

Supporting Information for

Doubly β -functionalized meso-meso Directly Linked Porphyrin Dimer Sensitizers for Photovoltaics

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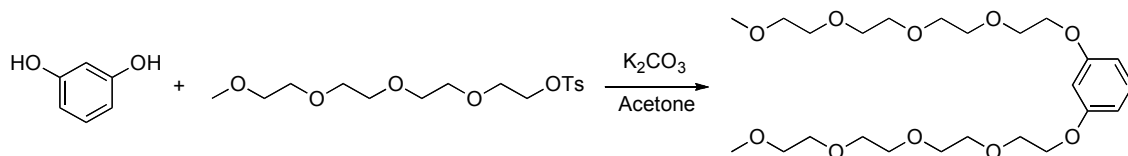
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This PDF file includes:

(Synthetic procedure for **PEG-2b-bd-Zn2** and normalized emission of diporphyrins. Cyclic voltammogram of ester form of all porphyrins. DFT calculation of **2b-FB-Zn**, **2b-Zn2**, **4b-Zn2**, **2b-bd-FB-Zn**, and **2b-bd-Zn2**.)

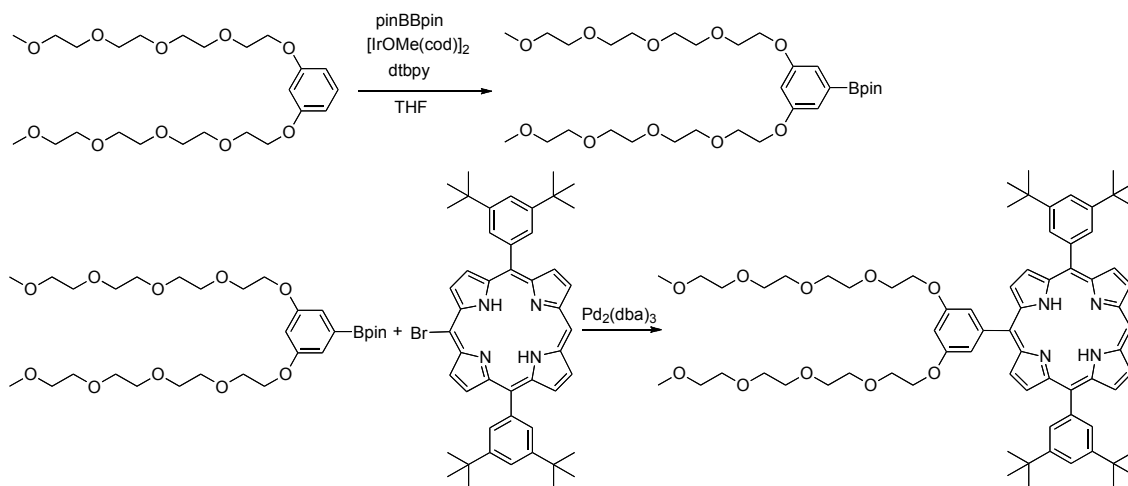
(1) Synthetic Procedure for PEG-2b-bd-Zn2.

3,5-di-PEG-benzene



Resorcinol (500 mg, 4.6 mmol, 1.0 equiv), a tosylate of tetraethylene glycol monomethyl ether (4.2 g, 11.6 mmol, 2.5 equiv), K_2CO_3 (3.18 g, 23 mmol, 5.0 equiv), and dried acetone (20 mL) were added to a 50-mL two-necked flask and purged with argon for 15 min. The resulting mixture was refluxed for 20 h under argon. The reaction mixture was quenched with water and extracted with ethyl acetate (3 times). The organic layer was dried over anhydrous Na_2SO_4 . The crude product was concentrated and purified by silica gel column chromatography (eluent: ethyl acetate). Removal of the solvent under vacuum gave the product (1.4 g) as colorless oil in 62% yield. 1H NMR ($CDCl_3$): δ 3.37–4.09 (m, 38H), 6.49–6.51 (m, 3H), 7.13–7.16 (t, J = 5.1 Hz, 1H).

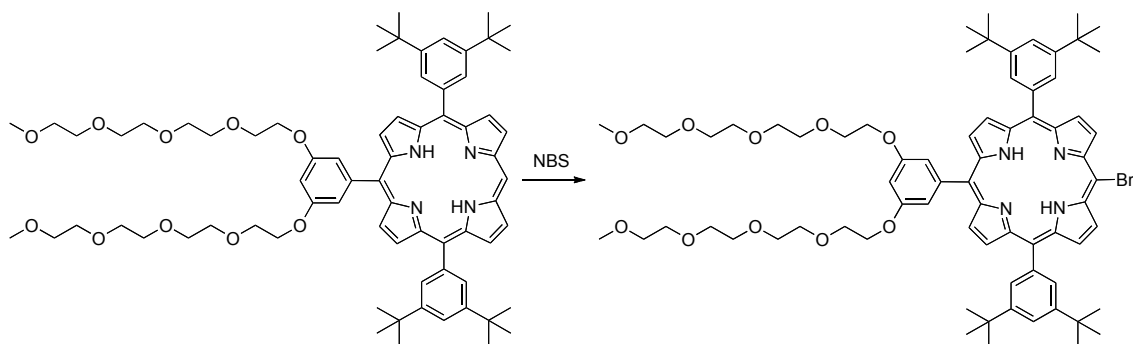
PEG-porphyrin monomer



3,5-di-PEG-benzene (808 mg, 1.65 mmol, 1.0 equiv), bis(pinacolato)diboron (419 mg, 1.65 mmol, 1.0 equiv), 4,4'-di-*tert*-butyl-2,2'-bipyridyl (2.2 mg, 0.0082 mmol, 0.005 equiv), and $[IrOMe(cod)]_2$ (2.7 mg, 0.0041 mmol, 0.0025 equiv) were added to a Schlenk flask and purged with argon, and then charged with 4.0 mL of dry THF. The mixture was stirred at reflux for 24 h under argon. The solvent was removed under vacuum and the crude product was used for the following reaction without separation. The crude product was a mixture of the desired borylated compound (66%) and the starting material (34%) according to the 1H NMR spectrum. The borylated PEG-benzene (1.07 mmol, 1.3 equiv), *meso*-

