Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Porphyrin Sensitized Solar Cells: TiO_2 Sensitization With a Π-Extended Porphyrin Possessing Two Anchoring Groups

by

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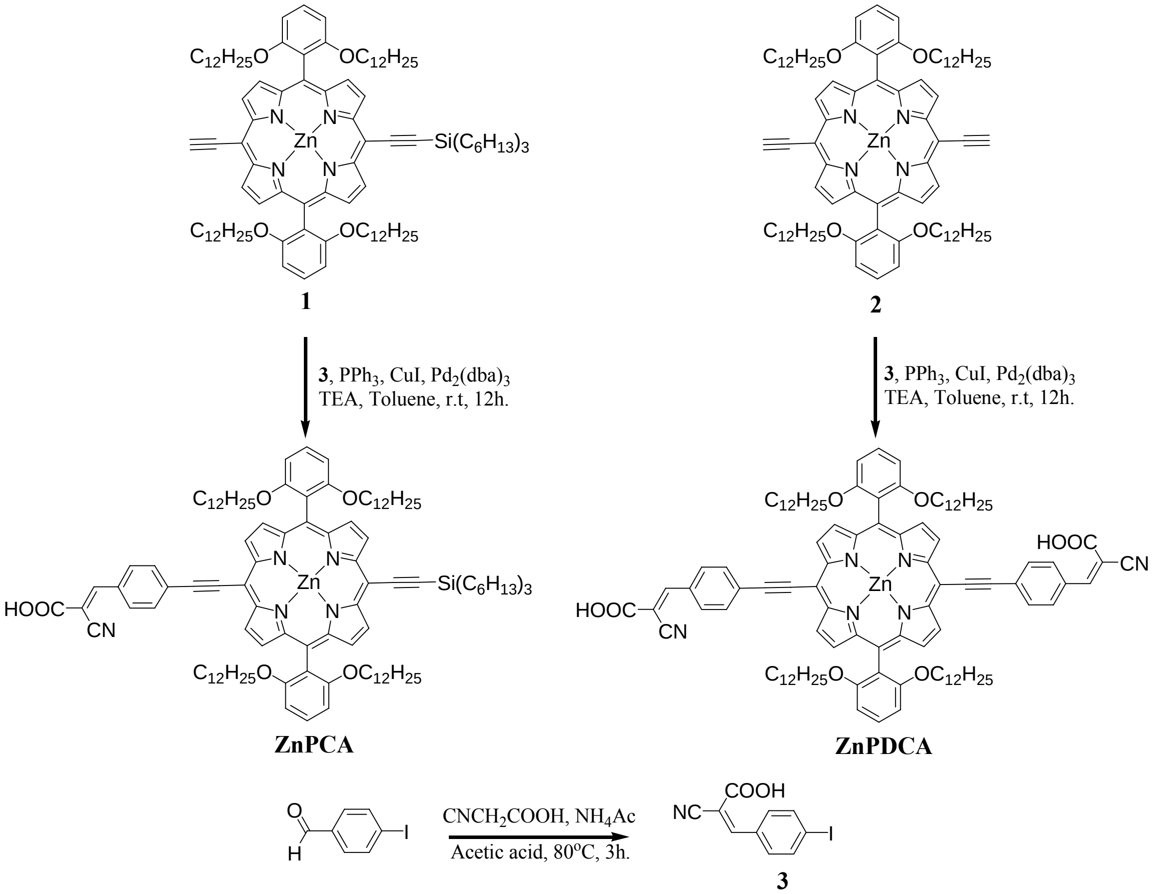
Experimental Section

Materials and General Procedures

All chemicals were obtained from commercial sources and used without further purification. All of the reactions and manipulations were carried out under N_2 with the use of standard inert-atmosphere and Schlenk techniques. Solvents used in reactions were dried by standard procedures. Absorbance spectra were obtained using a Varian Cary 5000 UV-Vis-NIR spectrophotometer. Nuclear magnetic resonance (NMR) spectra for all the synthesized compounds were recorded on a Varian INOVA 500 NMR spectrometer (499.773 MHz for ^{1}H NMR, 125.669 MHz for ^{13}C NMR). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a PE Voyager DE-Pro MALDI-TOF mass spectrometer in positive, reflector ionization mode, using dithranol as a matrix. Atomic layer deposition (ALD) was performed with a Savannah 100 instrument (Cambridge Nanotech Inc.). Compounds **1** and **2** were synthesized according to the published procedures.[1]

Porphyrin Synthesis

Details of the synthetic method are displayed in Scheme 1.



Scheme 1. Synthetic procedures for **ZnPCA** and **ZnPDCA.**

2-Cyano-3-(4-iodophenyl)acrylic Acid 3. 4-Iodobenzaldehyde (100 mg, 0.43 mmol) and cyanoacetic acid (44 mg, 0.52 mmol) were added to a stirred solution of ammonium acetate (11 mg, 0.14 mmol) in 1 ml of acetic acid and the resulting solution was refluxed for 12 h. After cooling to room temperature, the desired product was crystallized from the solution. The precipitate was filtered, washed by distilled water. Recrystallization from methylene chloride and hexane yielded the compound 3 as white solid (77 mg, 60% yield). ^{1}H NMR (DMSO) δ 8.29 (s, 1H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.78 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (DMSO) δ 163.09, 153.38, 138.21, 131.97, 130.91, 115.94, 104.45, 101.42.

