

Electronic supplementary information

Insight into quinoxaline containing D- π -A dyes for dye-sensitized solar cells with cobalt and iodine based electrolytes: the effect of π -bridge on the HOMO energy level and photovoltaic performance

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Materials

All chemicals and reagents were from commercial sources without purification. Solvents for chemical synthesis were purified by distillation. All chemical reactions were carried out under an argon atmosphere. The starting materials [4-bis(2',4'-bis((2-ethylhexyl)oxy)biphenyl-4-yl)amino]phenylborate¹ and 5,8-dibromo-2,3-diphenylquinoxaline² were synthesized according to the published procedures.

Characterization

¹H NMR and ¹³C NMR spectra were recorded on Bruker AM-400 MHz instruments with tetramethylsilane (TMS) as internal standard. HRMS were performed by using a Waters LCT Premier XE spectrometer. The absorption spectra of the sensitizer dyes in solution and adsorbed on TiO₂ films were measured with a Varian Cary 500 spectrophotometer. The stability and redox behaviors of dye molecules were analyzed by cyclic voltammetry (CV) in CH₂Cl₂ solutions without deoxidization. The cyclic voltammograms (CV) were determined by using a CHI660C electrochemical workstation (Chenhua Co. Ltd, Shanghai, China) in a three-electrode cell. Working electrode was glassy carbon electrode, used in conjunction with a Pt auxiliary electrode and an Ag/AgCl wire pseudo-reference electrode. All the experiments were performed in CH₂Cl₂ solutions containing 0.1 M tetrabutylammonium perchlorate (TBAP) at a scan rate of 100 mV s⁻¹. The ferrocenium/ferrocene (Fc/Fc⁺) redox couple was used as an external potential reference.

Fabrication and Photovoltaic measurements

4 or 8 μ m TiO₂ films composed of 20 nm nanoparticle, α -terpineol and ethyl cellulose, and a 4 μ m scattering layer (60% nanoparticles of 20 nm and 40% large particles of 100 nm) in thickness was prepared according to the established method.³ These nanocrystal titania films were treated with 40 mM TiCl₄ aqueous solution at room temperature overnight, following by sintering at 450 °C for 30 min. After cooling down to room temperature, these films were dipped into a 3 \times 10⁻⁴ M solution of dyes in chloroform/ethanol (v/v: 3/7) mixed solvent with 5 mM CDCA for 3 h. After this, the electrodes were rinsed with CH₂Cl₂ and ethanol and then dried. The size of the electrodes was 0.12 cm². The counter electrode (Pt-coated TCO) and the working electrode (dye-loaded TiO₂ film) were sealed together by a hot-melt 30 μ m thick spacer under heat. The Pt-counter electrodes were prepared following the literature.⁴ Iodide electrolyte containing: 0.1 M LiI, 0.03 M I₂, 0.5 M 1-butyl-3-methylimidazolium iodide (BMII), 0.1 M guanidine isothiocyanate, and 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile:

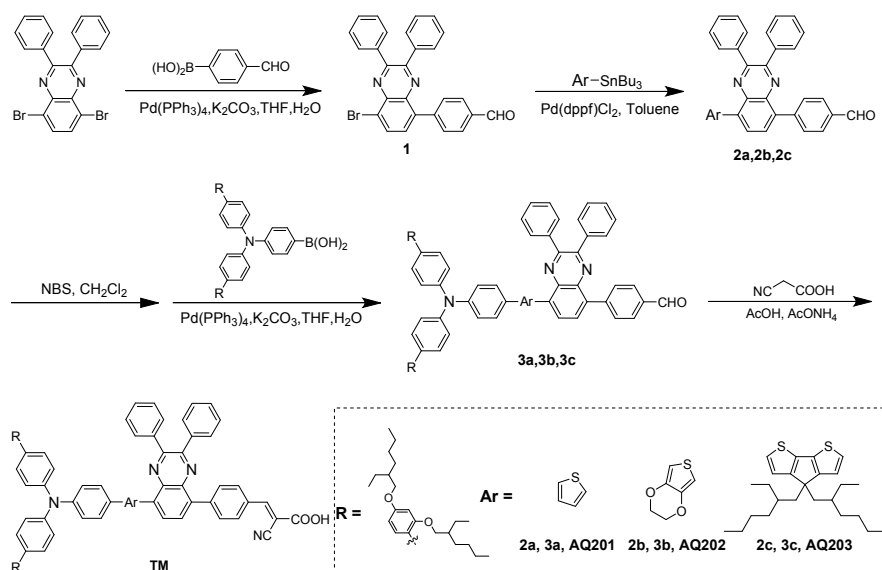
valeronitrile (85:15, v/v), cobalt electrolyte containing: 0.22 M [Co(II)(bpy)₃](TFSI)₂, 0.06 M [Co(III)(bpy)₃](TFSI)₃, 0.1 M LiClO₄, and 0.5 M 4-*tert*-butylpyridine in acetonitrile, (bpy=2,2'-bipyridine, TFSI=bis(trifluoromethane)sulfonamide).