bromoporphyrin (620 mg, 0.81 mmol, 1.0 equiv), Cs₂CO₃ (528 mg, 1.62 mmol, 2.0 equiv), Pd₂(dba)₃ (37 mg, 0.04 mmol, 0.05 equiv), PPh₃ (42 mg, 0.16 mmol, 0.2 equiv), CsF (246 mg, 1.62 mmol, 2.0 equiv) were added to a Schlenk flask and purged with argon, and then charged with 2.5 mL of dry DMF and 5 mL of dry toluene. The solution was deoxygenated via three freeze-pump-thaw degas cycles, and the resulting mixture was heated at 80 °C for 24h under argon. The reaction mixture was quenched with water and extracted with CH₂Cl₂ (3 times). The organic layer was dried over anhydrous Na₂SO₄. The crude product was concentrated and filter through a short pad of silica gel (eluent: CH₂Cl₂/CH₃OH = 30/1) to get rid of insoluble salts and high polar materials. The mixture was purified by GPC column (BioRad Bio-Beads SX-1, packed in THF in a 3.0 × 60 cm gravity-flow column; eluent: THF) to afford PEG-porphyrin monomer (710 mg) in 75% yield. ¹H NMR (CDCl₃): δ -2.95 (s, 2H, NH), 1.56 (s, 36H, 12 × CH₃), 3.28–4.28 (m, 38H, PEG-H), 6.93 (m, 1H, ArH), 7.42 (m, 2H, ArH), 7.82 (m, 2H, ArH), 8.11 (s, 4H, ArH), 8.93 (d, *J* = 4.6 Hz, 2H, β-H), 8.94 (d, *J* = 4.6 Hz, 2H, β-H), 9.06 (d, *J* = 4.6 Hz, 2H, β-H), 9.33 (d, *J* = 4.6 Hz, 2H, β-H), 10.21 (s, 1H, *meso*-H); MS (MALDI-TOF): *m/z* 1167.8 (M⁺), calcd. *m/z* 1174.70.

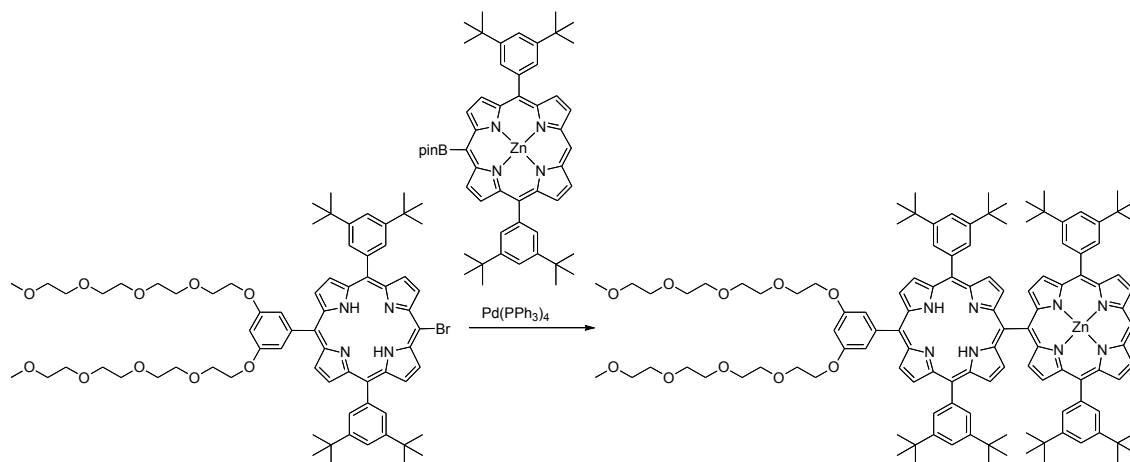
Br-PEG-porphyrin monomer



To a 300-mL two-necked flask equipped with stirrer and ice bath (0–2 °C) was added PEG-porphyrin monomer (458 mg, 0.39 mmol, 1.0 equiv), CHCl₃ (150 mL), and pyridine (0.5 mL). Then a solution of N-bromosuccinimide (NBS, 76.3 mg, 0.43 mmol, 1.1 equiv) in CHCl₃ (30 mL) was added dropwise over a period of 30 min at 0–2 °C. Stirring of the solution was continued for additional 15 min in ice bath. Then the reaction was quenched by an addition of 2 mL of acetone. The solution was then washed with water, dried over anhydrous sodium sulfate, evaporated to dryness to get the product (500 mg) as a purple solid quantitatively. ¹H NMR (CDCl₃): δ -2.67 (s, 2H, N-H), 1.62 (s, 36H, 12 × CH₃), 3.28–4.27 (m, 38H, PEG-H), 6.92 (m, 1H, ArH), 7.37 (m, 2H, ArH), 7.82 (m, 2H, ArH), 8.05 (s, 4H, ArH), 8.82 (br, 2H, β-H), 8.87 (br, 2H, β-H), 8.94 (br, 2H, β-H), 9.67 (d, *J* = 4.6 Hz, 2H, β-H); MS (MALDI-TOF): *m/z* 1254.4

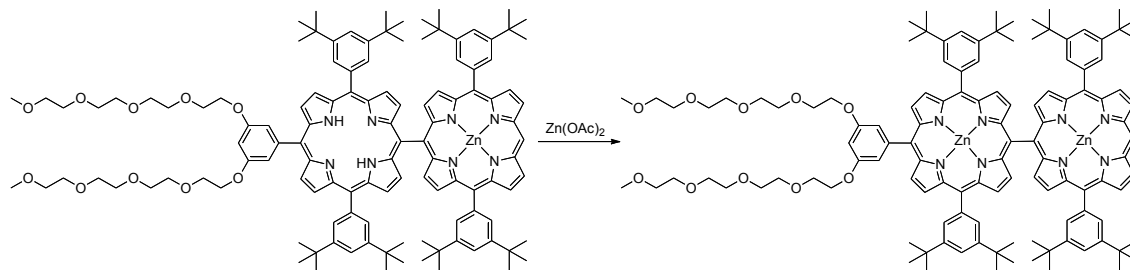
(M⁺), calcd. *m/z* 1252.60.

