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有机染料敏化太阳电池中激发态弛豫和电子注入的超快光谱研究

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Ultrafast Spectroscopic Studies of Excited State Relaxation and Electron Injection in Organic Dye-Sensitized Solar Cells

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1. Synthesis of LY-1 and LY-2

Tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$), [1,1′-bis(diphenylphosphino)ferrocene] dichloropalladium(II) ($Pd(dppf)Cl_2$), palladium(II) acetate ($Pd(OAc)_2$), bis(triphenylphosphine)palladium(II) chloride ($Pd(PPh_3)_2Cl_2$), 2-(2,6-dimethoxybiphenyl)-dicyclohexylphosphine (Sphos), 2-dicyclohexylphosphino-2′,6′-diisopropoxy-1,1′-biphenyl (Ruphos), Pd/C, hydrazine hydrate (80%(*w*)), iodobenzene, iodine (I_2), periodic acid (H_5IO_6), 4,4,4′,4′,5,5,5′,5′-octamethyl-2,2′-bi(1,3,2-dioxaborolane), *t*-butyllithium (*t*-BuLi), chlorotrimethylstannane, potassium hydroxide (KOH), sodium carbonate (Na_2CO_3), sodium *tert*-butoxide (NaO*t*-Bu), potassium acetate (KOAc), and potassium phosphate (K_3PO_4) were purchased from Sigma-Aldrich. *N*,*N*-Dimethylformide (DMF), ethanol, dimethyl sulfoxide (DMSO), dioxane, tetrahydrofuran (THF), and toluene were distilled before use. 1-((2-Hexyldecyl)oxy)-4-iodobenzene[S1], 2-hexyldecyl 4-methylbenzenesulfonate[S2], 3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine[S3], butyl 4-(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)benzoate[S4], and *tert*-butyl 4-(7-bromopyrido[3,4-*c*][1,2,5]thiadiazol-4-yl)benzoate[S5] were synthesized according to the respective literature procedures. Other chemicals are purchased and used without further purification. The synthetic routes of **LY-1** and **LY-2** are illustrated in Scheme S1 and the preparation details are described as follows.

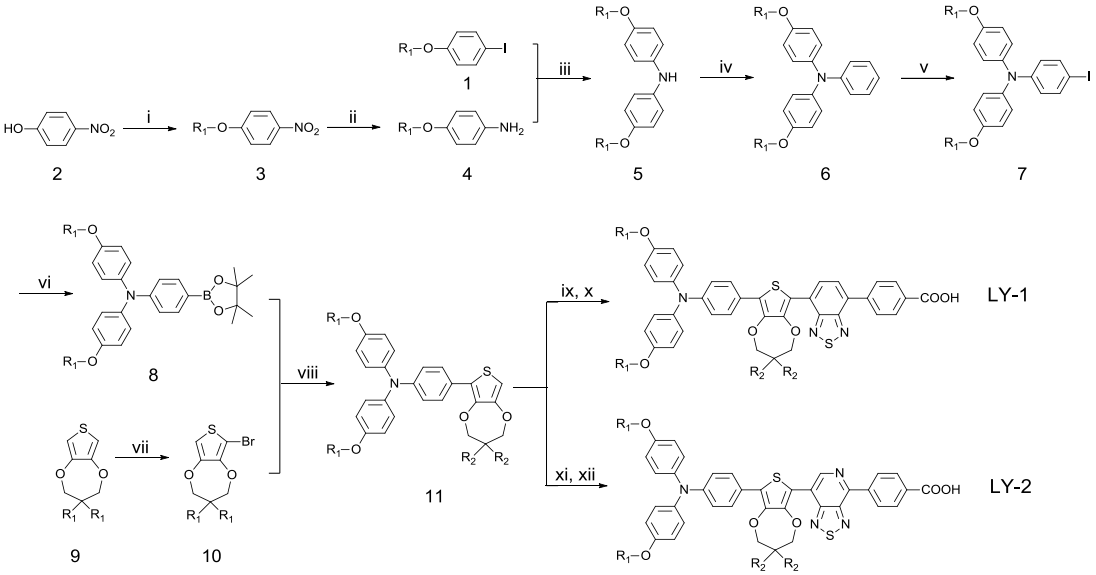

Fig.S1 Synthetic routes to LY-1 and LY-2

Herein R_1 represents the 2-hexyldecyl substituent, and R_2 is *n*-hexyl. [a] Reagents and conditions: (i) 2-hexyldecyl 4-methylbenzenesulfonate, K_2CO_3, DMF, 100 ℃, 3 h; (ii) Pd/C, hydrazine hydrate, ethanol, reflux, overnight; (iii) $Pd_2(dba)_3$, Ruphos, NaO*t*-Bu, toluene, reflux, overnight; (iv) iodobenzene, $Pd_2(dba)_3$, Ruphos, NaO*t*-Bu, toluene, reflux, overnight; (v) I_2, H_5IO_6, ethanol, reflux, overnight; (vi) 4,4,4′,4′,5,5,5′,5′-octamethyl-2,2′-bi(1,3,2-dioxaborolane), $Pd(dppf)Cl_2$, KOAc, DMSO, 45 ℃, 5 h; (vii) NBS, hydroquinone, THF, RT, 5 h; (viii) $Pd(OAc)_2$, Sphos, K_3PO_4, dioxane/H_2O (*V*/*V*, 5/1), reflux, overnight; (ix) *t*-BuLi, THF, −78 ℃, 1 h; chlorotrimethylstannane, −78 ℃ to RT, 12 h; butyl 4-(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)benzoate, $Pd(PPh)_2Cl_2$, toluene, reflux, 12 h; (x) NaOH, THF/H_2O (*V*/*V*, 3/1), reflux, overnight; then HCl. (xi) *t*-BuLi, THF, −78 ℃, 1 h; chlorotrimethylstannane, −78 ℃ to RT, 12 h; *tert*-butyl 4-(7-bromopyrido[3,4-*c*][1,2,5]thiadiazol-4-yl)benzoate, $Pd(PPh)_2Cl_2$, toluene, reflux, 12 h; (xii) HCl, THF, RT, 24 h.

1-((2-Hexyldecyl)oxy)-4-nitrobenzene **(3)**: **2** (1.40 g, 10.06 mmol), 2-hexyldecyl 4-methylbenzenesulfonate

(4.00 g, 10.06 mmol), and K_2CO_3 (6.97 g, 50.30 mmol) were dissolved in DMF (50 mL) in a three-neck round-bottom flask. The resulting mixture was stirred for 3 h at 100 ℃ and then cooled to room temperature. The mixture was extracted into dichloromethane, and the organic layer was washed with water and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum ether 60-90 ℃, 1/20, *V/V*) on silica gel to yield a colorless oil as the desired product **3** (3.52 g, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (d, J = 7.2 Hz, 2H), 6.94 (d, J = 9.2 Hz, 2H), 3.92 (d, J = 5.6 Hz, 2H), 1.81 (m, 1H), 1.27 (m, 24H), 0.87 (t, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.48, 141.27, 125.84, 114.40, 71.77, 37.82, 31.89, 31.81, 31.25, 31.23, 29.95, 29.62, 29.54, 29.34, 29.30, 26.79, 26.77, 22.66, 22.65, 14.07. MS (ESI) *m*/*z* calcd. for ($C_{22}H_{37}NO_3$): 363.28. Found: 364.28 ([M+H]$^+$). Anal. Calcd. for $C_{22}H_{37}NO_3$: C, 72.69%; H, 10.26%; N, 3.85%. Found: C, 72.61%; H, 10.22%; N, 3.82%.