ZnPCA. A solution of **1** (112 mg, 0.070 mmol), **3** (21 mg, 0.070 mmol), CuI (7 mg, 0.037 mmol), and PPh_3 (18 mg, 0.069 mmol) in 10 ml of TEA/Toluene (1:5 v/v) was degassed with N_2

stream for 10 min. $Pd_2(dba)_3$ (16 mg, 0.017 mmol) was added all at once and then stirred for 12 h. Solvent was evaporated in vacuo and then dark residue was purified by silica-gel column chromatography silica-gel column chromatography (dichloromethane/methanol (95:5 v/v)) to afford pure **ZnPCA**, (74 mg, 60% yield). ^1H NMR ($CDCl_3$) δ 9.69 (d, *J* = 4.5 Hz, 2H), 9.61 (d, *J* = 4.5 Hz, 2H), 8.93 (d, *J* = 4.5 Hz, 2H), 8.83 (d, *J* = 4.5 Hz, 2H), 8.36(s, 1H), 8.23 (br, 2H), 8.10 (br, 2H), 7.61 (br, 2H), 6.95 (d, *J* = 7 Hz 4H), 3.81 (br, 8H) 1.76-1.79 (m, 6H), 1.54-1.57 (m, 6H), 1.39-1.44 (m, 12H), 0.73-1.19 (br, 75H), 0.37-0.58 (br, 32H). MS (MALDI-TOF) *m/z* 1763 (M + H^+).

ZnPDCA A solution of **2** (90 mg, 0.070 mmol), **3** (46 mg, 0.15 mmol), CuI (6 mg, 0.071 mmol), and PPh_3 (37 mg, 0.140 mmol) in 10 ml of TEA/Toluene (1:5 v/v) was degassed with N_2 stream for 10min. $Pd_2(dba)_3$ (32 mg, 0.035 mmol) was added all at once and then stirred for 12h. Solvent was evaporated in vacuo and then dark residue was purified by silica-gel column chromatography silica-gel column chromatography (dichloromethane/methanol (2:1 v/v)) to afford pure **ZnPDCA**, (63 mg, 55% yield). ^1H NMR ($CDCl_3/CD_3OD$) δ 9.40 (d, *J* = 4.5 Hz, 4H), 8.59 (d, *J* = 4.5 Hz, 4H), 8.03 (s, 2H), 7.93 (d, *J* = 8 Hz, 4H), 7.86 (d, *J* = 8 Hz, 4H), 7.49 (t, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 4H), 3.66 (t, *J* = 6.0 Hz, 8H), 0.92-0.97 (m, 10H), 0.65-0.87 (br, 38H), 0.56-0.63 (br, 20H) 0.40-0.45 (m, 8H), 0.23-0.29 (m, 16H), 0.15-0.17 (m, 8H), (MALDI-TOF) *m/z* 1652 (M + H^+).

Preparation of dye-sensitized solar cells. Photoelectrodes were prepared on 12 Ω cm^{-2} FTO-coated glass (Hartford glass). Blocking layers of TiO_2 were deposited using 400 ALD cycles of titanium isopropoxide (Aldrich), TIP, and water as precursors. TiO_2 was grown at 200 °C using reactant exposure times of 1 and 0.02 s for TIP and H_2O, respectively, and nitrogen purge times of 10 s between exposures. A transparent TiO_2 nanoparticle layer (12 μm, measured using a Tencor P10 profilometer) was prepared by doctor blading a paste of TiO_2 nanoparticles (DSL 18NR-T, Dyesol) on the FTO. A scattering layer (4 μm) of TiO_2 nanoparticles (WER4-O, Dyesol) was subsequently deposited on top of the transparent layer. The resulting electrodes were annealed at 500 °C in air for 30 min. After annealing, the TiO_2 electrodes were immediately immersed in a 0.5 mM solution of **ZnPCA** and **ZnPDCA** in chloroform/ethanol (3:1). After 2 h, they were rinsed with chloroform/ethanol and dried with N_2. A Surlyn frame (25 μm) was sandwiched between the open-pore side of the membrane and a platinized FTO electrode. Light pressure was applied to seal the cell while heating the cell at 130 °C. A solution of 0.60 M butylmethylimidazolium iodide, 0.03 M I_2, 0.10 M guanidinium thiocyanate, 0.50 M 4-*tert*-butylpyridine and 0.1 M LiI in 3 mL acetonitrile:valeronitrile (85:15) was introduced into the TiO_2 cells. Additional Surlyn and a microscope cover slide sealed the electrolyte into the cell. Cells were illuminated through an Oriel 81092 filter by a Xe lamp in a Jobin Yvon fluorimeter (Fluorolog 3). Broadband excitation using the grating at zeroth order was 98 mW cm^{-2}. Optical power was measured with an Ophir 3A-SH radiometer. A CH Instruments 1200A potentiostat was used to measure current-voltage curves.

Electrochemical measurements. Cyclic voltammetry was carried out on a CH Instruments CH900 Electrochemical Analyzer using a conventional three-electrode system consisting of a **ZnPCA**/TiO_2 or **ZnPDCA**/TiO_2 as the working electrode, a platinum wire electrode, and a pseudo Ag/AgCl reference electrode. Ferrocene/ferrocenium (+0.64 V vs NHE) was used as an internal reference. All measurements were performed at ambient temperature under a nitrogen atomosphere in dry deoxygenated 0.1 M tetrabutylammonium hexafluorophosphate solution in CH_2Cl_2.