PEG-porphyrin dimer



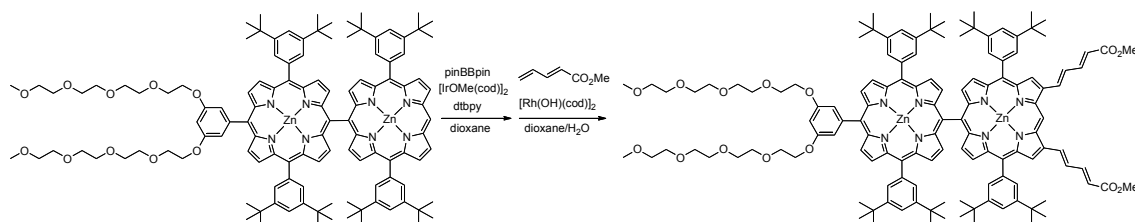
Porphyrin bromoate (193 mg, 0.22 mmol, 1.0 equiv), Br-PEG-porphyrin (325 mg, 0.26 mmol, 1.2 equiv), Cs₂CO₃ (143 mg, 0.44 mmol, 2.0 equiv), and Pd(PPh₃)₄ (25 mg, 0.022 mmol, 0.1 equiv) were added to a Schlenk flask and purged with argon, and then charged with dry DMF (2.5 mL) and dry toluene (5 mL). The solution was deoxygenated via three freeze-pump-thaw degas cycles, and the resulting mixture was heated at 80 °C for 48 h under argon. The reaction mixture was quenched with water and extracted with CH₂Cl₂ (3 times). The organic layer was dried over anhydrous Na₂SO₄. The mixture was purified by GPC column to afford PEG-porphyrin dimer (335 mg) in 79% yield. ¹H NMR (CDCl₃): δ -2.16 (s, 2H, N-H), 1.43–1.56 (m, 72H, 24 × CH₃), 3.30–4.33 (m, 38H, PEG-H), 6.97 (m, 1H, ArH), 7.50 (m, 2H, ArH), 7.69 (m, 2H, ArH), 7.72 (m, 2H, ArH), 8.00 (d, *J* = 4.3 Hz, 2H, β-H), 8.06 (m, 4H, ArH), 8.10 (m, 4H, ArH), 8.19 (d, *J* = 5.0 Hz, 2H, β-H), 8.56 (d, *J* = 4.1 Hz, 2H, β-H), 8.76 (d, *J* = 4.6 Hz, 2H, β-H), 8.90 (d, *J* = 4.6 Hz, 2H, β-H), 8.99 (d, *J* = 5.0 Hz, 2H, β-H), 9.18 (d, *J* = 4.6 Hz, 2H, β-H), 9.49 (d, *J* = 4.6 Hz, 2H, β-H), 10.38 (s, 1H, *meso*-H); MS (MALDI-TOF): *m/z* 1922.9 (M⁺), calcd. *m/z* 1921.03.

Zinc insertion of PEG-porphyrin dimer

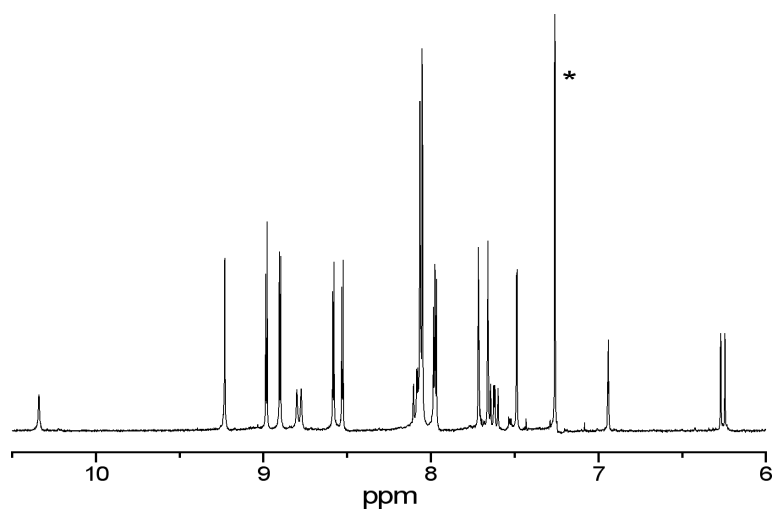
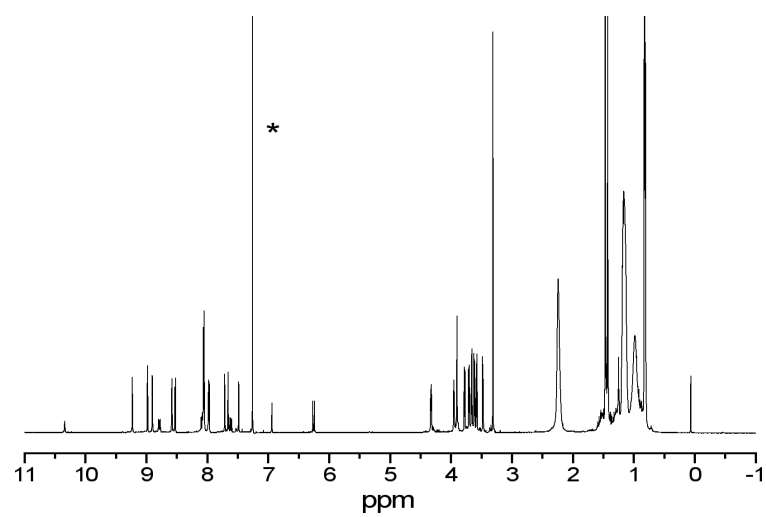


