

Electronic Supporting Information

Factors influencing the photoelectrochemical device performance sensitized by ruthenium polypyridyl dyes

Indra Purnama,^a Salmahaminati,^{b,c} Minori Abe,^b Masahiko Hada,^b Yuji Kubo,^{a,d} Jacob Y. Mulyana^{*a,d}

^aDepartment of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami Osawa, Hachioji, Tokyo 192-0397, Japan

^bDepartment of Chemistry, Graduate School of Science, Tokyo Metropolitan University, 1-1 Minami Osawa, Hachioji, Tokyo 192-0397, Japan

^cDepartment of Chemistry, Faculty of Mathematics and Natural Sciences, Islamic University of Indonesia, Yogyakarta, 55581, Indonesia

^dResearch Center for Hydrogen Energy-based Society, Tokyo Metropolitan University, Japan

Table of contents

1. General	S2
2. Materials	S2
3. Synthesis and characterization of P3	S2
4. Film preparation	S4
5. Electrochemistry & Photoelectrochemistry	S4
6. Measurements of H ₂	S4
7. IPCE Measurements	S5
8. Lifetime phosphorescence	S5
9. Theoretical calculation	S5
10. References	S6
11. Scheme S1 Synthetic pathway of P3	S3
12. Table S1 Reorganization energy measured in acetonitrile	S9
13. Figure S1 Absorption and emission spectra of PS in solution and FTO/TiO ₂ film	S7
14. Figure S2 A photograph of the custom-made DSPEC compartment	S7
15. Figure S3 Cyclic voltammograms of PS in solution and FTO/TiO ₂ film	S8

16. Figure S4 Cyclic voltammograms of EDTA	S8
17. Figure S5 Linier sweep voltammograms of PS in solution and FTO/TiO ₂ film	S8
18. Figure S6 The IPCE value of FTO/TiO ₂ / PS in comparison with their absorption spectra	S9
19. Figure S7 Lifetime decay profiles of PS in FTO/TiO ₂ film	S10
20. Figure S8 Lifetime decay profiles of PS in solution	S10
21. Figure S9 Time courses of photocurrent density generated by the FTO/TiO ₂ / PS	S11
22. Figure S10 Amount of H ₂ evolved for 30 min photolysis in absence of EDTA	S11
23. Figure S11 Gas chromatogram	S12
24. Figure S12 ¹ H NMR spectrum of P1	S13
25. Figure S13 ESI mass spectrum of P1	S14
26. Figure S14 ¹ H NMR spectrum of P2	S15
27. Figure S15 ESI mass spectrum of P2	S16
28. Figure S16 ¹ H NMR spectrum of P3	S17
29. Figure S17 ¹³ C NMR spectrum of P3	S18
30. Figure S18 ESI mass spectrum of P3	S19
31. Figure S19 ¹ H NMR spectrum of P4	S20
32. Figure S20 ESI mass spectrum of P4	S21

1. General

UV-Vis and fluorescence spectra were recorded on a Shimadzu UV-3600 UV-Vis spectrophotometer and JASCO FP-6300 spectrofluorometer, respectively. ¹H NMR and ¹³C NMR spectra were collected at 298 K using Bruker instrument (500 MHz). Electro spray ionization mass spectrometry (ESI-MS) spectra were measured on a Bruker micrOTOF II. Elemental analysis was carried out on an Exeter Analytical, Inc. CE-440F elemental analyzer.

