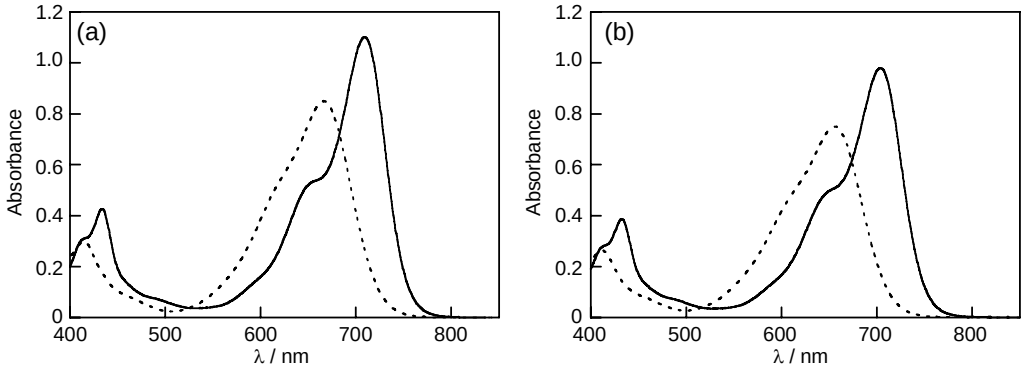

Figure S5. (a) Absorption spectra of 0.11 mM of ***i*Pr-PMI** in CH_2Cl_2 before (solid line) and after (dashed line) addition of 100 equivalent of Bu_4NOH. (b) Absorption spectra of 0.069 mM of **Cy-PMI** in CH_2Cl_2 before (solid line) and after (dashed line) addition of 90 equivalent of Bu_4NOH. Further addition of Bu_4NOH did not change the spectra.

S6.

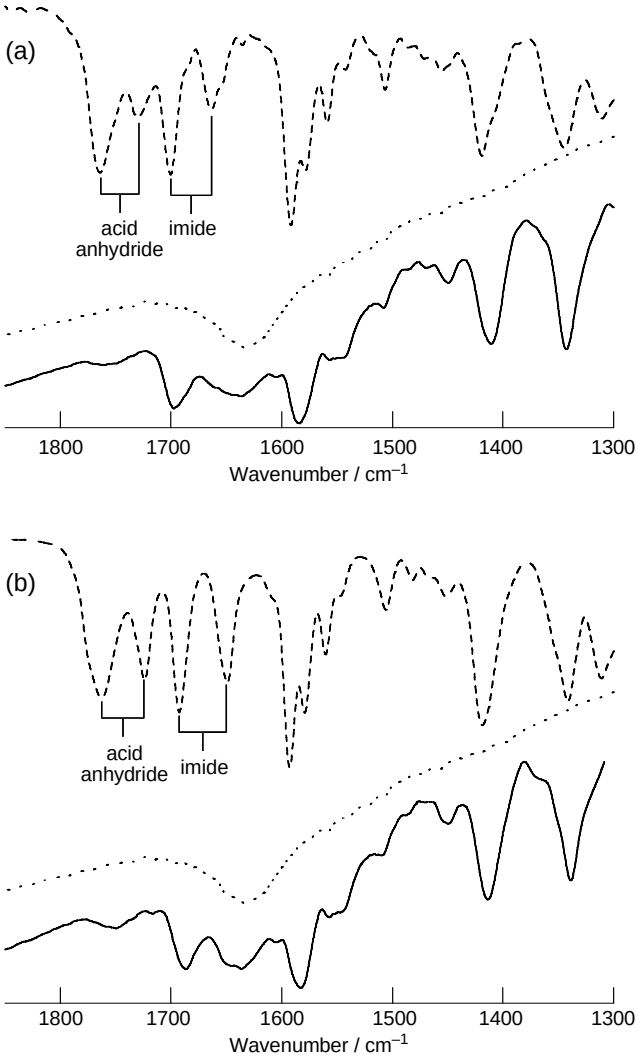

Figure S6. IR spectra of (a) ***i*Pr-PMI** and (b) **Cy-PMI** in KBr pallet (dashed line) and on surface of TiO_2 (solid line). IR spectra of TiO_2 (dotted line) are also shown for comparison. The peaks at around 1770-1720 cm^{-1} and 1700-1660 cm^{-1} are assigned to symmetric and asymmetric vibration of C=O of acid anhydride and that of imide, respectively. The peaks due to the acid anhydride disappear after adsorption of the dyes on the TiO_2 electrode, while those due to the imide remain intact.

S7.

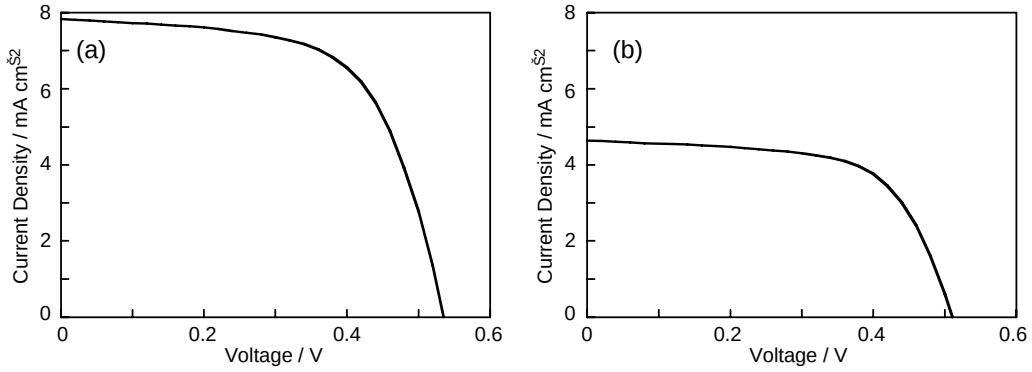

Figure S7. Current-voltage characteristics of (a) ***i*Pr-PMI** and (b) **Cy-PMI**-sensitized TiO_2 cells. Conditions: electrolyte 0.1 M LiI, 0.05 M I_2, 0.6 M 2,3-dimethyl-1-propyl imidazolium iodide, and 0.5M 4-*t*-butylpyridine in CH_3CN; input power: AM 1.5 under simulated solar light (100 mW cm^{-2}).