Supporting Information

Facile One-pot Synthesis of Unprecedented β, β'-linked Porphyrin-Chlorin Heterodimers

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Experimental Section

Materials and Instruments. Acenaphthenequinone and tetrachloro-1,4-benzoquinone were used as received. Pyrrole and $BF_3·OEt_2$ were freshly distilled before use. $CHCl_3$ were purified by washing with concentrated sulfuric acid, then with water until the aqueous layer was neutral, dried with $MgSO_4$, and then distilled over P_2O_5. Other solvents were used as received. UV-vis spectra were measured on a Shimadzu UV-3150 spectrometer. Fluorescence spectra were measured on a FLS920 spectrometer. ^1H NMR spectra were carried out using a Bruker AVANCE 400 spectrometer in $CDCl_3$ without tetramethylsilane (TMS) as the internal standard, Chemical shifts are expressed in ppm relative to chloroform (7.26 ppm). Mass spectra were taken with Agilent 6220 Accurate-Mass TOF LC/MS. Cyclic voltammetric measurements were performed on a RST3000 electrochemical system (Suzhou Risetech Instrument Co., Ltd. Suzhou, China). A three-electrode system was used and consisted of a platinum disk working electrode, a platinum wire counter electrode and a saturated calomel reference electrode (SCE). All the measurements were carried out in CH_2Cl_2 medium using 0.1 M or 0.5 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Porphyrin concentrations were maintained at 1 mM. All the solutions were purged with argon gas prior to electrochemical measurements and all the experiments were performed at room temperature.

Preparation

The reaction was carried out under anaerobic condition. Acenaphthenequinone (6.9 mmol), aldehyde (21 mmol, benzaldehyde for **1a** and **2a**, tolualdehyde for **1b** and **2b**) and pyrrole (1.9 mL, 28 mmol) were dissovled in pure chloroform (500 mL). $BF_3{\cdot}OEt_2$ (1.0 mL, 7.9 mmol) was added to the above solution and stirred for 1 h at room temperature, then tetrachloro-1,4-benzoquinone (7.61 g, 27.6 mmol) was added. After 2 h under reflux, triethylamine (4.0 mL) was added, and the mixture was stirred for another half hour. When it was cooled down to room temperature, it was filtered by sintered glass funnel. The filtrate was rotorevaporated to dryness, the black solid was further purified by column chromatography (silica, CH_2Cl_2/petroleum ether = 1:1) . The first green band (**2a** or **2b**) and second purple band (**1a** or **1b**) were collected, and evaporated to dryness. For 1a, yield 0.17 g (3.8%, based on pyrrole). Anal. Calc. for $C_{93}H_{60}N_8O{\cdot}1.7CH_2Cl_2$: C, 78.45; H, 4.41; N, 7.73%. Found: C, 78.14; H, 4.28; N, 7.72%. ^{1}H NMR (400 MHz; $CDCl_3$)：δ 8.78(2 H, s), 8.72(1 H, d), 8.65(1 H, d), 8.60(1 H, d), 8.55(1 H, d), 8.53(1 H, d), 8.46(1 H, d), 8.44(2 H, d), 8.39(2 H, t),8.26(6 H, m), 8.20(1 H, s),8.11(1 H, s), 8.04(1 H, d), 7.74(24 H, m), 7.35(4 H, m), 6.80(1 H, s), 6.46(1 H, t), 6.29(1 H, s), 6.25(1 H, t), 5.64(1 H, s), 5.32 (3H, s) -1.23(2 H, s), -2.88(2 H, s). UV-vis (CH_2Cl_2): λ_{max}, nm ($M^{-1}.cm^{-1}$): 421(2.69×10^5), 435(2.56×10^5), 521(2.88×10^4), 557(1.75×10^4), 601(1.03×10^4), 658(2.71×10^4). LC-ESI-MS: *m/z* calcd for $C_{93}H_{60}N_8O$ 1304.49; found 653.25$[M+2H]^{2+}$, 1305.49 $[M+H]^+$.

For **1b**, yield 0.16 g (3.4%). Anal. Calc. for $C_{100}H_{74}N_8O{\cdot}0.2CH_2Cl_2$: C, 84.71; H, 5.28; N, 7.89%. Found: C, 84.64; H, 5.29; N, 7.89%. ^{1}H NMR (400 MHz; $CDCl_3$)：δ 8.83(2 H, s), 8.72(2 H, t), 8.64(1 H, d), 8.58(3 H, m), 8.47(2 H, t), 8.38(1 H, d), 8.30(1 H, d), 8.23(3 H, m), 8.14(3 H, d),8.05(6 H, m), 7.93(1 H, d),7.86(2 H, t), 7.70-7.41(14H, m), 7.09(3 H, t), 6.86(1 H, s), 6.72(1 H, d), 6.47(1 H, s), 5.86(1 H, d), 5.81(1 H, s), 2.91(3 H, s), 2.67(12 H, m), 2.15(3H, s),1.35(3H, s), -1.20(2 H, s) , -2.81(2 H, s). UV-vis (CH_2Cl_2): λ_{max}, nm ($M^{-1}.cm^{-1}$): 422(2.54×10^5), 436(2.50 x

10^5), 523(2.62 x 10^4), 559(1.99 x 10^4), 603(1.18 x 10^4), 657(2.89 x 10^4). LC-ESI-MS: *m/z* calcd for $C_{100}H_{74}N_8O$ 1402.60; found 702.31 $[M+2H]^{2+}$, 1403.61 $[M+H]^+$.

