Electronic Supporting Information (ESI)

Porphyrins containing a tetraphenylethylene-substituted phenothiazine donor for fabricating efficient dye sensitized solar cells with high photovoltages

Jiazhi Zou[‡ a], Yunyu Tang[‡b], Glib Baryshnikov[c] Zhen Yang[a], Rui Mao[a], Weifang Feng[a], Jian Guan[a], Chengjie Li*[a], Yongshu Xie*[a]

[a] Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science & Technology, Shanghai 200237, P. R. China.

[b] Laboratory of Quality Safety and Processing for Aquatic Product, East China Sea Fisheries Research Institute, Chinese Academy of Fishery Sciences, Shanghai, 200090, P. R. China.

[c] Linköping University, Department of Science and Technology, Laboratory of Organic Electronics, Norrköping, SE - 60174 Sweden.

‡These authors contributed equally to the work.

*Email: yshxie@ecust.edu.cn; chengjie.li@ecust.edu.cn

Contents

1. Experiment Section

1.1. Materials and Reagent

All reagents and solvents were obtained from commercial sources and used without further purification unless otherwise noted. The TiO_2 paste (18NR-T and 18NR-AO) and FTO conducting glass (fluorine-doped SnO_2, transmission > 90% in the visible range, sheet resistance 15 Ω / square) were purchased from Advanced Election Technology Co. Ltd. The FTO conducting glass was washed with a detergent solution, deionized water, acetone, and ethanol successively under ultra-sonication for 30 min before use.

1.2. Equipment and Apparatus

^1H NMR and ^{13}C NMR spectra were obtained using a Bruker AM 400 spectrometer. FT-IR spectra were recorded in the region of 400−4000 cm^{-1} on a Thermo Electron Avatar 380 FT-IR instrument (ATR). HRMS measurements were performed using a Waters LCT Premier XE spectrometer. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was measured using a Shimadzu-Kratos model Axima CFR+ mass spectrometer using dithranol as the matrix. UV-Vis absorption spectra were recorded on a Varian Cary 100 spectrophotometer and a Varian Cray Eclipse fluorescence spectrophotometer. The cyclic voltammograms (CV) of the dyes were obtained in acetonitrile with a Versastat II electrochemical workstation (Princeton Applied Research) using 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte, the sensitizer attached to a nanocrystalline TiO_2 film deposited on the conducting FTO glass as the working electrode, a platinum wire as the counter electrode, and a silver chloride electrode in saturated KCl solution as the reference electrode. The scan rate was 50 $mV·s^{-1}$.

1.3. Synthetic details

Scheme S1 Synthetic routes for donor group.
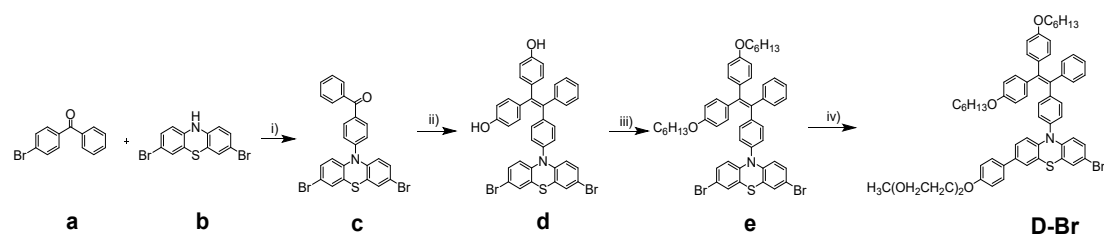
Reaction conditions: i) $Pd_2(dba)_3$, $^tBu_3P·HBF_4$, ^tBuONa, THF, reflux; ii) bis(4-hydroxyphenyl)methanone, Zn, $TiCl_4$, THF, reflux; iii) 1-bromohexane, K_2CO_3, DMF, 80 °C; iv) (4-(2-methoxyethoxy)phenyl)boronic acid, $Pd(PPh_3)_4$, K_2CO_3, THF/H_2O, reflux.
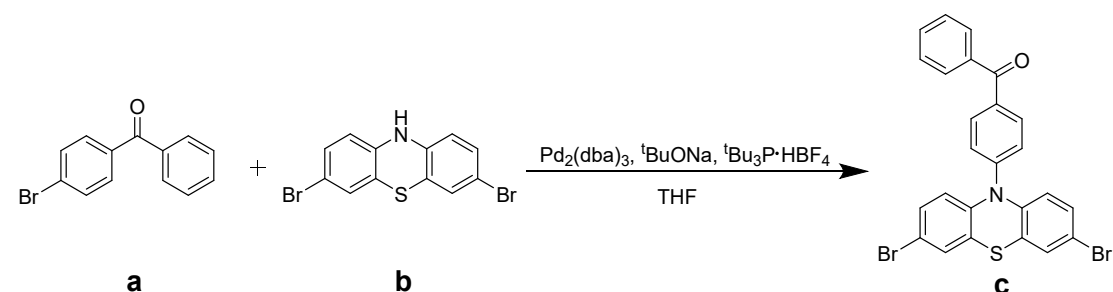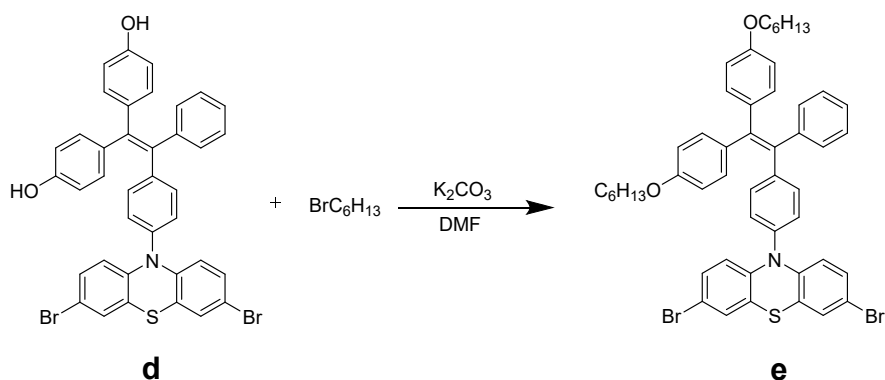

c: To a 250 mL Schlenk flask were added **a** (1.5 g, 5.6 mmol), **b** (1 g, 2.8 mmol), $Pd_2(dba)_3$ (77 mg, 0.08 mmol), $^tBu_3P·HBF_4$ (83 mg, 0.28 mmol), ^tBuONa (374 mg, 3.9 mmol) and THF (40 mL) under nitrogen. The mixture was stirred and heated to reflux for 12 h. After cooling to room temperature, the mixture was extracted with dichloromethane (DCM, 3×50 mL), and the organic layer was dried over Na_2SO_4.

Then the solvent was removed under vacuum and the residue was purified on a silica gel column using petroleum ether : ethyl acetate (PE:EA) = 10:1 as the eluent to give a yellow solid. Yield: 761 mg, 50%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, J = 8.6 Hz, 2H), 7.83 (d, J = 7.0 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 2.3 Hz, 2H), 7.15 (dd, J = 8.7, 2.3 Hz, 2H), 6.50 (d, J = 8.7 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 195.39, 145.58, 141.73, 137.37, 135.23, 132.65, 132.61, 130.14, 129.96, 129.93, 128.43, 126.75, 124.98, 121.08, 116.73. HRMS (EI, m/z). Calcd for C$_{25}$H$_{15}$Br$_2$NOS ([M]$^+$): 534.9241. Found: 534.9235. FT-IR (ATR, cm^{-1}): 3054 (w), 2951 (w), 2850 (w), 1731 (w), 1652 (m), 1596 (m), 1577 (m), 1503 (m), 1453 (s), 1377 (m), 1301 (m), 1272 (s), 1173 (m), 1146 (m), 1082 (m), 1018 (m), 917 (m), 841 (m), 800 (m), 738 (m), 697 (s), 673 (m), 576 (m), 534 (m), 480 (m). m.p. 54.2–56.4 °C.
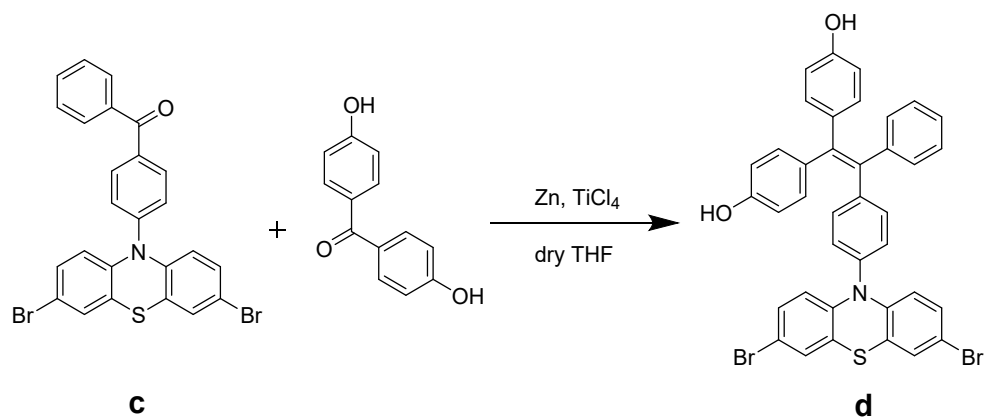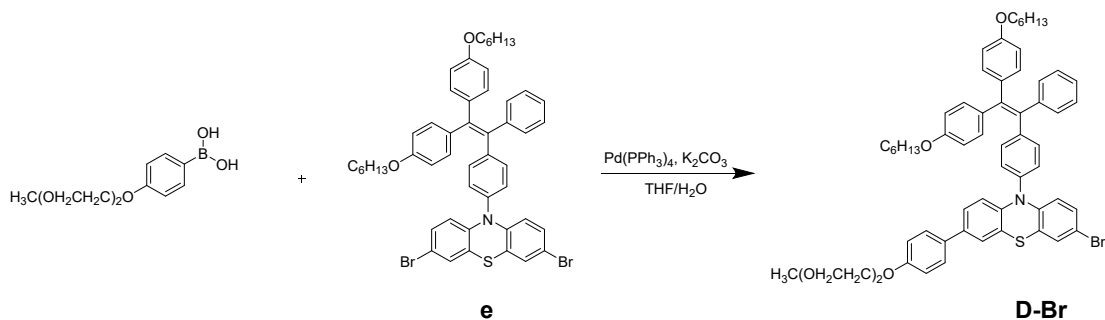

d: To a 250 mL Schlenk flask were added zinc powder (2.0 g, 30 mmol), TiCl$_4$ (0.33 mL, 3 mmol) and dry THF (10 mL) under nitrogen. The mixture was stirred at -15 ~ -10 °C for 2 h. Then the solution was kept stirring at room temperature for another 2 h for the next McMurry reaction without any purification.[1] Thus, a THF (10 mL) solution of **c** (400 mg, 0.75 mmol) and bis(4-hydroxyphenyl)methanone (240 mg, 1.1 mmol) was injected to the pre-prepared mixture *via* a syringe. The solution was stirred and heated to reflux for 12 h. After cooling to room temperature, the mixture was filtered through celite. Then the filtrate was extracted with DCM (3×50 mL). The organic layer was dried over Na$_2$SO$_4$. Then the solvent was removed under vacuum and the residue was purified on a silica gel column using PE:EA = 10:1 as the eluent to give a yellow solid 272 mg, yield 51%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.48 (s, 1H), 9.42 (s, 1H), 7.28 (d, J = 2.3 Hz, 2H), 7.24 – 7.19 (m, 4H), 7.17 – 7.15 (m, 3H), 7.15 – 7.13 (m, 2H), 7.11 – 7.08 (m, 2H), 6.83 (d, J = 8.6 Hz, 2H), 6.76 (d, J = 8.5 Hz, 2H), 6.55 (dd, J = 8.5, 5.6 Hz, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.76, 143.64, 142.76, 142.50, 136.57, 135.37, 133.68, 132.21, 131.98, 131.24, 130.72, 129.99, 129.49, 129.17, 128.29, 127.87, 125.89, 120.27, 117.03, 115.22, 114.97, 114.72, 113.99. HRMS (ESI, m/z). Calcd for C$_{38}$H$_{26}$Br$_2$NO$_2$S ([M + H]$^+$): 718.0051. Found: 718.0043. FT-IR (ATR, cm^{-1}): 3328 (m), 2922 (m), 2852 (m), 1886 (w), 1701 (m), 1656 (m), 1596 (m), 1506 (s), 1454 (s), 1375 (m), 1301 (m), 1235 (s), 1170 (s), 1098 (m), 1037 (m), 919 (m), 803 (s), 744 (m), 698 (s), 647 (m), 578 (m), 532 (m), 449 (m), 418 (m). m.p. 42.7–55.4 °C.

e: To a 250 mL Schlenk flask were added **d** (200 mg, 0.28 mmol), 1-bromohexane (0.1 mL, 0.7 mmol), K$_2$CO$_3$ (77 mg, 0.56 mmol) and DMF (10 mL) under nitrogen. The mixture was stirred and heated to 80

°C for 12 h. After cooling to room temperature, the mixture was extracted with EA (3×50 mL), and the organic layer was dried over Na_2SO_4. Then the solvent was removed under vacuum and the residue was purified on a silica gel column using PE:EA = 20:1 as the eluent to give a yellow oil. Yield: 201 mg, 81%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25 (d, J = 9.3 Hz, 2H), 7.19 – 7.11 (m, 5H), 7.06 (d, J = 2.3 Hz, 2H), 7.03 (d, J = 8.3 Hz, 2H), 6.99 – 6.90 (m, 6H), 6.64 (dd, J = 8.8, 6.8 Hz, 4H), 5.94 (d, J = 8.8 Hz, 2H), 3.92 – 3.85 (m, 4H), 1.79 – 1.70 (m, 4H), 1.49 – 1.39 (m, 4H), 1.36 – 1.29 (m, 8H), 0.93 – 0.86 (m, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 158.01, 157.98, 145.51, 143.30, 143.06, 141.80, 137.99, 137.54, 135.91, 135.26, 134.00, 132.70, 132.52, 131.24, 129.82, 129.68, 128.70, 127.97, 126.47, 121.05, 117.01, 114.59, 113.62, 113.43, 67.99, 67.86, 31.64, 29.29, 25.77, 22.63, 14.09. HRMS (ESI, m/z). Calcd for $C_{50}H_{50}Br_2NO_2S$ ([M + H]$^+$): 886.1929. Found: 886.1924. FT-IR (ATR, cm^{-1}): 2954 (m), 2922 (m), 2853 (m), 1727 (m), 1604 (m), 1507 (m), 1461 (m), 1363 (m), 1340 (m), 1243 (m), 1177 (m), 1121 (m), 1076 (m), 1019 (m), 964 (m), 891 (m), 828 (m), 746 (m), 700 (m), 644 (m), 616 (m), 530 (m), 443 (m).

