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Supporting Information

Benzo[1,2-*b*:4,5-*b'*]difuran-based sensitizers for dye-sensitized solar cells

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Experimental

Materials and equipment

The compounds **I**[1], **III**[2,3] and **IV**[3] were prepared according to the literature procedures. All other chemicals and solvents were purchased from commercial sources and used without further purification. All ^{1}H NMR and ^{13}C NMR spectra were measured at 300 and 75.5 MHz, respectively. Chemical shifts (δ) were calibrated against residual solvent signals. UV-vis absorption and emission spectra were recorded on a Perkin-Elmer Lambda 900 spectrometer and a Perkin-Elmer Spectrophotometer LS50B. Melting points were performed and not corrected. HRMS data was obtained with ESI (electrospray ionization) mode. Powder X-ray diffraction (PXRD) patterns were recorded on a STOE spellmann generator type DF4 with a Cu anode.

*2.2. Synthesis of compound **II***

A mixture of 4-bromobenzaldehyde (54 mg, 0.29 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.015 mmol), CuI (3 mg, 0.015 mmol) in Et_3N (20 mL) was purged with Argon for 20 min. To this mixture was dropwise added a solution of compound **I** (103 mg, 0.15 mmol) in THF (15 mL) under reflux. The resulting solution was refluxed for 3 h. After removing the solvents, the residue was poured into a silica gel column, eluting with gradients of *n*-hexane/CH_2Cl_2 (from 1:1 to 1:8) to obtain **II** as a red solid (87 mg,

74%): mp 131.5°C-131.6°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.02 (s, 1 H), 7.86 (m, 4 H), 7.68 (m, 2 H), 7.35 (m, 3 H), 3.65 (t, *J* = 7.59 Hz, 8H), 1.79 (m, 8H), 1.36 (m, 24H), 0.89 (t, *J* = 7.02 Hz, 12H); ^{13}C-NMR (75.5 MHz, $CDCl_3$): δ = 191.4, 163.2, 163.1, 145.2, 145.0, 135.5, 131.9, 131.6, 129.6, 129.4, 128.7, 128.4, 123.6, 123.2, 123.0, 116.5, 116.3, 100.3, 98.6, 96.9, 95.0, 84.0, 79.7, 62.6, 62.5, 50.4, 50.3, 31.5, 29.7, 28.6, 26.2, 22.6, 13.9; HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{53}H_{62}N_4O_3$ 802.4816; found 802.4817.

2.3. Synthesis of ***Dye-1***

A mixture of compound **II** (80 mg, 0.10 mmol) and cyanoacetic acid (85 mg, 1.0 mmol), ammonium acetate (23 mg, 0.3 mmol), and glacial acetic acid (20 mL) was purged with Argon for 15 min, and then stirred at 135°C for 24 h. After cooling to room temperature, the mixture was poured into ice water and the resulting precipitate was filtered off, washed with water several times and dried under vacuum. A red solid was obtained (57 mg, 66%): mp 248.6°C-248.7 °C; ^{1}H-NMR (400 MHz, DMSO-d_6, 80°C): δ = 8.36 (s, 1 H), 8.11 (d, *J* = 8.34 Hz, 2 H), 7.67 (d, *J* = 8.34 Hz, 2 H); 7.59 (m, 2 H), 7.47 (m, 3 H); ^{13}C-NMR (100 MHz, DMSO-d_6, 80°C): δ = 162.6, 130.9, 130.6, 128.1, 114.8, 61.2, 49.5, 30.4, 27.5, 25.1, 21.5, 13.1; HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{56}H_{63}N_5O_4$ 869.4875; found 869.4870.

2.4. Synthesis of ***Dye-2***

A mixture of compound **IV** (100 mg, 0.12 mmol) and cyanoacetic acid (102 mg, 1.2 mmol), ammonium acetate (23 mg, 0.3 mmol), and glacial acetic acid (50 mL) was purged by Ar for 15 mins, and then stirred at 135°C for 24 h. After cooling to room temperature, the mixture was poured into ice water and the resulting precipitate was filtered off, washed with water several times and dried under vacuum, a red solid was obtained (108 mg, 93%). mp 289.1°C-289.2 °C; ^{1}H-NMR (400 MHz, DMSO-d_6,

80°C): δ = 8.32 (s, 2 H), 8.09 (d, *J* = 8.92 Hz, 4 H), 7.76 (d, *J* = 8.92 Hz, 4 H), 3.65 (t, *J* = 8.04 Hz, 8 H), 1.76 (m, 8 H), 1.34 (m, 24 H), 0.86 (t, *J* = 6.72 Hz, 12 H); HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{60}H_{64}N_6O_6$ 964.4882; found 964.4874.