For **2a**, yield 0.38 g (8.0%). Anal. Calc. for $C_{49}H_{30}N_4O{\cdot}0.1CH_2Cl_2$: C, 84.33; H, 4.35; N, 8.01%. Found: C, 84.57; H, 4.15; N, 8.13%. ^{1}H NMR (400 MHz; $CDCl_3$)：δ 9.59(1 H, s),9.37(1 H, d), 8.81(1 H, d), 8.74(3 H, d), 8.68(1 H, s), 8.57(2 H, s), 8.50(3 H, s), 8.20(1 H, d), 7.96(2 H, d), 7.77(12 H, d), 6.95(1 H, d), -1.49(2 H, s). UV-vis (CH_2Cl_2): λ_{max}, nm ($M^{-1}.cm^{-1}$): 456(1.56 x 10^5), 549(1.10 x 10^4), 610(1.28 x 10^4), 697(1.20 x 10^4). LC-ESI-MS: *m/z* calcd for $C_{49}H_{30}N_4O$ 690.24; found 691.25 $[M+H]^+$.

For **2b**, yield 0.36 g (7.1%). Anal. Calc. for $C_{52}H_{36}N_4O{\cdot}0.1CH_2Cl_2$: C, 84.41; H, 4.92; N, 7.56%. Found: C, 84.23; H, 4.85; N, 7.56%. ^{1}H NMR (400 MHz; $CDCl_3$)：δ 9.57(1 H, s),9.33(1 H, d), 8.83(1 H, d), 8.74(3 H, d), 8.69(1 H, s), 8.54(1 H, s), 8.48(2 H, d), 8.35(2 H, d), 8.17(1 H, d),7.96(1 H, t), 7.83(2 H, d),7.53(8 H, m) 6.95(1 H, d), 2.70(9 H, m), -1.49(2 H, s). UV-vis (CH_2Cl_2): λ_{max}, nm ($M^{-1}.cm^{-1}$): 457(1.44 x 10^5), 550(9.7 x 10^3), 612(1.16 x 10^4), 699(1.23 x 10^4). LC-ESI-MS: *m/z* calcd for $C_{52}H_{36}N_4O$ 732.29; found 733.29 $[M+H]^+$.

X-ray Structure Determinations.

X-ray data collection was made on a Rigaku Mercury CCD X-ray diffractometer by using graphite monochromated Mo Ka (λ =0.071073 nm) at 223(2) K. For both **1a** and **2a**, their structures were solved by direct methods and refined on F^2 using full matrix least-squares methods with SHELXTL version 97.[1] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were idealized with the standard SHELXL-97 idealization methods. Complete crystallographic details, atomic coordinates, anisotropic thermal parameters, and fixed hydrogen atom coordinates are given in the cif file. For **1a,** the asymmetric unit contains two independent porphyrin-chlorin dimmer molecule and methylene chloride molecules were was found as the interstitial solvent. The CH_2Cl_2 was badly disordered. No models could satisfy this disorder. SQUEEZE[2] was used to model this disordered methylene chloride. Electron counts within the interporphyrins voids of 227e (corresponding to roughly to 1.5 molecules of CH_2Cl_2 per heterodimer). The presence of methylene chloride is also consistent with the results of ^{1}H NMR and elemental analyses.

[1] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structure, University of Göttingen, Germany, 1997.

[2] Spek, A. L. J. Appl. Crystallogr. 2003, 36,7.

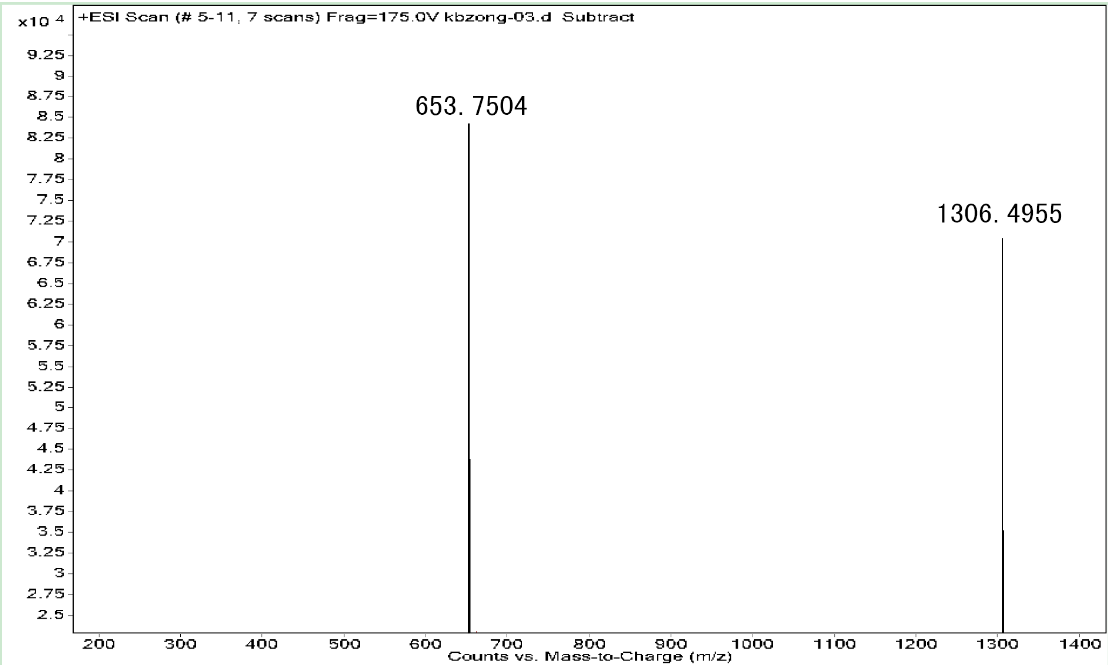


Figure S1a. Mass spectrum of the 1**a**.