D-Br: In a 250 mL Schlenk flask were added **e** (201 mg, 0.23 mmol), (4-(2-methoxyethoxy)phenyl)boronic acid (60 mg, 0.27 mmol), Pd(PPh$_3$)$_4$ (13 mg, 0.01 mmol) and 2 M aqueous K_2CO_3 (313 g, 23 mmol) solution were refluxed in THF (10 mL) for 12 h under nitrogen. After cooling to room temperature, the mixture was extracted with DCM (3×50 mL). The organic layer was dried over Na_2SO_4.Then the solvent was removed under reduced pressure and the residue was purified on a silica gel column using EA:PE = 1:4 as the eluent to give a yellow oil. Yield: 102 mg, 34%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38 (d, J = 8.8 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.19 – 7.12 (m, 6H), 7.10 – 7.07 (m, 2H), 7.04 (dd, J = 8.6, 2.1 Hz, 1H), 7.00 – 6.91 (m, 8H), 6.65 (d, J = 8.6 Hz, 4H), 6.15 (d, J = 8.6 Hz, 1H), 5.95 (d, J = 8.8 Hz, 1H), 4.19 – 4.15 (m, 2H), 3.92 – 3.84 (m, 6H), 3.76 – 3.71 (m, 2H), 3.61 – 3.57 (m, 2H), 3.40 (s, 3H), 1.78 – 1.70 (m, 4H), 1.45 – 1.39 (m, 4H), 1.35 – 1.26 (m, 8H), 0.93 – 0.85 (m, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 158.17, 157.99, 157.94, 145.22, 143.41, 143.30, 142.46, 141.65, 138.11, 137.96, 135.95, 135.38, 135.34, 133.89, 132.71, 132.54, 132.42, 131.27, 129.95, 129.42, 128.71, 128.11, 127.94, 127.31, 126.73, 126.42, 125.15, 124.60, 121.63, 119.28, 116.91, 116.12, 114.91, 114.20, 113.62, 113.46, 71.97, 70.78, 69.78, 67.86, 67.49, 59.13, 59.11, 31.63, 29.28, 25.76, 25.74, 22.62, 22.58, 14.07. HRMS (ESI, m/z). Calcd for $C_{61}H_{65}BrNO_5S$ ([M + H]$^+$): 1002.3767. Found: 1002.3768. FT-IR (ATR, cm^{-1}): 3033 (w), 2924 (m), 2865 (m), 1602 (m), 1504 (m), 1459 (s), 1382 (m), 1286 (m), 1239 (s), 1173 (m), 1107 (s), 1060 (m), 1023 (m), 922 (m), 831 (m), 808 (m), 748 (m), 696 (m), 636 (m), 613 (m), 573 (m), 542 (m), 513 (m), 430 (m).

1.4. Fabrication of the DSSCs

The procedure for preparation of TiO$_2$ electrodes and fabrication of the sealed cells for photovoltaic measurements were adapted from that reported by Grätzel and coworkers.[2] The photoelectrode was made by a screen-printed double layer of TiO$_2$ particles. A 12 μm thick film of 13 nm sized TiO$_2$ particles was first printed on the FTO conducting glass, which was kept in a clean box for 10 minutes, and then dried at 130 °C over 5 min, and further coated with a second layer of 5 μm thick 400 nm sized light-scattering anatase particles. Finally, the electrodes coated with the TiO$_2$ pastes were gradually sintered in a muffle furnace at 275 °C for 5 min, at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min and at 500 °C for 15 min, respectively. The size of the TiO$_2$ film was 0.12 cm^2. These films were immersed into a 40 mM aqueous TiCl$_4$ solution at 70 °C for 30 min, washed with deionized water and ethanol, and then heated again at 450 °C for 30 min. The films were then immersed into 0.2 mM solutions of the **XW71** and **XW72** in a mixture of toluene and ethanol (1/4, v/v) and 0.2 mM solutions of the porphyrin dyes **XW73** in a mixture of chloroform and ethanol (3/2, v/v) at 25 °C for 12 h. For coadsorption, the films were immersed into 0.2 mM solutions of the porphyrin dyes with various concentrations of CDCA at 25

°C for 12 h. For cosensitization, the films were immersed into 0.2 mM solutions of the porphyrin dyes with various concentrations of CDCA at 25 °C for 12 h, washed with ethanol, dried in air, and then immersed in a 0.3 mM solution of the co-sensitizer **XC3** in ethanol at 25 °C for the indicated time. The counter electrode was prepared according to the procedure reported in our previous work. Finally, the DSSCs were assembled, with an iodine electrolyte. The electrolyte containing 0.1 M LiI, 0.05 M I_2, 0.6 M 1-methyl-3-propyl-imidazolium iodide (PMII) and 0.5 M 4-(tert-butyl)pyridine (TBP) in CH_3CN.

1.5. Theoretical calculations

We employed density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations to optimize the ground state geometries and the frontier molecular orbital profiles of the **XW71** and **XW43**, using the hybrid B3LYP functional and the 6-31G* basis set.[3-4] Considering the similar structures of **XW71–XW73**, the theoretical calculations of **XW72** and **XW73** were not performed.

1.6. Photovoltaic behavior measurements

Photovoltaic measurements were performed by employing an AM 1.5 solar simulator equipped with a 300 W xenon lamp (model no. 91160, Oriel). The power of the simulated light was calibrated to 100 mW·cm^{-2} using a Newport Oriel PV reference cell system (model 91150 V). J–V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a model 2400 source meter (Keithley Instruments, Inc. USA). The voltage step and delay time of the photocurrent were 10 mV and 40 ms, respectively. Action spectra of the incident monochromatic photon-to-electron conversion efficiency (IPCE) for the solar cells were obtained with a Newport-74125 system (Newport Instruments). The intensity of monochromatic light was measured with a Si detector (Newport-71640). The electrochemical impedance spectroscopy (EIS) measurements of all the DSSCs were performed using a Zahner IM6e Impedance Analyzer (ZAHNER-Elektrik GmbH & CoKG, Kronach, Germany), with the frequency range of 100 mHz – 1 MHz and the alternative signal of 100 mV. The ZSimpWin software was used to fit the experimental EIS data of the DSSCs.

2. Energy levels of the molecular orbitals

Table S1. Electrochemical data and frontier orbital levels of the porphyrin dyes.

dye	HOMO[a]/V (vs NHE)	E_{0-0}[b]/V	LUMO[c]/V (vs NHE)
XW71	0.81	1.89	−1.08
XW72	0.81	1.90	−1.09
XW73	0.85	1.90	−1.05

[a] The HOMO levels were measured by cyclic voltammetry, see the experimental section for more details. [b] E_{0-0} was obtained from the equation of $E_{0-0} = 1240/\lambda_{inter}$, where λ_{inter} is the intersection point of the emission and the normalized absorption spectra (Figure S3). [c] The LUMO levels were calculated by subtracting E_{0-0} from the HOMO.

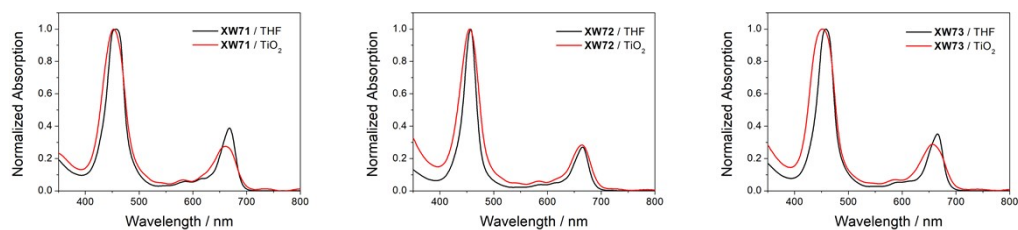## 3. Photovoltaic performance of the DSSCs based on the organic dyes

XC3
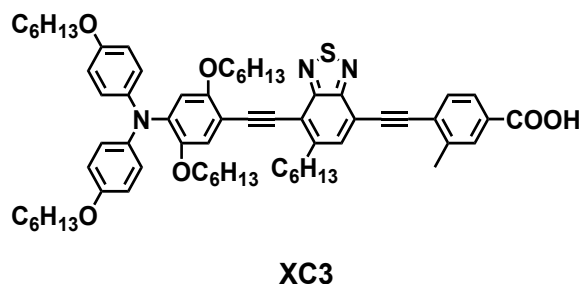
Figure S1. Molecular structure of **XC3**[5].

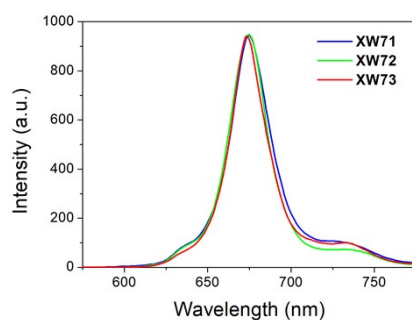**Table S2.** The photovoltaic performance of the DSSCs based on **XC3**.

Dye[*]	V_{oc} [V]	J_{sc} [mA·cm^{-2}]	Fill Factor [%]	PCE [%]
XC3	0.763 ± 0.002	16.95 ± 0.09	69.96 ± 0.15	9.05 ± 0.14

[*] The data were reported in our previous work.[5]

4. Emission and UV-vis spectra

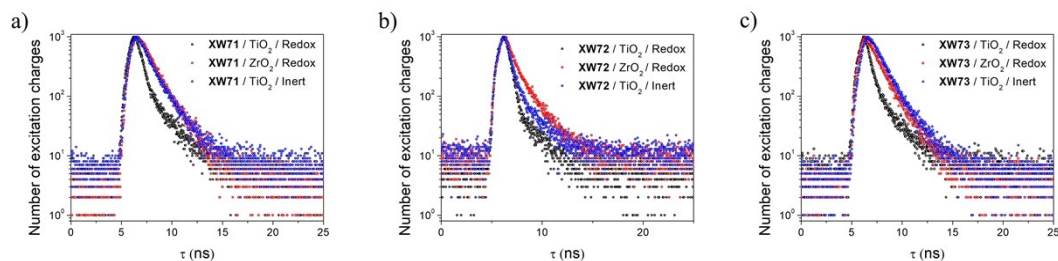**Figure S2.** Normalized absorption spectra of **XW71**–**XW73** in THF and on the TiO$_2$ films (3 μm).

Figure S3. Emission spectra of **XW71**–**XW73** in THF.

5. Cyclic voltammetry curves
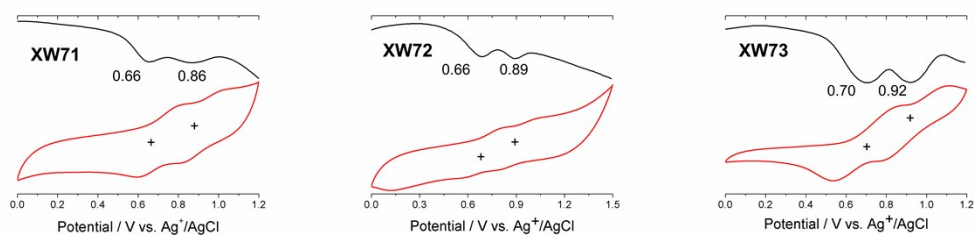
Figure S4. Cyclic voltammetry and differential pulse voltammetry curves of **XW71**–**XW73** adsorbed on the TiO$_2$ films.

6. PL decay traces

Figure S5. PL decay traces of dye-grafted TiO$_2$ films immersed in an iodine electrolyte and in an inert electrolyte as well as dye-grafted ZrO$_2$ films immersed in an iodine electrolyte. Excitation wavelength: 520 nm, emission wavelength 680 nm. (a) **XW71**; (b) **XW72**; (c) **XW73**.