2.5. Cyclic voltammetry

Cyclic voltammetry was conducted on an Autolab PGSTAT 101 electrochemical analyzer. An Ag/AgCl electrode containing 2M LiCl (in ethanol) served as the reference electrode with a glassy carbon electrode as the counter electrode and a Pt disk as the working electrode. Cyclic voltammetric experiments were performed at room temperature under Argon in $CHCl_3$ with 0.1 M *n*-Bu_4NPF_6 as a supporting electrolyte.

2.6. Fabrication of DSSCs

Electrodes with 4 μm transparent layer and 5 μm scattering layer of TiO_2 were screen-printed on fluorine-doped tin oxide (FTO) as reported in the literature.[5] After sintering at 500°C for 0.5 h and cooling to room temperature, the electrodes were treated with 33 mM $TiCl_4$ solution at 70°C for 0.5 h. The films were sintered at 500°C for 0.5 h and cooled to 80°C before dipping into dye solution (0.1 mM dye with or without 0.3 mM chenodeoxycholic acid in a mixture of 1:1 THF and ethanol) for 12 h. After the sensitization, the electrodes were rinsed with acetonitrile and dried in air. The cells were sealed with a Surlyn film and Platinized FTO counter electrode. The composition of electrolyte of this study is 0.2 M $[Co(bpy)_3][B(CN)_4]_2$, 0.05 M $[Co(bpy)_3][B(CN)_4]_3$, 0.1 M LiOTf, 0.5 M 4-*tert*-butylpyridine in acetonitrile.

Computational studies: All of the theoretical calculations were carried out within the density functional theory approach by using A.02 revision of Gaussian 09 program package[6] with the Coulomb Attenuated Methods for Density Functional Theory by means of the hybrid functional B3LYP (CAM-B3LYP)[7] and the basis set 6-31 +

G(d,p).[8] This method includes long range correction into the non-coulomb part of exchange functional which gives a correct description of electron excitation and charge transfer. To reduce computational costs, the alkyl groups of BDF were substituted by methyl groups. First we optimized the ground-state geometry of **dye-1** and **dye-2** in THF using the PCM model (polarized continuum model)[9-12] with CAM-B3LYP methods without any symmetry restriction. The obtained structures for **dye-1** and **dye-2** are both planar giving to **dye-2** a C_i symmetry. Once the geometries were optimized, we performed excited state calculations using time-dependent CAM-B3LYP Methods.