4-((2-Hexyldecyl)oxy)aniline **(4)**: **3** (1.50 g, 4.13 mmol) was dissolved in ethanol (30 mL) in a three-neck round-bottom flask. Then hydrazine hydrate (2 mL) and Pd/C (100 mg) were added. The resulting mixture was stirred overnight at reflux and then cooled to room temperature. The mixture was filtrated and the filtrate was concentrated under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum ether 60-90 ℃, 1/20, *V/V*) on silica gel to afford a colorless oil as the desired product **4** (1.34 g, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.75 (d, J = 8.8 Hz, 2H), 6.63 (d, J = 8.8 Hz, 2H), 3.75 (d, J = 5.8 Hz, 2H), 3.38 (s, 2H), 1.74 (m, 1H), 1.31 (m, 24H), 0.89 (t, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.92, 139.87, 116.61, 115.90, 71.94, 38.28, 32.12, 32.07, 31.60, 30.25, 29.92, 29.88, 29.85, 29.80, 29.54, 27.05, 27.02, 22.88, 14.31. MS (ESI) *m*/*z* calcd. for ($C_{22}H_{39}NO$): 333.30. Found: 333.29 ([M]$^+$). Anal. Calcd. for $C_{22}H_{39}NO$: C, 79.22%; H, 11.79%; N, 4.20%. Found: C, 79.23%; H, 11.76%; N, 4.21%.

Bis(4-((2-hexyldecyl)oxy)phenyl)amine **(5)**: **1** (1.62 g, 3.65 mmol) and **4** (1.34 g, 4.02 mmol) were dissolved in toluene in a dried Schlenk tube. Then $Pd_2(dba)_3$ (100 mg, 0.11 mmol), Ruphos (62 mg, 0.13 mmol) and NaO*t*-Bu (950 mg, 9.89 mmol) were added to the reaction mixture in a glove box, which was stirred at reflux overnight under argon. After cooling to room temperature, water was added and the mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum ether 60-90 ℃, 1/20, *V/V*) on silica gel to yield a brown oil as the desired product **5** (2.16 g, 91% yield). ^{1}H NMR (400 MHz, C_6D_6-d_6) δ: 6.89 (m, 8H), 5.00 (s, 1H), 3.76 (d, J = 5.5 Hz, 4H), 1.81 (m, 2H), 1.51 (m, 4H), 1.30 (m, 44H), 0.91 (t, J = 5.5 Hz 12H). ^{13}C NMR (100 MHz, C_6D_6-d_6) δ: 154.88, 138.94, 120.27, 116.14, 71.77, 38.99, 32.68, 32.63, 32.31, 30.89, 30.54, 30.45, 30.42, 30.16, 27.74, 23.49, 23.46, 14.74, 14.72. MS (ESI) *m*/*z* calcd. for ($C_{44}H_{75}NO_2$): 649.58. Found: 649.55 ([M]$^+$). Anal. Calcd. for $C_{44}H_{75}NO_2$: C, 81.29%; H, 11.63%; N, 2.15%. Found: C, 81.26%; H, 11.60%; N, 2.14%.

4-((2-Hexyldecyl)oxy)-*N*-(4-((2-hexyldecyl)oxy)phenyl)-*N*-phenylaniline **(6)**: **5** (725 mg, 1.12 mmol) and iodobenzene (910 mg, 4.46 mmol) were dissolved in toluene in a dried Schlenk tube. Then $Pd_2(dba)_3$ (31 mg, 0.03 mmol), Ruphos (19 mg, 0.04 mmol) and NaO*t*-Bu (322 mg, 3.45 mmol) were added to the reaction mixture in a glove box, which was stirred at reflux overnight under argon. After cooling to room temperature, water was added and the mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum ether 60-90 ^{o}C, 1/50, *V/V*) on silica gel to yield a colorless oil as the desired product **6** (664 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17 (m, 2H), 7.05 (d, J = 8.8 Hz, 4H), 6.96 (d, J = 8.0 Hz, 2H), 6.84 (m, 5H), 3.82 (d, J = 5.6 Hz, 4H), 1.77 (m, 2H), 1.45 (m, 4H),

1.31 (m, 44H), 0.91 (t, *J* = 6.4 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.79, 149.13, 141.12, 129.07, 126.63, 120.95, 120.55, 115.46, 71.36, 38.28, 32.14, 32.10, 31.63, 30.26, 29.82, 29.56, 27.10, 27.08, 22.91, 14.33. MS (ESI) *m*/*z* calcd. for ($C_{50}H_{79}NO_2$): 725.61. Found: 726.60 ($[M+H]^+$). Anal. Calcd. for $C_{50}H_{79}NO_2$: C, 82.70%; H, 10.97%; N, 1.93%. Found: C, 82.71%; H, 10.95%; N, 1.90%.

4-((2-Hexyldecyl)oxy)-*N*-(4-((2-hexyldecyl)oxy)phenyl)-*N*-(4-iodophenyl)aniline **(7)**: I_2 (119 mg, 0.47 mmol) and H_5IO_6 (36 mg, 0.16 mmol) were dissolved in ethanol (14 mL) in a two-neck round-bottom flask. Then **6** (664 mg, 0.91 mmol) was added to the resulting mixture, which was stirred at reflux overnight under argon. After cooling to room temperature, the saturated $Na_2S_2O_3$ aqueous solution was added to remove the excess iodine. Then water was added and the mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum ether 60-90 ℃, 1/50, *V/V*) on silica gel to yield a colorless oil as the desired product **7** (717 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.42 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 4H), 6.84 (d, *J* = 8.6 Hz, 4H), 6.71 (d, *J* = 8.8 Hz, 2H), 3.84 (d, *J* = 5.5 Hz, 4H), 1.81 (m, 2H), 1.49 (m, 4H), 1.34 (m, 44H), 0.94 (t, *J* = 6.4 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 156.21, 148.91, 140.29, 137.66 126.90, 122.25, 115.56, 81.88, 71.30, 38.25, 32.13, 32.09, 31.63, 30.25, 29.92, 29.82, 29.56, 27.10, 27.08, 22.90, 14.34. MS (ESI) m/z calcd. for ($C_{50}H_{78}INO_2$): 851.51. Found: 852.52 ($[M+H]^+$). Anal. Calcd. for $C_{50}H_{78}INO_2$: C, 70.48%; H, 9.23%; N, 1.64%. Found: C, 70.45%; H, 9.21%; N, 1.62%.