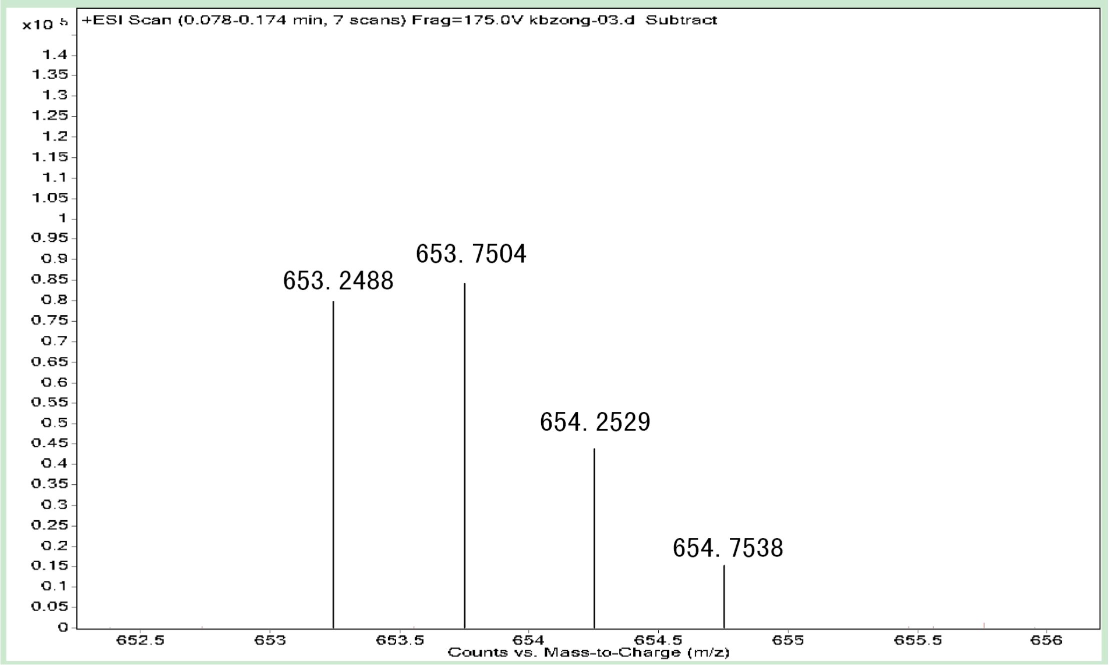


Figure S1b. Expanded mass spectrum of the 1**a** around m/z = 653.

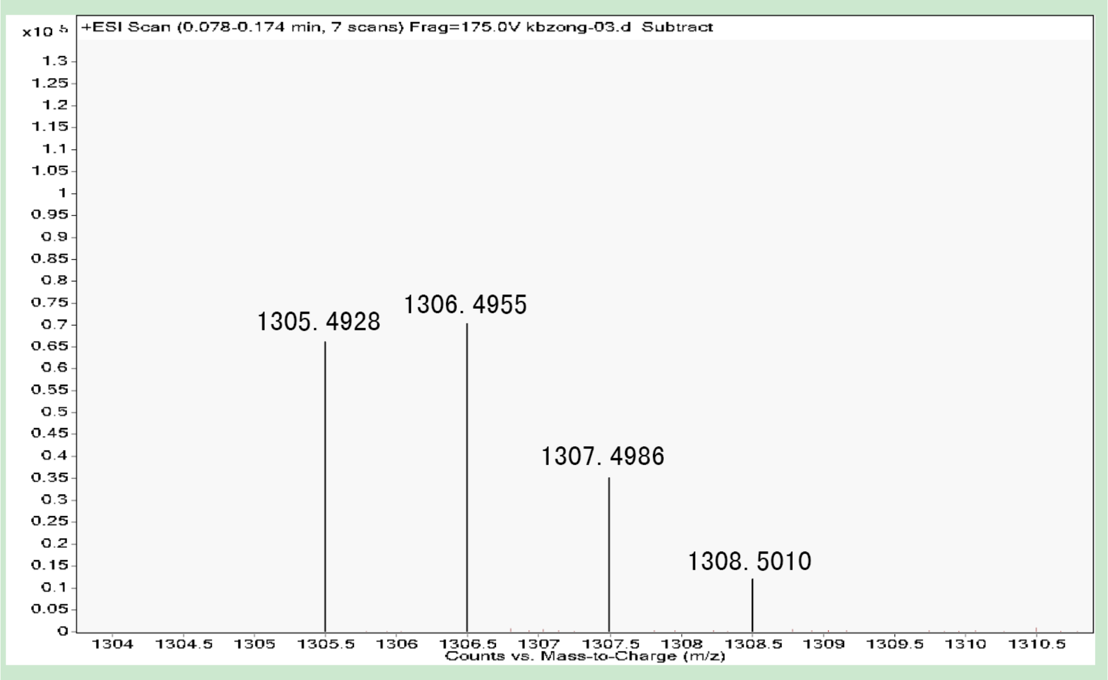


Figure S1c. Expanded mass spectrum of the 1**a** around m/z = 1306.