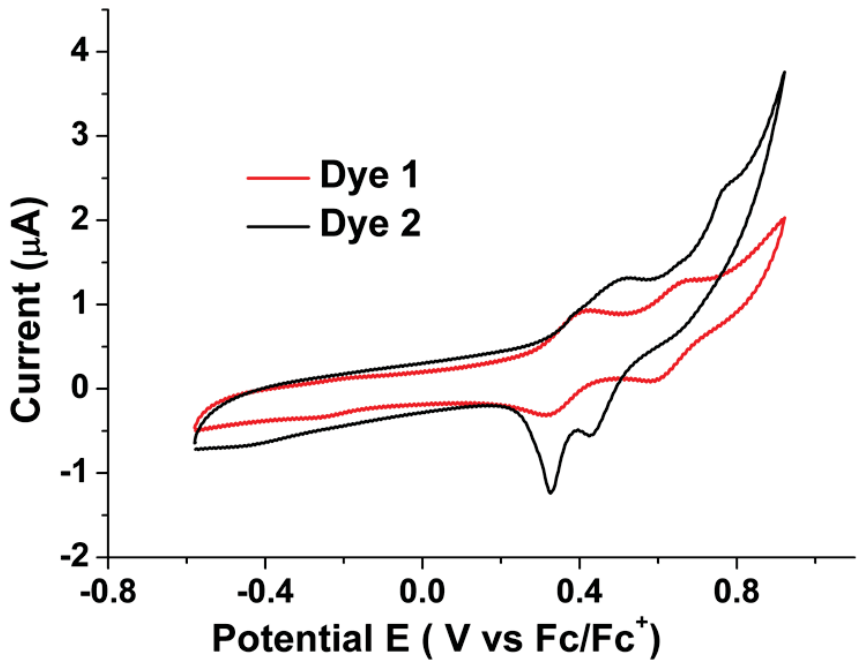

Figure S1. Cyclic voltammograms of **Dye-1** (1×10^{-4} M, black line) and **Dye-2** (1×10^{-4} M, red line) in $CHCl_3$ (0.1 M $Bu_4N(PF_6)$; Pt-disk working electrode; scan rate 100 mVs^{-1}).

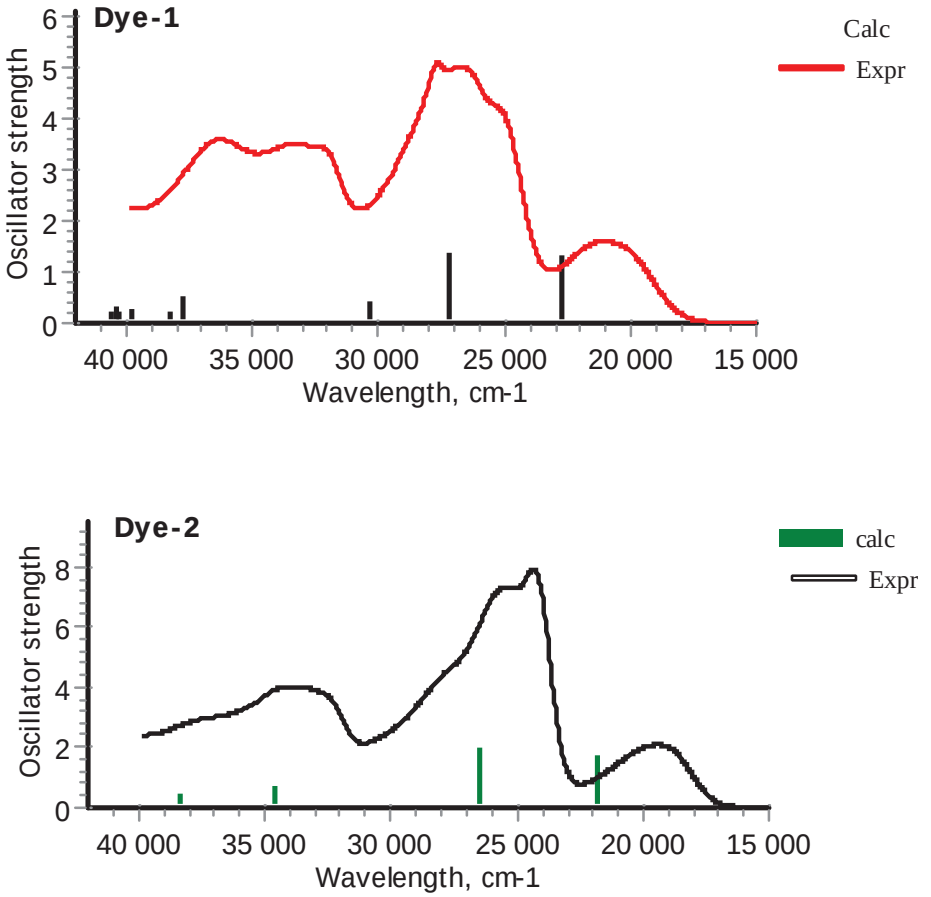

Figure S2. Electronic absorption spectra of **Dye-1** (top) and **Dye-2** (bottom) in THF solution, together with the calculated $S_0 \rightarrow S_n$ transitions at the CAM-B3LYP /6-31G(d,p) level of theory.