PEG-porphyrin dimer (210 mg, 0.11 mmol, 1.0 equiv) was dissolved in CHCl₃ (10 mL), and the solution was purged with nitrogen for 10 min. A solution of Zn(OAc)₂·2H₂O (119 mg, 0.55 mmol, 5.0 equiv) in MeOH (2 mL) was added to the porphyrin solution in one portion, and the reaction mixture was stirred at room temperature for 30 min. The reaction was quenched with saturated NaHCO₃ aq. and extracted with CHCl₃ for 3 times. The organic layer was washed with water and dried over Na₂SO₄. The solvent was removed in vacuo to give PEG-porphyrin dimer biszinc(II) (210 mg) in 97% yield. ¹H NMR(CDCl₃): δ 1.43–1.56 (m, 72H, 24 × CH₃), 2.97–4.35 (m, 38H, PEG-H), 6.96 (m, 1H, ArH), 7.53 (m, 2H, ArH), 7.68 (m, 2H, ArH), 7.71 (m, 2H, ArH), 8.06 (m, 4H, ArH), 8.07 (d, *J* = 4.3 Hz, 2H, β-H), 8.11 (m, 4H, ArH), 8.18 (d, *J* = 4.8 Hz, 2H, β-H), 8.67 (d, *J* = 4.6 Hz, 2H, β-H), 8.75 (d, *J* = 4.6 Hz, 2H, β-H), 8.99 (d, *J* = 4.6 Hz, 2H, β-H), 9.08 (d, *J* = 4.6 Hz, 2H, β-H), 9.19 (d, *J* = 4.6 Hz, 2H, β-H), 9.49 (d, *J* = 4.6 Hz, 2H, β-H), 10.38 (s, 1H, *meso*-H); MS (MALDI-TOF): *m/z* 1985.7 (M⁺), calcd. *m/z* 1982.94.

PEG-porphyrin dimer diester



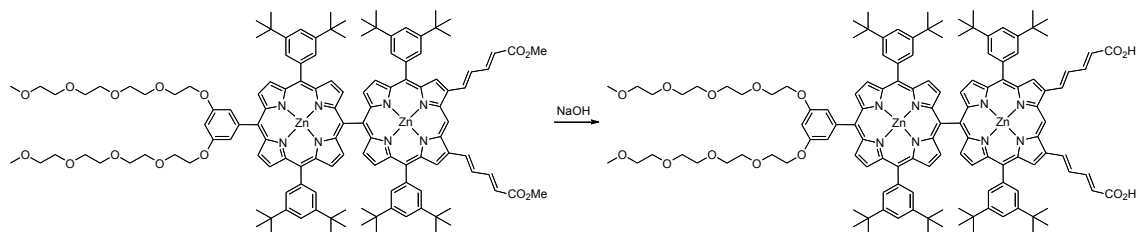
PEG-porphyrin dimer biszinc(II) (105 mg, 0.052 mmol, 1.0 equiv), bis(pinacolato)diboron (132 mg, 0.52 mmol, 10.0 equiv), 4,4'-di-*tert*-butyl-2,2'-bipyridyl (2.8 mg, 0.0104 mmol, 0.2 equiv), and [IrOMe(cod)]₂ (3.4 mg, 0.0052 mmol, 0.1 equiv) were added to a Schlenk flask and purged with argon, and then charged with 1,4-dioxane (1.5 mL). The mixture was stirred at reflux for 48 h under argon. The solvent was removed under vacuum and the crude product was used for the following reaction without separation. The crude product was a mixture of diborylated compound (78%) and monoborylated compound (12%) according to the ¹H NMR spectrum. The borylated mixture and [Rh(cod)OH]₂ (2.0 mg, 0.0044 mmol, 0.08 equiv) were added to a Schlenk flask and purged with argon, and charged with 1,4-dioxane (2 mL), H₂O (200 μL), and methyl 2,4-pentadienoate (154 μL, 1.32 mmol, 40 equiv). The mixture was stirred at room temperature for 3 days under argon. The solvent was removed under vacuum and the crude product was dissolved in CH₂Cl₂ (5 mL) and DDQ (20 mg) was added. The mixture was stirred for 5 min and quenched with saturated NaHCO₃ aq. and extracted with CHCl₃ for 3 times. The crude product was purified by silica gel chromatography with CH₂Cl₂/methanol = 50/1 as eluent to give PEG-porphyrin dimer diester (32.7 mg) in 28% yield for two steps. ¹H NMR (CDCl₃ in the presence of *n*-BuNH₂): δ 1.43–1.47 (m, 72H, 24 × CH₃), 3.90 (s, 6H, OMe), 3.31–4.33 (m, 38H, PEG-H), 6.25 (d, *J* = 15.1 Hz, 2H, double bond), 6.94 (m, 1H, ArH), 7.49 (m, 2H, ArH), 7.64 (dd, *J* = 15.1, 11.0 Hz, 2H, double bond), 7.66 (m, 2H, ArH), 7.71 (m, 2H, ArH), 7.97 (m, 4H, β-H), 8.06 (m, 8H, ArH), 8.10 (dd, *J* = 15.1, 11.0 Hz, 2H, double bond), 8.52 (d, *J* = 4.6 Hz, 2H, β-H), 8.58 (d, *J* = 4.6 Hz, 2H, β-H), 8.78 (d, *J* = 15.1 Hz, 2H, double bond), 8.90 (d, *J* = 4.6 Hz, 2H, β-H), 8.98 (d, *J* = 4.6 Hz, 2H, β-H), 9.23 (s, 2H, β-H), 10.34 (s, 1H, *meso*-H); MS (MALDI-TOF): *m/z* 2209.5 (M⁺), calcd. *m/z* 2203.02.



