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Electronic Supporting Information

A detailed experimental and theoretical investigation of the role of cyano group in the π-bridged acceptor of sensitizers for use in dye-sensitized solar cells (DSCs)

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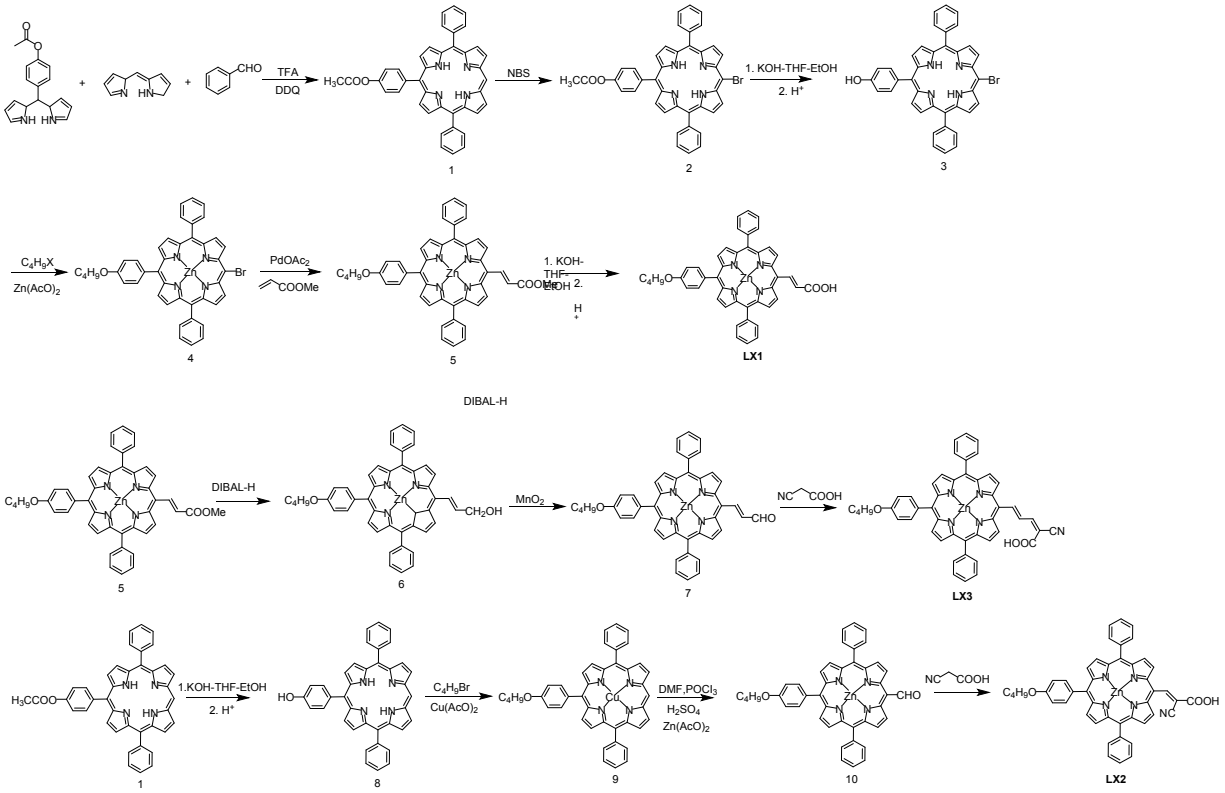
Synthesis



Scheme S1 Synthesis of **LX1**, **LX2** and **LX3**

Firstly, the free base porphyrin **1** containing ester group at the para position of the meso benzo ring was obtained via MacDonald [2+2] porphyrin synthesis. Bromination and base hydrolysis afforded porphyrin **3**, which was used to introduce the long alkyl chain via a well-known procedure and zinc metal leading to compound **4**.[S1] The following heck coupling afforded **5**, and subsequent hydrolysis furnished the final sensitizer **LX1** with a meso acrylic acid group as the π-bridged acceptor in 90% yield. Reduction of the ester group in **5** with DIBAL-H led to compound **6** which was oxidized to aldehyde **7** by using MnO_2. The subsequent Knoevenagel condensation with cyanoacetic acid afforded sensitizer **LX3** containing the meso α-cyanopentadienoic acid acceptor with a yield of 84%.[S2]

Synthesis of **LX2** started with the free base porphyrin **1**. The base hydrolysis followed by O-butylation and copper complexation resulting in copper porphyrin **9**. Vilsmeier reaction furnished aldehyde functional group at the porphyrin meso

position.[S3] De-metalation with a strong sulfuric acid removed copper and the following zinc complexation with $Zn(OAc)_2$ afforded porphyrin **10**. The sensitizer **LX2** containing the meso acrylic acid acceptor was then obtained via a Knoevenagel condensation of **10** with the cyano acetic acid in 84% yield.