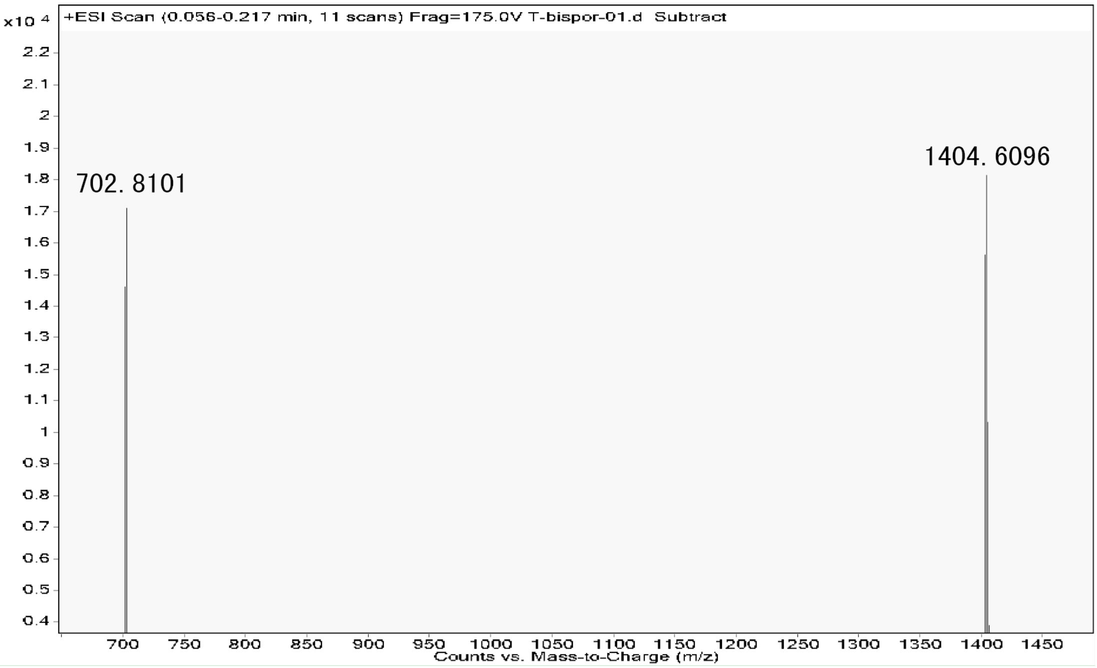


Figure S2a. Mass spectrum of the 1**b**.

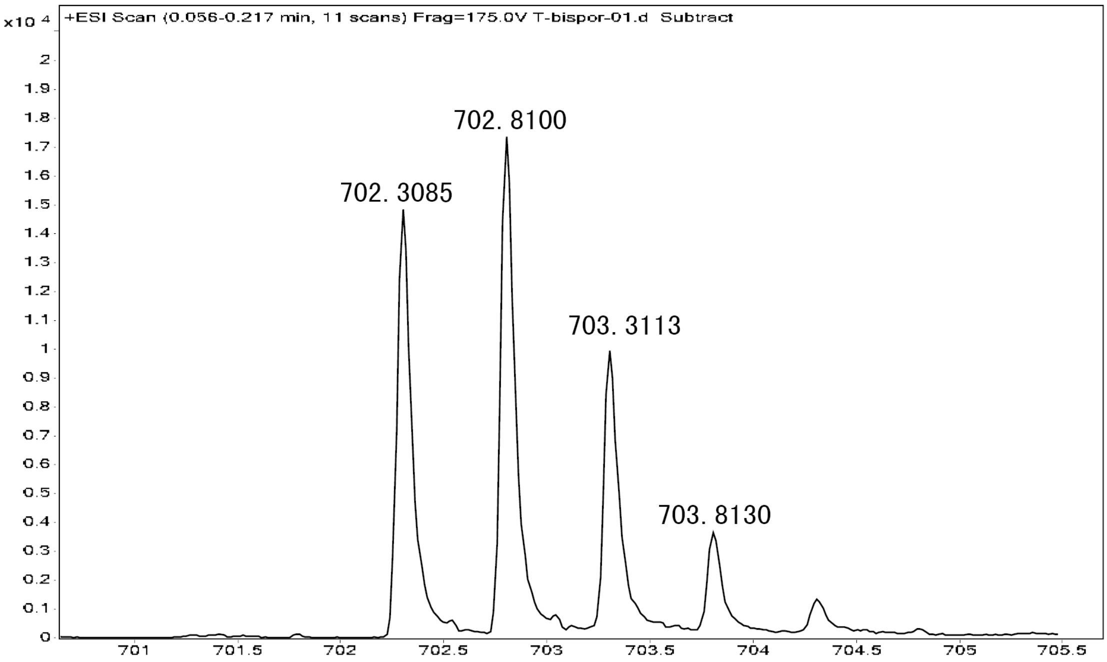


Figure S2b. Expanded mass spectrum of the 1**b**.