The DSSCs were evaluated by recording the *J-V* curves with a Keithley 2400 source meter under the illumination of Air Mass 1.5G simulated solar light coming from a solar simulator (Oriel-91160 equipped with a 300 W Xe lamp). Incident monochromatic IPCE spectra were obtained with an Oriel-74125 system and the intensity of incident monochromatic was measured with a Si detector (Oriel-71640). Electrical impedance experiments (EIS) were performed in the dark. The spectra were scanned in a frequency range from 0.1 Hz to 100 kHz at room temperature with applied potential set at open circuit. The alternate potential amplitude was set at 10 mV.

Photoinduced Charge-Transfer Dynamics

The nanosecond laser flash photolysis technique was applied to the dye-sensitized, 4 μm thick, transparent TiO₂ mesoporous films deposited on normal flint glass. The samples were excited by pulses produced at a repetition rate of 30 Hz by a broad-band optical parametric oscillator (GWU OPO-355) pumped by a Powerlite 7030 frequency-tripled Q-switched Nd:YAG laser (Continuum, Santa Clara, California, USA). The output excitation wavelength was tuned at λ_{exc} = 530 nm with a pulse width of 7 ns (fwhm). The laser beam was expanded by a planoconcave lens to irradiate a large cross-section of the sample, whose surface was kept at a 45 degree angle to the excitation beam. The probe light, produced by a continuous wave xenon arc lamp, was first passed through a monochromator tuned in 20 nm steps throughout the 420-740 nm range of the VIS light spectrum. The probe light passed various optical elements, the sample, and then a second monochromator, before being detected by a fast photomultiplier tube (Hamamatsu, R9110). Data waves were recorded on a DSA 602A digital signal analyzer (Tektronix, Beaverton, Oregon, USA). Satisfactory signal-to-noise ratios were typically obtained by averaging over 1500 laser shots. The transient absorption measurements were performed on the previously described dye-sensitized, 4 μm-thick, transparent TiO₂ either immersion with [Co(bpy)₃]^{2+/3+} or I⁻/I₃⁻ based electrolyte.

Dye Synthesis



Scheme S1. Synthetic Procedure of the Dyes AQ201, AQ202, and AQ203.

Synthesis of 2. Under an argon atmosphere, compound **1** (439 mg, 1.0 mmol), K₂CO₃ (5 mL, 2 M aqueous

solution) and Pd(PPh₃)₄ (42 mg, 0.036 mmol) were dissolved in 20 mL of THF. After stirring for half an hour, the mixture was heated to 50 °C and a solution of (4-formylphenyl)boronic acid (1.0 mmol) in THF (5 mL) was added slowly. The mixture was then refluxed for 12 h before cooling to room temperature and extracted with CH₂Cl₂. The organic layers were washed with brine water and dried over anhydrous Na₂SO₄. After removing the solvent under reduced pressure, the residue was chromatographed on a silica gel column with PE/CH₂Cl₂ (3/1-1/1, v/v) as eluent to give compound **2** (260 mg, 56 % yield). ¹H NMR(400 MHz, CDCl₃, ppm): δ = 10.15 (s, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.8 Hz, 2H), 7.75-7.71 (m, 3H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.44-7.32 (m, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 192.19, 153.26, 153.01, 143.81, 139.03, 138.74, 138.68, 138.29, 138.23, 135.47, 132.92, 131.44, 130.34, 130.19, 130.00, 129.46, 129.37, 129.33, 128.38, 128.29, 124.51. HRMS (m/z): [M+H⁺] calcd for C₂₇H₁₈N₂OBr, 465.0602; found: 465.0538.