2. Materials

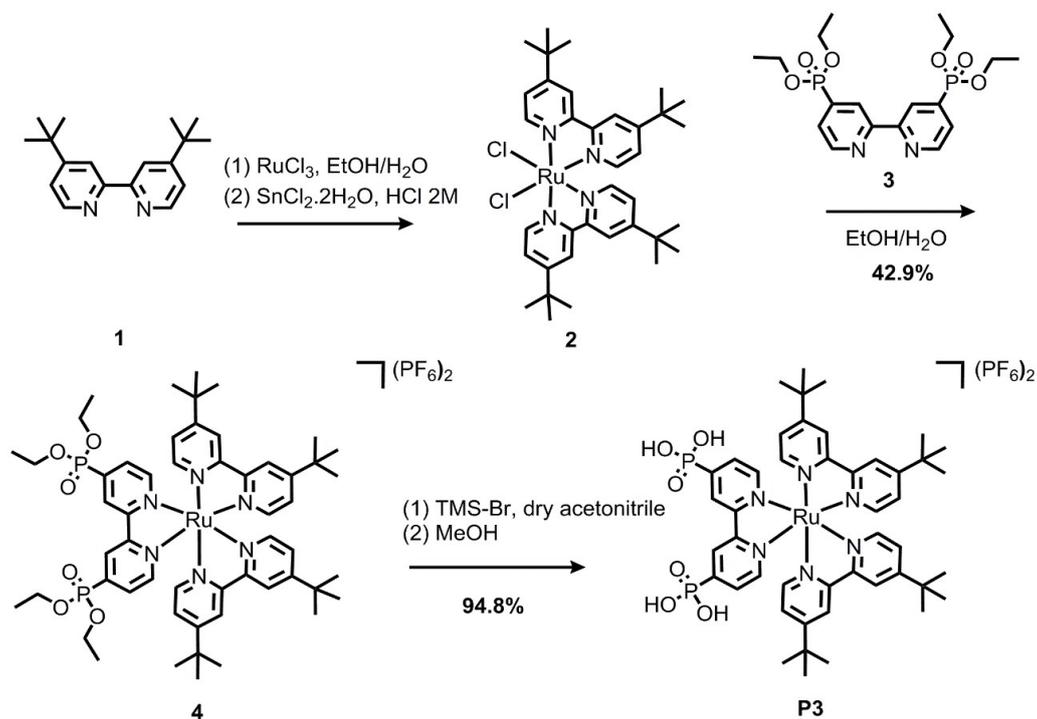
Transparent titania paste and RuCl₃ hydrate were purchased from Sigma Aldrich. 4,4'-Di-*tert*-butyl-2,2'-bipyridyl **1** was purchased from Tokyo Chemical Industry Co., Ltd. Other chemicals were purchased from Kanto Chemical and Wako. Organic solvents were dried and distilled according to the standard methods when necessary. The organic syntheses were carried out under a N₂ atmosphere using Schlenk techniques. Ruthenium complex **P1** and **P2** were

prepared according to the previous report¹ with slight modification using methanol for the reaction and acetonitrile for the hydrolysis. **P4**² and 4,4'-bis(diethylphosphonate)-2,2'-bipyridine **3**³ were prepared according to the procedure described in the literature.

3. Synthesis and characterization of P3

Synthesis of complex 2. The synthesis of complex **2** follows the “ruthenium blue” method reported previously.⁴ Compound **1** (1.06 g, 3.95 mmol) in 10 mL EtOH along with HCl (2 mL) was added to the prepared “ruthenium blue” solution (RuCl₃, 396 mg, 1.91 mmol) in 30 mL EtOH/H₂O (2:1) while the temperature was maintained at 80 °C.⁴ This mixture was refluxed for 0.5 hr under nitrogen, after which the color of the solution turned dark brown. After evaporating the solvent using a rotary evaporator, the deep brown crystals were deposited, collected by filtration and washed with water. The formed ruthenium(III) complex was suspended in 30 mL 2M HCl and 0.24 g of SnCl₂·2H₂O solid was added followed by heating at 90 °C while stirring until the dark precipitate was formed. The solid material **2** was collected by filtration, washed with water, and dried without further purification.

Scheme S1 Synthetic pathway of **P3**



Synthesis of complex 4. A mixture of complex **2** (300 mg) and compound **3** (108 mg, 0.25 mmol) in a 15 mL mixed solution of $\text{EtOH}/\text{H}_2\text{O}$ (2:1) was refluxed for 6 h under nitrogen. The solvents were removed by rotary evaporator and the product was isolated by column chromatography on silica gel. The main fraction was collected and eluted by 10% CH_3OH in