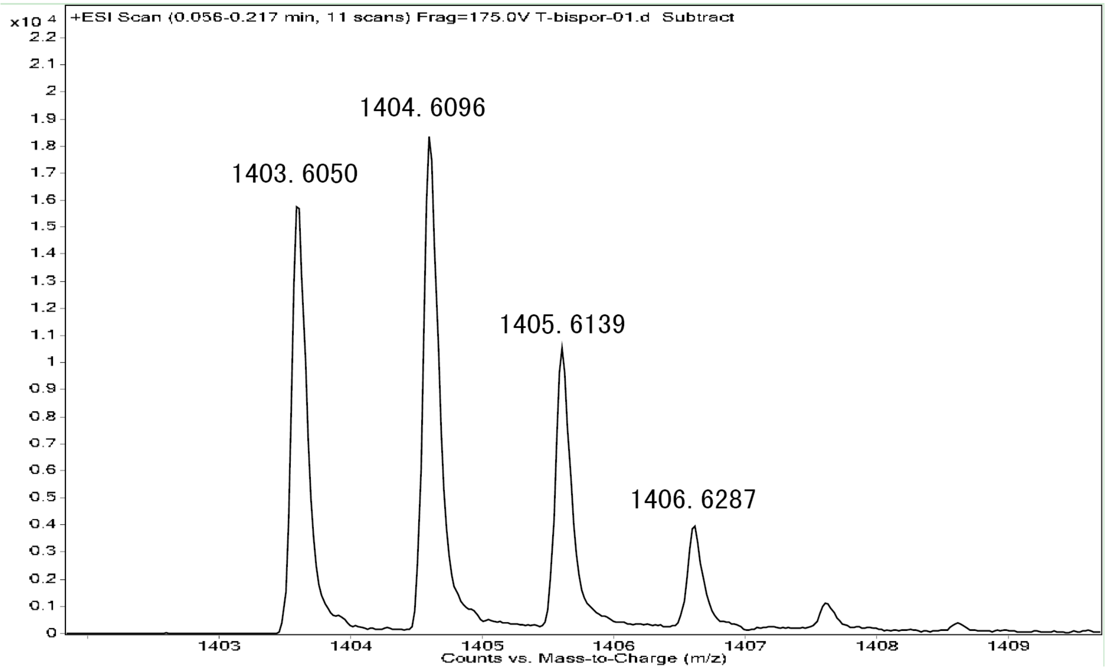


Figure S2c. Expanded mass spectrum of the 1**b** around m/z = 1404.

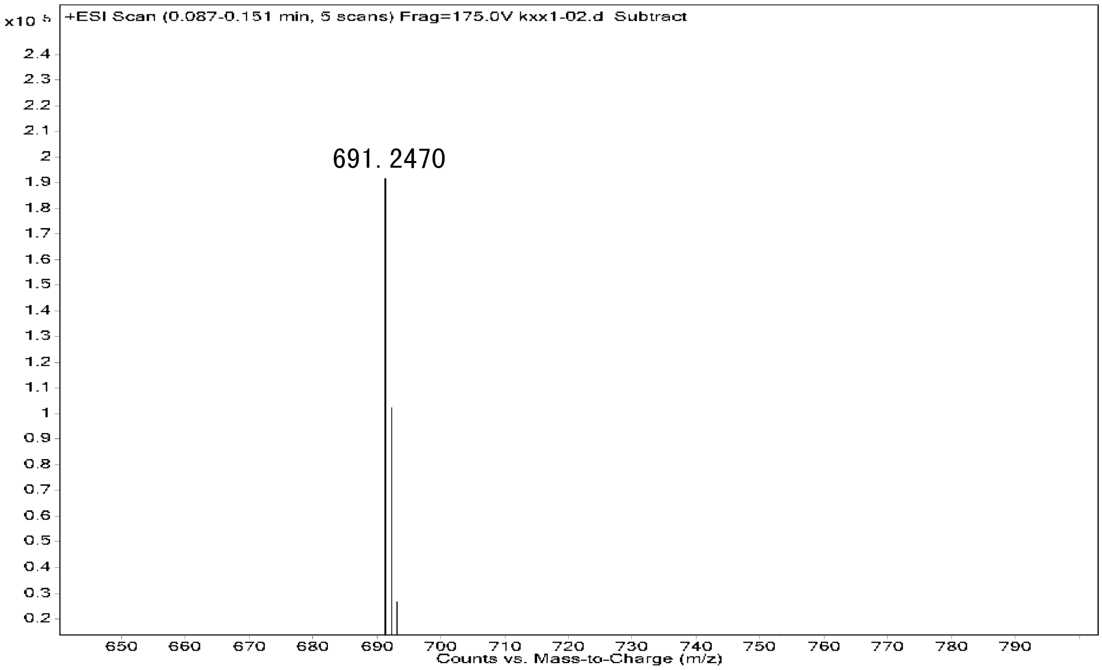


Figure S3. **M**ass spectrum of the 2**a**.