Table S3. Injection and regeneration time and efficiencies for DSSCs based on **XW71–XW73**.

dye	$\tau_{\text{TiO}_2/\text{redox}}^{a}$ (ns)	$\tau_{\text{ZrO}_2/\text{redox}}^{b}$ (ns)	$\tau_{\text{TiO}_2/\text{inert}}^{c}$ (ns)	φ_{inj}^{d}	φ_{reg}^{e}
XW71	0.21	2.76	2.93	92%	93%
XW72	0.21	2.01	2.27	90%	91%
XW73	0.24	2.63	2.47	91%	90%

[a] In the presence of a redox mediator and grafted on TiO$_2$ films. [b] In the redox mediator and grafted on ZrO$_2$ films. [c] In the inert electrolyte and grafted on TiO$_2$ films. [d] φ_{inj} was estimated from the equation of $\varphi_{\text{inj}} = 1-(\tau_{\text{TiO}_2/\text{redox}}/\tau_{\text{ZrO}_2/\text{redox}})$. [e] φ_{reg} was estimated from the equation of $\varphi_{\text{reg}} = 1-(\tau_{\text{TiO}_2/\text{redox}}/\tau_{\text{TiO}_2/\text{inert}})$.

7. Nyquist plots and estimated charge collection efficiencies of the devices based on XW71-XW73
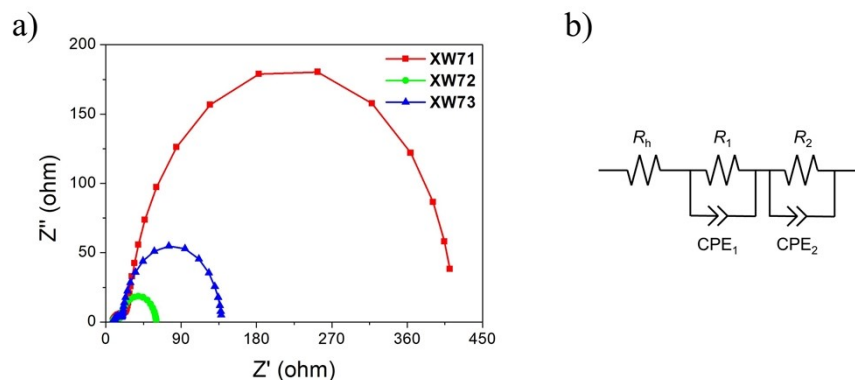
Figure S6. EIS Nyquist a) and equivalent circuit b) for the devices based on **XW71-XW73** measured at -0.75 V in the dark.

Table S4. Charge collection efficiencies estimated from the EIS plots at a bias potential of -0.75 V.

dye	$R_{\text{tr}}/\Omega\cdot\text{cm}^{-2}$	$R_{\text{rec}}/\Omega\cdot\text{cm}^{-2}$	η_{cc}
XW71	15.5	387.1	96%
XW72	8.2	43.7	84%
XW73	9.7	119.5	92%

R_{tr}: transport resistance at counter electrode. R_{rec}: charge recombination resistance. η_{cc} was estimated by $\eta_{\text{cc}} = (1+R_{\text{tr}}/R_{\text{rec}})^{-1}$

8. Photovoltaic parameters

Table S5. The dye loading amounts for the cells based on individual dyes.

Dyes	Dye Loading Amount [10^{-7} mol/cm^2]
XW71	1.67
XW72	1.37
XW73	1.40

Table S6. Photovoltaic parameters of the **XW72** based DSSCs using electrolytes with various concentrations of Li$^+$.

Electrolytes*	V_{oc} [V]	J_{sc} [mA·cm^{-2}]	Fill Factor [%]	PCE [%]
0.1 M LiI + 0.6 M PMII	0.772 ± 0.009	19.23 ± 0.23	69.23 ± 0.21	10.3 ± 0.2
0.2 M LiI + 0.5 M PMII	0.770 ± 0.005	19.36 ± 0.47	69.55 ± 0.13	10.4 ± 0.2
0.5 M LiI + 0.2 M PMII	0.768 ± 0.004	19.38 ± 0.45	68.47 ± 0.48	10.2 ± 0.1

* The concentration of PMII was adjusted to maintain the constant total concentration of I$^-$ at 0.7 M.

Table S7. The photovoltaic data for the porphyrin dyes with different concentrations of CDCA.

Dyes*	V_{oc} [V]	J_{sc} [mA·cm^{-2}]	Fill Factor [%]	PCE [%]	Dye Loading Amount [10^{-7} mol/cm^2]
XW71 [a]	0.770 ± 0.004	20.59 ± 0.13	71.22 ± 0.12	11.3 ± 0.2	1.52
XW71 [b]	0.780 ± 0.002	20.55 ± 0.10	70.89 ± 0.05	11.4 ± 0.4	1.47
XW71 [c]	0.771 ± 0.009	20.45 ± 0.05	71.05 ± 0.11	11.2 ± 0.4	1.33
XW72 [a]	0.779 ± 0.007	19.23 ± 0.11	70.14 ± 0.12	10.5 ± 0.1	1.22
XW72 [b]	0.768 ± 0.005	19.05 ± 0.08	69.33 ± 0.05	10.1 ± 0.2	1.13
XW72 [c]	0.759 ± 0.003	18.90 ± 0.13	70.22 ± 0.04	10.1 ± 0.1	1.05
XW73 [a]	0.780 ± 0.004	19.85 ± 0.14	71.68 ± 0.12	11.0 ± 0.2	1.33
XW73 [b]	0.789 ± 0.003	19.83 ± 0.13	71.44 ± 0.17	11.2 ± 0.3	1.25
XW73 [c]	0.785 ± 0.012	19.76 ± 0.05	71.55 ± 0.09	11.1 ± 0.1	1.19

* The photovoltaic data are the averaged values of three parallel cells. The TiO$_2$ electrode was dipped in 0.2 mM of the porphyrin dye with [a] 1 mM CDCA; [b] 2 mM CDCA; [c] 3 mM CDCA for 12 h, then rinsed with ethanol.

Table S8. Photovoltaic parameters of the porphyrin sensitized solar cells with simultaneous coadsorption and cosensitization.

Dyes*	V_{oc} [V]	J_{sc} [mA·cm^{-2}]	Fill Factor [%]	PCE [%]
XW71 [a]	0.767 ± 0.005	20.65 ± 0.11	73.22 ± 0.15	11.6 ± 0.2
XW71 [b]	0.777 ± 0.004	21.13 ± 0.17	73.89 ± 0.25	12.1 ± 0.3
XW71 [c]	0.773 ± 0.003	20.35 ± 0.15	73.55 ± 0.31	11.5 ± 0.1
XW72 [a]	0.770 ± 0.008	19.89 ± 0.13	73.14 ± 0.23	11.2 ± 0.1
XW72 [b]	0.775 ± 0.002	20.21 ± 0.05	72.33 ± 0.15	11.3 ± 0.3
XW72 [c]	0.763 ± 0.001	20.01 ± 0.19	72.22 ± 0.11	11.0 ± 0.1
XW73 [a]	0.777 ± 0.001	20.34 ± 0.11	74.68 ± 0.22	11.8 ± 0.1
XW73 [b]	0.780 ± 0.010	21.21 ± 0.10	74.44 ± 0.11	12.3 ± 0.4
XW73 [c]	0.781 ± 0.002	20.76 ± 0.07	74.55 ± 0.39	12.1 ± 0.3

* The photovoltaic data are the averaged values of three parallel cells. The TiO$_2$ electrode was first dipped in 0.2 mM of the porphyrin dye with 2 mM CDCA (XW71 and XW73) or 1 mM CDCA (XW72) for 12 h, rinsed with ethanol, and then immersed in a 0.3 mM of XC3 in ethanol for [a] 1.5 h, [b] 2 h, [c] 2.5 h, then rinsed with ethanol.
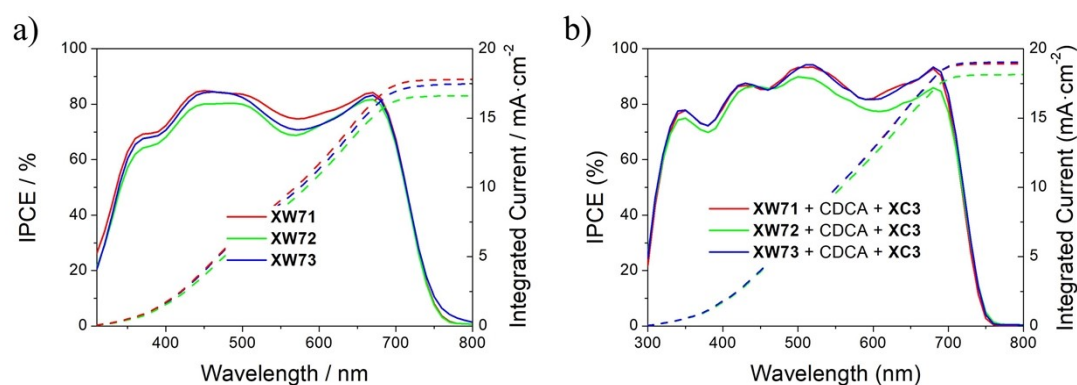
Table S9. The dye loading amounts for the simultaneously coadsorbed and cosensitized solar cells.

| Devices	Porphyrin dyes [10^{-7} mol·cm^{-2}]	XC3 [10^{-7} mol·cm^{-2}]
XW71 + CDCA + **XC3**	0.55	0.99
XW72 + CDCA + **XC3**	0.45	0.85
XW43 + CDCA + **XC3**	0.66	1.02

Dyes dipped with 2 mM CDCA (**XW71**, **XW73**) or 1 mM CDCA (**XW72**) and then 0.3 mM **XC3**.

9. J-V characteristics and IPCE action spectra

Figure S7. IPCE spectra of (a) **XW71**-**XW73** and (b) **XW71** (12 h) + 2 mM CDCA + 0.3 mM **XC3** (2 h), **XW72** (12 h) + 1 mM CDCA + 0.3 mM **XC3** (2 h), **XW73** (12 h) + 2 mM CDCA + 0.3 mM **XC3** (2 h) and their corresponding integrated current curves (dashed line).

10. Chemical capacitance and electron lifetimes
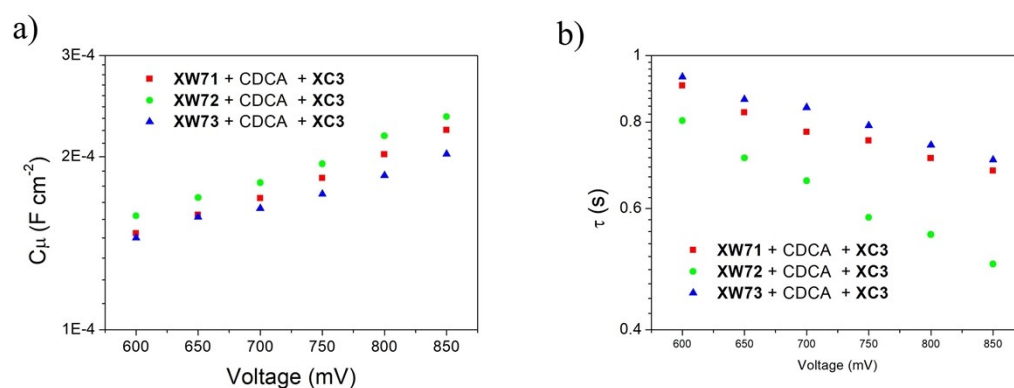
Figure S8. Plots of (a) C_μ and (b) τ versus potential bias for DSSCs based on **XW71** (12 h) + 2 mM CDCA + 0.3 mM **XC3** (2 h), **XW72** (12 h) + 1 mM CDCA + 0.3 mM **XC3** (2 h), **XW73** (12 h) + 2 mM CDCA + 0.3 mM **XC3** (2 h).