Compound **1**

4-(Di(1H-pyrrol-2-yl)methyl)phenyl acetate[4] (280 mg, 1 mmol), dipyrromethane (146 mg, 1 mmol) and benzaldehyde (212 mg, 2 mmol) were dissolved in 150 mL dichloromethane. Trifluoroacetic acid (90 μL, 1.2 mmol) was quickly added by syringe and the solution was stirred at room temperature for 3 h. After that, DDQ (680 mg, 3 mmol) was added and the solution was stirred for another 4 hours. The solvent was evaporated and the crude product was eluted through a short pad of silica gel by dichloromethane to remove most of the tar. The mixture was further purified by column chromatography using PE/CH_2Cl_2 (2/1) as eluent to give pure product **1** (65mg, 11 %).

^{1}H NMR (400 MHz, CDCl3) δ 10.25 (s, 1H), 9.37 (d, J = 4.6 Hz, 2H), 9.05 (d, J = 4.6 Hz, 2H), 8.93 (q, J = 4.7 Hz, 4H), 8.25 (dd, J = 11.2, 8.0 Hz, 6H), 7.81 (d, J = 6.0 Hz, 6H), 7.52 (d, J = 8.2 Hz, 2H), 2.52 (s, 3H), -2.99 (s, 2H). MS (MALDI-TOF, m/z): $(M+H)^+$ calcd for $C_{40}H_{28}N_4O_2$, 596.22; found, 596.38.

Compound **2**

A mixture of compound **1** (59.6 mg, 0.1 mmol) in dry $CHCl_3$ (20 mL) and pyridine (3 drops) was cooled to 0°C for 15 min, and then NBS (26.69 mg, 0.15 mmol) was added to the mixture. The solution was stirred at room temperature for 1 h. The solvent was removed in vacuum. The residue was purified by column chromatography using CH_2Cl_2/PE (1/2) as eluent to give product **2** (21.69 mg, 91%).

^{1}H NMR (400 MHz, CDCl3) δ 9.69 (d, J = 4.8 Hz, 2H), 8.92 (d, J = 4.3 Hz, 2H), 8.83 (d, J = 3.0 Hz, 4H), 8.25 – 8.17 (m, 6H), 7.80 (d, J = 7.3 Hz, 6H), 7.51 (d, J = 8.3 Hz, 2H), 2.51 (s, 3H), -2.74 (s, 2H). MS (MALDI-TOF, m/z): (M+H)+ calcd for $C_{40}H_{27}BrN_4O_2$, 674.13; found, 674.19.

Compound **3**

Compound **2** (33.7 mg, 0.05 mmol) and KOH (57.7 mg, 1.00 mmol) were dissolved in THF/EtOH/H_2O (2:2:1, 30 mL) and the solution was refluxed for 1 hour. The reaction mixture was then cooled to room temperature and then acidified with aqueous HCl (pH≈3) and extracted with CH_2Cl_2. The organic phase was washed with water several times and dried with anhydrous Na_2SO_4. The residue was purified by column chromatography using CH_2Cl_2/PE (2/1) as eluent to give **3** (56.8 mg, 90 %) as a purple solid.

^{1}H NMR (400 MHz, CDCl3) δ 9.69 (d, J = 4.6 Hz, 2H), 8.92 (d, J = 4.1 Hz, 2H), 8.90 – 8.77 (m, 4H), 8.22 (d, J = 6.4 Hz, 4H), 8.06 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 7.1 Hz, 6H), 7.22 (d, J = 8.2 Hz, 2H), 5.22 (s, 1H), -2.72 (s, 2H). MS (MALDI-TOF, m/z): (M+H)+ calcd for $C_{38}H_{25}BrN_4O$, 632.12; found, 632.20.

Compound **4**

A mixture of compound 3 (63.2 mg, 0.1 mmol), K_2CO_3 (27.6 mg, 0.2 mmol) and n-butyl bromide (17 mg, 0.12 mmol) in dry DMF (20 mL) was heated at 80°C for 8 h. Then the reaction was quenched with water (100 mL), and the mixture was extracted with CH_2Cl_2 (3 × 50mL). The solvent was removed in vacuum. The residue was then dissolved in the mixed solution of CH_2Cl_2/methanol (2:1, 30mL). After that, zinc acetate dihydrate (88mg, 0.4mmol) was added. The solution was refluxed for 1 hour. The solvent was evaporated and the crude product was extracted with CH_2Cl_2. The organic layer was washed with brine several times and dried with anhydrous Na_2SO_4. The filtrate was evaporated under vacuum to give **4** (54 mg, 72 %).

^{1}H NMR (400 MHz, CDCl3) δ 9.79 (d, J = 4.6 Hz, 2H), 9.01 (d, J = 4.5 Hz, 2H), 8.97 (d, J = 4.6 Hz, 2H), 8.92 (d, J = 4.5 Hz, 2H), 8.22 (d, J = 6.4 Hz, 4H), 8.09 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 7.1 Hz, 6H), 7.30 (s, 2H), 4.28 (t, J = 6.3 Hz, 2H), 2.10 – 1.92 (m, 2H), 1.69 (m, 2H), 1.13 (t, J = 7.3 Hz, 3H). MS (MALDI-TOF, m/z): (M+H)+ calcd for $C_{42}H_{31}BrN_4OZn$, 750.10; found, 749.87.