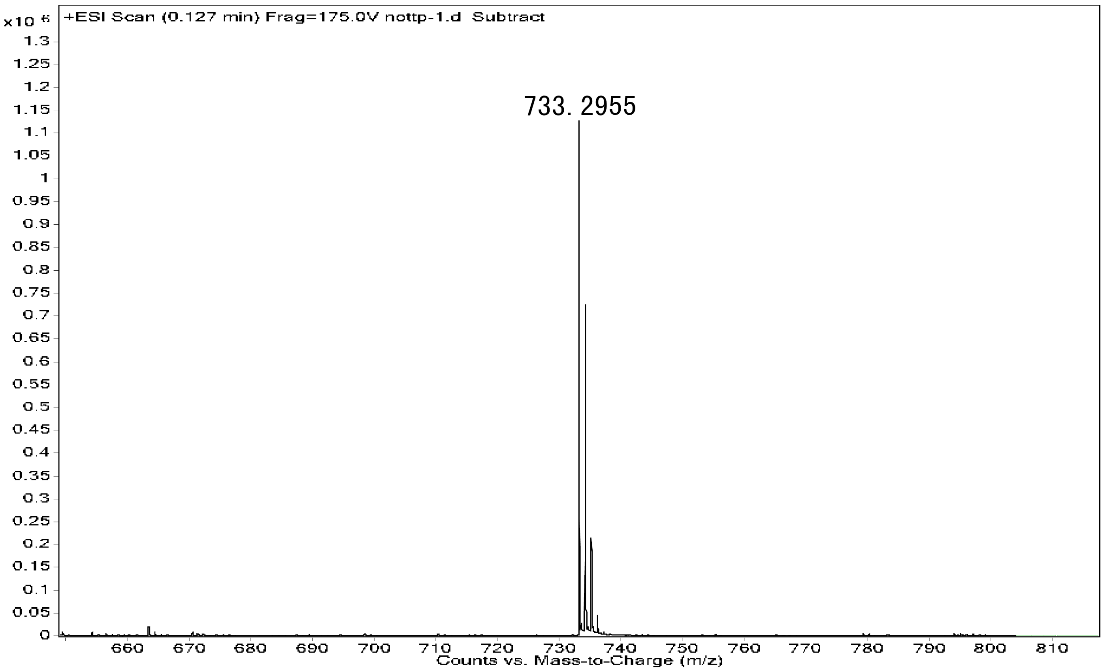


Figure S4. Mass spectrum of the 2**b**.

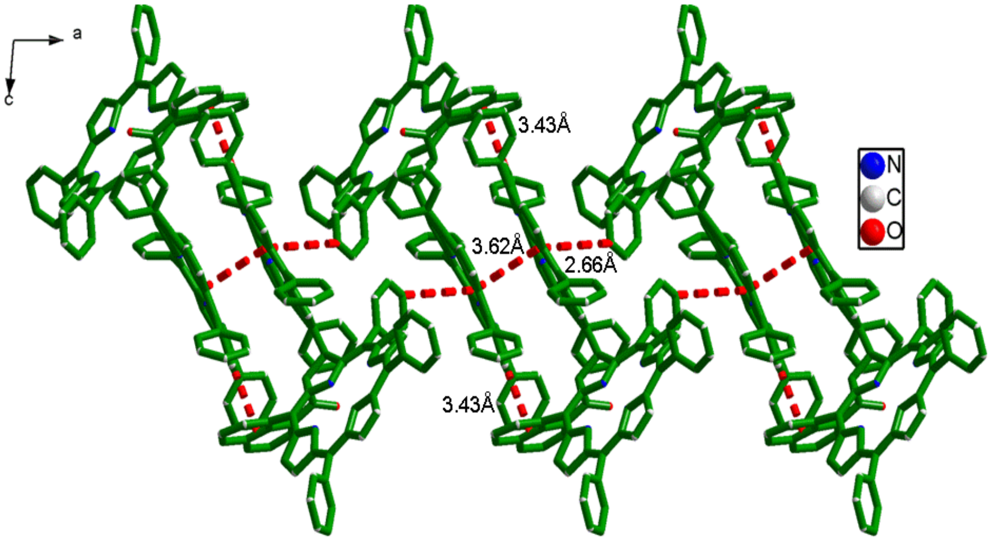


Figure S5. Packing diagram of **1a** along *a* axis, showing edge to face and π-π stacking interactions: 1) edge to face, distance between C(144#1) (symmetry operator #1: x, -1/2+y, -1+z) and plane of N(21), N(22), N(23), N(24): 2.66 Å ; and distance between C(2b5#2) (symmetry operator #2: x, -1/2+y, -1+z) and nathphyl ring (including C(111), C(112), C(113), C(114), C(115), C(116), C(117), C(118), C(119), C(120)): 3.43Å; 2) π-π, the center to center distance between N(21), N(22), N(23), N(24) and N(21#2), N(22#2), N(23#2), N(24#2): 3.62 Å

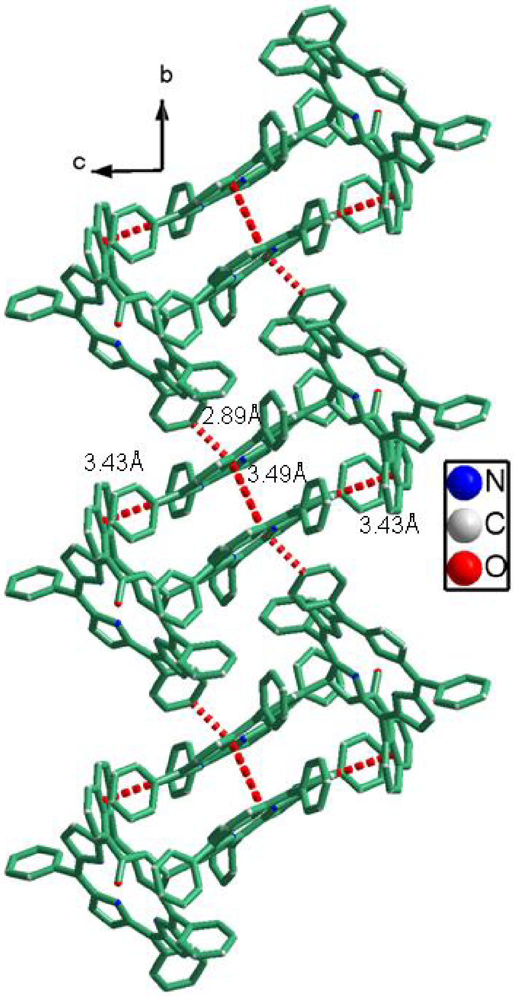


Figure S6. Packing diagram of compound **1a** along *b* axis, showing edge to face and π-π stacking interactions: 1) edge to face, distance between C(334#1) (symmetry operator #1: 2-x, 2-y, 1-z) and plane of N(21), N(22), N(23) and N(24): 2.89 Å ; and distance between C(2b5#2) (symmetry operator #2: -1+x, -1+y, z) and nathphyl ring (including C(111), C(312), C(313), C(314), C(315), C(316), C(317), C(318), C(319), C(320)): 3.43Å; 2) π-π, the center to center distance between N(21), N(22), N(23), N(24) and N(21#2), N(22#2), N(23#2), N(24#2): 3.49 Å