11. Characterization spectra for the compounds
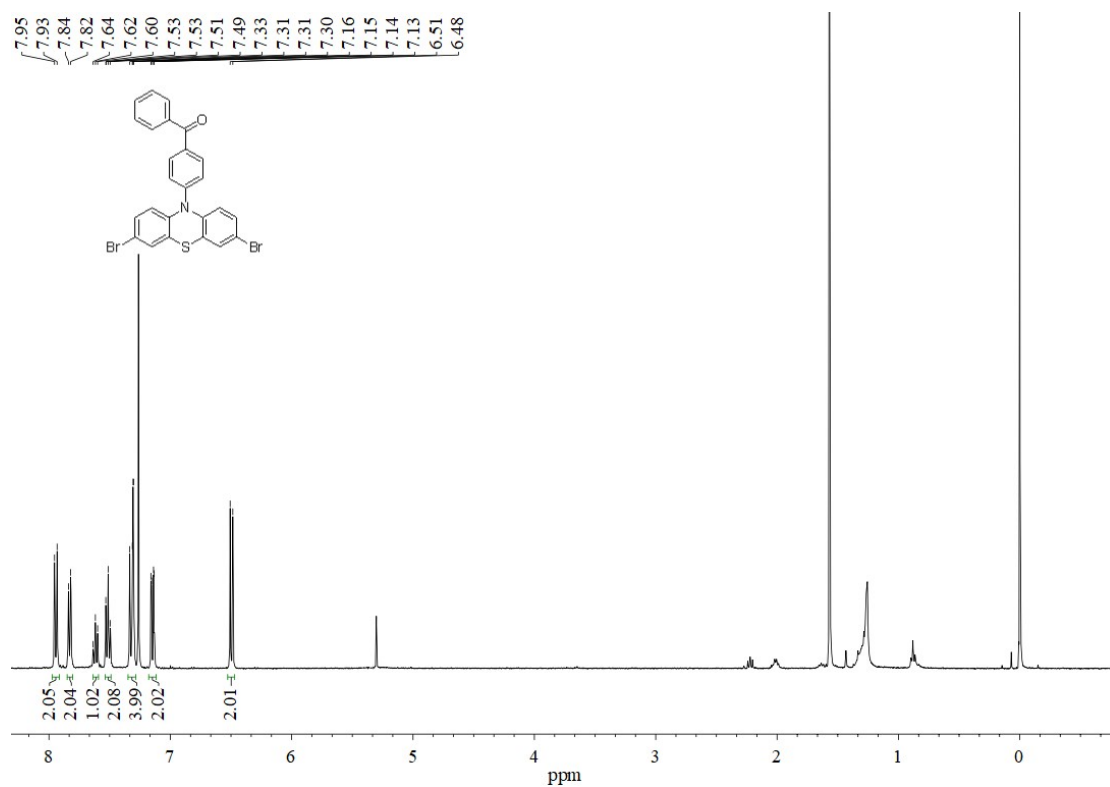
Figure S9. The ^{1}H NMR spectrum of **c** in CDCl$_3$.
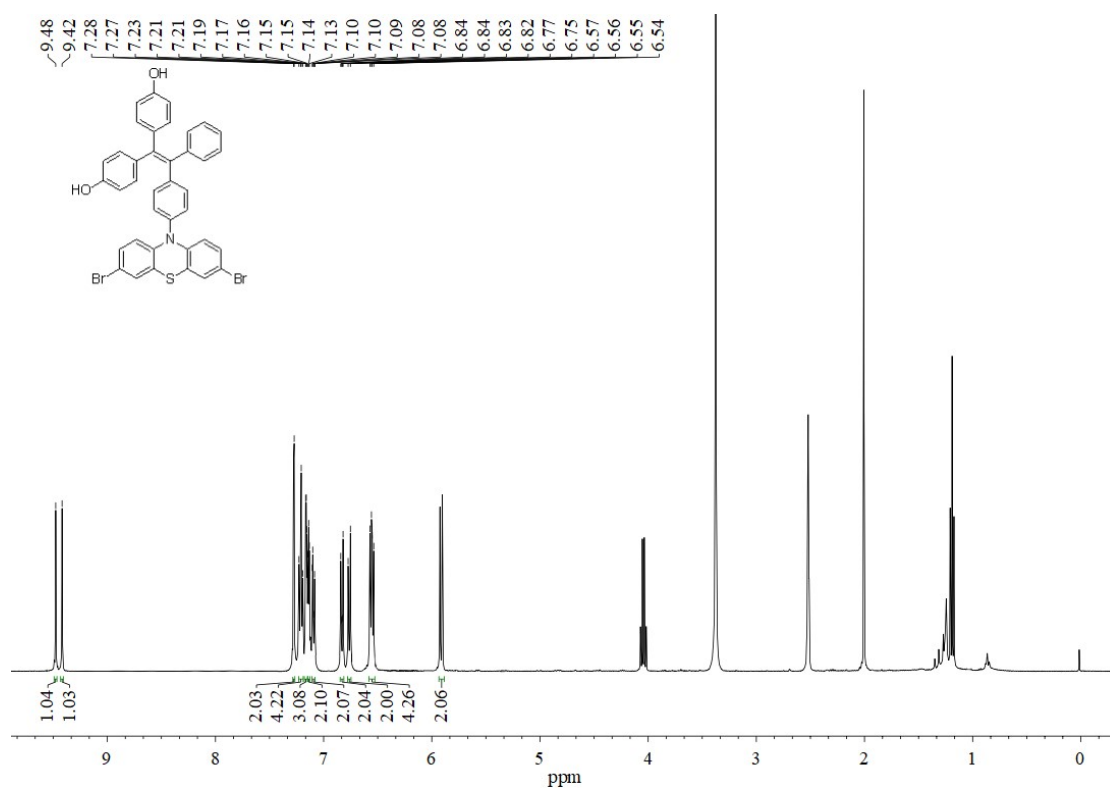
Figure S10. The ^{1}H NMR spectrum of **d** in DMSO-d_6.
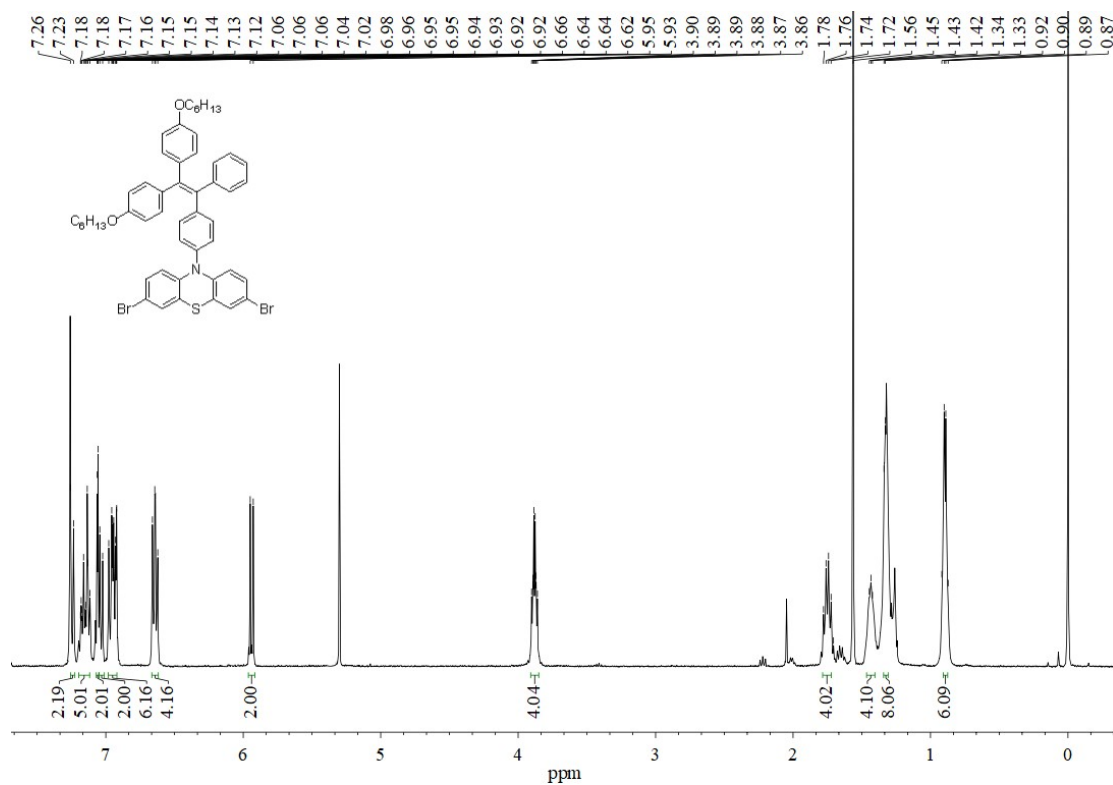
Figure S11. The ^{1}H NMR spectrum of **e** in CDCl$_3$.
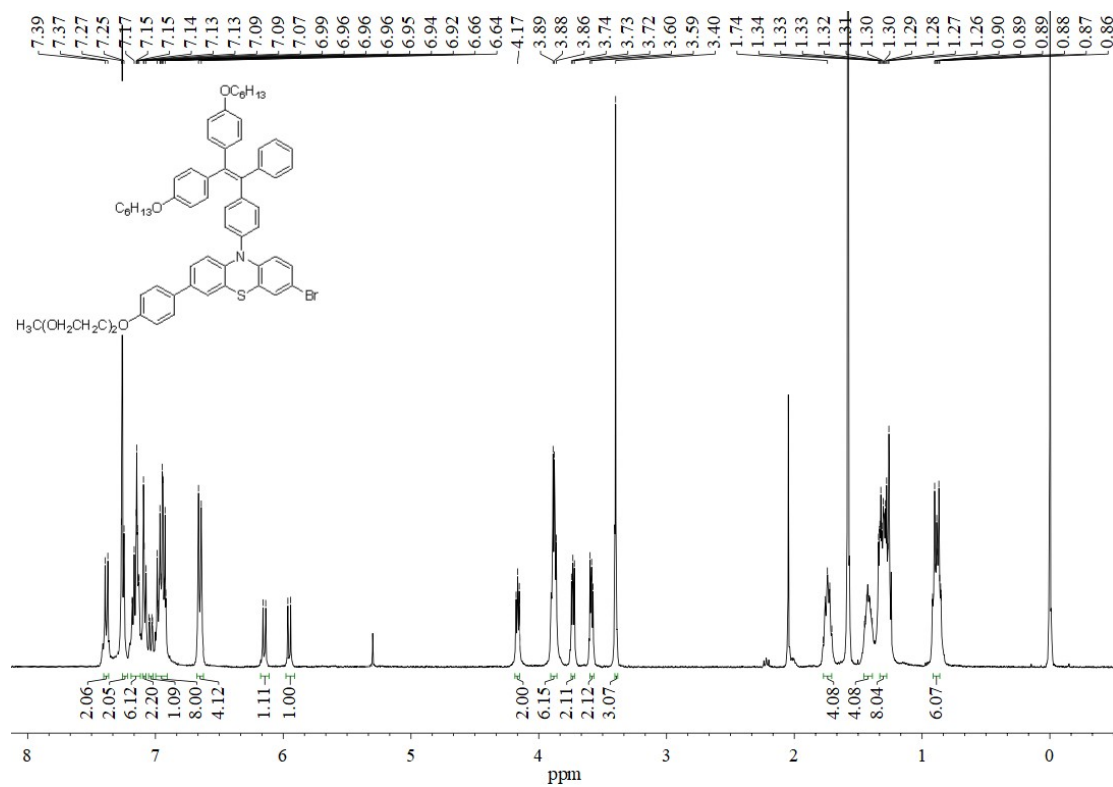
Figure S12. The ^{1}H NMR spectrum of **D-Br** in CDCl$_3$.
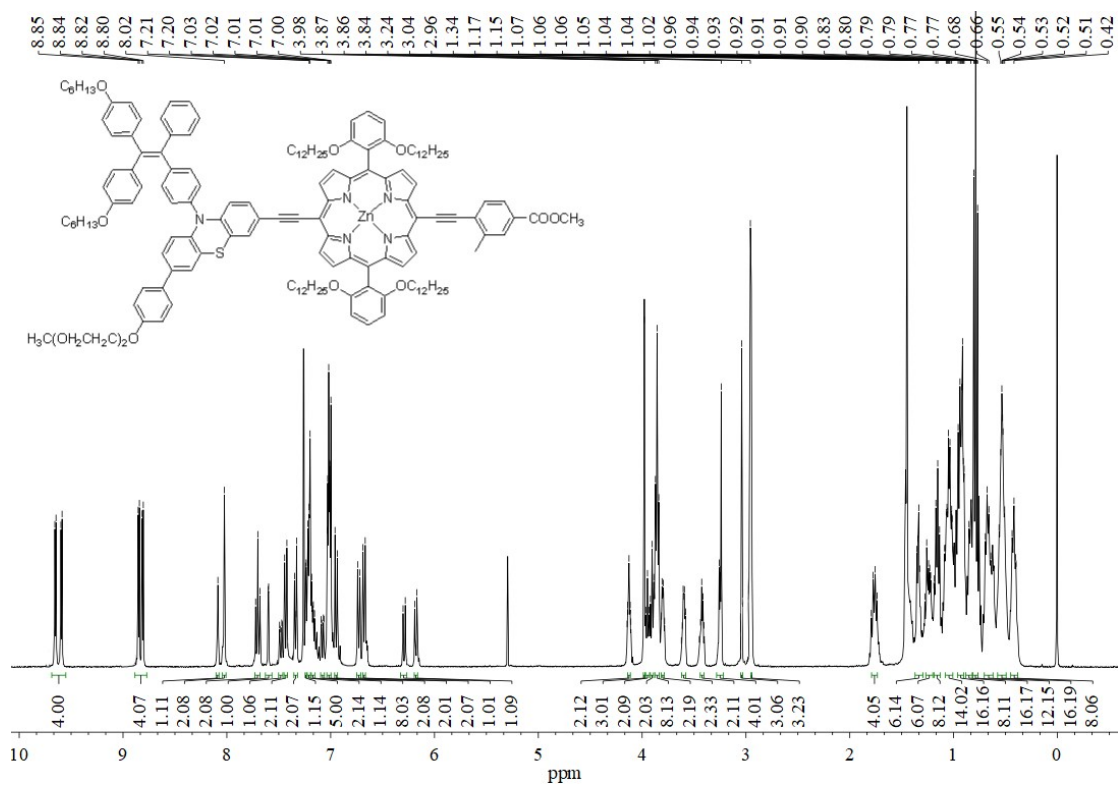
Figure S13. The ^{1}H NMR spectrum of **2a** in CDCl$_3$.
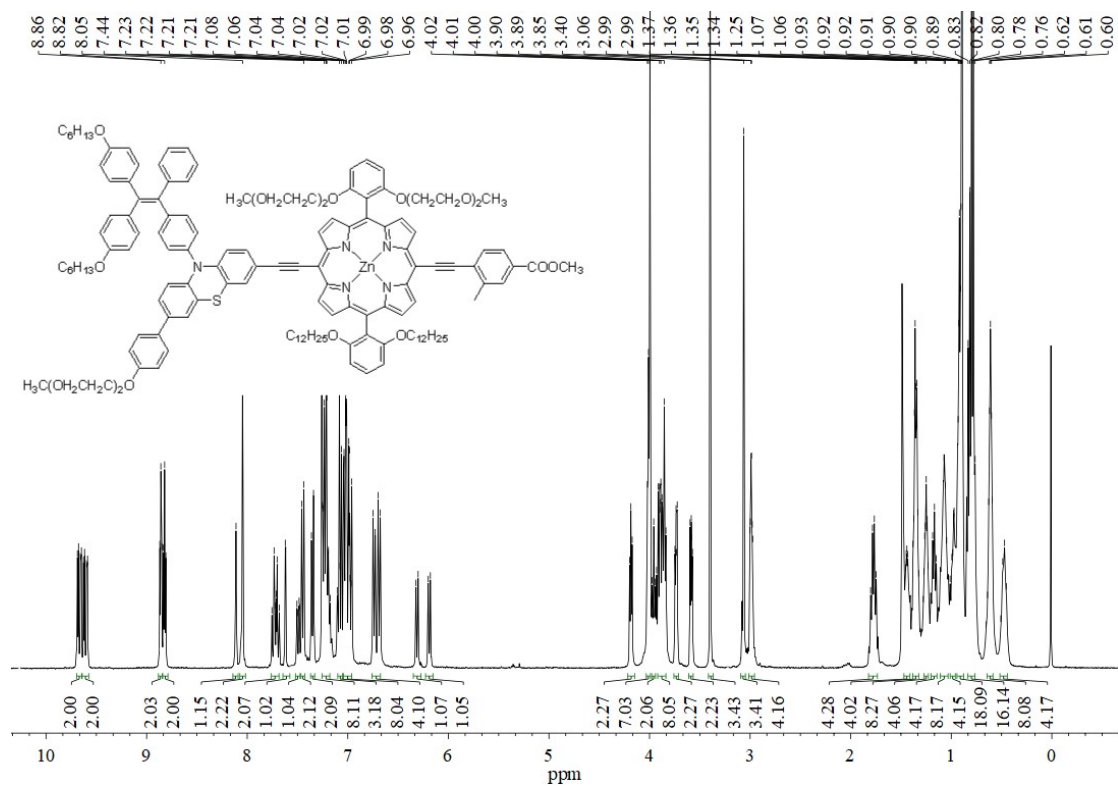
Figure S14. The ^{1}H NMR spectrum of **2b** in CDCl$_3$.
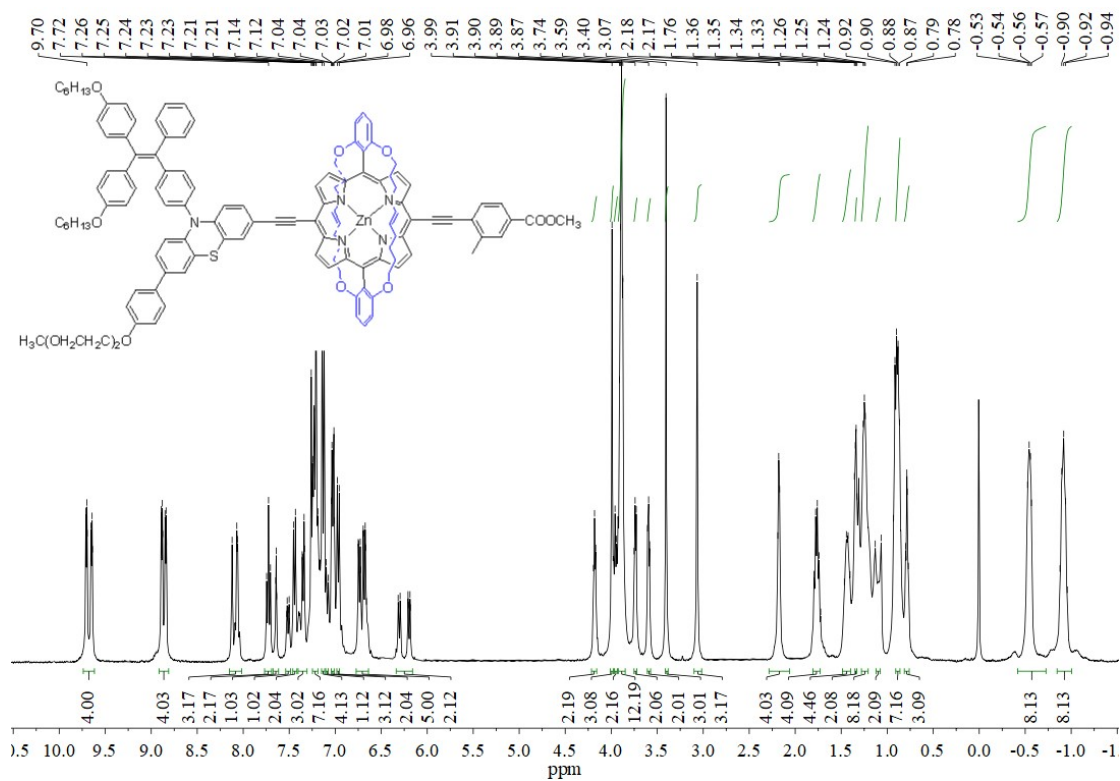
Figure S15. The ^{1}H NMR spectrum of **2c** in CDCl$_3$.
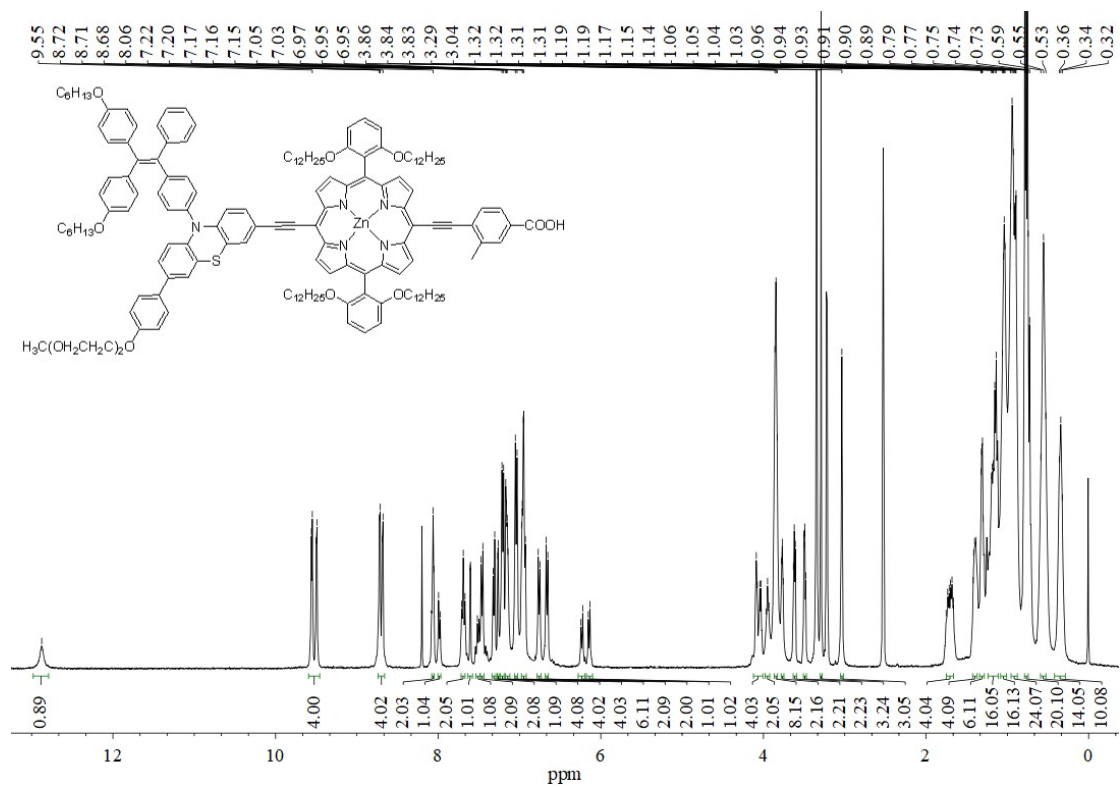
Figure S16. The ^{1}H NMR spectrum of **XW71** in a mixture of DMSO-d_6 and CDCl$_3$ (2:1).
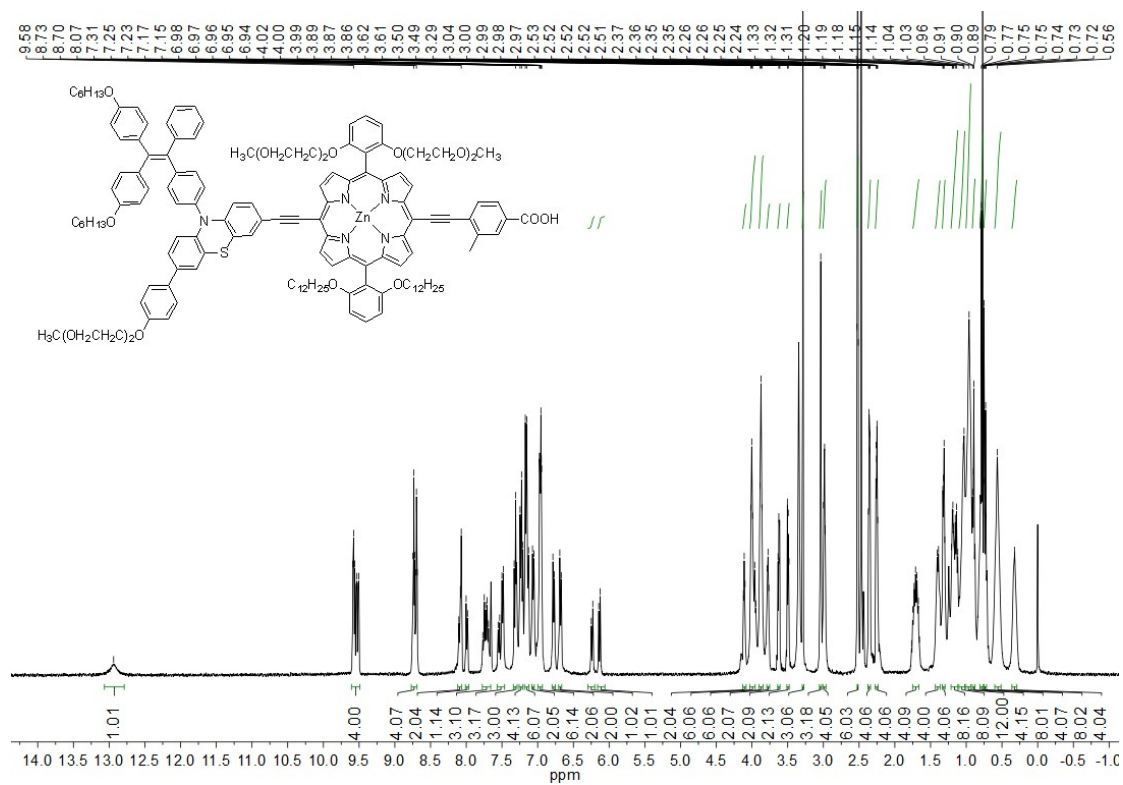
Figure S17. The ^{1}H NMR spectrum of **XW72** in a mixture of DMSO-d_6 and CDCl$_3$ (2:1).
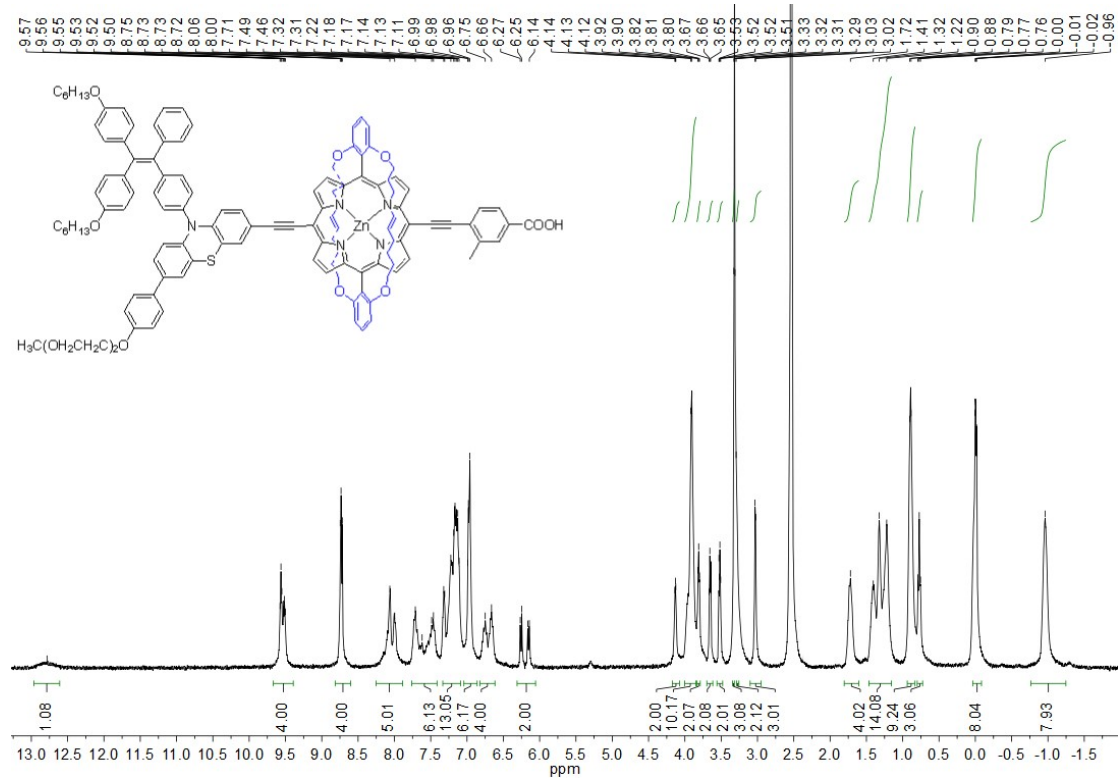