Compound **5**

A flask was charged with a mixture of **4** (75.0 mg, 0.1 mmol) and methyl acrylate (27.2 μL, 0.3 mmol), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), PPh3 (8.3 mg, 0.027 mmol), DMF (5 mL), anhydrous toluene(5 mL) and K_2CO_3 (20.7 mg, 0.15 mmol). The flask was degassed and purged with Ar. The mixture was heated at 130 °C for 4 h under Ar. Then the reaction was quenched with water (100 mL), and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined extracts were washed with water and dried with anhydrous Na_2SO_4. The solvent was removed in vacuum. The residue was purified by column chromatograph using CH_2Cl_2/PE (2/1) as eluent. Recrystallization from CH_2Cl_2/methanol gave **5** (49%).

^{1}H NMR (400 MHz, CDCl3) δ 10.29 (d, J = 15.7 Hz, 1H), 9.56 (d, J = 4.7 Hz, 2H), 9.02 (d, J = 4.7 Hz, 2H), 8.96 (d, J = 4.6 Hz, 2H), 8.89 (d, J = 4.6 Hz, 2H), 8.21 (d, J = 6.3 Hz, 4H), 8.08 (d, J = 8.5 Hz, 2H), 7.85 – 7.72 (m, 6H), 7.27 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 15.7 Hz, 1H), 4.26 (t, J = 6.5 Hz, 2H), 4.01 (s, 3H), 2.04 – 1.92 (m, 2H), 1.68 (dt, J = 14.8, 7.2 Hz, 2H), 1.10 (t, J = 7.4 Hz, 3H). MS (MALDI-TOF, m/z): $(M+H)^+$ calcd for $C_{46}H_{36}N_4O_3Zn$, 756.21; found, 756.64

Compound **LX1**

Compound **5** (37.8 mg, 0.05 mmol) and KOH (57.7 mg, 1.00 mmol) were dissolved in THF/EtOH/H_2O (2:2:1, 30 mL) and the solution was refluxed for 1 hour. The reaction mixture was then cooled to room temperature and then acidified with aqueous HCl(pH≈3) and extracted with CH_2Cl_2. The organic phase was washed with water several times and dried with anhydrous Na_2SO_4. The residue was purified by column chromatography using CH_2Cl_2/MeOH (100/1) as eluent to give **LX1** (90%). ^{1}H NMR (400 MHz, DMSO) δ 10.19 (d, J = 15.7 Hz, 1H), 9.55 (d, J = 4.7 Hz, 2H), 8.83 (d, J = 4.7 Hz, 2H), 8.79 (d, J = 4.6 Hz, 2H), 8.71 (d, J = 4.6 Hz, 2H), 8.21 – 8.13 (m, 4H), 8.04 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 5.7 Hz, 6H), 7.32 (d, J = 8.4 Hz, 2H), 4.25 (t, J = 6.3 Hz, 2H), 1.94 – 1.84 (m, 2H), 1.60 (dq, J = 14.7, 7.5 Hz, 2H), 1.05 (t, J = 7.4 Hz, 3H). MS (MALDI-TOF, m/z): $(M+H)^+$ calcd for $C_{45}H_{34}N_4O_3Zn$, 742.19; found, 742.50.

Compound **6**

A solution of DIBAL-H (1.5 M in toluene, 0.2 mL, 0.30 mmol) was added dropwise to a solution of compound **5** (75.6 mg, 0.10mmol) in anhydrous toluene (30 mL) under argon atmosphere. The reaction mixture was stirred in ice-bath for 0.5 h and then the reaction was allowed to warm to room temperature. After another 30 min, the reaction was quenched with water. After the aqueous layer was removed, the organic layers were dried with anhydrous Na_2SO_4. The filtrate was then evaporated under vacuum and purified by column chromatography using CH_2Cl_2 as eluent to give compound **6** (61.1 mg, 84%) as a red solid.

^{1}H NMR (400 MHz, CDCl3) δ 9.42 (d, J = 4.7 Hz, 2H), 8.96 (dd, J = 9.0, 4.5 Hz, 5H), 8.90 (d, J = 4.6 Hz, 2H), 8.21 (d, J = 6.5 Hz, 4H), 8.08 (d, J = 8.4 Hz, 2H), 7.83 – 7.69 (m, 6H), 7.25 (d, J = 10.8 Hz, 2H), 6.28 (dt, J = 15.7, 5.4 Hz, 1H), 4.50 (d, J = 5.0 Hz, 2H), 4.24 (t, J = 6.5 Hz, 2H), 3.35 (d, J = 5.1 Hz, 1H), 2.02 – 1.91 (m, 2H), 1.67 (dq, J = 147.5 Hz, 2H), 1.10 (t, J = 7.3 Hz, 3H). MS (MALDI-TOF, m/z): $(M+H)^+$ calcd for $C_{45}H_{36}N_4O_2Zn$, 728.21; found, 728.48