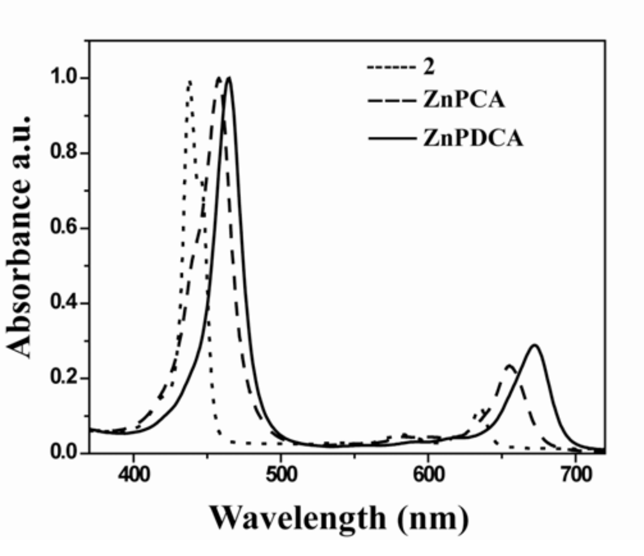


Fig. S1. UV-Vis spectra of **2**, **ZnPCA** and **ZnPDCA** in chloroform-ethanol (3:1).

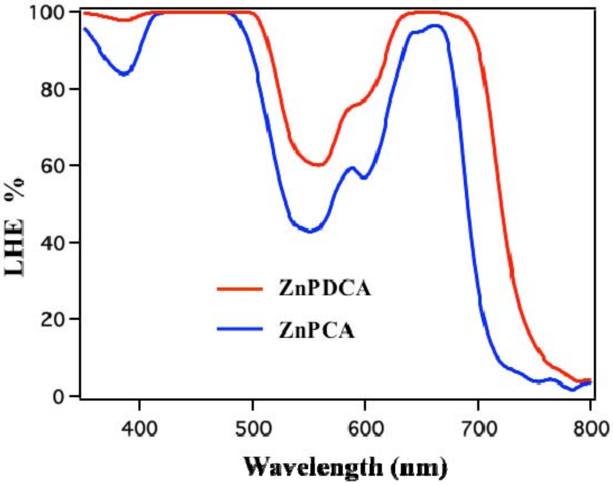


Fig. S2. Light harvesting efficiency (LHE) for **ZnPCA** and **ZnPDCA** on 12 μm TiO_2 films. (Reflection by FTO and scattering by 400 nm particles are not taken into account.)

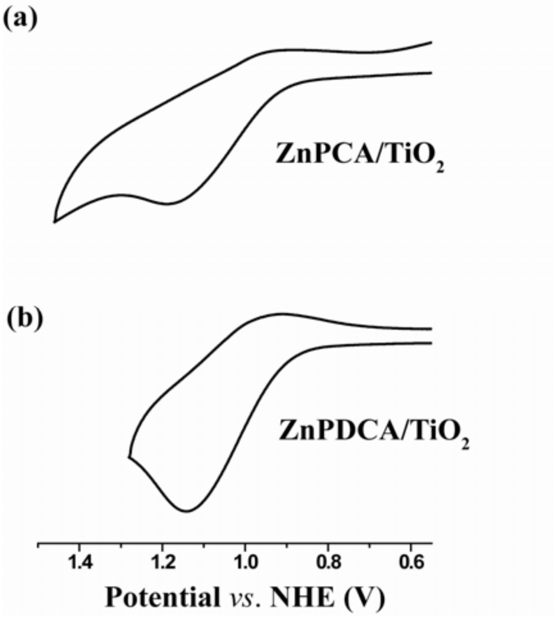
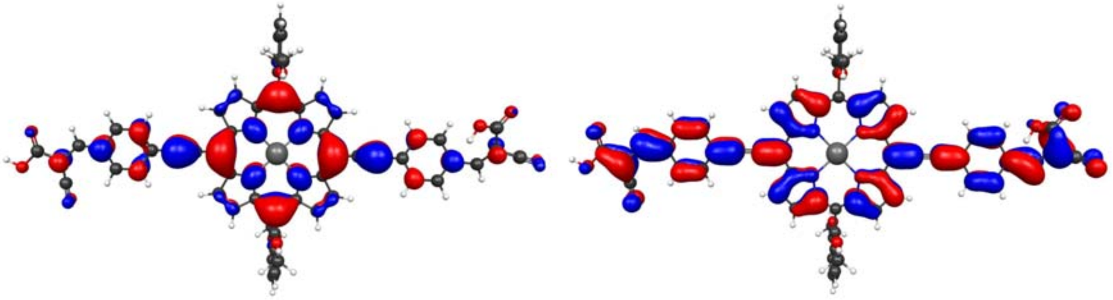
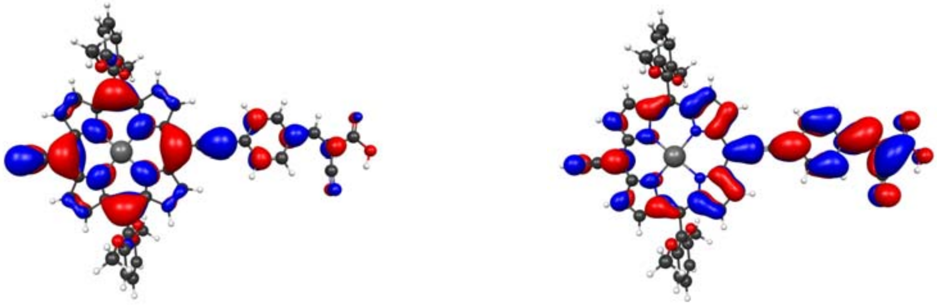


Fig. S3. Cyclic voltammograms of **ZnPCA** (a) and **ZnPDCA** (b) on TiO_2 (scan rate = 0.1 V/s).