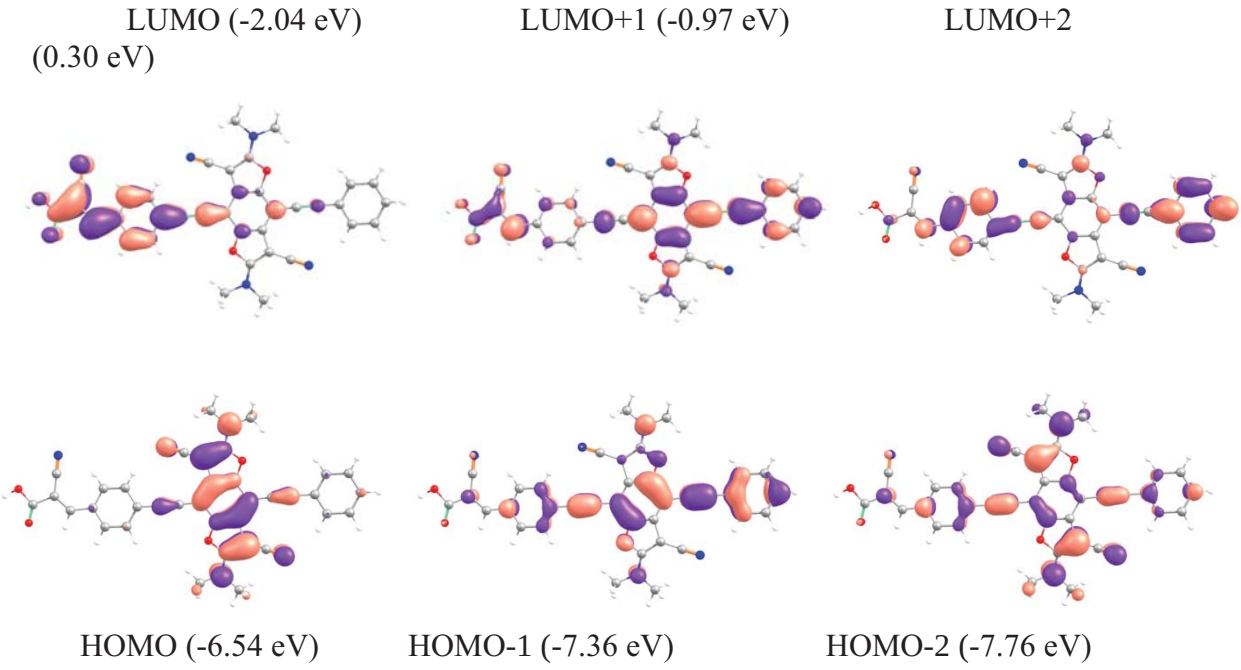

Figure S3. Frontier molecular orbitals of the π-conjugated skeletons of **Dye-1**.