Compound **7**

Activated MnO_2 (87 mg, 1 mmol) was added to a solution of 6 (72.8 mg, 0.1 mmol) in dry CH_2Cl_2 (4.0 mL) and stirred at room temperature for 19 h. The solvent was removed under vacuum and the residue was purified by column chromatography using CH_2Cl_2/PE(4:1) as eluent to give compound **7** (64.6 mg, 89%) as a green solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (dd, J = 11.7, 6.3 Hz, 2H), 9.42 (d, J = 4.7 Hz, 2H), 8.98 (d, J = 4.7 Hz, 2H), 8.95 (d, J = 4.6 Hz, 2H), 8.87 (d, J = 4.6 Hz, 2H), 8.19 (d, J = 6.6 Hz, 4H), 8.07 (d, J = 8.4 Hz, 2H), 7.78 (dq, J = 13.9, 7.0 Hz, 6H), 7.30 – 7.22 (m, 2H), 6.83 (dd, J = 15.6, 7.9 Hz, 1H), 4.25 (t, J = 6.5 Hz, 2H), 2.02 – 1.91 (m, 2H), 1.67 (dq, J = 14.7, 7.4 Hz, 2H), 1.10 (t, J = 7.4 Hz, 3H). MS (MALDI-TOF, m/z): $(M+H)^+$ calcd for $C_{45}H_{34}N_4O_2Zn$, 726.20; found, 726.11.

Compound **LX3**

A solution of **7** (72.6 mg, 0.1 mmol), cyanoacetic acid (42.5 mg, 0.5 mmol), and

piperidine (235 uL, 2.4 mmol) in methanol (15 mL) was heated at reflux temperature for 50 min under Ar. While the solution was cooled to room temperature, CH_2Cl_2 (50 mL) and H_2O (100 mL) were added, and the solution was shaken vigorously, adjusting the pH of the aqueous layer to pH= 2 with H_3PO_4 (1.0 mL). The organic phase was washed with water several times and dried with anhydrous Na_2SO_4. The filtrate was concentrated in vacuum to give **LX-3** (66.6 mg, 84%) as a green solid.

^{1}H NMR (400 MHz, DMSO) δ 10.47 (d, J = 14.6 Hz, 1H), 9.72 (d, J = 4.7 Hz, 2H), 8.90 – 8.84 (m, 3H), 8.79 (d, J = 4.6 Hz, 2H), 8.70 (d, J = 4.6 Hz, 2H), 8.24 – 8.17 (m, 4H), 8.06 (d, J = 8.4 Hz, 2H), 7.90 – 7.81 (m, 6H), 7.46 (dd, J = 14.5, 11.8 Hz, 1H),7.46(t, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 4.26 (s, 3H), 1.90 (dd, J = 14.0, 6.7 Hz, 2H), 1.62 (dq, J = 14.4, 7.3 Hz, 2H), 1.08 (t, J = 7.3 Hz, 3H). MS (MALDI-TOF, m/z): $(M+H)^+$ calcd for $C_{48}H_{35}N_5O_3Zn$, 793.20; found, 793.21.

Compound **8**

The preparation method was the same with that of compound **3** from **2**. The residue was purified by column chromatography using CH_2Cl_2/PE (2/1) as eluent to give 8 in 96% yield.

Compound **9**

The preparation method was the same with that of compound **4** from **3** except that $Cu(OAc)_2$ was employed in place of $Zn(OAc)_2$. The yield is 92% from **8**.

Compound **10**

$POCl_3$ (1 mL, 0.011 mmol) was added very slowly to dry DMF (1.25 mL, 0.016 mmol) at 0 °C within 4 hours. To that mixture, a solution of compound **9** (67.0 mg, 0.1 mmol) in $ClCH_2CH_2Cl$ (30mL) was added dropwise within 1 hour. Then the bath was heated to 90 °C and maintained for 4 h. After the reaction cooled to the room temperature, added 2 mL H_2SO_4 under the ice bath and stirred strongly for 30 min, then acidified with aqueous NaOH (pH≈7) and extracted with CH_2Cl_2. The organic phase was washed with water several times and dried with anhydrous Na_2SO_4. The

solvent was removed under vacuum. The residue was purified by column chromatograph using CH_2Cl_2/PE (2/1) as eluent. Recrystallization from CH_2Cl_2 /methanol. The purified product was then dissolved in the mixed solution of CH_2Cl_2/methanol (2:1, 30mL). After that, zinc acetate dihydrate (88mg, 0.4mmol) was added. The solution was refluxed for 1 hour. The solvent was evaporated and the crude product was extracted with CH_2Cl_2. The organic layer was washed with brine several times and dried with anhydrous Na_2SO_4. The filtrate was evaporated under vacuum to give **10** (43 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.40 (s, 1H), 10.00 (d, J = 4.9 Hz, 2H), 9.02 (d, J = 4.9 Hz, 2H), 8.90 (d, J = 4.5 Hz, 2H), 8.78 (d, J = 4.6 Hz, 2H), 8.16 (d, J = 6.4 Hz, 4H), 8.06 (d, J = 8.5 Hz, 2H), 7.77 (dd, J = 15.8, 8.6 Hz, 6H), 7.29 (d, J = 9.6 Hz, 2H), 4.25 (t, J = 6.6 Hz, 3H), 2.01 – 1.92 (m, 2H), 1.66 (dd, J = 14.9, 7.4 Hz, 2H), 1.10 (t, J = 7.4 Hz, 3H). MS (MALDI-TOF, m/z): $(M+H)^+$ calcd for $C_{43}H_{32}N_4O_2Zn$, 700.12; found, 700.08.