HOMO of ZnPDCA LUMO of ZnPDCA



HOMO of ZnPCA LUMO of ZnPCA

Fig. S4. Molecular orbitals of **ZnPCA** and **ZnPDCA** calculated at the B3LYP/6-31G* level.

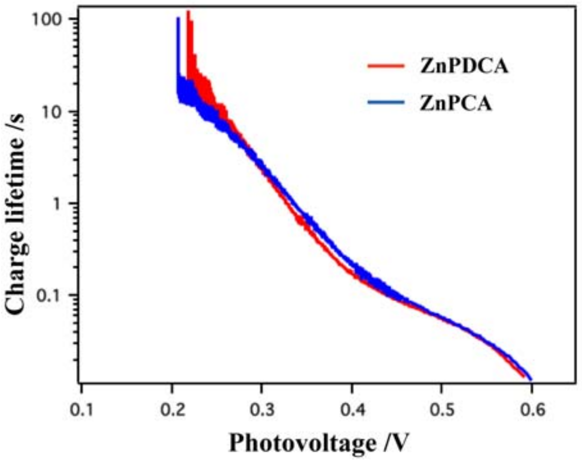
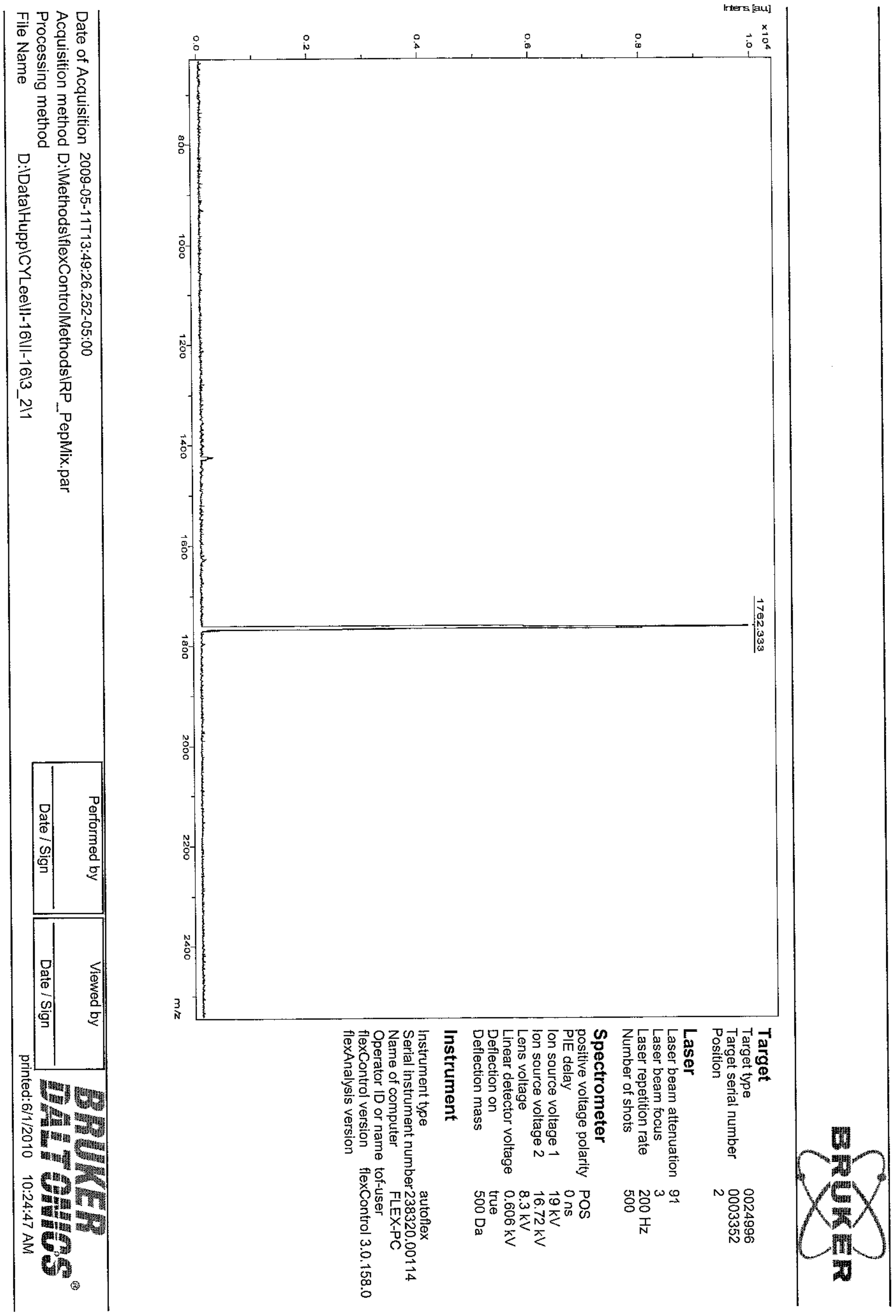


Fig. S5. Charge lifetimes vs. photovoltage for **ZnPDCA** and **ZnPCA** sensitized TiO_2 cells.