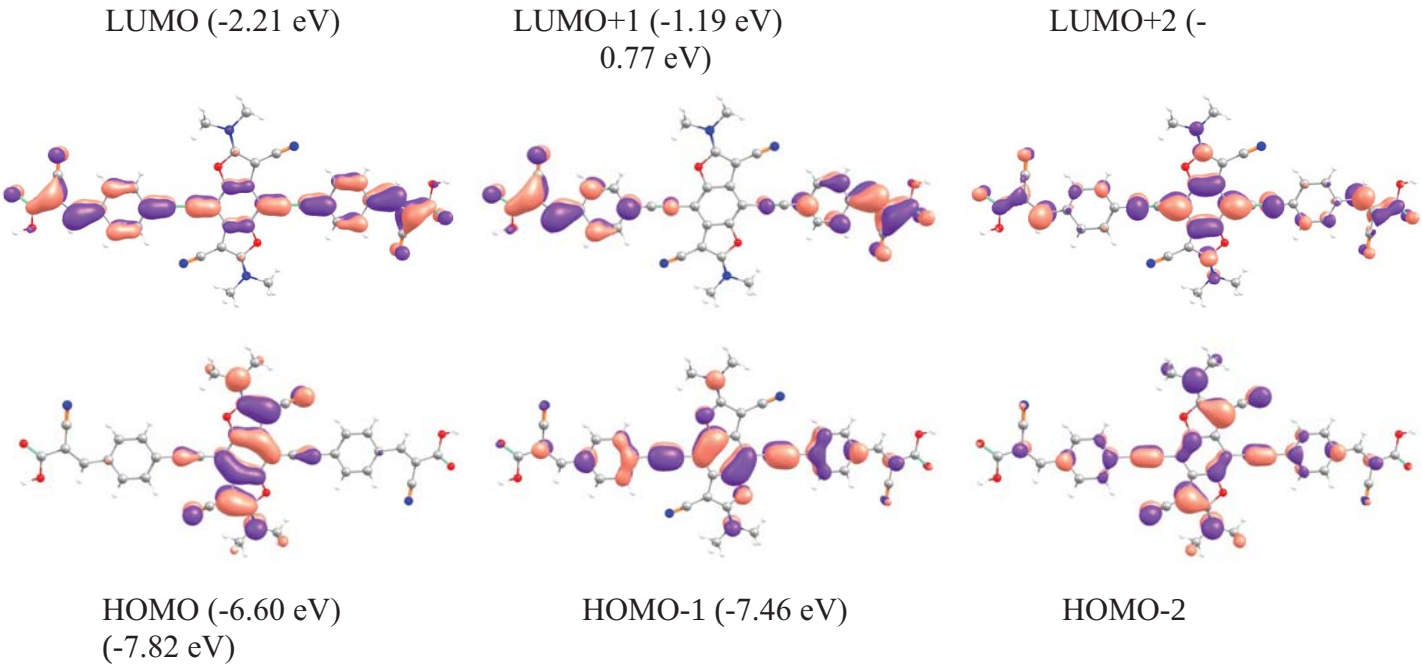

Figure S4. Frontier molecular orbitals of the π-conjugated skeletons of **Dye-2**.

Table S1. The vertical CAM-B3LYP calculated $S_0 \rightarrow S_n$ transitions for **Dye-1**.

State	Excitation energy [cm^{-1}]	Oscillator strength	Dominant contributions (%)
S_1	22 750	1.32	H→ L (72), H→L+1 (16), H-1→L (5), H-2→L (3)
S_2	27 211	1.38	H-1→L (54), H→L+1 (12), H-2→L (12) H-3→L (6), H-1→L+1 (6), H→L (2)
S_3	30 358	0.38	H→L+1 (42), H-1→L+1 (17), H→L (10), H-1→L (10), H-2→L (10), H-2→L+1 (3)
S_4	32 498	0.10	H-2→L (26), H→L+1 (23), H-1→L+1 (19), H→L (14), H-3→L (6), H-2→L+1 (4), H-5→L (3)
S_5	35 012	0.05	H-3→L (26), H-2→L+1 (22), H-2→L (18), H-1→L+1 (10), H-5→L (10), H-6→L (2)
S_6	35 485	0.03	H-6→L (82), H-6→L+1(2), H-1→L+3 (2), H-2→L+3 (2)
S_7	37 757	0.48	H→L+5 (23), H→L+2 (13), H-1→L+1 (8)
S_8	38 260	0.22	H-1→L+1 (23), H-1→L (17), H→L+5 (8)

Table S2. The vertical CAM-B3LYP calculated $S_0 \rightarrow S_n$ transitions for **Dye-2**.

State	Excitation energy [cm^{-1}]	Oscillator strength	Dominant contributions (%)
S_1	21 753	1.71	H→ L (77), H→L+2 (11), H-1→L (5), H-2→L+1 (2)
S_2	26 446	1.93	H-1→ L (70), H-3→L+1 (6), H-2→L+1 (5), H-1→L+2 (5), H→L (5), H→L+2 (4)
S_5	33 288	0.08	H→L+2 (65), H→L (10), H-1→L+2 (4)
S_7	34 632	0.69	H-4→ L (25), H-1→L+2 (23), H-3→L+1 (16), H-2→L+1 (12), H→L+2 (9), H→L (6),
S_9	35 491	0.08	H-6→ L (48), H-5→L+1 (35), H-1→L+4 (3), H-3→L+3 (2)
S_{11}	38 339	0.41	H→ L+6 (46), H→L+15 (13), H-2→L+1 (5), H→L+11 (5), H→L+12 (4), H→L+4 (4)