Synthesis of 3a. Under an argon atmosphere, 2-(tributylstanny)thiophene (193 mg, 0.52 mmol) and compound **2** (200 mg, 0.43 mmol) and Pd(dppf)Cl₂ (7.3 mg, 0.01 mmol) were dissolved in anhydrous toluene (20 mL) and refluxed for 12 h. The organic phase was extracted with CH₂Cl₂, washed with HCl (1 M), dried over Na₂SO₄ and concentrated under reduced pressure. The crude solid was purified by chromatography on silica gel using PE/CH₂Cl₂ (3/1-1/1, v/v) as eluent to give a yellow solid **3a** (180 mg, 89 % yield). ¹H NMR(400 MHz, CDCl₃, ppm): δ = 10.13 (s, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.04 (s, 4H), 7.93 (d, *J* = 4.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.76-7.74 (m, 2H), 7.59-7.56 (m, 3H), 7.41-7.29 (m, 6H), 7.22 (t, *J* = 4.2 Hz, 1H). ¹³C NMR (10 MHz, CDCl₃, ppm): δ = 192.27, 152.05, 151.79, 144.45, 138.69, 138.63, 138.53, 138.51, 137.21, 137.10, 135.27, 133.07, 131.48, 130.44, 130.27, 130.03, 129.75, 129.36, 129.14, 128.88, 128.31, 128.28, 126.90, 126.84, 126.72. HRMS (m/z): [M+H⁺] calcd for C₃₁H₂₁N₂OS, 469.1375; found: 469.1388.

Synthesis of 4a. Compound **3a** (160 mg, 0.34 mmol) and N-bromosuccinimide (**NBS**) (73 mg, 0.41 mmol) were dissolved in anhydrous CH₂Cl₂ in an ice bath for 2 h. Then, a Suzuki coupling reaction was performed with [4-bis(2',4'-bis((2-ethylhexyl)oxy)biphenyl-4-yl)amino]phenylborate by using a similar procedure to that of compound **2** to give an orange solid **4a** (210 mg, 45 % yield). ¹H NMR(400 MHz, CDCl₃, ppm): δ = 10.12 (s, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.04(s, 4H), 7.83 (d, *J* = 4.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.80-7.78 (m, 2H), 7.61-7.59 (m, 4H), 7.45 (d, *J* = 8.2 Hz, 4H), 7.41-7.39 (m, 3H), 7.36-7.27 (m, 6H), 7.22-7.18 (m, 6H), 6.57-6.55 (m, 4H), 3.89-3.86 (m, 8H), 1.76-1.68 (m, 4H), 1.45-1.26 (m, 32H), 0.97-0.87 (m, 24H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 192.26, 159.93, 157.27, 152.02, 151.56, 147.80, 147.67, 145.61, 144.51, 138.75, 138.66, 138.59, 137.04, 136.71, 135.23, 133.46, 133.12, 131.48, 130.77, 130.55, 130.48, 130.34, 130.08, 129.37, 129.21, 129.17, 128.30, 128.12, 126.42, 126.08, 123.96, 123.44, 123.17, 122.03, 105.22, 100.35, 70.75, 70.56, 39.54, 39.44, 30.70, 30.64, 29.20, 29.07, 24.13, 23.97, 23.16, 23.14, 14.21, 11.27, 11.25. HRMS (m/z): [M+H⁺] calcd for C₉₃H₁₀₆N₃O₅S, 1376.7853; found: 1376.7836.