Fig. S6. MALDI-TOF of **ZnPCA**



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Position	2

Laser

Laser beam attenuation	91
Laser beam focus	3
Laser repetition rate	200 Hz
Number of shots	500

Spectrometer

positive voltage polarity	POS
PIE delay	0 ns
Ion source voltage 1	19 kV
Ion source voltage 2	16.72 kV
Lens voltage	8.3 kV
Linear detector voltage	0.606 kV
Deflection on	true
Deflection mass	500 Da

Instrument

Instrument type	autoflex
Serial instrument number	238320.00114
Name of computer	FLEX-PC
Operator ID or name	tof-user
flexControl version	flexControl 3.0.158.0
flexAnalysis version	

Date of Acquisition	2009-05-11T13:49:26.252-05:00
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Processing method	
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Performed by	Viewed by
Date / Sign	Date / Sign

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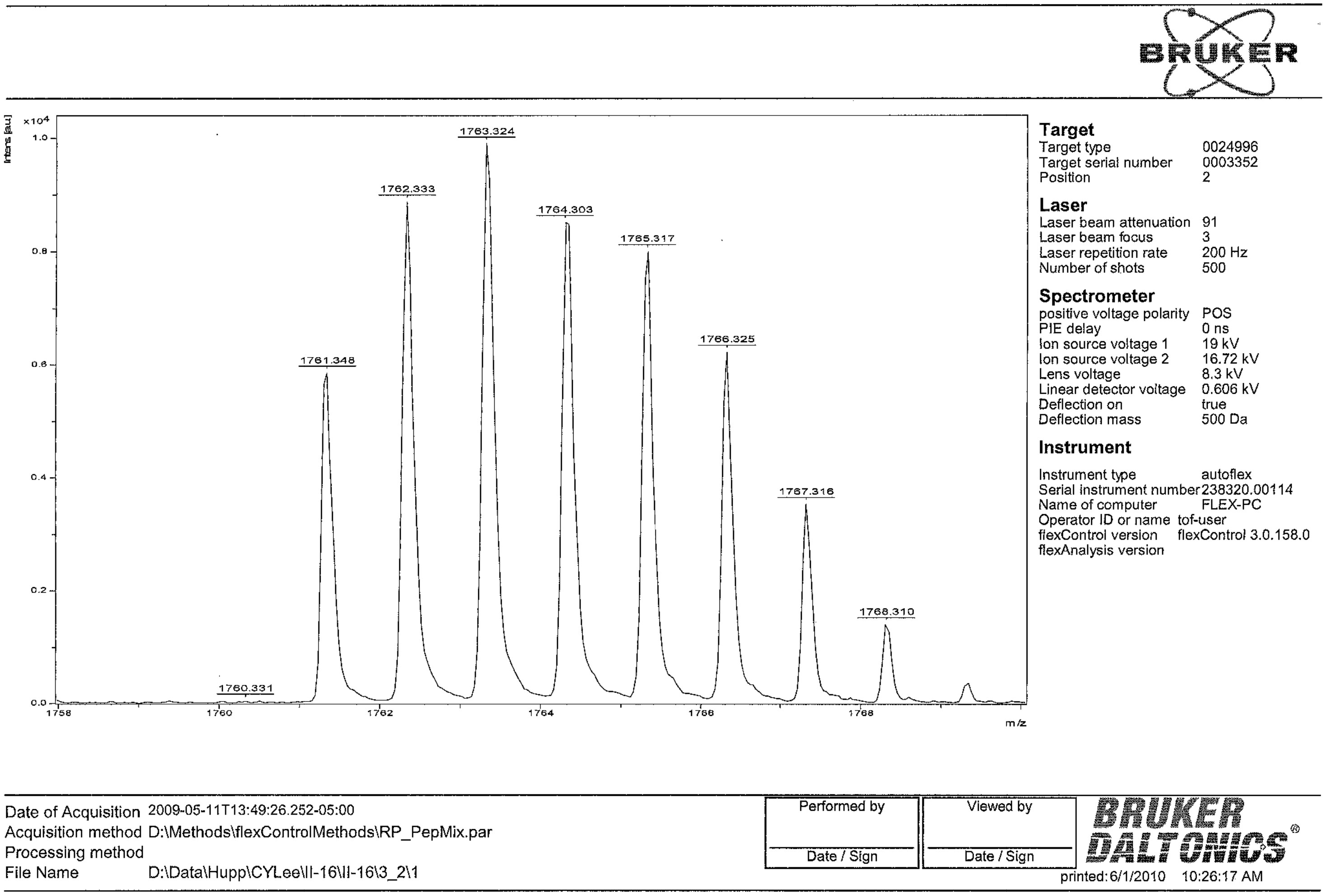
Fig. S7. Expanded MALDI-TOF of **ZnPCA**



Target

Target type	0024996
Target serial number	0003352
Position	2

Laser

Laser beam attenuation	91
Laser beam focus	3
Laser repetition rate	200 Hz
Number of shots	500

Spectrometer

positive voltage polarity	POS
PIE delay	0 ns
Ion source voltage 1	19 kV
Ion source voltage 2	16.72 kV
Lens voltage	8.3 kV
Linear detector voltage	0.606 kV
Deflection on	true
Deflection mass	500 Da

Instrument

Instrument type	autoflex
Serial instrument number	238320.00114
Name of computer	FLEX-PC
Operator ID or name	tof-user
flexControl version	flexControl 3.0.158.0
flexAnalysis version	