Table S3 XYZ coordinates and absolute energies of **Dye-1**

	X	Y	Z
C	-2.60591900	1.20145800	-0.01160200
C	-1.21322800	1.24896000	-0.01113400
C	-0.34882100	0.15633900	0.00655000
C	-1.00188800	-1.09160800	0.02357000
C	-2.39551400	-1.13776300	0.02278200
C	-3.25961600	-0.04655900	0.00435700
C	-0.56237500	-2.47275900	0.03565400
C	-1.72583000	-3.24391500	0.05619600
O	-2.82035500	-2.44476800	0.03777500
C	0.77529300	-2.91612400	0.00796500
N	1.88845200	-3.24836100	-0.01727200
N	-1.96241200	-4.55884900	0.11399700
C	-3.30298600	-5.08590400	-0.12858600
H	-4.05534300	-4.36367900	0.17814800
H	-3.42767700	-5.99583900	0.45949800
C	-0.85718300	-5.50511100	0.04289200
H	-1.21892500	-6.47536800	0.38203200
H	-0.04476000	-5.19732700	0.69943100
C	-3.04616000	2.58402100	-0.02301700
C	-1.88383900	3.35471500	-0.04444300
O	-0.78846700	2.55473600	-0.02656900
N	-1.64460200	4.67011800	-0.10401900
C	-0.30514500	5.19442600	0.14965400
H	-0.17802700	6.11014100	-0.42884300
H	0.44854800	4.47549200	-0.16165900
C	-2.74864800	5.61753000	-0.03312900
H	-3.56110300	5.31043600	-0.68991100
H	-2.38574000	6.58741100	-0.37224400
C	1.06219300	0.30513100	0.00558300
C	2.26716000	0.41791400	0.00441600
C	-4.38301700	3.03023700	0.00794400
N	-5.49363700	3.37056500	0.03619300
C	-4.67154200	-0.19831500	0.00158300
C	-5.87540800	-0.32097600	-0.00230600
C	-7.30217100	-0.41162300	-0.00666800
C	-7.94099300	-1.65997000	0.00228800
C	-8.07367000	0.76040100	-0.02008400
C	-9.32840500	-1.73178600	-0.00237000
H	-7.34404300	-2.56560300	0.01287400
C	-9.46066200	0.67742500	-0.02487300
H	-7.57440400	1.72368800	-0.02621600
C	-10.09109900	-0.56538600	-0.01605000
H	-9.81629200	-2.70101000	0.00470500
H	-10.05205500	1.58720500	-0.03531900
H	-11.17462400	-0.62517400	-0.01966200
C	3.69063000	0.49246600	0.00165900
C	4.34719000	1.73163400	-0.00262600
C	4.45067600	-0.68981900	0.00253700
C	5.72937200	1.77930500	-0.00606800
H	3.76790300	2.64782000	-0.00341600

C	5.83260600	-0.63441300	-0.00076700
H	3.94066200	-1.64702700	0.00528000
C	6.50067300	0.60326000	-0.00520100
H	6.22924600	2.74276100	-0.00955800
H	6.38757700	-1.56276500	-0.00015500
C	7.94227900	0.77282600	-0.00939400
C	8.96382400	-0.11742500	-0.00955900
H	8.27843400	1.80675500	-0.01314100
C	8.81514800	-1.53878000	-0.00504300
N	8.70679100	-2.69176900	-0.00138100
C	10.34973300	0.42283900	-0.01481100
O	10.62422800	1.60466900	-0.01905400
O	11.27535800	-0.54313500	-0.01433500
H	12.15456100	-0.12904000	-0.01789900
H	-0.16689100	5.42238000	1.21282500
H	-3.13006000	5.72037300	0.98891300
H	-3.44477700	-5.32422200	-1.18888600
H	-0.47641300	-5.60726300	-0.97935400