Synthesis of AQ201. Under an argon atmosphere, a mixture of **4a** (170 mg, 0.12 mmol), cyanoacetic acid (85 mg, 1 mmol), and ammonium acetate (120 mg) in acetic acid (25 mL) and THF (5 mL) was heated at reflux for 12 h. After cooling down, the mixture was poured into water. The precipitates were collected by filtration and washed with water. The residue was purified by column chromatography on silica gel with CH₂Cl₂/ethanol (10:1, v/v) to yield a red solid **AQ201** (120 mg, 69 % yield). ¹H NMR(400 MHz, Acetone-*d*₆, ppm): 8.45-8.43(m, 2H), 8.26 (d, *J* = 8.8 Hz, 2H), 8.14 (d, *J* = 8.2 Hz, 2H), 8.08-8.04 (m, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.51-7.49 (m, 5H), 7.45-7.44 (m, 3H), 7.40-7.35(m, 3H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 6H), 6.69 (s, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 3.96-3.94 (m, 8H), 1.76-1.68 (m, 4H), 1.50-1.30 (m, 32H), 0.98-0.86 (m, 24H). ¹³C NMR (100 MHz, Acetone-*d*₆, ppm): δ = 161.01, 158.17, 149.46, 146.41, 143.98, 134.76, 132.50, 131.43, 131.35, 130.92, 129.07, 129.02, 127.16, 124.71, 124.13, 123.68, 123.05, 106.71, 101.08, 71.35, 71.04, 40.43, 40.35, 31.51, 31.34, 24.61, 23.78, 23.76, 14.46, 14.39, 11.64, 11.48, 5.45. HRMS (m/z): [M+H⁺] calcd for C₉₆H₁₀₇N₄O₆S, 1443.7911; found: 1443.7953.

Synthesis of 3b. Compound **3b** was obtained by using a similar procedure to that of **3a** (150 mg, 75 % yield). ¹H NMR(400 MHz, CDCl₃, ppm): δ = 10.05 (s, 1H), 8.63 (d, J = 8.8 Hz, 1H), 7.96 (s, 4H), 7.82 (d, J = 4.4 Hz, 1H), 7.69 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.32-7.23 (m, 6H), 7.55 (s, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 191.25, 150.66, 150.06, 143.61, 140.35, 139.74, 137.71, 137.46, 137.25, 136.09, 134.83, 134.07, 130.63, 130.41, 129.48, 129.37, 128.98, 128.28, 127.98, 127.19, 126.64, 111.86, 102.97, 64.02, 63.27. HRMS (m/z): [M+H⁺] calcd for C₃₃H₂₃N₂O₃S, 527.1429; found: 527.1428.

Synthesis of 4b. Compound **4b** was obtained by using a similar procedure to that of **4a** (190 mg, 80 % yield). ¹H NMR(400 MHz, CDCl₃, ppm): δ = 10.11 (s, 1H), 8.74 (d, J = 8.8 Hz, 1H), 8.03(s, 4H), 7.88 (d, J = 8.4 Hz, 1H), 7.84-7.82 (m, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.8 Hz, 4H), 7.39-7.35 (m, 4H), 7.33-7.23 (m, 6H), 7.20-7.18 (m, 4H), 6.57-6.56 (m, 4H), 4.48-4.47 (m, 2H), 4.42-4.41(m, 2H), 3.90-3.87 (m, 8H), 1.77-1.70 (m, 4H), 1.45-1.27 (m, 32H), 0.98-0.87 (m, 24H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 192.31, 159.86, 157.23, 151.67, 150.82, 138.81, 138.49, 135.78, 135.08, 131.46, 130.67, 130.34, 130.06, 129.36, 129.14, 129.05, 128.26, 128.18, 125.55, 123.73, 123.19, 121.37, 105.18, 100.31, 70.72, 70.55, 64.94, 64.39, 39.50, 39.40, 34.25, 30.64, 30.59, 30.35, 29.73, 29.47, 29.15, 29.02, 24.08, 23.92, 23.11, 23.08, 14.15, 11.20, 11.19. HRMS (m/z): [M+H⁺] calcd for C₉₅H₁₀₈N₃O₇S, 1434.7908; found: 1437.7910.