acetone (10 drops of saturated KPF_6 in CH_3OH was added to 100 mL solution) to afford complex **4**. The pure fractions were collected to yield 42.9% (123 mg) of the complex. ^1H NMR (500 MHz, CD_3CN): 1.32 (12H, t, $J = 7.05$ Hz), 1.41 (18H, s), 1.42 (18H, s), 4.19 (8H, p, $J = 7.06$ Hz), 7.37 (2H, dd, $J = 2.07$ Hz, 6.02 Hz), 7.42 (2H, dd, $J = 2.12$ Hz, 6.08 Hz), 7.54 (4H, dd, $J = 6.00$ Hz, 11 Hz), 7.62 (2H, dd, $J = 5.73$ Hz, 12.4 Hz); 7.87 (2H, dd, $J = 4.12$ Hz, 5.50 Hz), 8.58 (4H, dd, $J = 1.85$ Hz, 7.05 Hz), 8.78 (2H, d, $J = 13.4$ Hz)

Synthesis of P3. Complex **4** (116 mg, 0.1 mmol) was dissolved in dry CH_3CN (25 mL) and $\text{Si}(\text{CH}_3)_3\text{Br}$ (0.13 mL, 1.0 mmol) was added dropwise at room temperature under a N_2 atmosphere. The mixture was heated to 45°C for 48 h and then cooled to room temperature. Dry CH_3OH (25 mL) was then added and the solution was stirred for another 3 h. The solvent was then removed under reduced pressure and the product was obtained after recrystallization from diethyl ether to yield 94.8% of the complex. ^1H NMR (500 MHz, CD_3OD): 1.44 (18H, s), 1.45 (18H, s), 7.51 (2H, dd, $J = 1.98$ Hz, 6.08 Hz), 7.55 (2H, dd, $J = 2.02$ Hz, 6.03 Hz), 7.65 (4H, dd, $J = 6.62$ Hz, 6.50 Hz), 7.74 (2H, dd, $J = 5.50$ Hz, 12.0 Hz); 7.96 (2H, dd, $J = 3.60$ Hz, 5.50 Hz), 8.73 (4H, dd, $J = 2.20$ Hz, 2.20 Hz), 8.88 (2H, d, $J = 13.3\text{Hz}$). ESI-MS: 951.29 [M-3H] $^-$. Calcd: 951.30. Elemental analysis: Calcd for $\text{C}_{46}\text{H}_{58}\text{F}_{12}\text{N}_6\text{O}_6\text{P}_4\text{Ru}\cdot\text{H}_2\text{O}$: C, 43.44; H, 4.83; N, 6.61. Found: C, 43.47; H, 4.84; N, 6.64.

4. Film Preparation

Transparent TiO_2 films of 9 mm x 9 mm size with 7 μm thickness printed on FTO (Fluorine-doped Tin Oxide) glass were made according to the previous report.⁵ The mesoporous films were cast through doctor blading onto an ethanol cleaned FTO substrate using tape as a spacer for consistent thickness. The films were first dried while covered for 30 min and then sintered at 450°C for 30 min. Film thicknesses (~ 7 μm) were determined using a Mitutoyo 156-101 micrometer stand. Titania films were submerged into concentrated CH_3OH solutions of **P1**, **P2**, **P3** or **P4** to allow the molecules to anchor to the nanocrystallite surface. The films were submerged for 4 h to achieve the optimum dye loading as monitored by UV-Vis spectroscopy. The amount of the dyes on TiO_2 surface (dye loading c_0 in cm^{-3}) were estimated according to the previously reported calculations and presented in Table 2 and Table S1.⁶ Prior to use, the films were soaked for ~ 30 min in neat CH_3OH to remove any weakly adsorbed molecules from the film.

5. Electrochemistry and photoelectrochemistry

Electrochemical and photoelectrochemical measurements of the dyes on TiO₂ were performed on a VersaSTAT 3 potentiostat (Princeton Applied Research), using FTO/TiO₂/dye as working electrode, Ag/AgCl reference electrode and platinum counter electrode, measured in a custom-made cell as shown in Figure S2 using 0.1 M acetate buffer pH 5 containing 0.1 M NaClO₄ as the supporting electrolyte. A Max-303 Xenon lamp (Asahi Spectra) 300 W with 400 nm long pass filter was used to irradiate the photoanodes from the FTO side. The light intensity 160 mW/cm² was used for irradiating the photoanode in photoelectrochemical experiments. For cyclic voltammetry measurements in solution, the dyes were dissolved in 0.1 M acetate buffer pH 5 and methanol (1:3) containing 0.1 M NaClO₄ supporting electrolyte. The potential values were converted to NHE ($E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.207$).⁷