E= - 1959.20392514 ua; μ = 5.564 Debye

Table S4 XYZ coordinates and absolute energies of **Dye-2**

	X	Y	Z
C	-0.66286000	-1.23332400	-0.00380900
C	0.72611900	-1.11728000	-0.01710200
C	1.45593300	0.06888100	-0.01589200
C	0.66286000	1.23332400	0.00380900
C	-0.72611900	1.11728000	0.01710200
C	-1.45593300	-0.06888100	0.01589200
C	0.93907300	2.65616800	0.02164500
C	-0.30640300	3.28675900	0.02977300
O	-1.30045100	2.36428700	0.03734500
C	2.21634400	3.25155300	0.04682900
N	3.28374100	3.71017300	0.06855800
N	-0.69512200	4.56543100	0.00773100
C	-2.08880300	4.92556800	0.25786200
H	-2.75136500	4.13173200	-0.07768400
H	-2.31608900	5.83355900	-0.30171200
C	0.29357300	5.63122400	0.10381100
H	1.12364900	5.44839000	-0.57723200
C	-0.93907300	-2.65616800	-0.02164500
C	0.30640300	-3.28675900	-0.02977300
O	1.30045100	-2.36428700	-0.03734500
N	0.69512200	-4.56543100	-0.00773100
C	2.08880300	-4.92556800	-0.25786200
H	2.31608900	-5.83355900	0.30171200
H	2.75136500	-4.13173200	0.07768400
C	-0.29357300	-5.63122400	-0.10381100
H	-1.12364900	-5.44839000	0.57723200
H	0.18538600	-6.56537800	0.18722300
C	2.87453900	0.08529800	-0.03393600
C	4.08417000	0.11340800	-0.05044600
C	-2.21634400	-3.25155300	-0.04682900
N	-3.28374100	-3.71017300	-0.06855800
C	-2.87453900	-0.08529800	0.03393600
C	-4.08417000	-0.11340800	0.05044600
C	-5.50659100	-0.20645600	0.06887700
C	-6.30278300	0.94966700	0.10739400
C	-6.12383600	-1.46631100	0.04865000
C	-7.68211700	0.85379200	0.12541800
H	-5.82864200	1.92440000	0.12338400
C	-7.50429100	-1.55430600	0.06698700
H	-5.51145800	-2.36088800	0.01868400
C	-8.31160500	-0.40349900	0.10531300
H	-8.26419300	1.76445400	0.15557400
H	-7.97377800	-2.53283800	0.05118100
C	5.50659100	0.20645600	-0.06887700
C	6.30278300	-0.94966700	-0.10739400
C	6.12383600	1.46631100	-0.04865000
C	7.68211700	-0.85379200	-0.12541800
H	5.82864200	-1.92440000	-0.12338400
C	7.50429100	1.55430600	-0.06698700
H	5.51145800	2.36088800	-0.01868400
C	8.31160500	0.40349900	-0.10531300

H	8.26419300	-1.76445400	-0.15557400
H	7.97377800	2.53283800	-0.05118100
C	9.74899600	0.61916300	-0.12166000
C	10.79287200	-0.24533400	-0.15285700
H	10.04001500	1.66481000	-0.10594300
C	10.67380900	-1.67129600	-0.17746100
N	10.58813600	-2.82555700	-0.19751000
C	12.19719100	0.23673000	-0.16391800
O	13.15995300	-0.50113900	-0.19045300
O	12.30382200	1.57204800	-0.14176200
H	13.24794700	1.80018500	-0.15043000
C	-9.74899600	-0.61916300	0.12166000
H	-10.04001500	-1.66481000	0.10594300
C	-10.79287200	0.24533400	0.15285700
C	-10.67380900	1.67129600	0.17746100
N	-10.58813600	2.82555700	0.19751000
C	-12.19719100	-0.23673000	0.16391800
O	-13.15995300	0.50113900	0.19045300
O	-12.30382200	-1.57204800	0.14176200
H	-13.24794700	-1.80018500	0.15043000
H	2.26111600	-5.11094300	-1.32406400
H	-0.67913500	-5.73462200	-1.12400200
H	-0.18538600	6.56537800	-0.18722300
H	0.67913500	5.73462200	1.12400200
H	-2.26111600	5.11094300	1.32406400