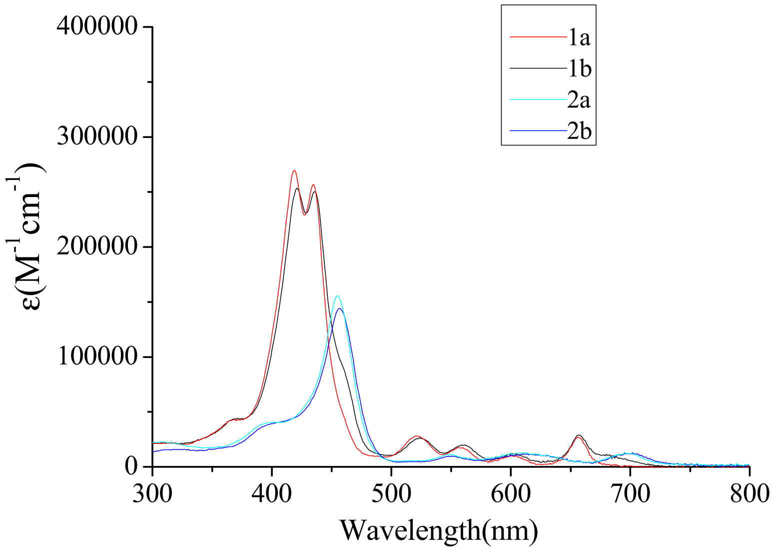


Figure S7. UV-visible absorption spectra of compounds 1**a**, 1**b,** 2**a** and 2**b** in CH_2Cl_2.

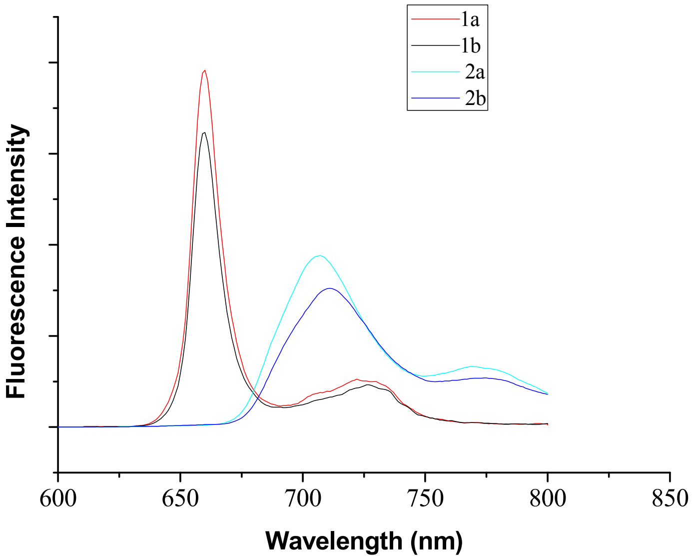


Figure S8. Fluorescence spectra of compounds 1**a**, 1**b,** 2**a** and 2**b** in toluene at room temperature. The excitation wavelength was 420, 422, 457 and 459 nm, respectively. The sample concentration was 2 × 10^{-7} mol/L.

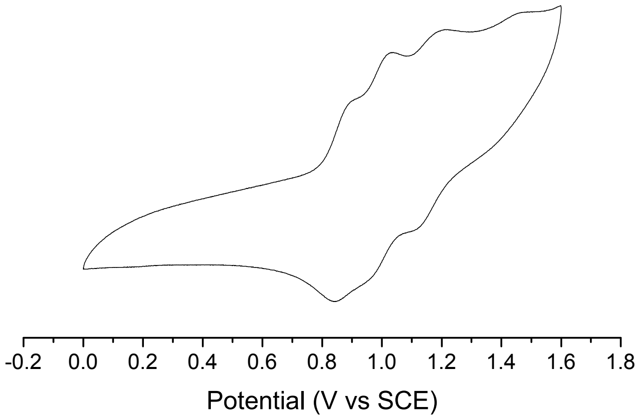


Figure S9. Cyclic voltammograms for **1a** as 1 mM solutions in CH_2Cl_2. The supporting electrolyte is tetra-n-butylammonium hexafluorophosphate (0.5 M). Scan rate 100 mV/s.