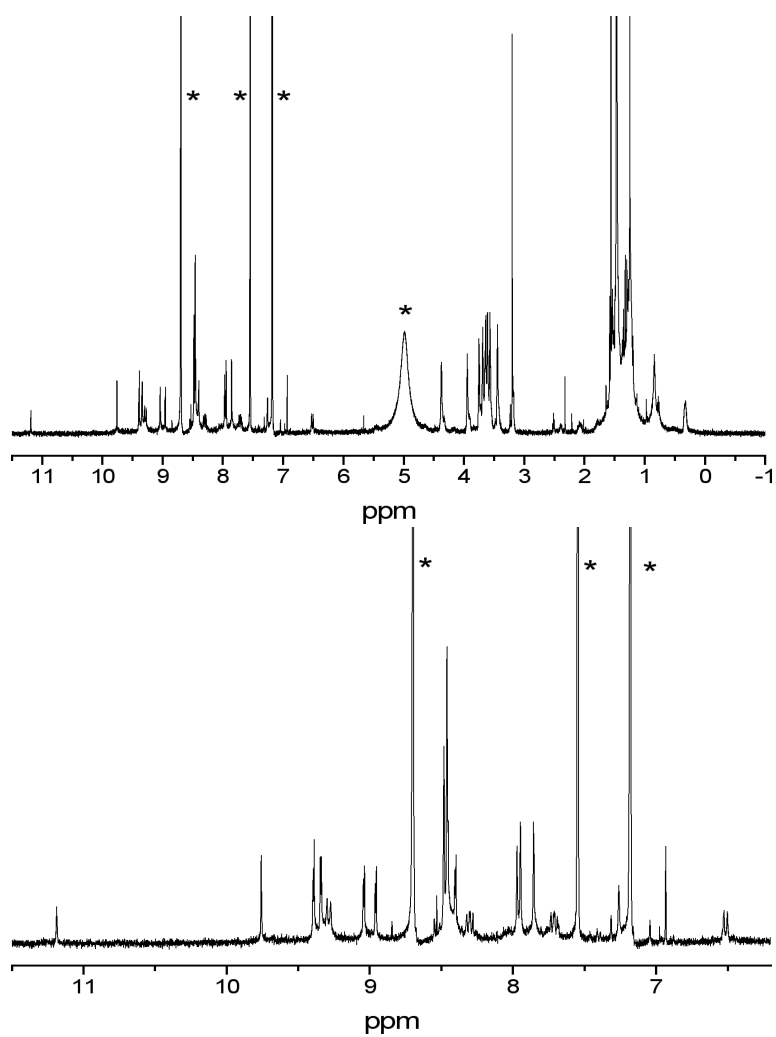
* solvent

FigureS1. ^1H NMR for PEG-porphyrin dimer diester in CDCl_3 in presence of $n\text{-BuNH}_2$.

PEG-2b-bd-Zn2



PEG-porphyrin dimer diester (32.7 mg, 0.015 mmol) was dissolved in THF (2 mL). Then ethanol (2 mL) and NaOH aq. (2.0 M, 2 mL) was added. The solution was stirred under N₂ atmosphere at 65–70 °C (oil bath) for 40 h. The solvent was removed in vacuo, and then about 30 mL of water was added to the solid. The dark solid was precipitated by the slow addition of HCl aq. (1.0 M) to the aqueous solution of the product until the solution became enough acidic (pH = 3). Then the solid was filtered to obtain desired product (26.0 mg) in 80% yield. ¹H NMR (pyridine-d₅): δ 1.25–1.56 (m, 72H, 24 × CH₃), 3.20–4.38 (m, 38H, PEG-H), 6.51 (d, *J* = 14.7 Hz, 2H, double bond), 6.93 (s, 1H, ArH), 7.72 (dd, *J* = 16.5, 11.0 Hz, 2H, double bond), 7.86 (s, 2H, ArH), 7.95 (s, 2H, ArH), 7.97 (s, 2H, ArH), 8.30 (dd, *J* = 15.6, 11.5 Hz, 2H, double bond), 8.40 (d, *J* = 4.6 Hz, 2H, β-H), 8.46 (m, 8H, ArH), 8.95 (d, *J* = 4.6 Hz, 2H, β-H), 9.04 (d, *J* = 4.6 Hz, 2H, β-H), 9.30 (d, *J* = 15.1, 2H, double bond), 9.34 (d, *J* = 4.6 Hz, 2H, β-H), 9.39 (d, *J* = 4.6 Hz, 2H, β-H), 9.76 (s, 2H, β-H), 11.18 (s, 1H, *meso*-H); MS (MALDI-TOF): *m/z* 2176.9 (M⁺), calcd. *m/z* 2174.99.



* solvent

FigureS2. ^1H NMR for **PEG-2b-bd-Zn2** in pyridine-d_5

(2) Normalized emission spectra in ethanol

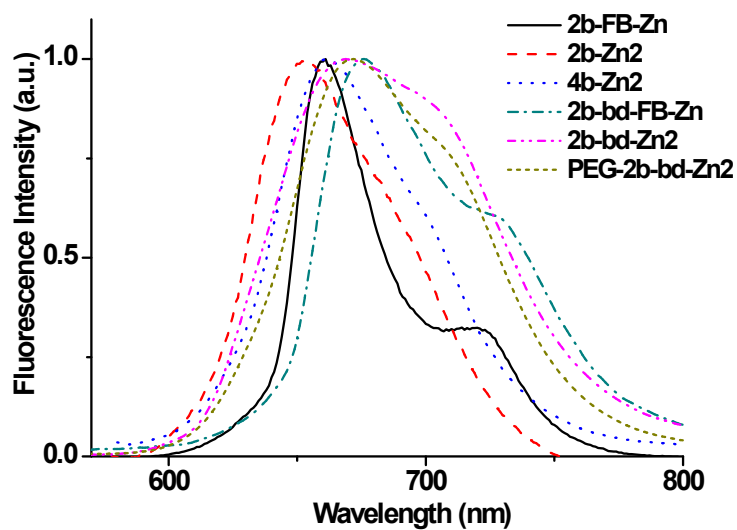
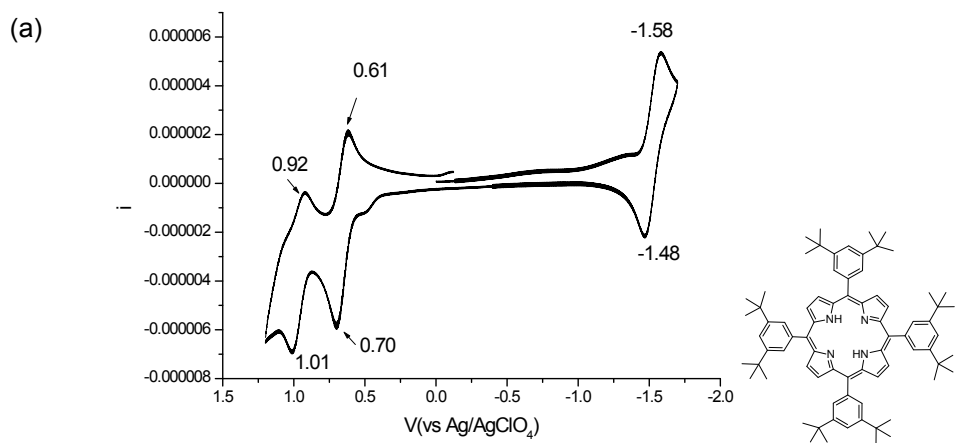
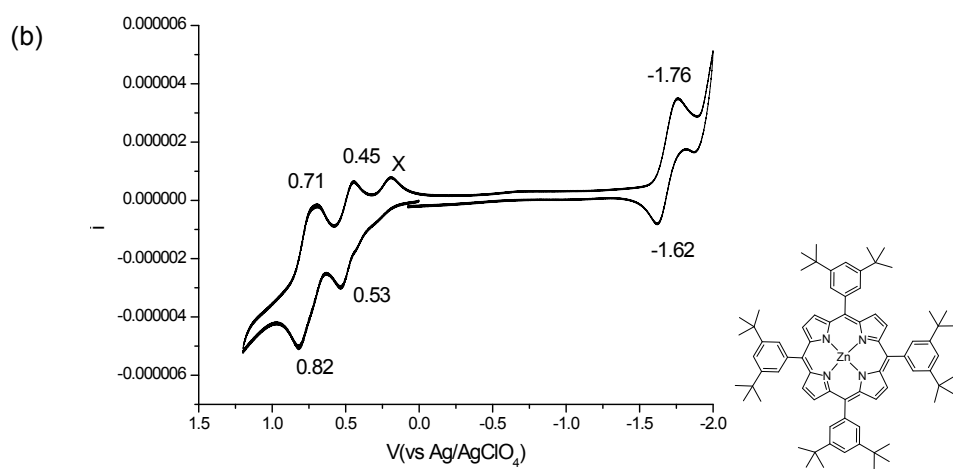