4-((2-Hexyldecyl)oxy)-*N*-(4-((2-hexyldecyl)oxy)phenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline **(8)**: **7** (460 mg, 0.54 mmol), 4,4,4′,4′,5,5,5′,5′-octamethyl-2,2′-bi(1,3,2-dioxaborolane) (441 mg, 1.62 mmol), Pd(dppf)Cl_2 (20 mg, 0.03 mmol), KOAc (159 mg, 1.62 mmol), and DMSO (10mL) were added to a three-neck round-bottom flask under argon. The reaction mixture was stirred at 45 ℃ for 5 h and then cooled to room temperature. The resultant mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the residue was purified by column chromatography (toluene/petroleum ether 60-90 ℃, 1/2, *V/V*) on silica gel to afford a colorless oil as the desired product **8** (390 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.62 (d, *J* = 8.6 Hz, 2H), 7.07 (d, *J* = 8.9 Hz, 4H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 4H), 3.83 (d, *J* = 5.6 Hz, 4H), 1.78 (m, 2H), 1.47 (m, 4H), 1.32 (m, 56H), 0.91 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 156.27, 151.69, 140.35, 135.94, 127.31, 118.68, 115.49, 83.54, 71.33, 38.27, 32.12, 32.08, 31.63, 30.24, 29.91, 29.80, 29.55, 27.09, 27.08, 25.04, 22.89, 14.32. MS (ESI) *m*/*z* calcd. for ($C_{56}H_{90}BNO_4$): 851.70. Found: 852.70 ($[M+H]^+$). Anal. Calcd. for $C_{56}H_{90}BNO_4$: C, 84.45%; H, 10.28%; N, 2.46%. Found: C, 84.42%; H, 10.29%; N, 2.43%.

6-Bromo-3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (**10**): **9** (1.55 g, 4.78 mmol) and hydroquinone (66 mg, 0.60 mmol) were dissolved in THF (10 mL) in a three-neck round-bottom flask under argon. Then NBS (851 mg, 4.78 mmol) was added. The reaction mixture was stirred at room temperature for 5 h. The resultant mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the residue was purified by column chromatography (toluene/petroleum ether 60-90 ℃, 1/10, *V/V*) on silica gel to afford a colorless oil as the desired product **10** (1.19 g, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 6.42 (s, 1H), 3.91 (s, 2H), 3.84 (s, 2H), 1.38 (m, 4H), 1.28 (m, 16H), 0.88 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 148.83, 147.64, 104.07, 92.53, 77.84, 77.69, 43.87, 31.74, 31.70, 30.08, 22.71, 22.62, 14.05. MS (ESI) *m*/*z* calcd. for ($C_{19}H_{31}BrO_2S$): 402.12. Found: 403.12 ($[M+H]^+$). Anal. Calcd. for $C_{19}H_{31}BrO_2S$: C, 56.57%; H, 7.75%. Found:

C, 56.60%; H, 7.78%.

4-(3,3-Dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-6-yl)-*N*,*N*-bis(4-((2-hexyldecyl)oxy)phenyl)aniline **(11)**: **8** (390 mg, 0.43 mmol), **10** (173 mg, 0.43 mmol), $Pd(OAc)_2$ (4 mg, 0.02 mmol), Sphos (7 mg, 0.02 mmol), K_3PO_4 (915 mg, 4.31 mmol) and dioxane/H_2O (10mL, 5/1, *V/V*) were added to a three-neck round-bottom flask under argon. The reaction mixture was refluxed overnight and then cooled to room temperature. The resultant mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the residue was purified by column chromatography (toluene/petroleum ether 60-90 ℃, 1/5, *V/V*) on silica gel to afford a colorless oil as the desired product **11** (391 mg, 87%). ^{1}H NMR (400 MHz, THF-d_8) δ: 7.90 (d, J = 8.8 Hz, 2H), 7.09 (d, J = 8.9 Hz, 4H), 6.98 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.9 Hz, 4H), 6.69 (s, 1H), 4.06 (s, 2H), 3.94 (s, 2H), 3.86 (d, J = 5.4 Hz, 4H), 1.78 (m, 2H), 1.49 (m, 8H), 1.40 (m, 12H), 1.32 (m, 46H), 0.89 (m, 18H). ^{13}C NMR (100 MHz, THF-d_8) δ: 167.68, 156.14, 154.86, 154.38 150.56, 149.10, 147.32, 144.49, 141.61, 131.38, 130.55, 129.55, 78.54, 78.19, 71.43, 44.48, 39.32, 33.01, 32.89, 32.52, 31.37, 31.08, 30.86, 30.73, 30.46, 29.18, 28.05, 23.90, 23.68, 14.48. MS (ESI) *m*/*z* calcd. for ($C_{69}H_{109}NO_4S$): 1047.81. Found: 1048.56 ($[M+H]^+$). Anal. Calcd. for $C_{69}H_{109}NO_4S$: C, 79.03%; H, 10.48%; N, 1.34%. Found: C, 79.01%; H, 10.50%; N, 1.32%.

4-(7-(8-(4-(Bis(4-((2-hexyldecyl)oxy)phenyl)amino)phenyl)-3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-6-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)benzoic acid **(LY-1)**: In a three-neck flame-dried round-bottom flask was dissolved **11** (300 mg, 0.28 mmol) in THF (15 mL) and cooled to −78 ℃ using a dry ice/acetone cold bath. Under argon, *t*-BuLi (0.19 mL, 1.3 M in hexanes, 0.30 mmol) was added dropwise to the reaction mixture, which was stirred for 1 h at −78 ℃ . After trimethylstannyl chloride (110 mg, 0.55 mmol) was added in one portion via syringe, the mixture was slowly warmed up and stirred for 12 h at room temperature. Water was slowly added to terminate the reaction and the mixture was extracted three times with diethyl ether before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude product was used in the subsequent reaction directly.

In a dried Schlenk tube were dissolved 4-(3,3-dihexyl-8-(trimethylstannyl)-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-6-yl)-*N*,*N*-bis(4-((2-hexyldecyl)oxy)phenyl)aniline (168 mg, 0.14 mmol) and butyl 4-(7-bromobenzo[*c*][1,2,5]thiadiazol-4-yl)benzoate (92 mg, 0.28 mmol) in toluene (10 mL). $Pd(PPh)_2Cl_2$ (6 mg, 0.01 mmol) was added to the reaction mixture, which was stirred at reflux for 12 h. Water was added to terminate the reaction and the mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude pruduct was purified by column chromatography (toluene/petroleum ether 60-90 ℃, 1/1, *V/V*) on silica gel to yield the desired butyl ester.

