Electronic Supplementary Information for:

Linearly π-extended squaraine dyes enable the spectral response of dye-sensitized solar cells in the NIR region over 800 nm

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1. Synthesis

Preparation of compound 1

3,4-Dihydroxy-3-cyclobutene-1,2-dione (0.50 g, 4.4 mmol) and 1-heptyl-5-iodo-2,3,3-trimethyl-3*H*-indolium iodide (4.72 g, 9.23 mmol) were dissolved in a mixture of 1-butanol (4 mL) and benzene (1 mL). Then a catalytic amount of quinoline was added and the solution was heated under reflux for 6 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent; $CHCl_3$/hexane/EtOAc, 7/2/1, v/v/v). Compound **1** was precipitated from $CHCl_3$/hexane solution as a green crystal (3.0 g, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60–7.57 (m, 4H), 6.72 (d, J = 8.2 Hz, 2H), 5.92 (s, 2H), 3.98-3.81 (m, 4H), 1.74 (m, 16H), 1.37–1.24 (m, 16H), 0.85 (t, J = 6.9 Hz, 6H). MALDI TOF-MS: m/*z* calcd for $[M(C_{40}H_{50}I_2N_2O_2) + H]^+$, 845.20; found 845.46. IR (KBr, cm^{-1}): 2952, 2920, 1601, 1499, 1452, 1342, 1275, 1171, 1084, 1042. Anal.Calcd. for $C_{40}H_{50}I_2N_2O_2$; C, 56.88; H, 5.97; N, 3.32 %. Found: C, 56.86; H, 5.64; N, 3.18 %.

Preparation of compound 3

In a two-necked round-bottom flask equipped with a condenser, **1** (0.30 g, 0.36 mmol), $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), and CuI (2.1 mg, 0.011 mmol) were dissolved in tetrahydrofuran (10 mL) under an N_2 atmosphere. To the solution was added 3-(1-methyl)ethyloxy-4-(tributylstannyl)cyclobut-3-ene-1,2-dione (**2**) (0.23 g, 0.53 mmol), and the mixture was stirred at 50 ºC for 27 h. After cooling, the solvent was removed at reduced pressure, and the residue was purified by silica gel column chromatography (eluent; $CHCl_3$/EtOAc, 9/1, v/v). Compound **3** was precipitated from $CHCl_3$/hexane solution as a green crystal (0.12 g, 38%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06 (d, J = 8.3 Hz, 1H), 7.97 (s, 1H), 7.66–7.63 (m, 2H), 7.04 (d, J = 8.4 Hz, 1H), 6.80 (d, J = 8.1 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 6.03 (s, 2H) 5.66–5.60 (m, 1H), 4.15–3.88 (m, 4H), 1.82–1.79 (m, 16H), 1.58 (d, J = 6.2 Hz, 6H), 1.38–1.28 (m, 16H), 0.88 (t, J = 6.6 Hz, 6H). MALDI TOF-MS: m/*z* calcd for $[M(C_{47}H_{57}IN_2O_5)]^+$, 856.33; found 855.99. IR (KBr, cm^{-1}): 2953, 2918, 1782, 1738, 1601, 1504, 1391, 1344, 1273, 1171, 1082, 1042. Anal.Calcd. for $C_{47}H_{57}IN_2O_5$: C, 65.88; H, 6.70; N, 3.27 %. Found: C, 65.70; H, 6.52; N, 3.15 %.

Preparation of compound 4

Compound **3** (0.40 g, 0.46 mmol) was dissolved in a mixture of THF–3.6% HCl aq. (THF/HCl aq., 10/1(v/v), 37 mL) and then stirred for 20 h at 60 ºC. After removal of solvent, the residue was washed with water and a mixture of $CHCl_3$ and hexane ($CHCl_3$/hexane, 1/2, v/v), and dried *in vacuo* to give **4** as a purple solid (0.37 g, 97%), which was used in the next step without further purification. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.02–7.98 (m, 2H), 7.87 (s, 1H), 7.64 (d, J = 9.8 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 8.5 Hz, 1H), 5.81 (s, 1H), 5.78 (s, 1H), 4.07–4.02 (m, 4H), 1.66–1.64 (m, 16H), 1.32–1.26 (m, 16H), 0.81 (t, J = 6.8 Hz, 6H). MALDI TOF-MS: m/z calcd for $[M(C_{44}H_{51}IN_2O_5)]^+$, 814.28; found 814.98. IR (KBr, cm^{-1}): 2953, 2926, 1765, 1599, 1580, 1502, 1400, 1344, 1273, 1169, 1105, 1086, 1041.