For the determination of Ru^{III}/Ru^{II} self-exchange energy (reorganization energy), variable-temperature cyclic voltammetry of FTO/TiO₂/dye electrodes⁶ was performed in 0.1 M acetate buffer pH 5 containing 0.1 M NaClO₄ and in dry acetonitrile containing 0.1 M TBAPF₆. The modeling to obtain the reorganization energies from the CV data was performed using Origin 9.0 software with the least-squares error minimization and Levenberg–Marquardt iteration method.⁶

6. Measurements of H₂

Hydrogen measurements were performed on a Shimadzu 2010 Plus with a BID detector. The evolved gas in the headspace of the DSPEC was withdrawn using a Vici pressure lock gas syringe and injected to the GC. The gas mixture was separated using a miropacked ST column at oven temperature 35 °C using helium gas carrier. Hydrogen quantification was determined using 5% H₂ in argon and 5% O₂ in helium reference gases, purchased from Taiyo Nippon Sanso Co., Ltd. The Faradaic efficiency for the hydrogen production was calculated according to equation 1:

$$\eta_{\text{H}_2} = \frac{2nH_2}{Q} \quad (1)$$

where nH_2 is the mole of gas observed from the experiments and $Q = \text{charge} / 96485$.

7. IPCE measurements

The incident photon-to-charge carrier efficiencies (IPCE) of each dye on TiO₂ were measured manually in a custom-made two-electrode cell comprising of FTO/TiO₂/dye working electrode and Pt counter electrode loaded with 0.1 M acetate buffer pH 5 containing 0.1 M NaClO₄

electrolyte in the absence and presence of EDTA. Xenon light irradiation is filtered with appropriate bandpass filters to obtain monochromatic lights at the wavelengths between 460 and 670 nm. The light intensity was measured by ADCMT 8230E Optical Power Meter (ADC Corporation). The measurement was performed at 0.05 V vs. NHE external bias. The data parameters were collected and calculated according to equation 2.

$$\text{IPCE (\%)} = \frac{I(\text{mA})}{P(\text{mW})} \times \frac{1240}{\lambda(\text{nm})} \times 100 \quad (2)$$

8. Lifetime phosphorescence

The phosphorescence lifetime of the photoluminescence of the dyes in solution and in film was measured on a Quantaurus-Tau Fluorescence Spectrometer C11367. For solution, 14 μM of dye solution in methanol/acetate buffer pH 5 containing 0.1 M NaClO_4 (3:1) was purged by N_2 for 20 mins prior to measuring the phosphorescence decay. For films, FTO/ TiO_2 /dye was inserted in the cell at 45° position and purged by N_2 for 20 mins before the measurement. The cell is kept deaerated throughout the measurement.

9. Theoretical calculation

Theoretical energy levels were obtained using B3LYP functional, which uses Stuttgart ECP (SDD) basis set for Ru and 6-31G** for all other atoms (C, H, O, N, P), calculated in the polarizable continuum model (PCM) of methanol using Gaussian 09 package.⁸ The molecular orbitals were visualized using the Gauss view 5.0.8 program.

10. References

1. M. R. Norris, J. J. Concepcion, C. R. K. Glasson, Z. Fang, A. M. Lapidés, D. L. Ashford, J. L. Templeton, and T. J. Meyer. *Inorg. Chem.*, 2013, **52**, 12492–12501.
2. I. Purnama, Y. Kubo, and J. Y. Mulyana. *Inorg. Chim. Acta.*, 2018, **471**, 467-474.
3. I. Gillaizeau-Gauthier, F. Odobel, M. Alebbi, A. Roberto, E. Costa, G. A. Bignozzi, P. Qu, and G. J. Meyer. *Inorg. Chem.*, 2001, **40**, 6073.
4. N. Nagao, M. Tsuchida, H. Kumakura, K. Hisamatsu, F. S. Howell, and M. Mukaida. *Inorg. Chim. Acta.*, 1992, **195**, 221-225.