Figure S3. Fluorescence spectra of **2b-FB-Zn**, **2b-Zn₂**, **4b-Zn₂**, **2b-bd-FB-Zn₂**, **2b-bd-Zn₂** and **PEG-2b-bd-Zn₂** in ethanol. The spectra are normalized for comparison.

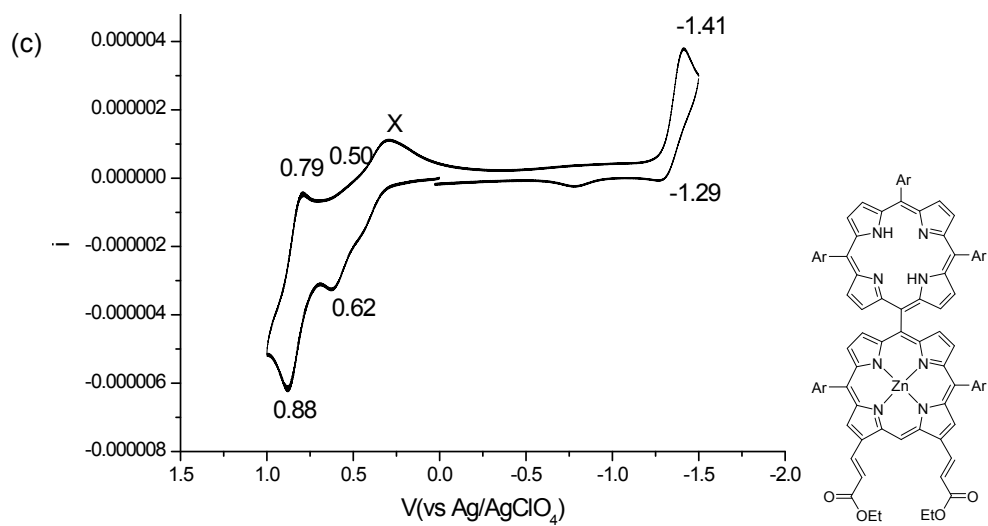
(3) Cyclic voltammetry



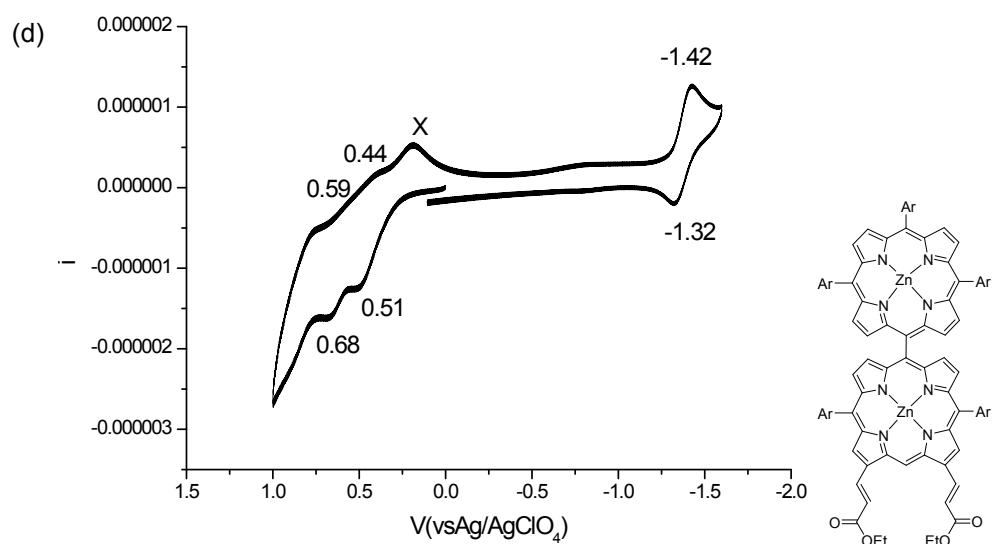
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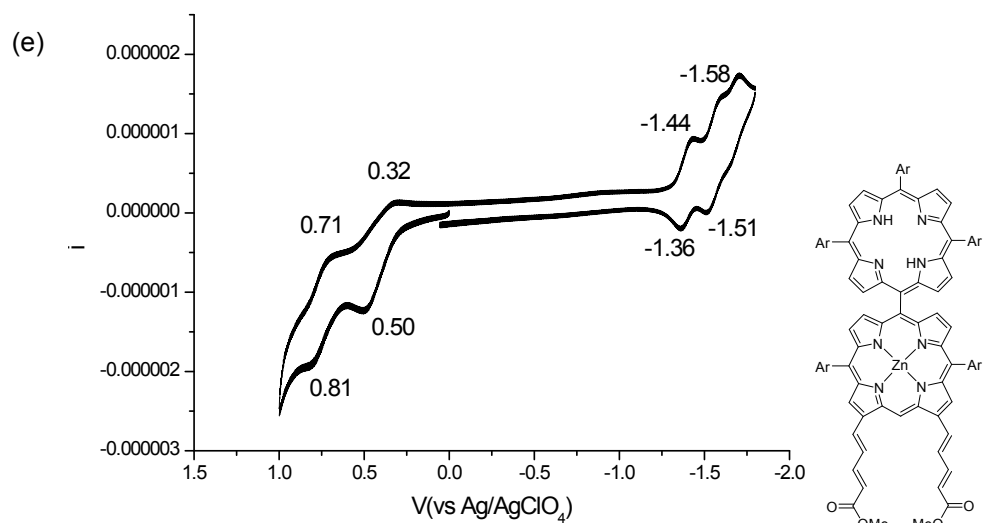
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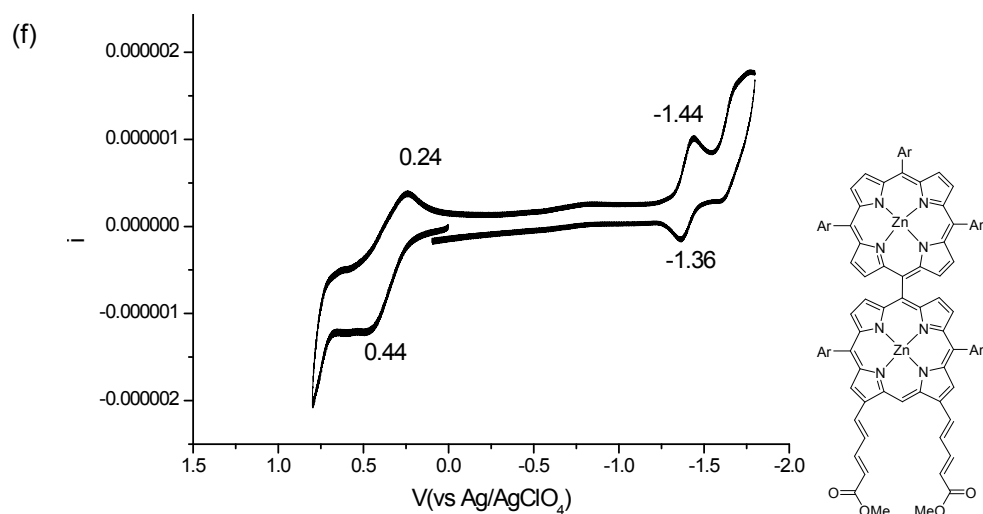