In a three-neck round-bottom flask were dissolved butyl ester and KOH (55 mg, 1.38 mmol) in a solvent mixture of THF/H_2O (10 mL, 3/1, *V/V*). The reaction mixture was refluxed overnight and then cooled to room temperature. Chloroform was added before the organic phase was washed with 0.1 M hydrochloric acid and water in turn and then dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude product was purified by column chromatography (chloroform/methanol, 10/1, *V/V*) on silica gel to yield a black solid as the desired product **LY−1** (109 mg, 74% yield). ^{1}H NMR (400 MHz, THF-d_8) δ: 8.48 (d, J = 7.6 Hz, 1H), 8.15 (m, 4H), 7.88 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 8.6 Hz, 2H), 7.05 (d, J = 8.7 Hz, 4H), 6.90 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.7 Hz, 4H), 4.13 (s, 2H), 4.03 (s, 2H), 3.84 (d, J = 5.2 Hz, 4H), 1.78 (m, 2H), 1.51 (m, 12H), 1.32 (m, 56H), 0.89 (m, 18H). ^{13}C NMR (100 MHz, THF-d_8) δ: 167.75, 157.14, 154.55, 154.06, 150.60,

149.19, 146.32, 142.49, 141.61, 131.38, 130.75, 129.85, 128.30, 127.66, 127.40, 127.29, 126.32, 125.55, 120.96, 116.19, 114.67, 78.47, 78.39, 71.72, 44.68, 39.33, 33.15, 33.02, 32.89, 32.57, 31.37, 31.18, 30.86, 30.73, 30.47, 28.18, 28.00, 23.92, 23.74, 14.65. HR-MS (MALDI) *m*/*z* calcd. for ($C_{82}H_{115}N_3O_6S_2$): 1301.82273. Found: 1301.81793. Anal. Calcd. for $C_{82}H_{115}N_3O_6S_2$: C, 75.59%; H, 8.90%; N, 3.23%. Found: C, 75.61%; H, 8.91%; N, 3.23%.

4-(7-(8-(4-(Bis(4-((2-hexyldecyl)oxy)phenyl)amino)phenyl)-3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-6-yl)-[1,2,5]thiadiazolo[3,4-*c*]pyridin-4-yl)benzoic acid **(LY−2)**: In a dried Schlenk tube were dissolved 4-(3,3-dihexyl-8-(trimethylstannyl)-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepin-6-yl)-*N*,*N*-bis(4-((2-hexyldecyl)oxy)phenyl)aniline (168 mg, 0.14 mmol) and *tert*-butyl 4-(7-bromopyrido[3,4-*c*][1,2,5]thiadiazol-4-yl)benzoate (92 mg, 0.28 mmol) in toluene (10 mL). $Pd(PPh)_2Cl_2$ (6 mg, 0.01 mmol) was added to the reaction mixture, which was stirred at reflux for 12 h. Water was added to terminate the reaction and the mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the crude pruduct was purified by column chromatography (toluene/petroleum ether 60-90 ℃, 1/1, *V*/*V*) on silica gel to yield the desired butyl ester.

In a three-neck round bottom flask were dissoved the *t*-butyl ester and concentrated hydrochloric acid (3 mL) in THF (9 mL). The mixture was stirred at room temperature for 24 h. Water was added and the mixture was extracted three times with chloroform before the organic phase was washed with water and dried over anhydrous sodium sulfate. After solvent removal under reduced pressure, the residue was purified by column chromatography (chloroform/methanol, 15/1, *V*/*V*) on silica gel to yield a black solid **LY-2** （100 mg, 71% yield). ^{1}H NMR (400 MHz, THF-d_8) δ: 9.46 (s, 1H), 8.87 (m, 2H), 8.17 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 4H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 4H), 4.19 (s, 2H), 4.05 (s, 2H), 3.85 (d, *J* = 5.2 Hz, 4H), 1.78 (m, 2H), 1.53 (m, 12H), 1.32 (m, 56H), 0.90 (m, 18H). ^{13}C NMR (100 MHz, THF-d_8) δ:. 167.75, 157.24, 156.09, 150.91, 150.42, 149.38, 148.41, 146.29, 142.30, 141.85, 141.53, 132.93, 130.69, 130.58, 130.29, 128.30, 127.76, 126.62, 126.07, 122.28, 120.79, 116.22, 112.39, 78.42, 71.74, 44.72, 39.35, 36.39, 33.20, 33.03, 32.91, 32.58, 31.39, 31.19, 30.87, 30.80, 30.74, 30.64, 30.48, 28.19, 28.01, 26.59, 23.94, 23.75, 14.65. HR-MS (MALDI) *m*/*z* calcd. for ($C_{81}H_{114}N_4O_6S_2$): 1302.81798. Found: 1302.81457. Anal. calcd. for $C_{81}H_{114}N_4O_6S_2$: C, 74.61%; H, 8.81%; N, 4.30%. Found: C, 74.60%; H, 8.84%; N, 4.31%.

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(S2) Matthews, C. J.; Leese, T. A.; Thorp, D.; Lockhart, J. C. *J. Chem. Soc., Dalton Trans.*, **1998,** 79.

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2. Additional data

Table S1 Measured and calculated energy levels, energy-gaps, and electronic absorption properties of LY-1 and LY-2

Dye	E_H/eV [a]	E_L/eV [a]	E_{H-1}/eV [b]	E_H/eV [b]	E_L/eV [b]	$\Delta E_{H/L}$/eV [b]	$\Delta E_{H-1/L}$/eV [b]	λ_{abs}^{meas}/nm [c]	λ_{abs}^{cacl}/nm [d]	Transition [d]
LY-1	−5.00	−3.19	−5.90	−5.11	−2.68	2.43	3.22	507	511	H→L (85%) H−1→L (15%)
LY-2	−5.01	−3.50	−5.97	−5.14	−3.02	2.12	2.95	555	568	H→L (87%) H−1→L (13%)

[a] Measured frontier orbital energies with respect to vacuum were calculated *via* $E = -4.88 - eE_{onset}$, where E_{onset} is the onset potential (Fig.2a) of oxidation and reduction of the ground state of a dye measured with cyclic voltammetry. H and L represent HOMO and LUMO, respectively; [b] Frontier orbital energies with respect to vacuum were calculated at the PBE0/6-311G(d,p) level for a dye in THF; [c] λ_{abs}^{meas}, ε_{abs}^{meas} were measured for a dye in THF; [d] λ_{abs}^{cacl} and corresponding transition assignments were derived from the TDDFT calculation at the MPW1K/6-311G(d,p) level for a dye in THF.