Compound **LX2**

The preparation method was the same with that of **LX-3**. The yield is 84% from **10**.

^{1}H NMR (400 MHz, DMSO) δ 10.84 (s, 1H), 9.50 (d, J = 4.7 Hz, 2H), 8.86 (d, J = 4.7 Hz, 2H), 8.83 (d, J = 4.6 Hz, 2H), 8.73 (d, J = 4.6 Hz, 2H), 8.25 – 8.18 (m, 4H), 8.09 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 5.9 Hz, 6H), 7.37 (d, J = 8.5 Hz, 2H), 4.29 (t, J = 6.4 Hz, 2H), 1.97 – 1.87 (m, 2H), 1.64 (dq, J = 14.6, 7.4 Hz, 2H), 1.09 (t, J = 7.4 Hz, 3H). MS (MALDI-TOF, m/z): $(M+H)^+$ calcd for $C_{46}H_{33}N_5O_3Zn$, 767.19; found, 767.16.

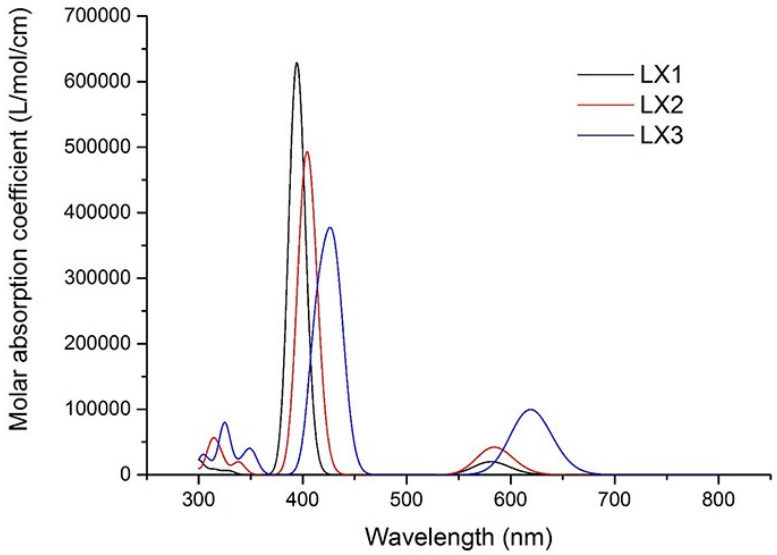


Fig. S1 The UV-vis of isolated **LX1-3** dyes simulated at TD-CAM-B3LYP/6-311G(d) level in the ethanol solution.

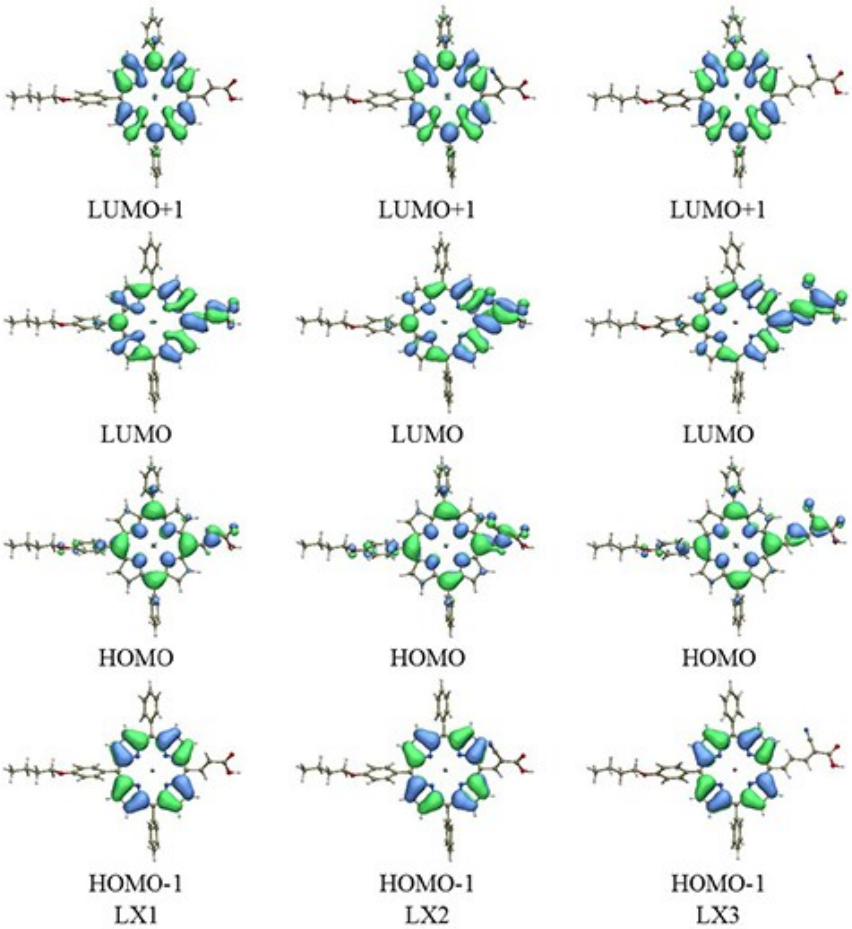


Fig. S2 Molecular orbital distributions for **LX1-3.**

Table S1. The calculated excited energy (EEXC), absorption wavelength (λmax), oscillator strengths (*f*) and transition contributions for **LX1-3** calculated at TD-CAM-B3LYP/6-311G(d) in ethanol.