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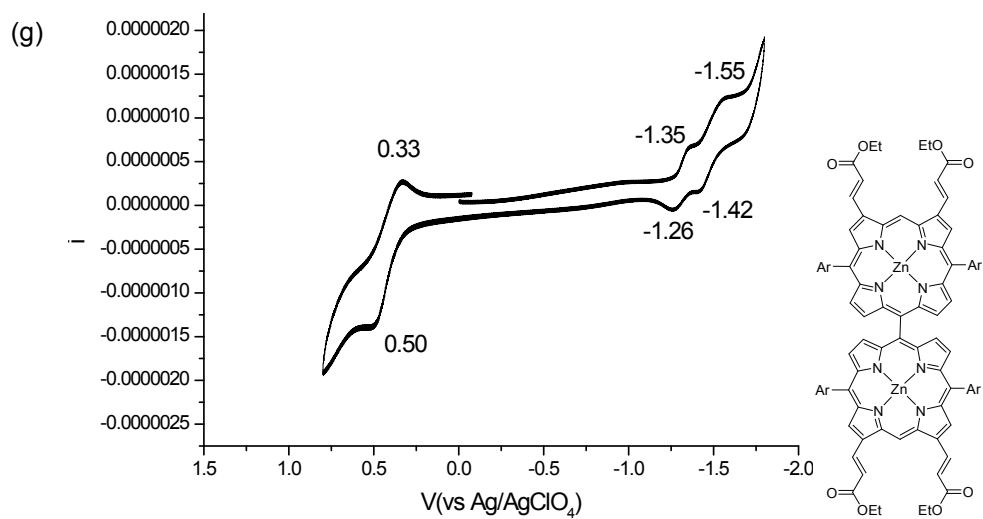
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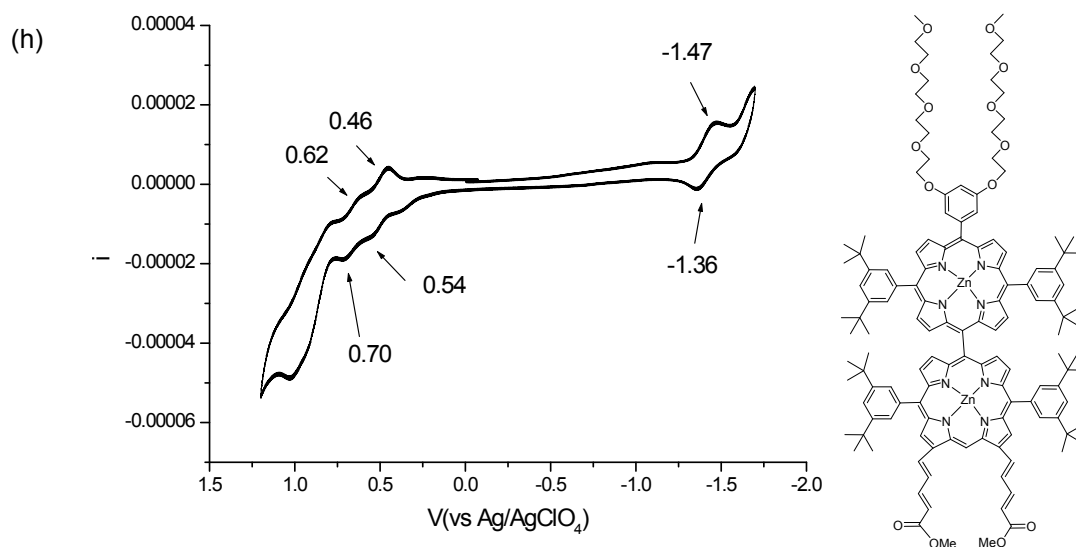
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<Oxidation and reduction for **2b-bd-Zn2**>



<Oxidation and reduction for **4b-Zn2**>



<Oxidation and reduction for **PEG-2b-bd-Zn2**>

Figure S4. Cyclic voltammogram of all ester derivatives in dichloromethane reported versus Ag/AgClO₄ (V).