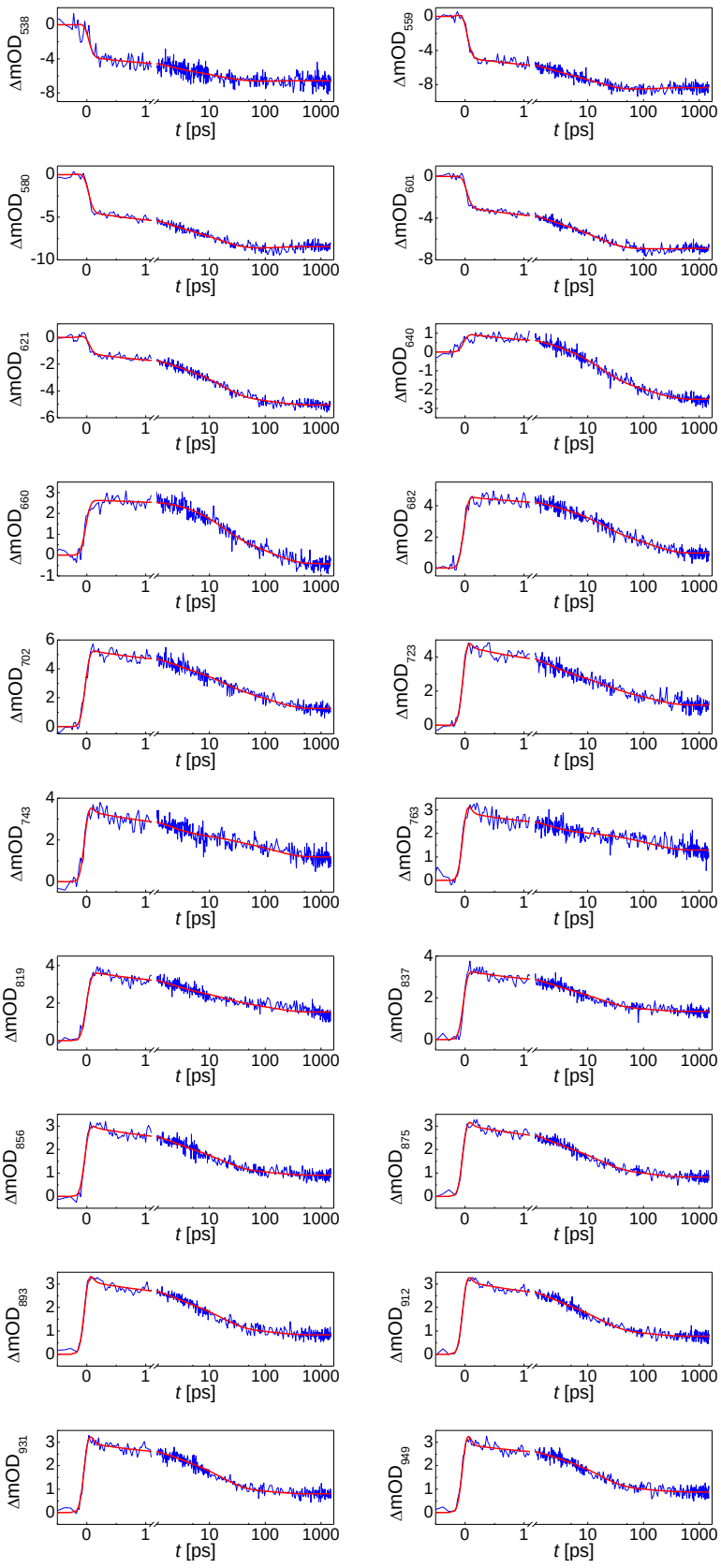

Fig.S2 Selected kinetic traces (blue) at different wavelengths for a 2.1-μm-thick, LY-1 grafted titania film immersed in a realistic cobalt electrolyte

The red lines are fittings obtained from target analysis.

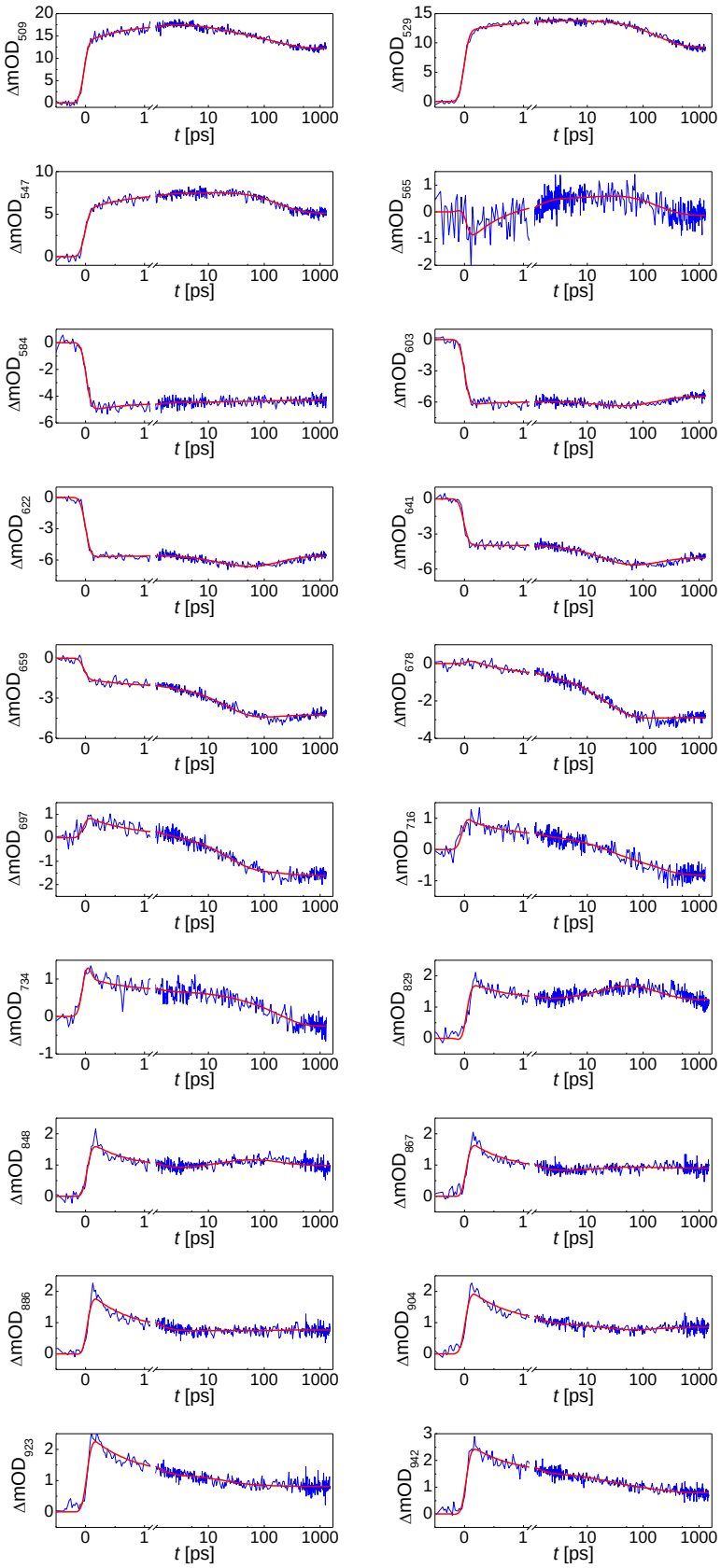

Fig.S3 Selected kinetic traces (blue) at different wavelengths for a a 2.1-μm-thick, LY-2 grafted titania film immersed in a realistic cobalt electrolyte

The red lines are fittings obtained from target analysis.