Synthesis of AQ202. Compound **AQ202** was obtained by using a similar procedure to that of **AQ201** (90 mg, 78 % yield). ¹H NMR (400 MHz, Acetone-*d*₆, ppm): δ = 8.73 (s, 1H), δ = 8.37 (s, 1H), 8.18 (d, J = 8.8 Hz, 1H), 8.06 (d, J = 8.8 Hz, 1H), 7.88-7.72 (m, 5H), 7.59 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 4.2 Hz, 4H), 7.36-7.28 (m, 6H), 7.23 (d, J = 8.4 Hz, 2H), 7.12-7.18 (m, 6H), 6.66-6.56 (m, 4H), 4.43-4.36 (m, 4H), 3.92-3.91 (m, 8H), 1.73-1.66 (m, 4H), 1.44-1.28 (m, 32H), 0.97-0.84(m, 24H). ¹³C NMR (100 MHz, Acetone-*d*₆, ppm): δ = 160.92, 158.14, 155.10, 146.51, 139.87, 139.47, 134.39, 132.43, 131.58, 131.45, 131.32, 131.25, 130.97, 129.74, 128.93, 127.75, 124.41, 123.74, 116.75, 106.65, 103.72, 101.13, 71.38, 71.04, 65.16, 40.40, 40.35, 31.50, 31.34, 24.84, 24.61, 23.77, 14.49, 14.42, 11.65, 11.50. HRMS (m/z): [M+H⁺] calcd for C₁₁₄H₁₄₀N₃O₅S₂, 1501.7966; found: 1501.7733.

Synthesis of 3c. Compound **3c** was obtained by using a similar procedure to that of **3a** (320 mg, 47 % yield). ¹H NMR(400 MHz, CDCl₃, ppm): δ = 10.12 (s, 1H), 8.22-8.20 (m, 1H), 8.03 (s, 4H), 7.88-7.86 (m, 2H), 7.79-7.77(m, 2H), 7.58 (d, J = 4.4 Hz, 2H), 7.45-7.44 (m, 3H), 7.35-7.29 (m, 3H), 7.20 (d, J = 4.2 Hz, 1H), 6.99-6.97 (m, 1H), 1.97-1.93 (m, 4H), 1.29-1.22 (m, 2H), 1.01-0.88 (m, 16H), 0.78-0.60 (m, 12H).

Synthesis of 4c. Compound **4c** was obtained by using a similar procedure to that of **4a** (250 mg, 65 % yield). ¹H NMR(400 MHz, CDCl₃, ppm): δ = 10.05 (s, 1H), 8.13 (s, 1H), 7.97 (s, 4H), 7.80 (d, J = 8.4 Hz, 2H), 7.72-7.70(m, 2H), 7.51 (d, J = 8.8 Hz, 2H), 7.42-7.35 (m, 9H), 7.28-7.21 (m, 5H), 7.10 (d, J = 8.2 Hz, 7H), 6.49-6.48 (m, 4H), 3.82-3.78 (m, 8H), 1.94-1.86 (m, 4H), 1.69-1.61 (m, 4H), 1.35-1.18 (m, 34H), 0.95-0.80 (m, 40H), 0.68-0.55(m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ = 192.29, 159.86, 157.21, 138.79, 138.65, 135.12, 133.28, 131.42, 130.69, 130.49, 130.38, 130.05, 129.39, 129.07, 128.37, 128.26, 125.92, 123.73, 123.15, 105.15, 100.27, 70.69, 70.52, 43.43, 39.48, 39.39, 35.21, 34.19, 30.63, 30.57, 29.14, 29.01, 28.61, 27.45, 24.04, 23.90, 23.10, 23.07, 22.84, 14.14, 11.17, 10.70. HRMS (m/z): [M+H⁺] calcd for C₁₁₄H₁₄₀N₃O₅S₂, 1695.0234; found: 1695.0217.