(4) DFT calculation

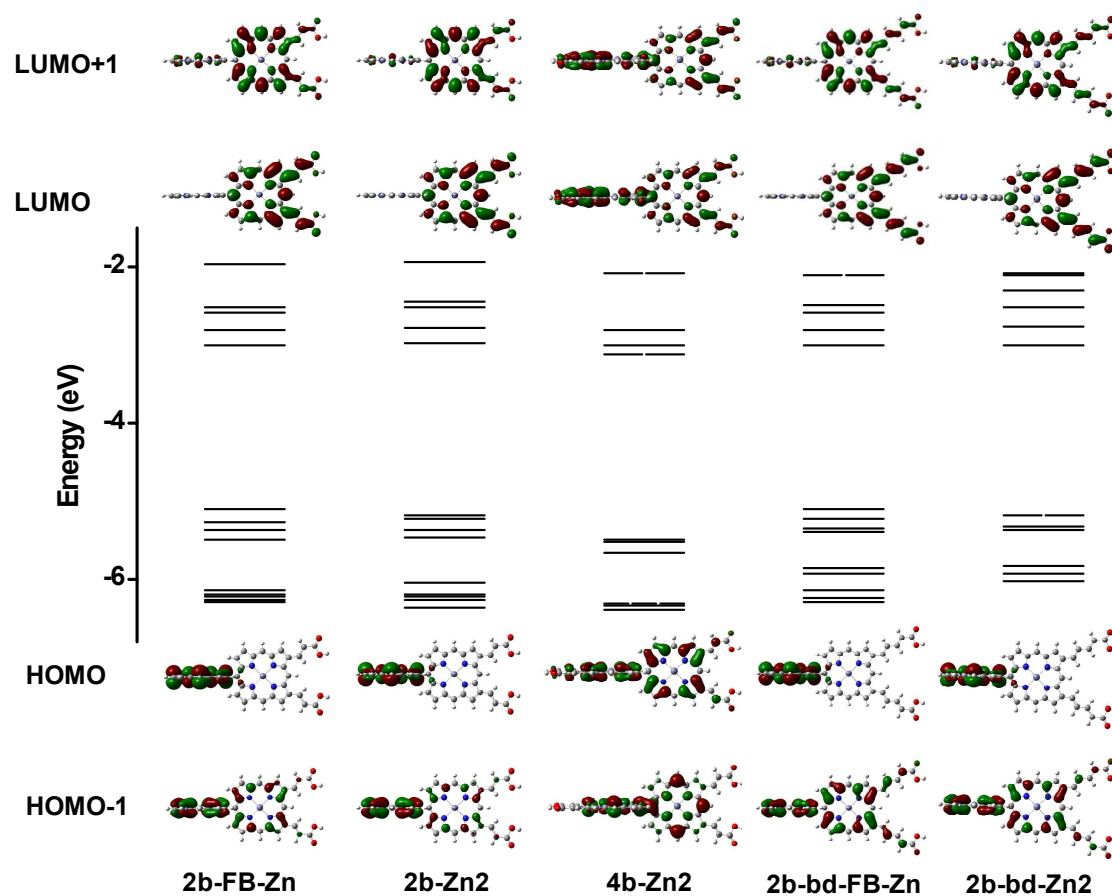


Figure S5. Selected four molecular orbitals for carboxylic acid porphyrin dimers calculated at B3LYP/6-31G level. The aryl groups were replaced by hydrogen before calculation.

Table S1. Redox potentials of porphyrin dimers.^a

Compound	$E_{1/2, \text{ox}}$ (V)	$E_{1/2, \text{red}}$ (V)	$\Delta E_{\text{HOMO-LUMO}}^b$ (V)	$E_{1/2, \text{ox}}^*$ (eV) ^c
FbP^d	0.44	−1.75	2.19	—
ZnP^d	0.27	−1.91	2.18	—
2b-FB-Zn	0.34	−1.57	1.91	−1.54
2b-Zn2	0.26	−1.59	1.85	−1.64
4b-Zn2	0.20	−1.53	1.63	−1.68
2b-bd-FB-Zn	0.19	−1.62	1.81	−1.64
2b-bd-Zn2	0.12	−1.62	1.74	−1.73
PEG-2b-bd-Zn2	0.28	−1.64	1.92	−1.57

^aThese values were measured by cyclic voltammetry using a platinum working electrode, a platinum wire counter electrode and Ag/0.01M AgClO₄ reference electrode. The measurements were carried out in dichloromethane solutions containing 0.1M Bu₄NBF₆ as a supporting electrolyte. (in V vs ferrocene/ferrocenium ion pair). ^b $\Delta E_{\text{HOMO-LUMO}} = E_{1/2, \text{ox}} - E_{1/2, \text{red}}$. ^c $E_{1/2, \text{ox}}^* = E_{1/2, \text{ox}} - E_{0-0}$. ^dAryl groups are 3,5-di-*tert*-butylphenyl.

Table S2. Energy levels from DFT calculation.^a

Compound	HOMO−1 (eV)	HOMO (eV)	LUMO (eV)	LUMO+1 (eV)	ΔE_{cal} (eV) ^b
2b-FB-Zn	−5.52	−5.33	−2.97	−2.75	2.36
2b-Zn2	−5.47	−5.42	−2.94	−2.72	2.48
4b-Zn2	−5.80	−5.77	−3.10	−3.10	2.67
2b-bd-FB-Zn	−5.47	−5.33	−2.97	−2.75	2.36
2b-bd-Zn2	−5.42	−5.42	−2.97	−2.70	2.45
PEG-2b-bd-Zn2	— ^c	— ^c	— ^c	— ^c	— ^c

^aCalculated at B3LYP/6−31G level. ^bDifference in the HOMO-LUMO energy. ^cNot calculated.