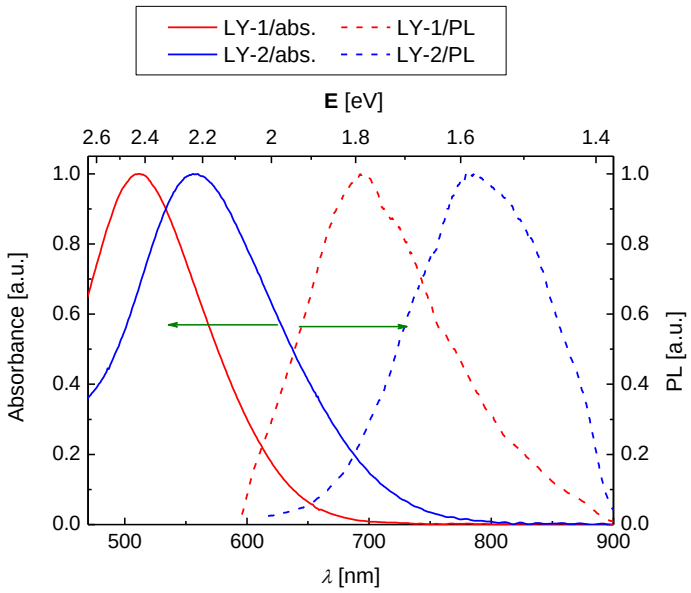

Fig.S4 Normalized electron absorption spectra (solid lines) and PL spectra (dash lines) of LY−1 and LY−2 grafted titania films immersed in a realistic cobalt electrolyte

The absorption of a titania film has been substracted for clarity of presentation. The PL spectra recorded with an ICCD camera are ecited with 490 nm laser.

Table S2 Measured and calculated electronic absorption/photoluminescence properties of LY-1 and LY-2 grafted on titania and further immersed in a cobalt electrolyte

Dye	λ_{max}^{abs} /nm [a]	λ_{max}^{PL} /nm [a]	Stokes shift/eV [a]	λ_{max}^{abs} /nm [b]	f^{abs} [c]	Transition [c]	λ_{max}^{PL} /nm [b]	f^{PL} [c]	Transition [d]	Stokes shift/eV [b]
LY-1	511	695	0.6	509	1.00	H→L (85%)	689	1.44	L→H (93%)	0.6
LY-2	556	785	0.6	565	0.95	H→L (88%)	764	1.34	L→H (93%)	0.6

[a] Measured maximum absorption (λ_{max}^{abs}), maximum PL (λ_{max}^{PL}), and Stokes shift; [b] Calculated maximum absorption (λ_{max}^{abs}), maximum PL (λ_{max}^{PL}), and Stokes shift at the TD-MPW1K/6-311G(d,p) level for a dye in acetonitrile; [c] Oscillator strength (f^{abs}) and transition assignment were derived from the TDDFT calculations on absorption spectra; [d] Oscillator strength (f^{PL}) and corresponding transition assignments were derived from the TDDFT calculations on PL spectra.

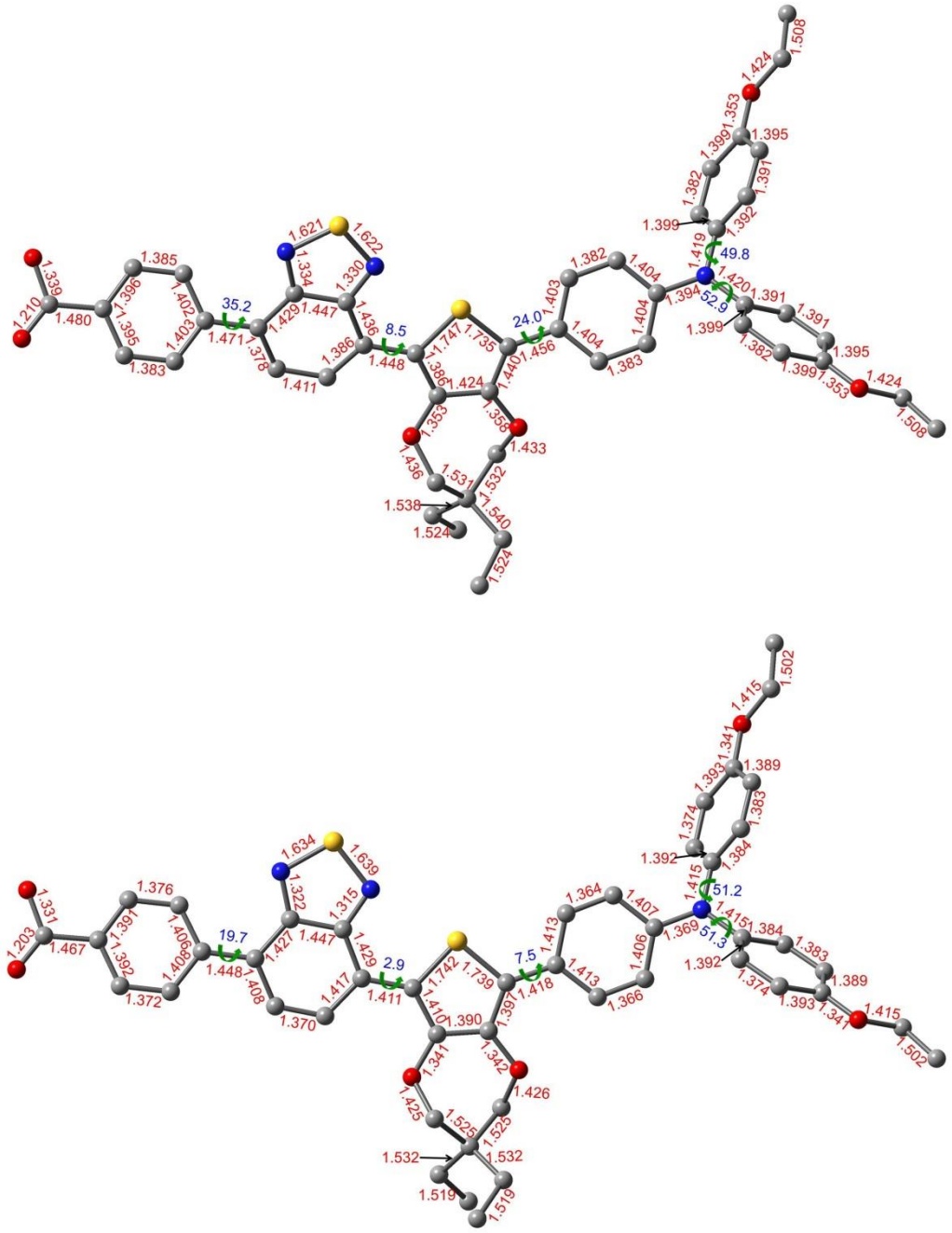

Fig.S5 Optimized geometies of S_0 (top) and S_1 (bottom) for LY-1 at the PBE0/6-311G(*d*,*p*) and TD-MPW1K/6-311G(*d*,*p*) levels

The key parameters of bond lengths in angstroms (red numbers) and dihedral angles in degrees (blue numbers) are included.