Dye	States	E_{EXC} (eV)	λmax (nm)	f	Transitions
LX1	S1	2.14	581	0.1098	H-0->L-0 (67%), H-1->L+1 (32%)
	S2	2.17	572	0.0005	H-0->L+1 (50%), H-1->L-0 (49%)
	S3	3.14	395	1.6938	H-1->L-0 (30%), H-0->L+1 (30%), H-1->L+1 (26%), H-0->L-0 (13%)
	S4	3.15	393	1.8300	H-1->L+1 (40%), H-0->L+1 (20%), H-1->L-0 (20%), H-0->L-0 (20%)
LX2	S1	2.12	584	0.2078	H-0->L-0 (71%), H-1->L+1 (24%)
	S2	2.14	580	0.0265	H-1->L-0 (61%), H-0->L+1 (34%)
	S3	3.04	408	1.6112	H-1->L+1 (58%), H-0->L-0 (20%)
	S4	3.10	400	1.4317	H-0->L+1 (54%), H-1->L-0 (32%)
LX3	S1	2.00	619	0.5487	H-0->L-0 (80%), H-1->L+1 (17%)
	S2	2.10	591	0.0146	H-1->L-0 (59%), H-0->L+1 (37%)
	S3	2.88	430	1.7452	H-1->L+1 (63%), H-0->L+2 (17%), H-0->L-0 (15%)
	S4	3.00	414	1.2369	H-0->L+1 (58%), H-1->L-0 (40%)

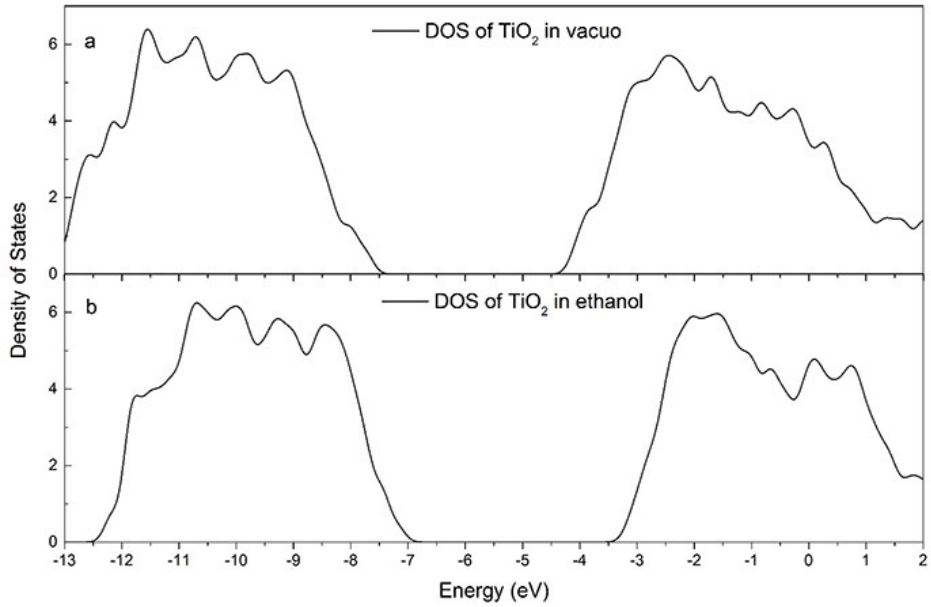


Fig. S3 DOS of bare TiO_2 in vacuo and ethanol simulated at B3LYP/6-311G(d) level.