Figure S18. The ^{1}H NMR spectrum of **XW73** in a mixture of DMSO-d_6 and CDCl$_3$ (2:1).
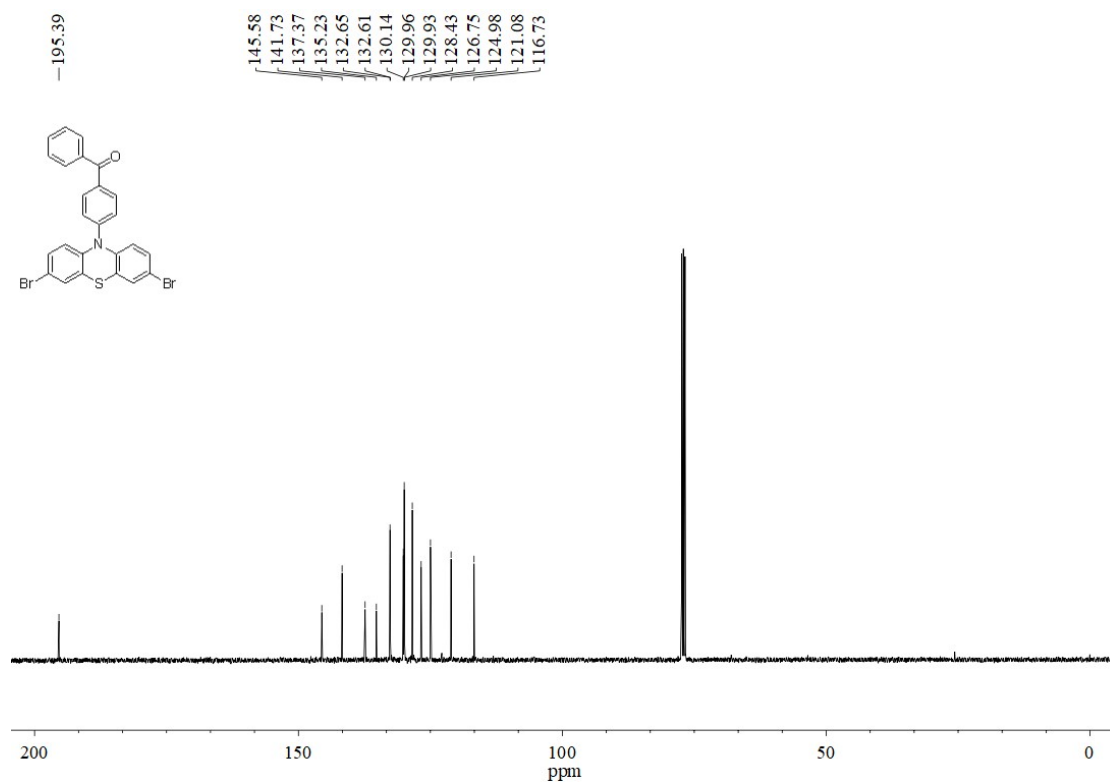
Figure S19. The ^{13}C NMR spectrum of **c** in CDCl$_3$.
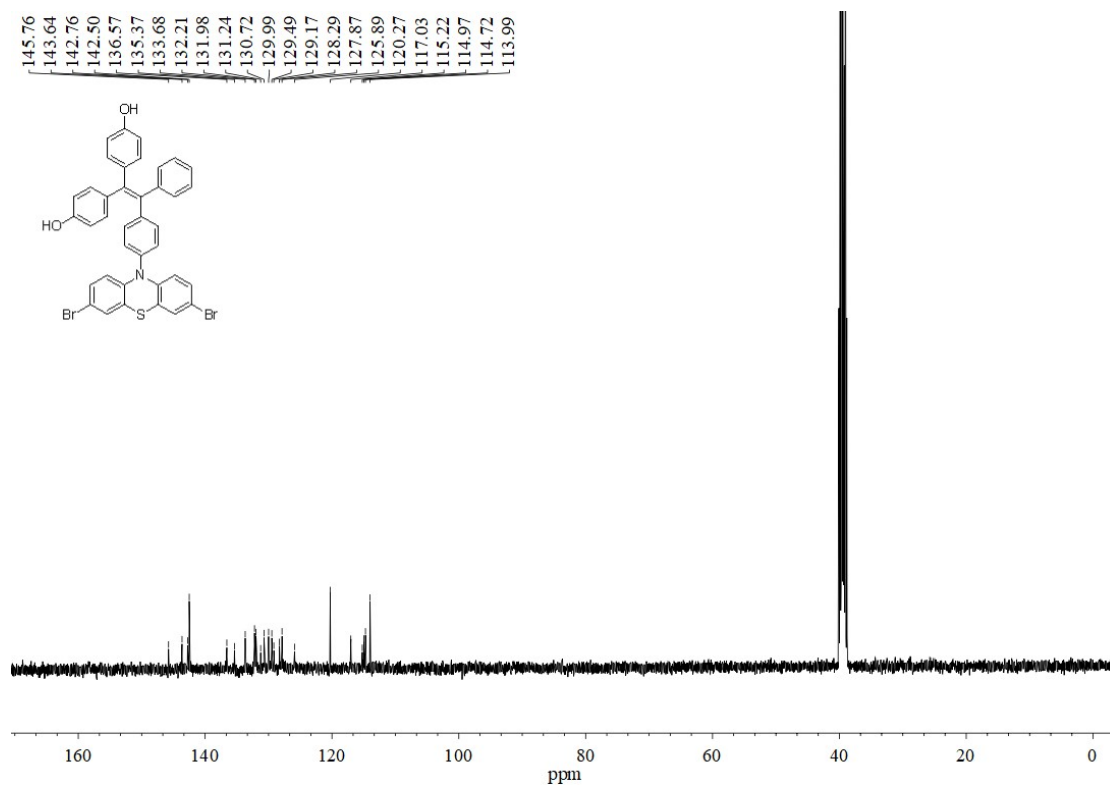
Figure S20. The ^{13}C NMR spectrum of **d** in DMSO-d_6.
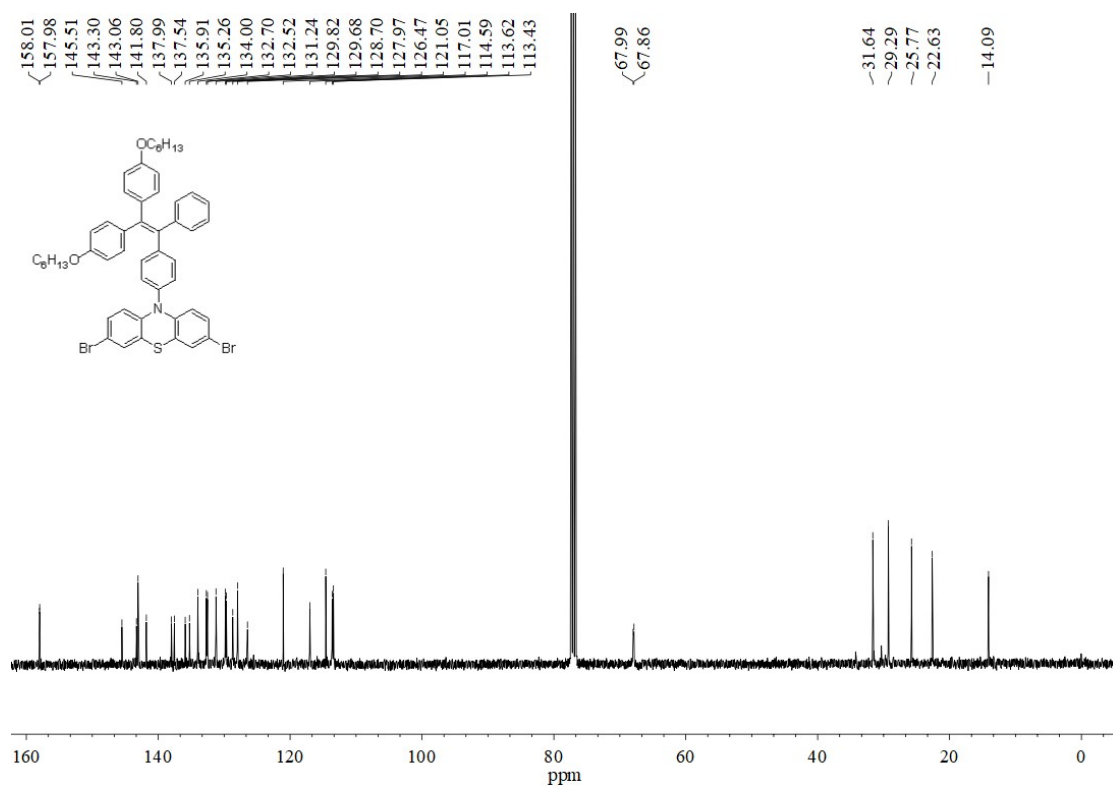
Figure S21. The ^{13}C NMR spectrum of **e** in CDCl$_3$.
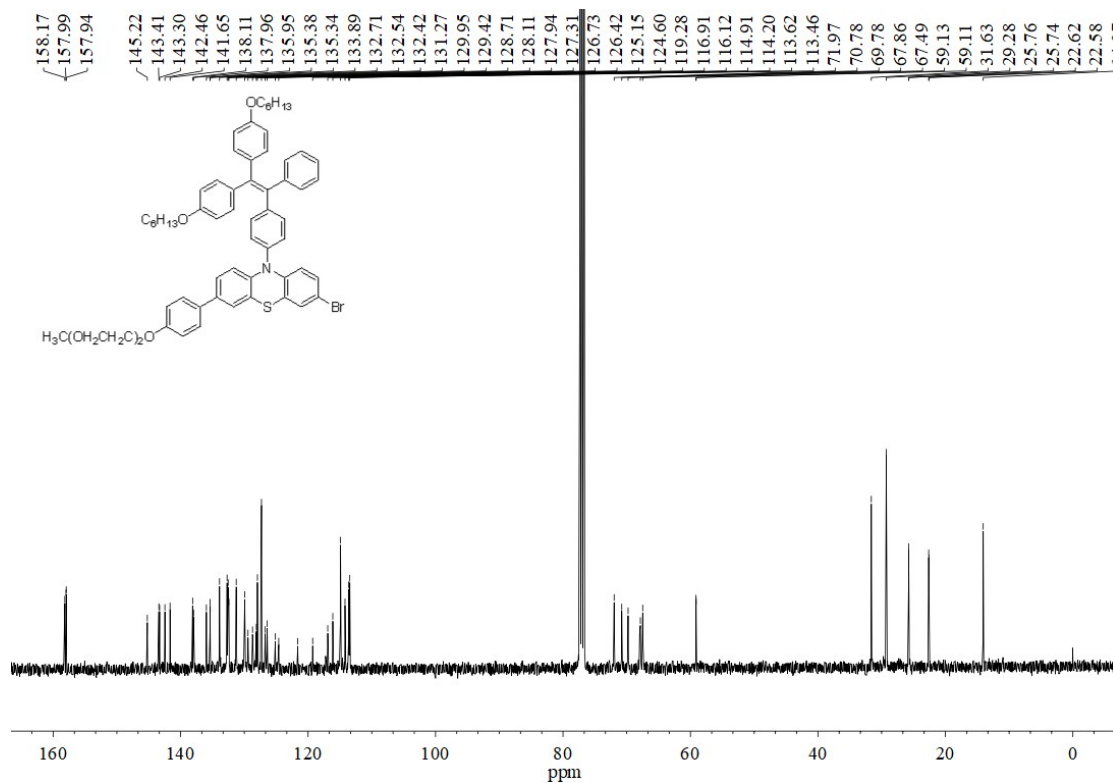
Figure S22. The ^{13}C NMR spectrum of **D-Br** in CDCl$_3$.
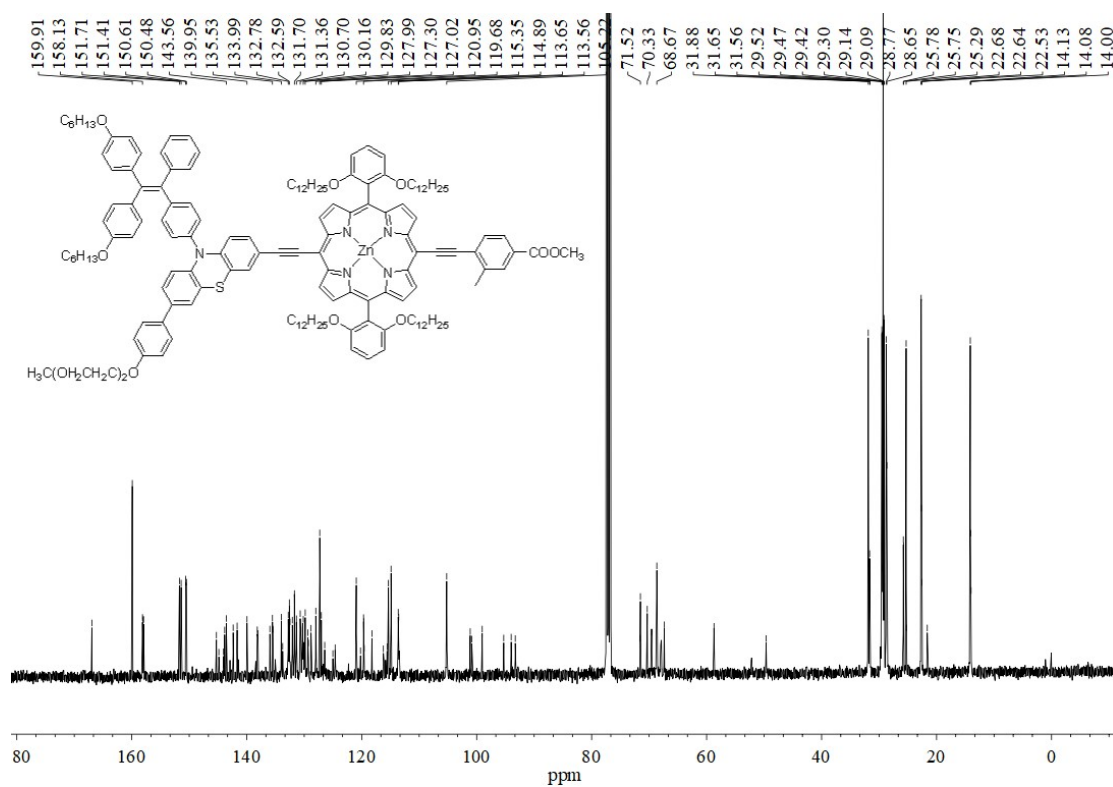
Figure S23. The ^{13}C NMR spectrum of **2a** in CDCl$_3$.
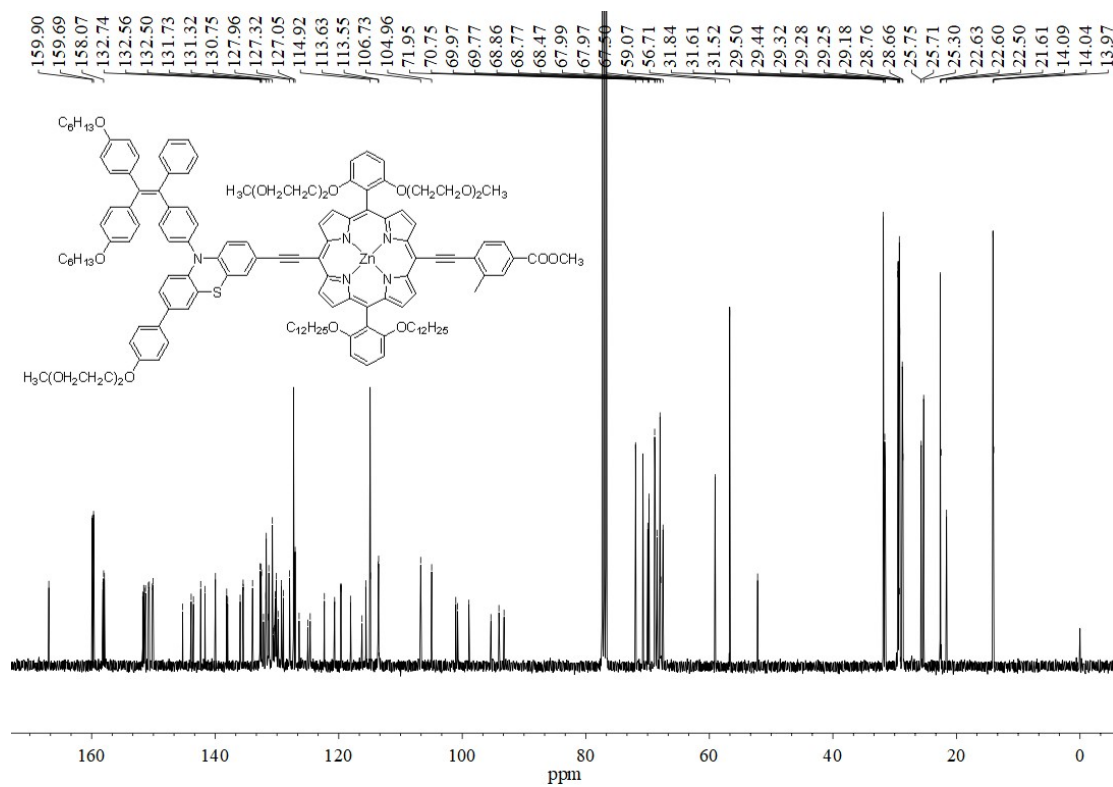
Figure S24. The ^{13}C NMR spectrum of **2b** in CDCl$_3$.
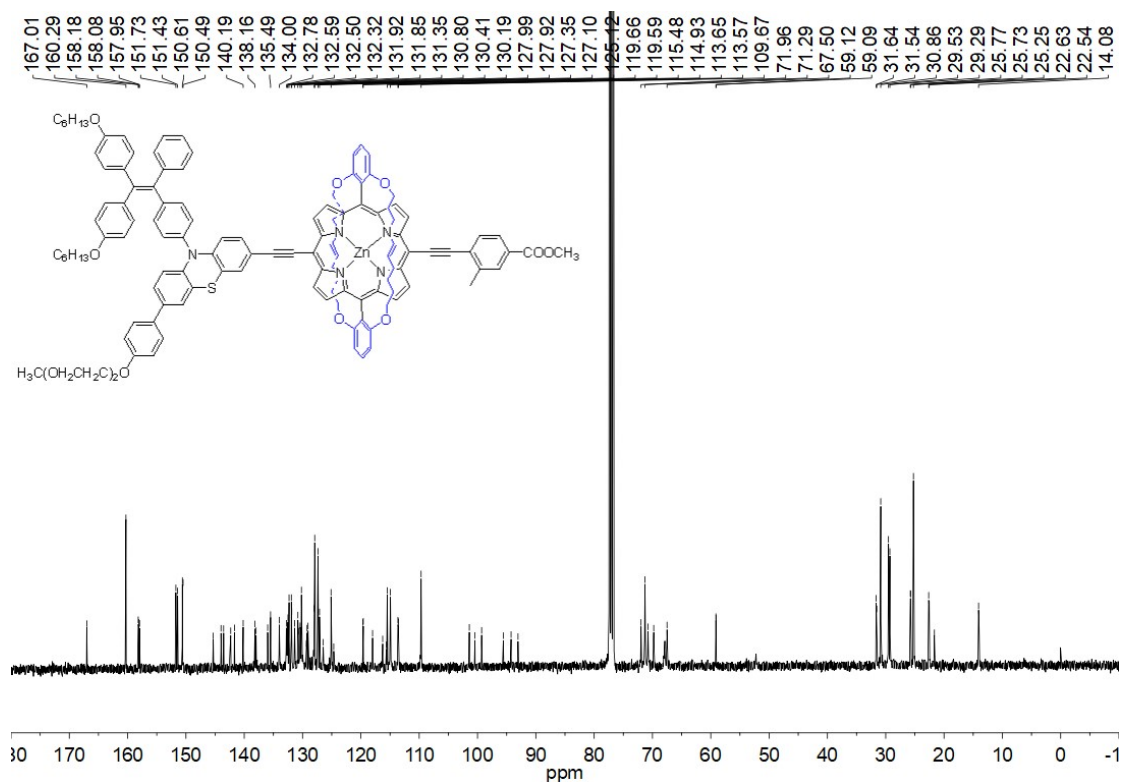
Figure S25. The ^{13}C NMR spectrum of **2c** in CDCl$_3$.
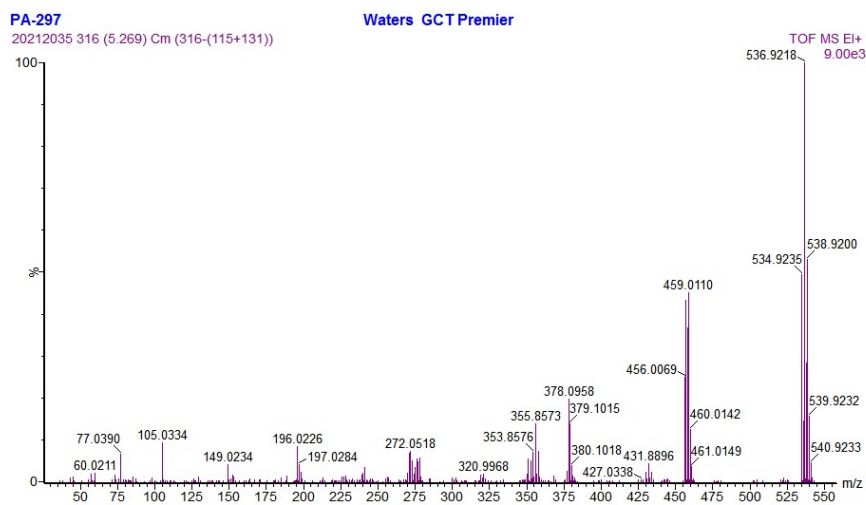
Figure S26. HRMS of **c**.
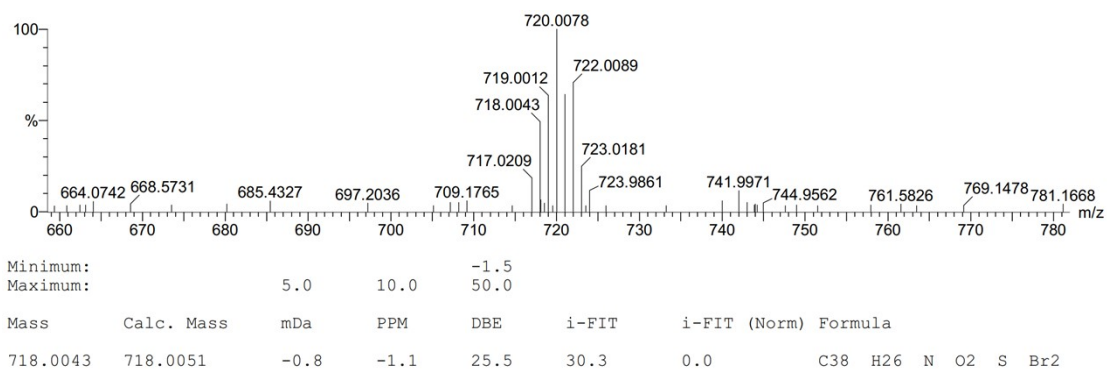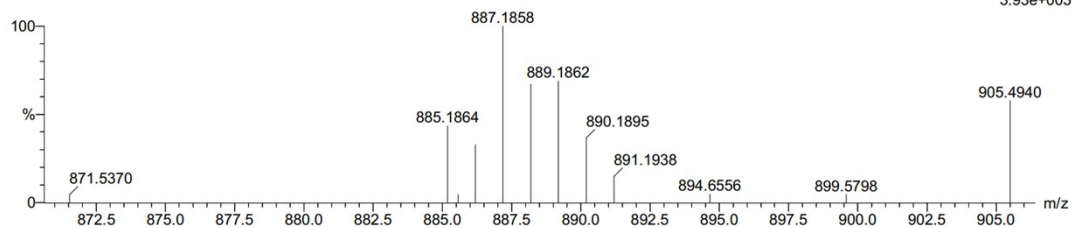
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
718.0043	718.0051	-0.8	-1.1	25.5	30.3	0.0	C38 H26 N O2 S Br2	