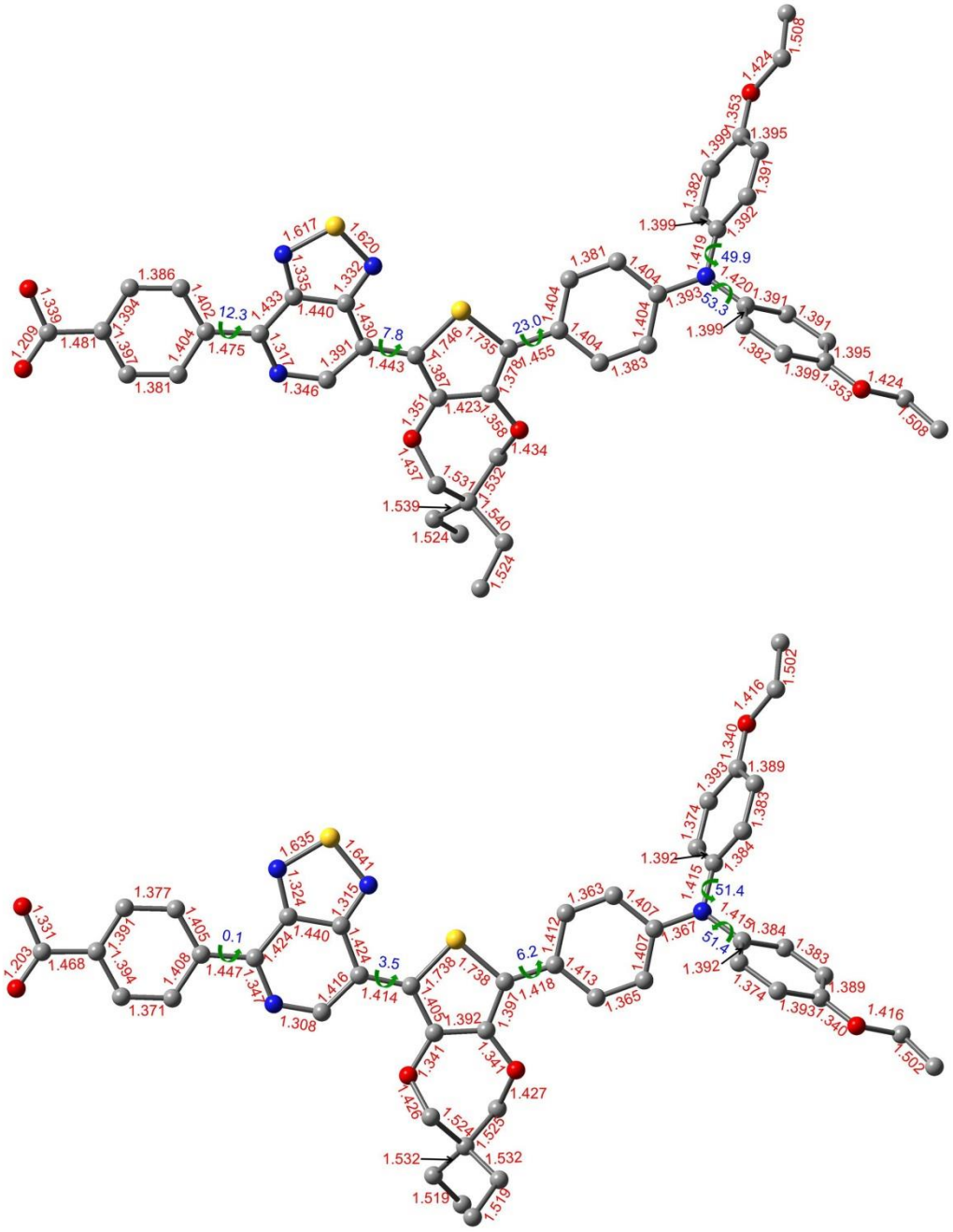

Fig.S6 Optimized geometies of S_0 (top) and S_1 (bottom) for LY-2 at the PBE0/6-311G(*d*,*p*) and TD-MPW1K/6-311G(*d*,*p*) levels

The key parameters of bond lengths in angstroms (red numbers) and dihedral angles in degrees (blue numbers) are included.

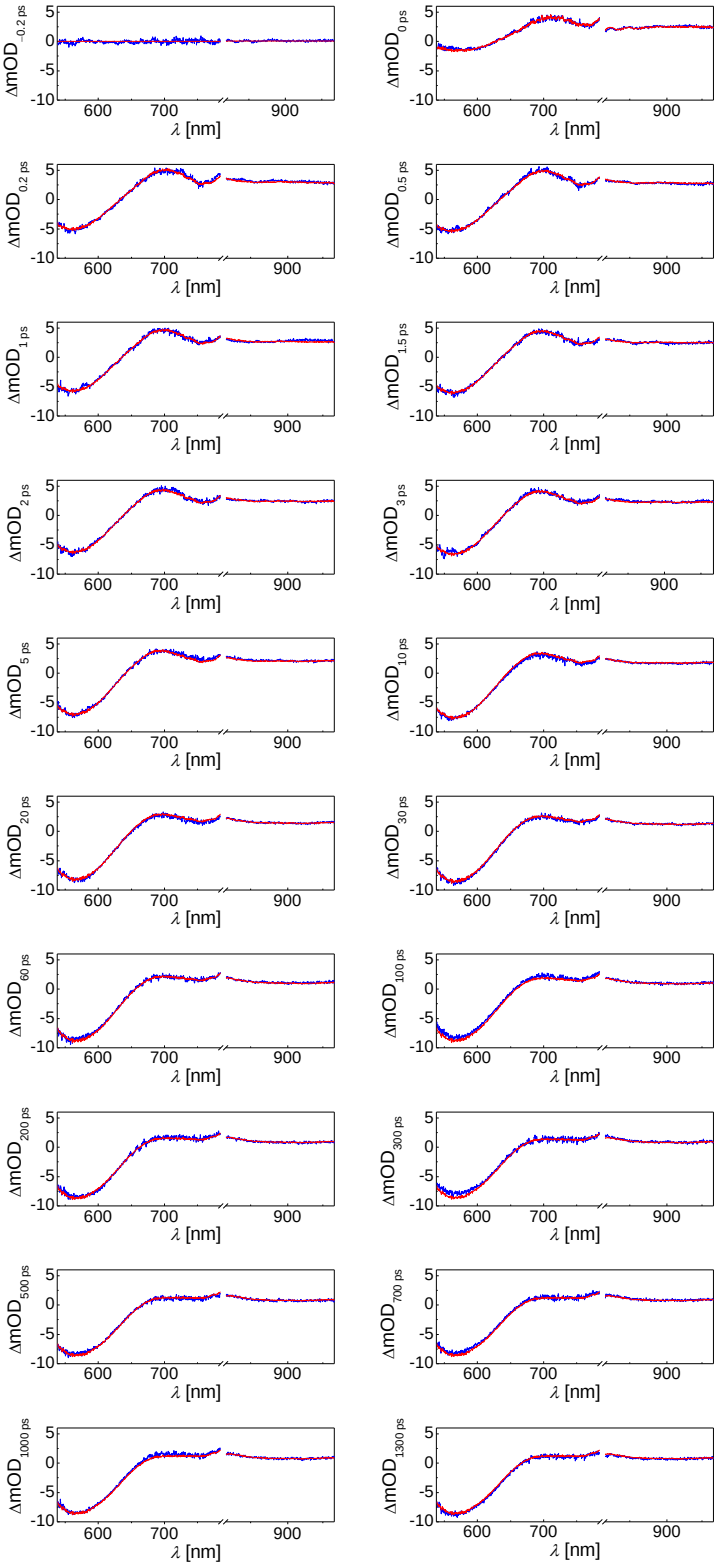

Fig.S7 Selected TA spectra (blue) at different time delays for a 2.1-μm-thick, LY-1 grafted titania film immersed in a realistic cobalt electrolyte

The red lines are fittings obtained from target analysis.