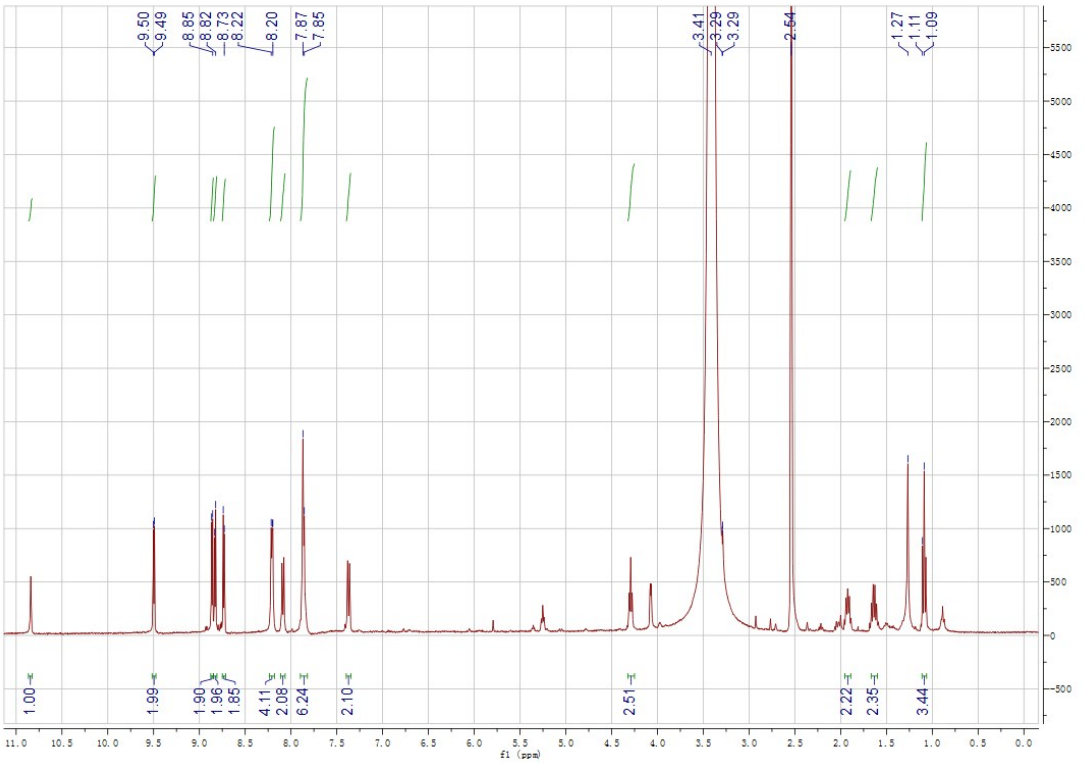


Fig. S4 [1]H- NMR spectra of **LX2** in DMSO-d6.

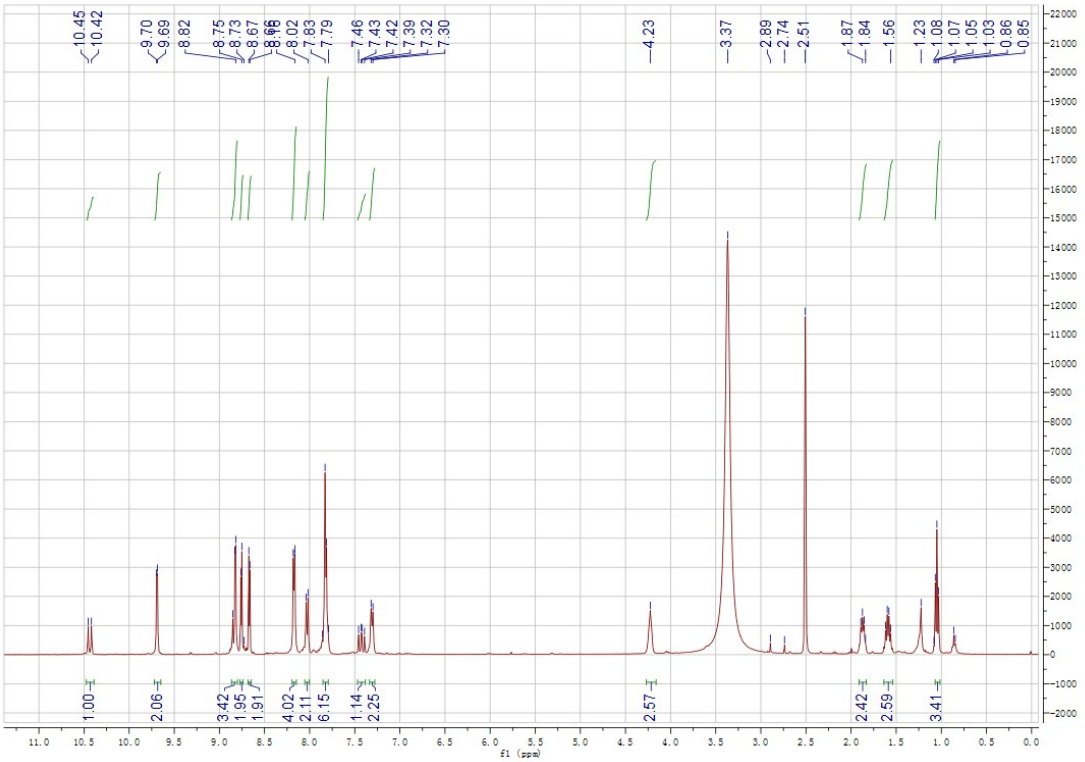


Fig. S5 [1]H- NMR spectra of **LX3** in DMSO-d6.