Figure S27. HRMS of **d**.
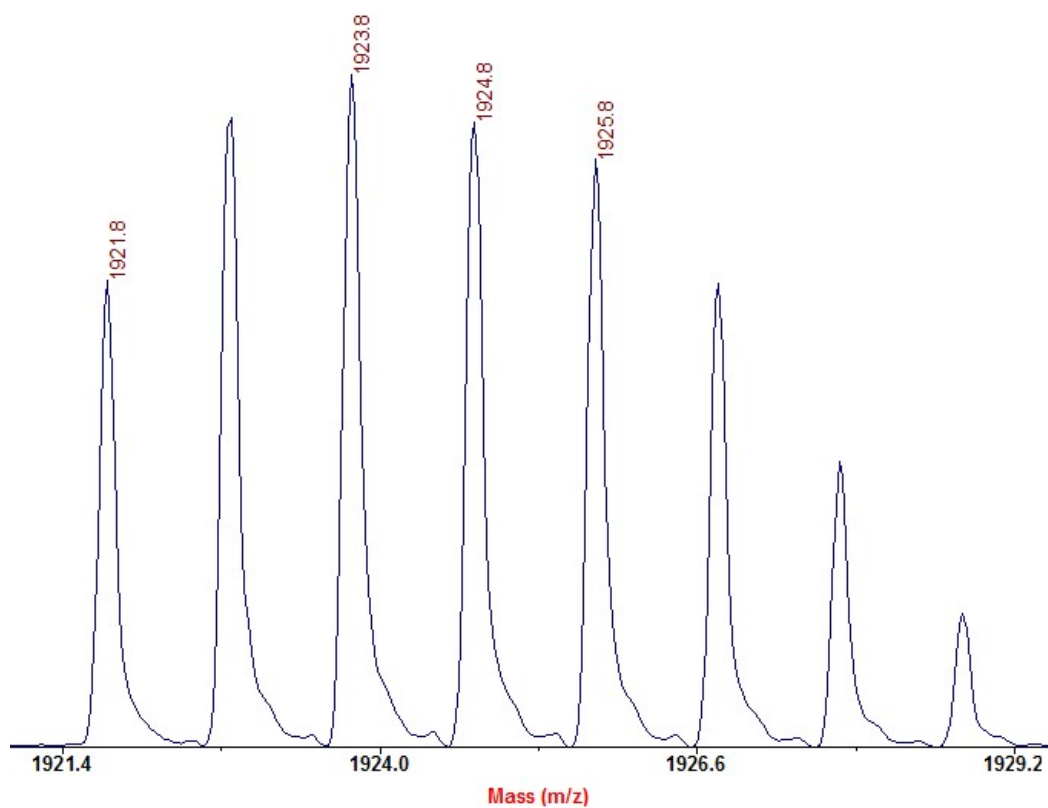
Figure S28. HRMS of **e**.