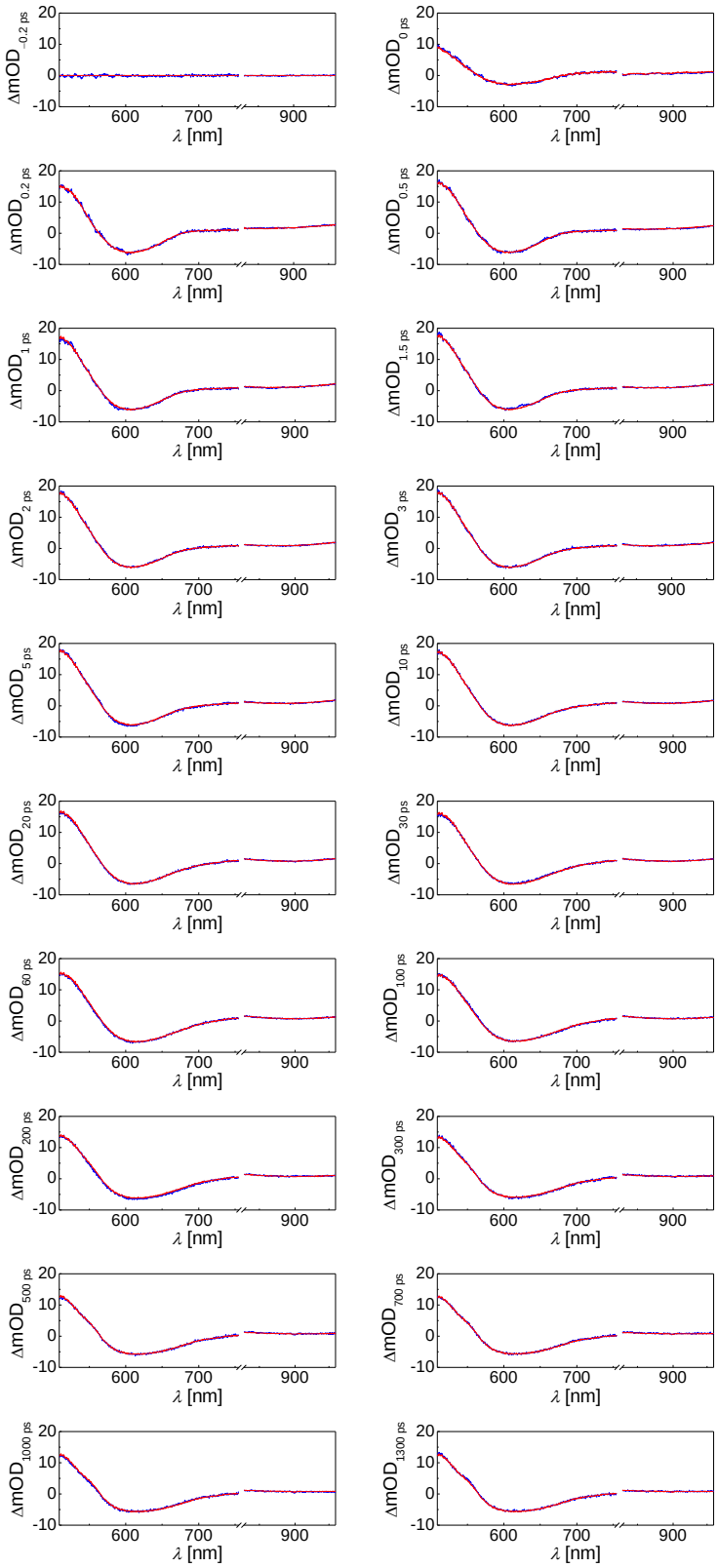

Fig.S8 Selected TA spectra (blue) at different time delays for a 2.1-μm-thick, LY-2 grafted titania film immersed in a realistic cobalt electrolyte

The red lines are fittings obtained from target analysis.

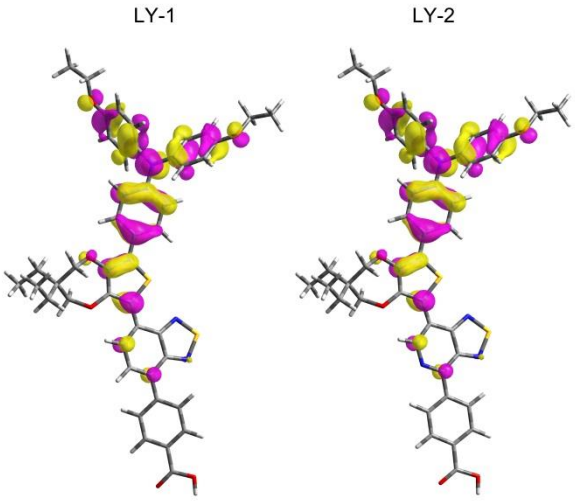

Fig.S9 Distribution profiles of holes on LY-1 and LY-2 at the single-electron oxidized states calculated at the UPBE0/6-311G(*d*,*p*) level of theory

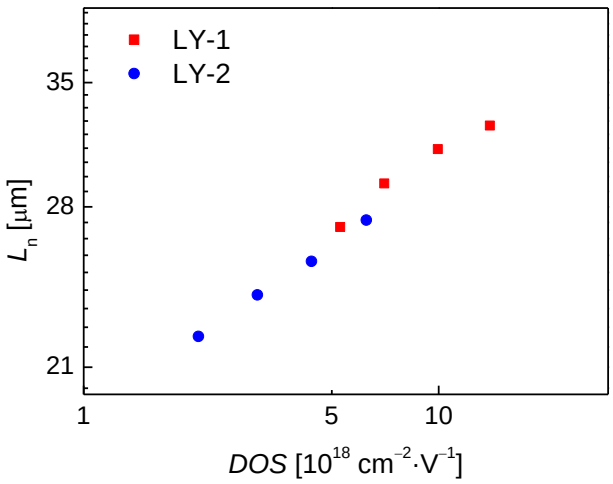

Fig.S10 Plots of electron diffusion length (L_n) *versus* density of states (DOS)

The data points are fitted data from electrical impedance spectroscopies