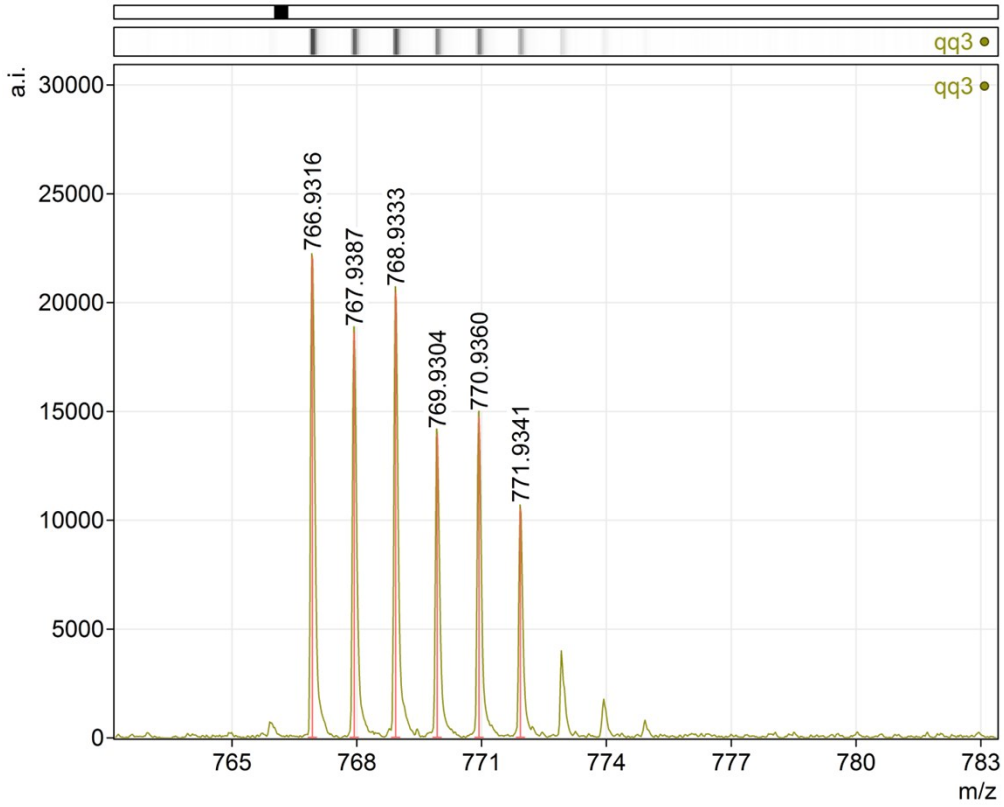


Fig. S6 MALDI-TOF MS of **LX2**

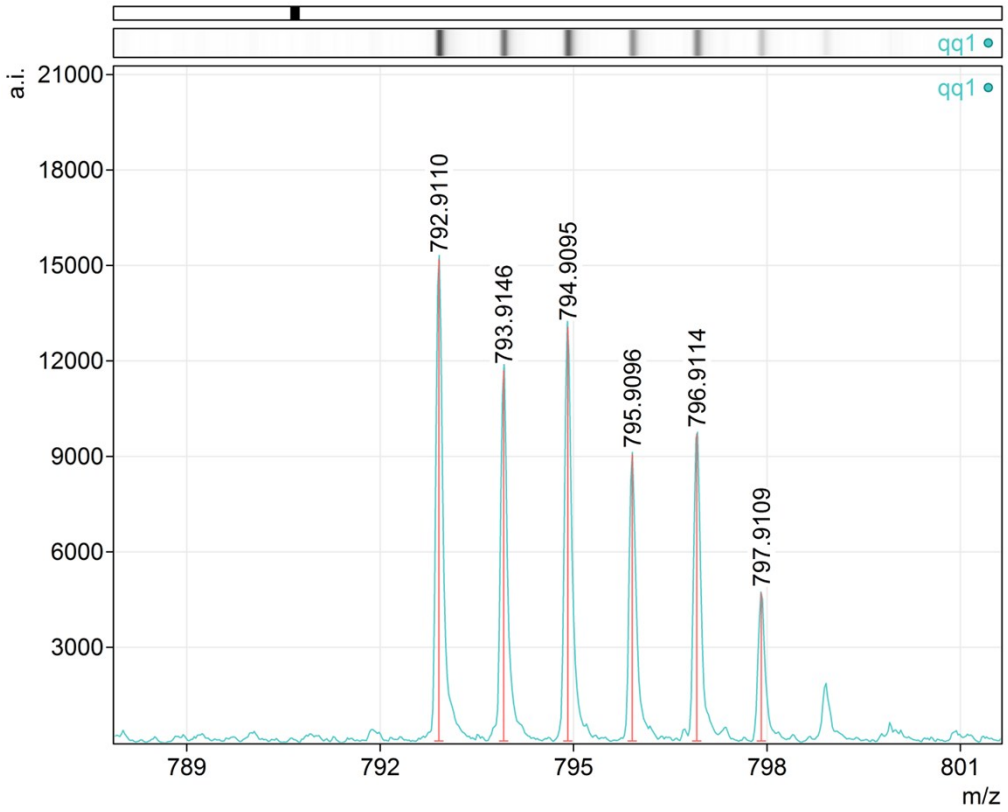


Fig. S7 MALDI-TOF MS of **LX3**

Notes and References

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