Figure S29. HRMS of **D-Br**.
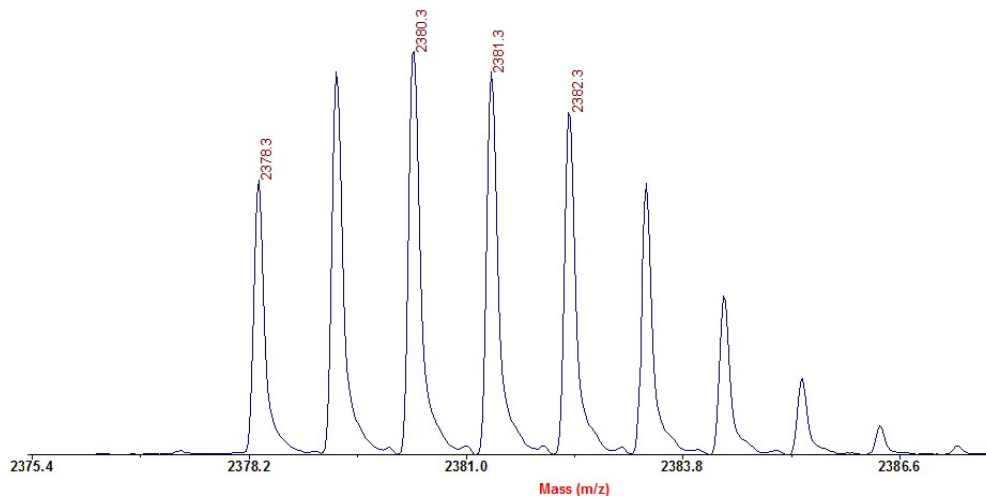
Figure S30. MALDI-TOF MS of **2a**.
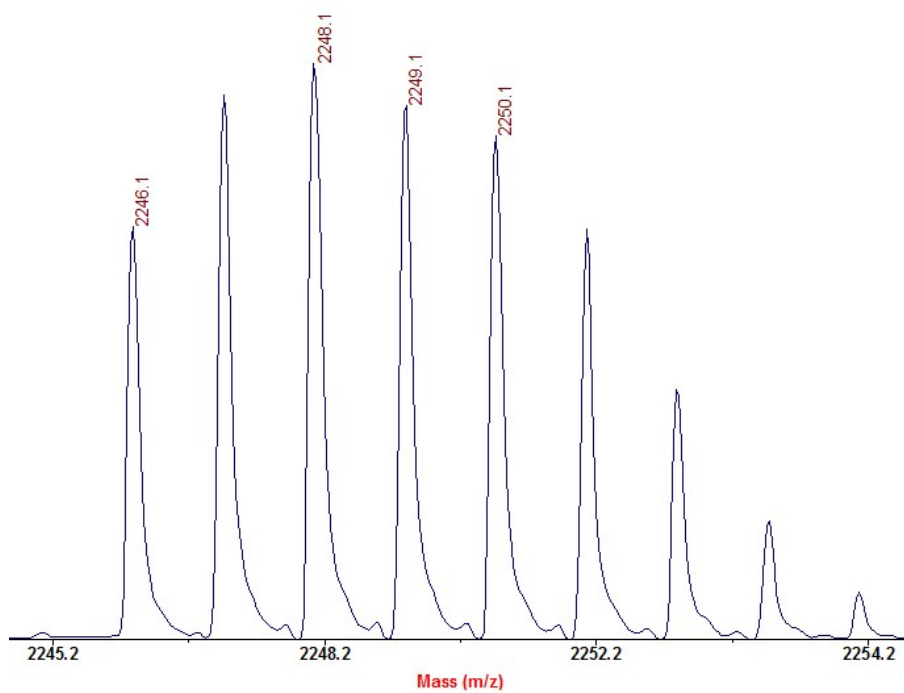
Figure S31. MALDI-TOF MS of **2b**.
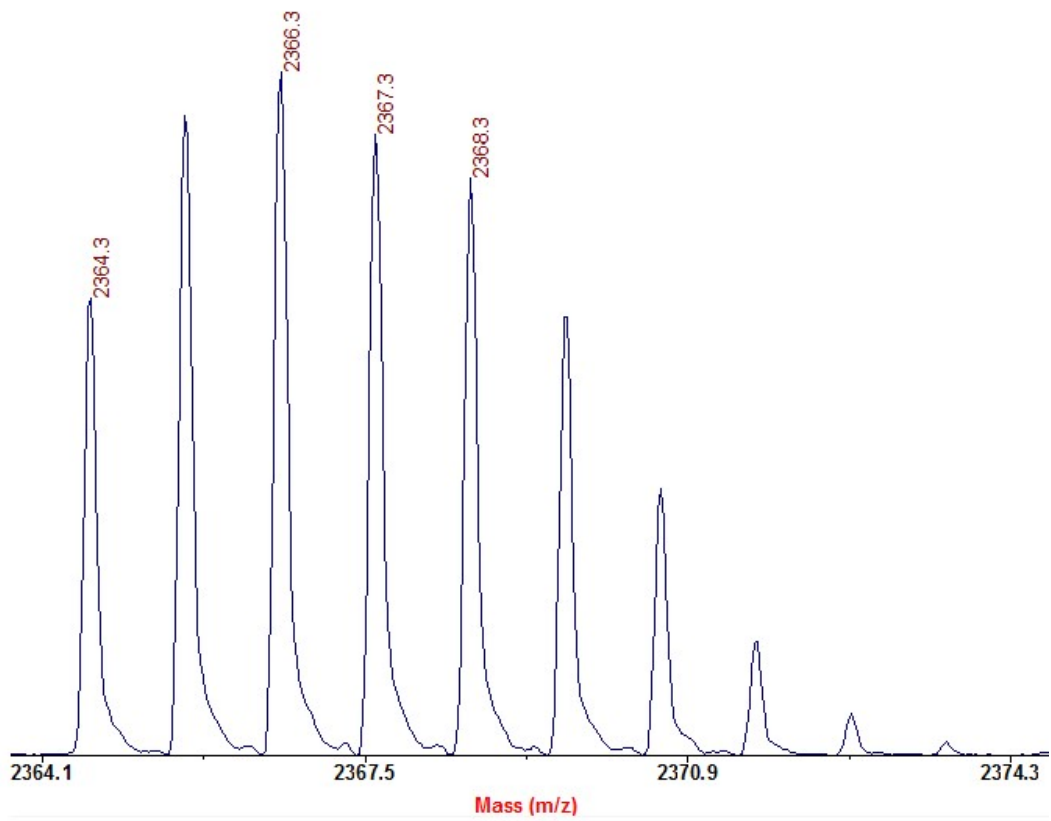