E= -2317.29880004 ua; μ = 0.000 Debye C_i Symmetry

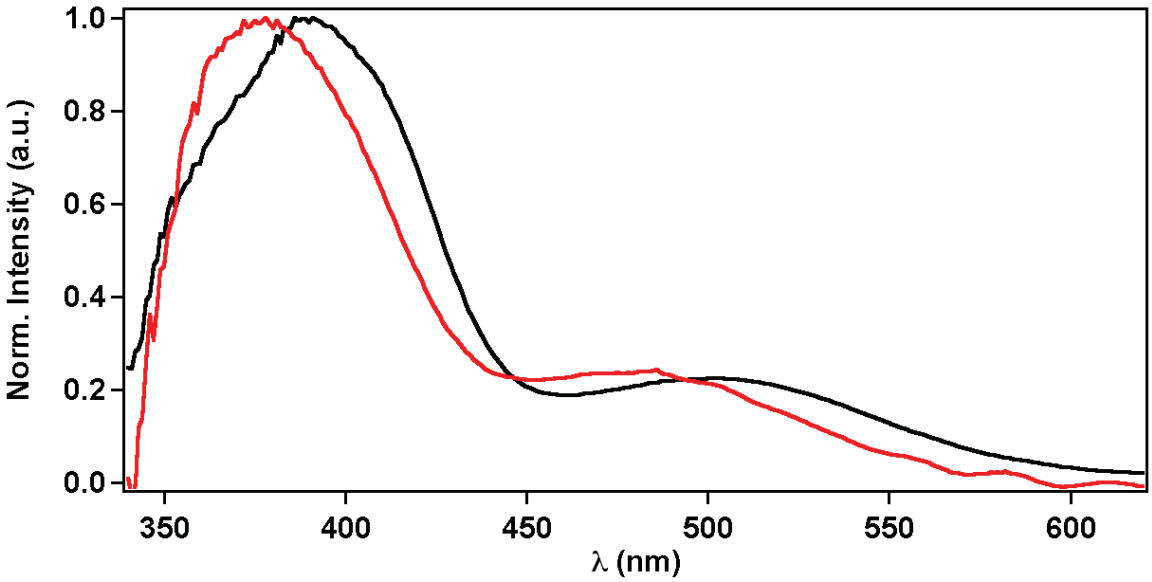

Figure S5. UV-Vis spectra of **Dye-1**(red) and **Dye-2** (black) adsorbed on the TiO_2 film.

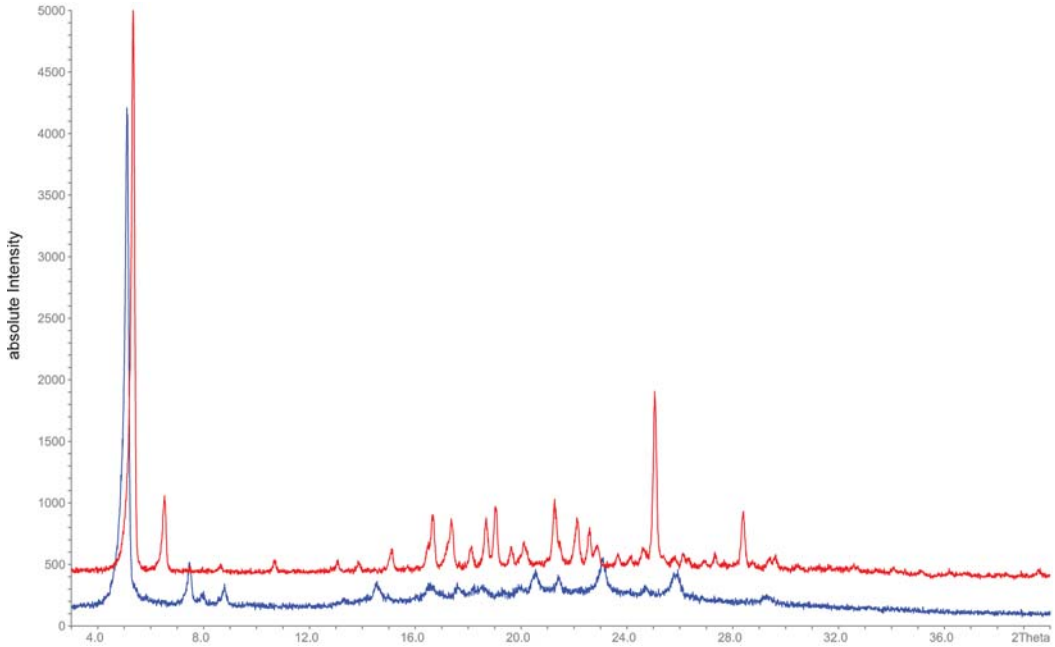

Figure S6. PXRD patterns of **Dye-1**(blue curve) and **Dye-2** (red curve).

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