Synthesis of AQ203. Compound **AQ203** was obtained by using a similar procedure to that of **AQ201** (85 mg, 63 % yield). ¹H NMR (400 MHz, Acetone-*d*₆, ppm): δ = 8.35 (d, J = 8.4 Hz, 1H), 8.29 (s, 1H), 8.16-8.12 (m, 3H), 8.03 (d, J = 8.8 Hz, 2H), 7.93 (d, J = 8.8 Hz, 1H), 7.69-7.67 (m, 2H), 7.54-7.50 (m, 4H), 7.37-7.35 (m, 7H), 7.24-7.22 (m, 3H), 7.15-7.13 (m, 3H), 7.04-7.00 (m, 6H), 6.56(s, 2H), 6.48(d, J = 8.8 Hz, 2H), 3.83-3.81 (m, 8H), 1.64-1.53 (m, 4H), 1.24-1.16 (m, 34H), 0.85-0.74 (m, 40H), 0.60-0.51 (m, 12H). ¹³C NMR (100 MHz, Acetone-*d*₆) δ = 160.98, 158.16, 146.42, 139.96, 134.61, 132.43, 131.43, 131.35, 130.92, 129.13, 129.00, 124.54, 123.69, 106.69, 101.09, 71.35, 71.05, 54.79, 43.91, 40.43, 40.34, 36.11, 35.02, 32.64, 31.51, 31.34, 24.82, 24.61, 23.78, 23.76, 23.57, 23.51, 23.34, 14.49, 14.41, 11.65, 11.50, 11.18. HRMS (m/z): [M+H⁺] calcd for C₁₁₇H₁₄₁N₄O₆S₂, 1762.0293; found: 1762.0281.

Additional data

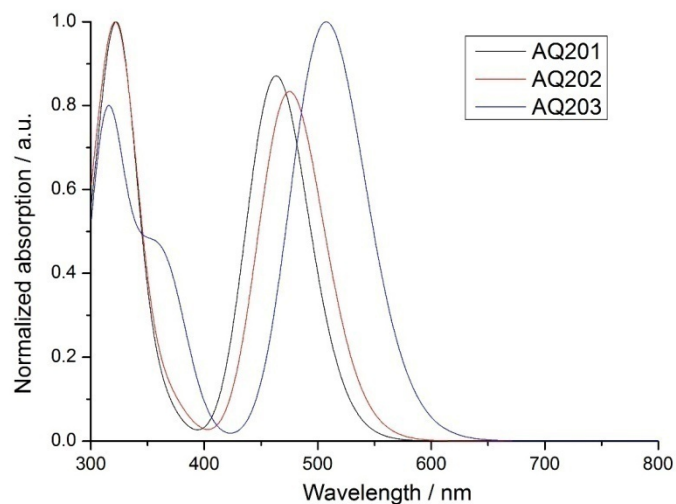


Fig. S1 Normalized simulated absorption spectra of AQ201, AQ202 and AQ203 from DT-DFT

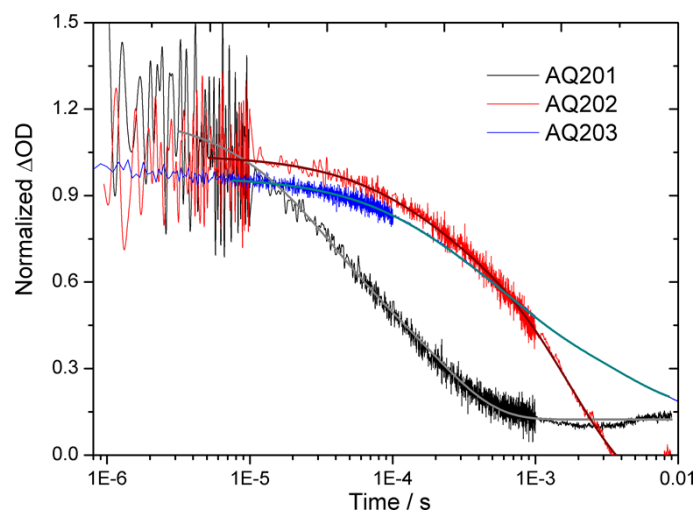


Fig. S2 Microsecond normalized transient absorption decays of AQ201, AQ202 and AQ203 dyes at 1050 nm in the presence of the iodide redox electrolyte

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