Figure S32. MALDI-TOF MS of **2c**.
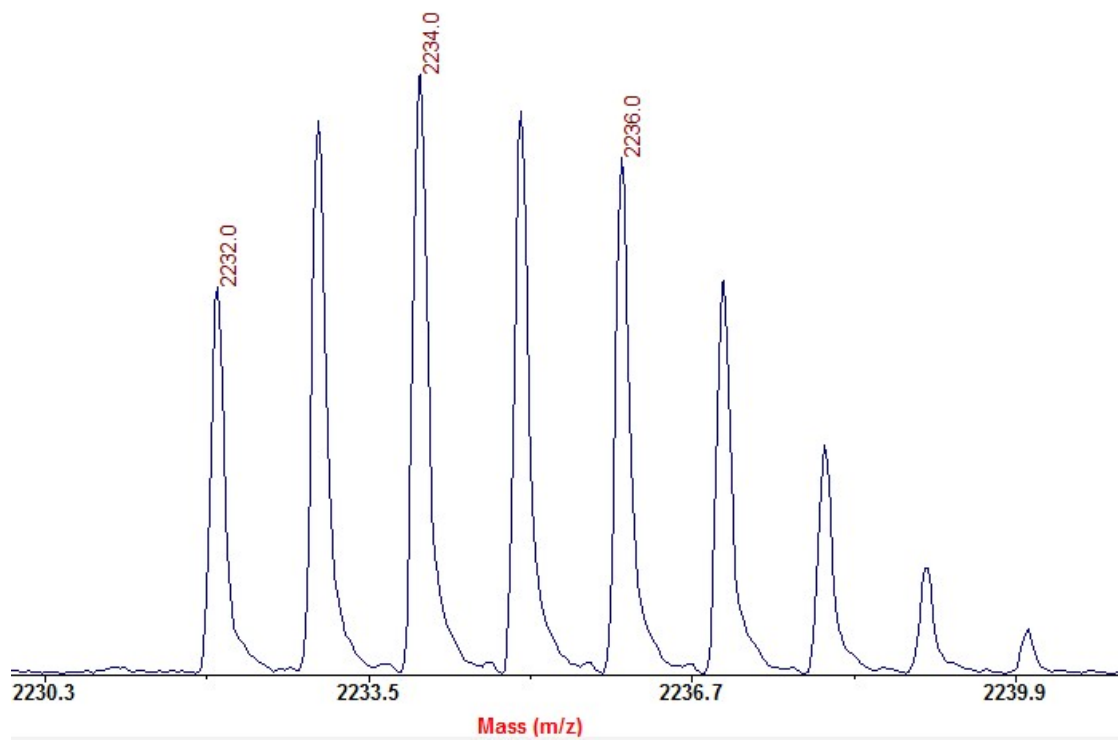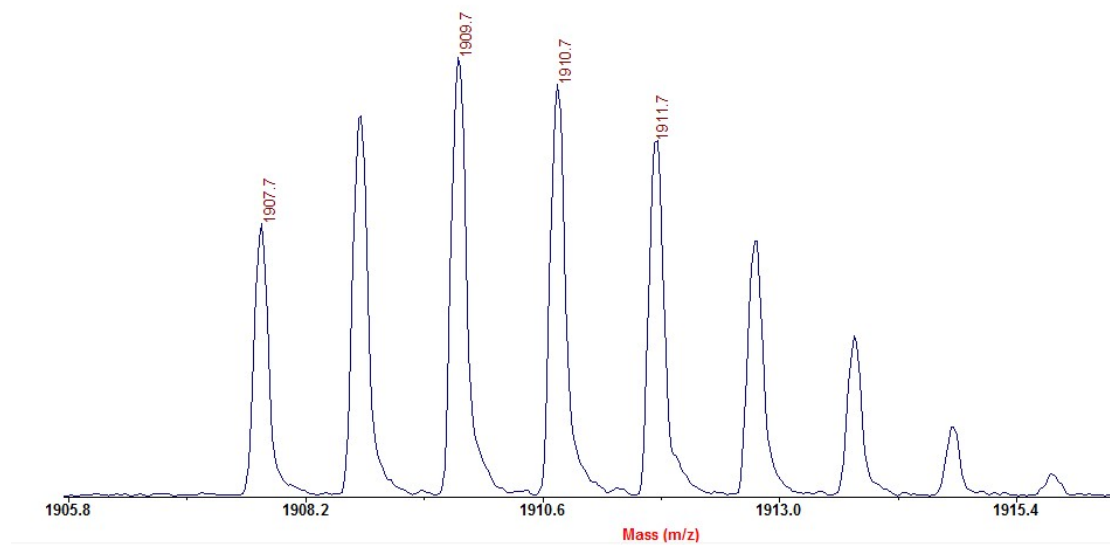
Figure S33. MALDI-TOF MS of **XW71**.

Figure S34. MALDI-TOF MS of **XW72**.

Figure S35. MALDI-TOF MS of **XW73**.

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