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Date / Sign	Date / Sign

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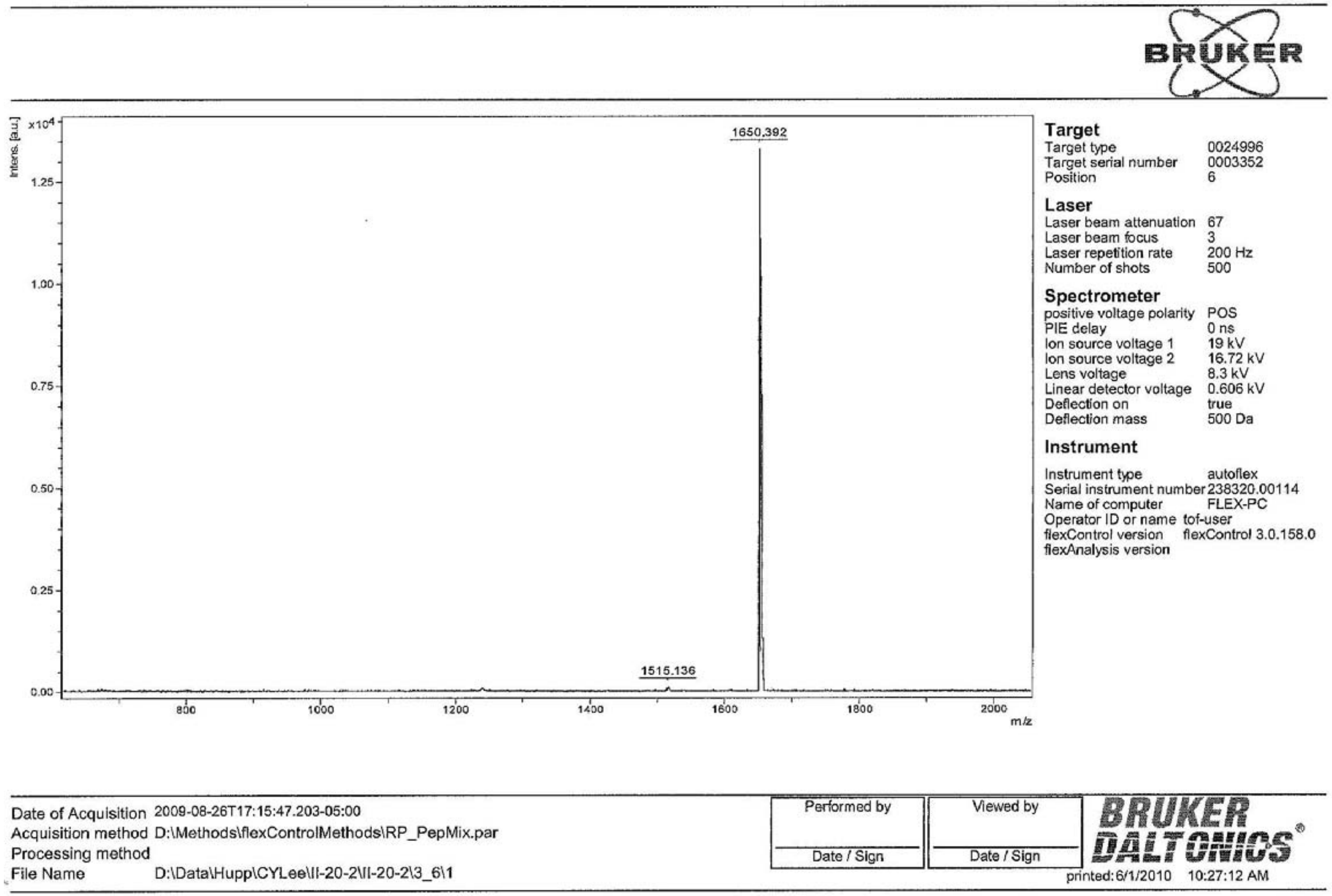
Fig. S8. MALDI-TOF of **ZnPDCA**



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Target serial number	0003352
Position	6

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Laser beam focus	3
Laser repetition rate	200 Hz
Number of shots	500

Spectrometer

positive voltage polarity	POS
PIE delay	0 ns
Ion source voltage 1	19 kV
Ion source voltage 2	16.72 kV
Lens voltage	8.3 kV
Linear detector voltage	0.606 kV
Deflection on	true
Deflection mass	500 Da

Instrument

Instrument type	autoflex
Serial instrument number	238320.00114
Name of computer	FLEX-PC
Operator ID or name	tof-user
flexControl version	flexControl 3.0.158.0
flexAnalysis version	