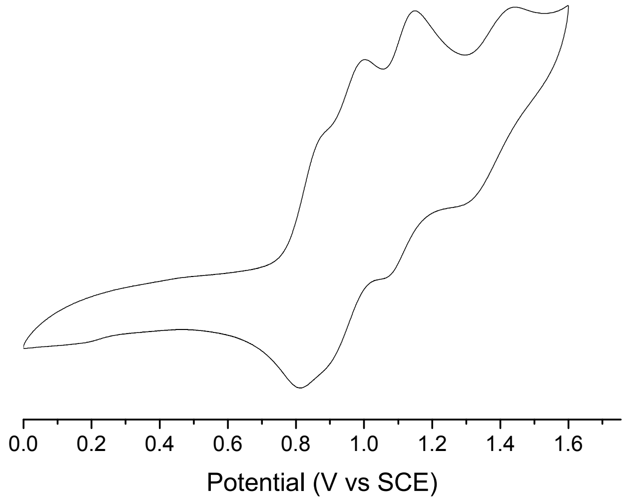
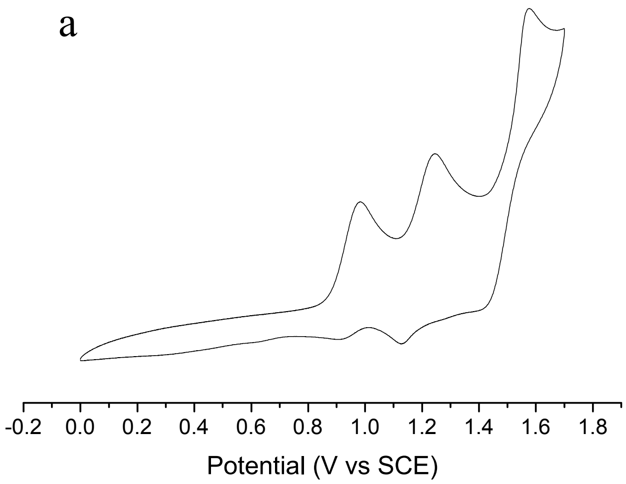


Figure S10. Cyclic voltammograms for **1b** as 1 mM solutions in CH_2Cl_2. The supporting electrolyte is tetra-n-butylammonium hexafluorophosphate (0.5 M). Scan rate 100 mV/s.



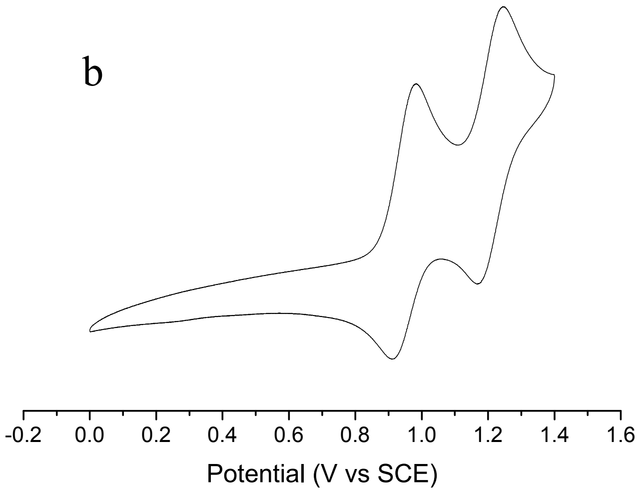


Figure S11. Cyclic voltammograms for **2a** as 1 mM solutions in CH_2Cl_2. The supporting electrolyte is tetra-n-butylammonium hexafluorophosphate (0.1 M). Scan rate 100 mV/s. a) 0-1700 mv; b) 0-1400 mv.

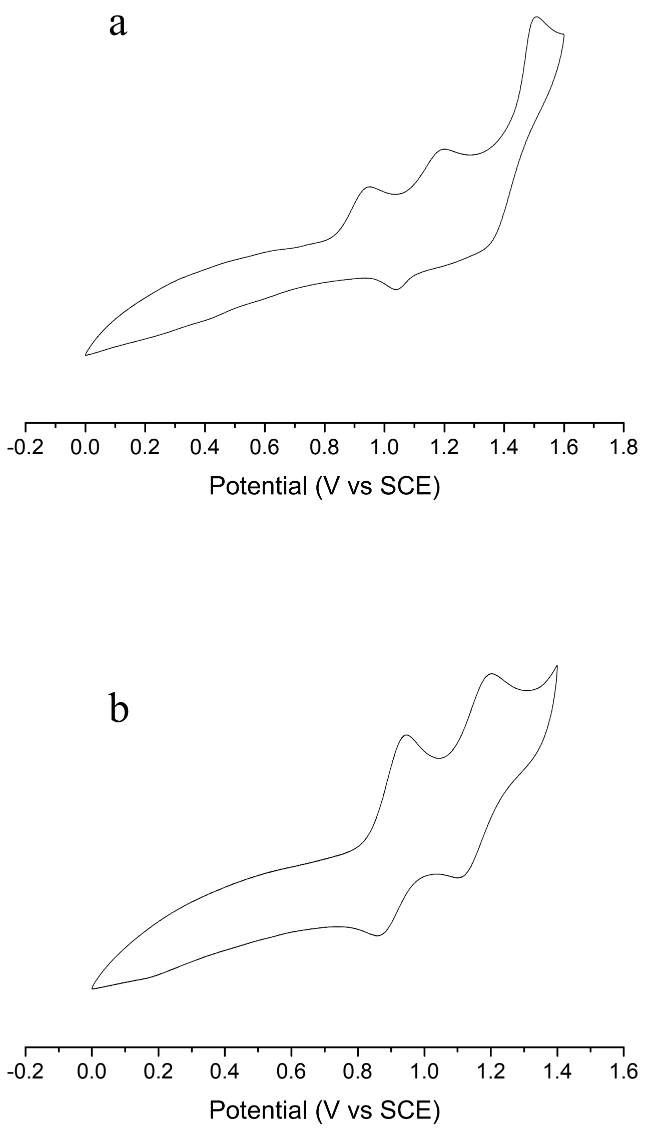


Figure S12. Cyclic voltammograms for **2b** as 1 mM solutions in CH_2Cl_2. The supporting electrolyte is tetra-n-butylammonium hexafluorophosphate (0.1 M). Scan rate 100 mV/s. a) 0-1700 mv; b) 0-1400 mv.