Preparation of compound 6a

Compound **4** (0.13 g, 0.17 mmol) and 1-butyl-2,3,3-trimethyl-3*H*-indolium iodide (**5a**) (68 mg, 0.20 mmol) were dissolved in a mixture of 1-butanol (6.0 mL) and benzene (1.5 mL). Then a catalytic amount of quinoline was added and the solution was heated at 65 ºC for 18 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent; $CHCl_3$/acetone, 4/1, v/v). Compound **6a** was precipitated from $CHCl_3$/hexane solution as a dark purple crystal (0.13 g, 75%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.13 (d, J = 8.8 Hz, 1H), 8.11 (s, 1H), 7.94 (s, 1H), 7.78–7.73 (m, 2H), 7.71 (d, J = 8.4 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.49–7.46 (m, 2H), 7.23 (d, J = 8.4 Hz, 1H), 6.30 (s, 1H), 5.86 (s, 2H), 4.51–4.40 (m, 2H), 4.18–4.01 (m, 4H), 1.79–1.68 (m, 24H), 1.45–1.25 (m, 18H), 0.95 (t, J = 7.3 Hz, 3H), 0.85 (t, J = 6.7 Hz, 6H). MALDI TOF-MS: m/z calcd for $[M(C_{59}H_{70}IN_3O_4)]^+$, 1011.44; found 1011.79. IR (KBr, cm^{-1}): 2953, 2926, 1742, 1612, 1558, 1493, 1394, 1342, 1319, 1265, 1167, 1082, 1038. Anal.Calcd. for $C_{59}H_{70}IN_3O_4$: C, 70.02; H, 6.97; N, 4.15 %. Found: C, 69.94; H, 7.01; N, 4.08 %.

Preparation of compound 6b

Compound **4** (0.15 g, 0.18 mmol) and 3-butyl-2-methyl-1,3-benzothiazol-3-ium iodide (**5b**) (74 mg, 0.22 mmol) were dissolved in a mixture of 1-butanol (3.7 mL) and benzene (0.9 mL). Then a catalytic amount of quinoline was added and the solution was heated at 90 ºC for 4.5 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified

by silica gel column chromatography (eluent; $CHCl_3$/EtOAc/CH_3OH, 40/10/1, v/v/v). Compound **6b** was precipitated from $CHCl_3$/hexane solution as a dark purple crystal (90 mg, 49%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.25–8.20 (m, 2H), 7.83 (d, J = 8.3 Hz, 1H), 7.64–7.58 (m, 3H), 7.53–7.50 (m, 2H), 7.02 (d, J = 8.3 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 6.44 (s, 1H), 6.01 (s, 1H), 5.96 (s, 1H), 4.41 (t, J = 7.9 Hz, 2H), 4.08–3.85 (m, 4H), 1.92–1.88 (m, 2H), 1.82–1.77 (m, 16H), 1.56–1.51 (m, 2H), 1.40–1.25 (m, 16H), 1.04 (t, J = 7.3 Hz, 3H), 0.88 (t, J = 6.7 Hz, 6H). MALDI TOF-MS: m/z calcd for $[M(C_{56}H_{64}IN_3O_4S)]^+$, 1001.37; found 1001.76. IR (KBr, cm^{-1}): 2953, 2926, 1738, 1601, 1493, 1393, 1340, 1265, 1167, 1081, 1038. Anal.Calcd. for $C_{56}H_{64}IN_3O_4S$: C, 67.12; H, 6.44; N, 4.19 %. Found: C, 67.49; H, 6.77; N, 4.08 %.

2. DFT Calculations of TSQa-b

The ground-state geometries of **TSQa-b** were optimized in the gas phase by DFT calculations with the Gaussian 09 program (**Fig. 5**).[1] The calculations were performed on the models in which alkyl substituents have been replaced by methyl groups with the B3LYP exchange-correlation functional under a 6-31G basis set.

1 Gaussian 09, Revision **A.1**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

3. ^{1}H-NMR Spectra