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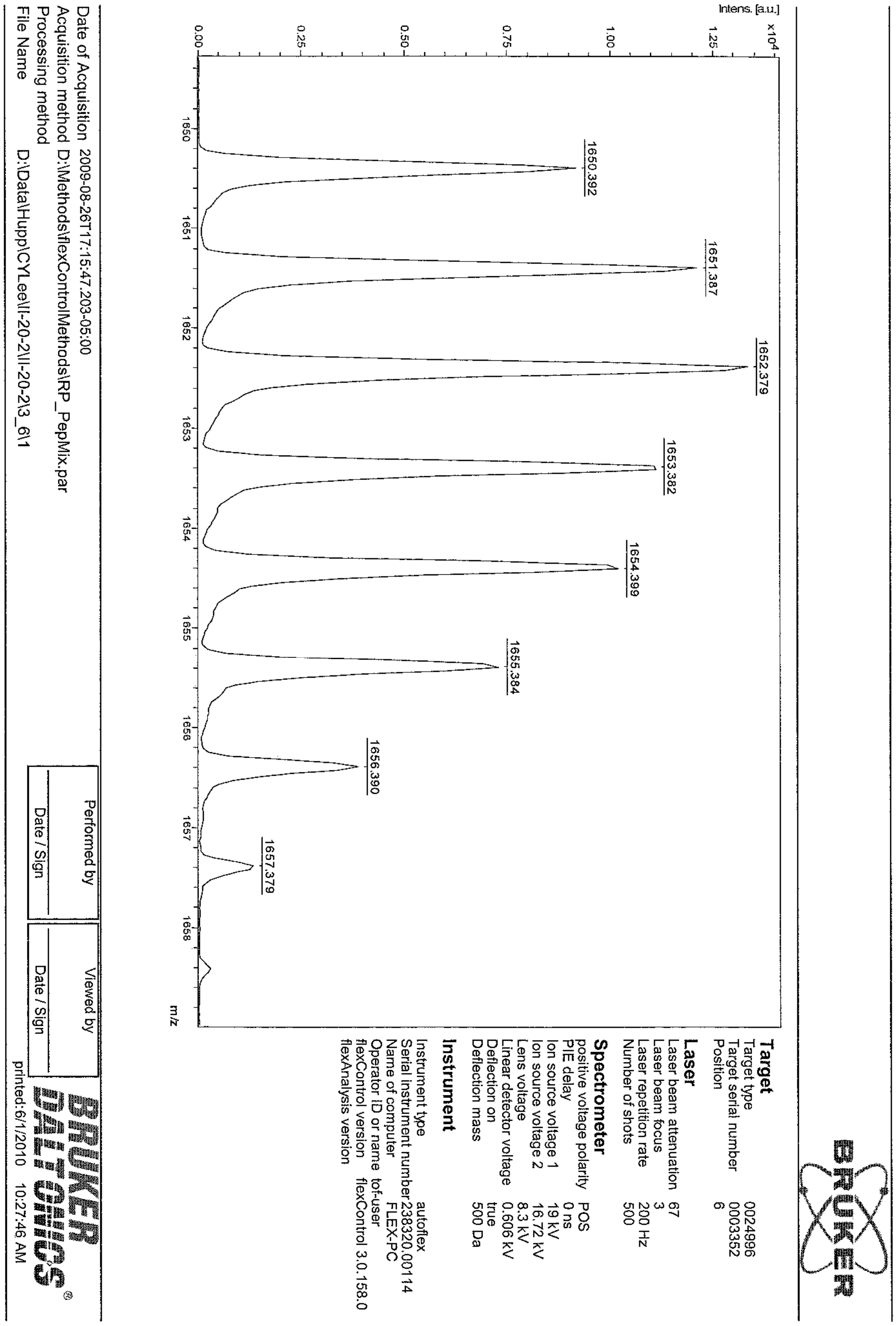
Fig. S9. Expanded MALDI-TOF of **ZnPDCA**



Target

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Target serial number	0003352
Position	6

Laser

Laser beam attenuation	67
Laser beam focus	3
Laser repetition rate	200 Hz
Number of shots	500

Spectrometer

positive voltage polarity	POS
PIE delay	0 ns
Ion source voltage 1	19 kV
Ion source voltage 2	16.72 kV
Lens voltage	8.3 kV
Linear detector voltage	0.606 kV
Deflection on	true
Deflection mass	500 Da

Instrument

Instrument type	autoflex
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Name of computer	FLEX-PC
Operator ID or name	tof-user
flexControl version	flexControl 3.0.158.0
flexAnalysis version	

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Acquisition method D:\Methods\flexControlMethods\RP_PepMix.par
Processing method
File Name D:\Data\Hupp\CYLee\I-20-2\I-20-2\3_6\1

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Date / Sign	Date / Sign

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Fig. S10. ^{1}H-NMR of **ZnPCA**

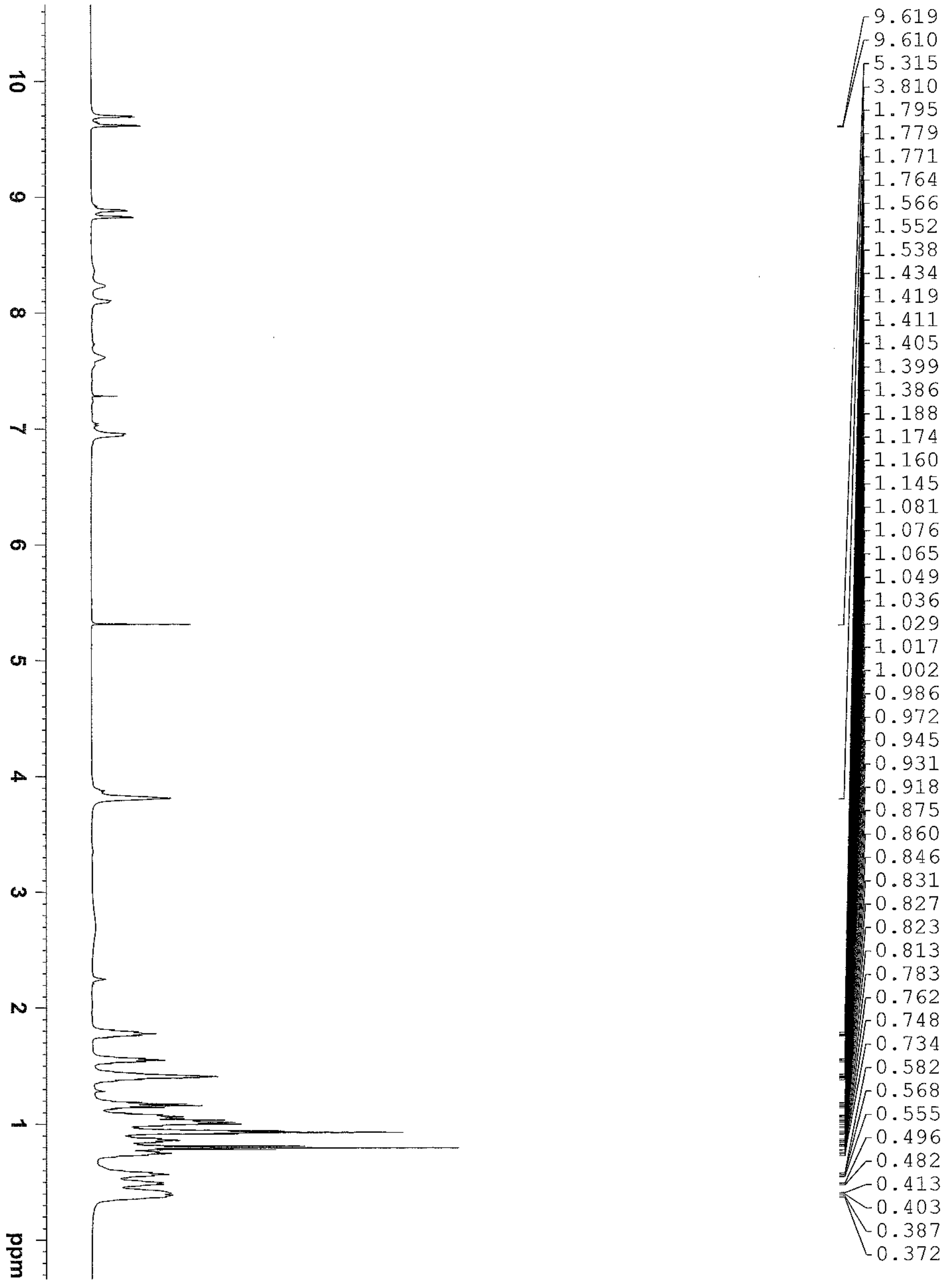
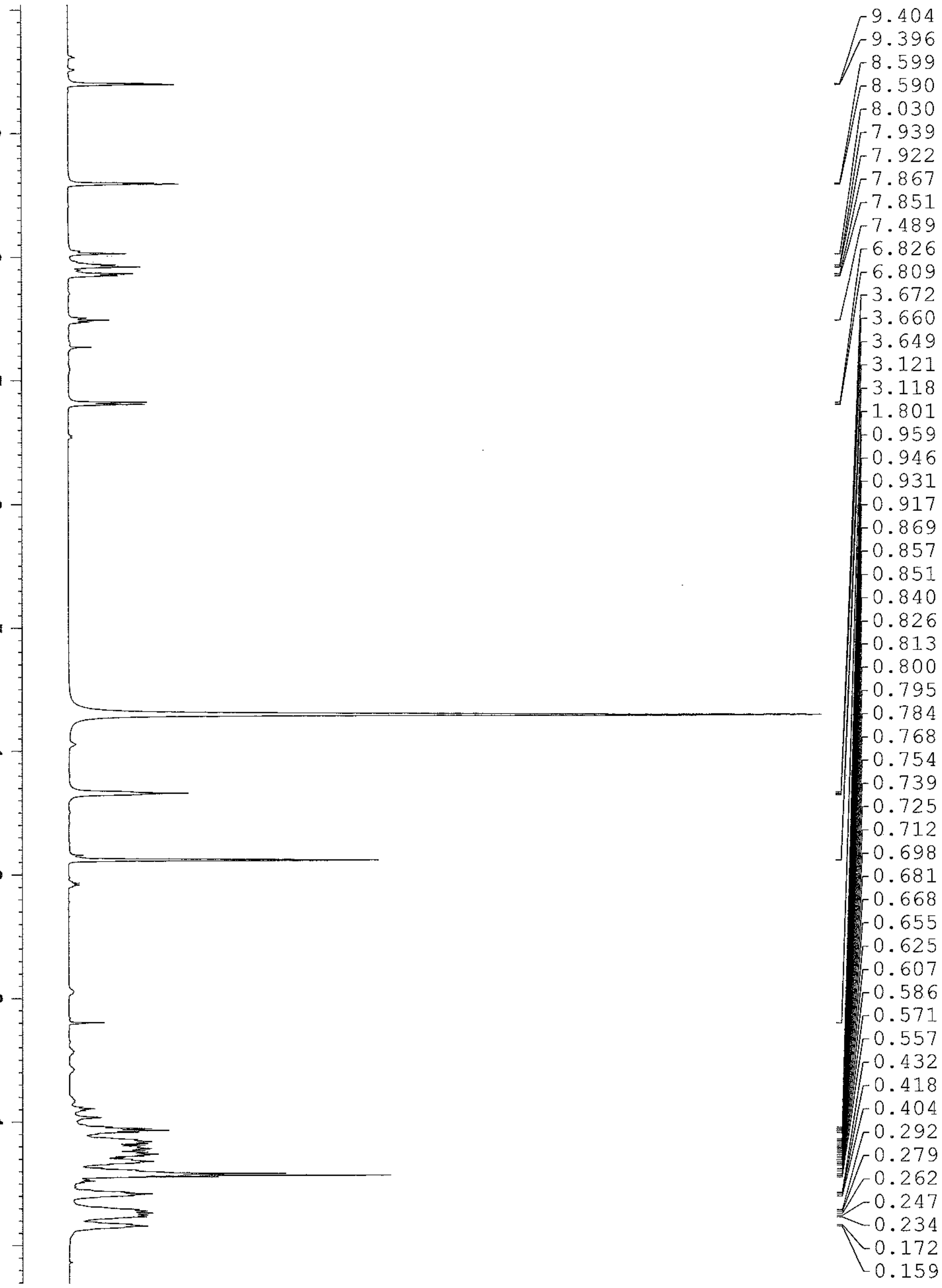


Fig. S11. ^{1}H-NMR of **ZnPDCA**



Reference:

1. C. Y. Lee and J. T. Hupp, *Langmuir*, 2010, **26**, 3760.

Caption for TOC figure: A dye-sensitized solar cell based on a π-extended porphyrin possessing two anchoring groups achieves a power conversion efficiency of 5.5 %.

TOC