5. D. Moia, V. Vaissier, I. Lopez-Duarte, T. Torres, M. K. Nazeeruddin, B. C. O'Regan, J. Nelson, and P. R. F. Barnes. *Chem. Sci.* 2014, **5**, 281.
6. B. N. DiMarco, T. C. Motley, R. S. Balok, G. Li, M. A. Siegler, R. M. O'Donnell, K. Hu, and G. J. Meyer. *J. Phys. Chem. C.* 2016, **120**, 14226.
7. T. Daeneke, A. J. Mozer, T. H. Kwon, N. W. Duffy, A. B. Holmes, U. Bach, and L. Spiccia. *Energy Environ. Sci.*, 2012, **5**, 7090.
8. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016

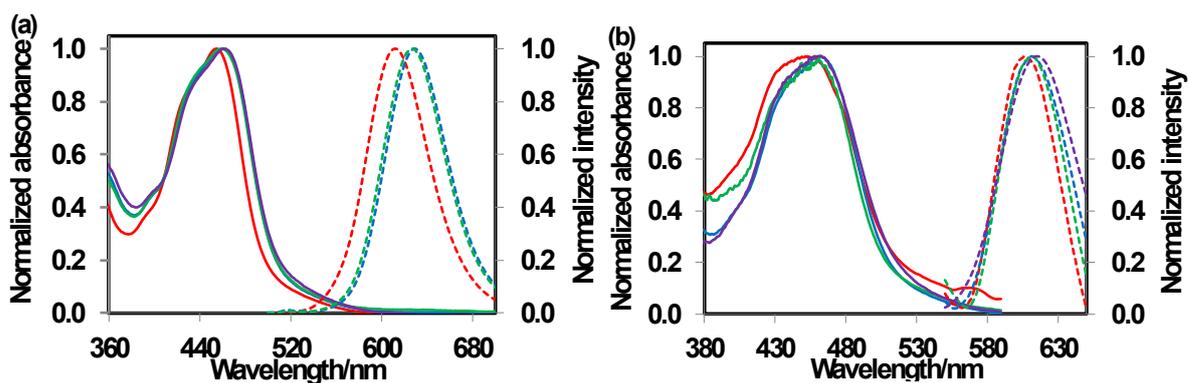


Figure S1 Absorption (solid) and emission (dashed) spectra of **P1** (red) **P2** (blue) **P3** (green) and **P4** (purple) measured in (a) 0.1 M acetate buffer pH 5 and methanol (1:3) containing 0.1 M NaClO₄ and in (b) FTO/TiO₂.

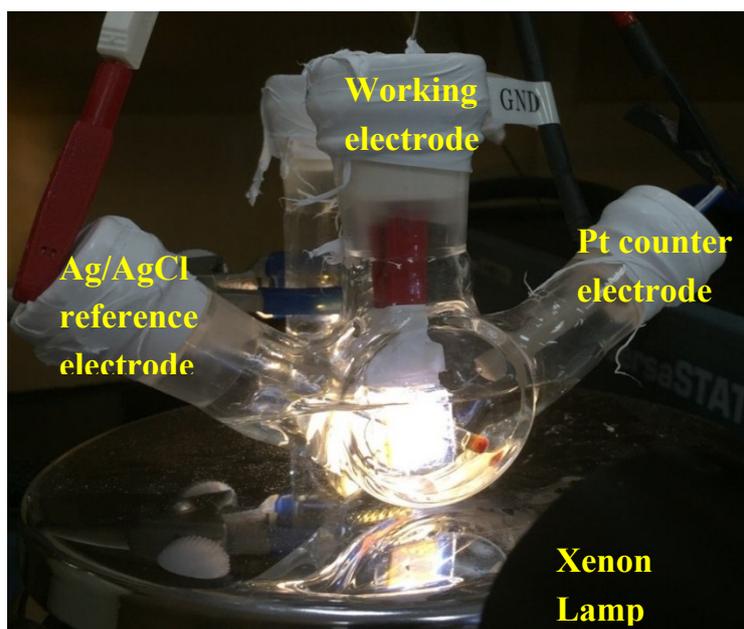


Figure S2 A photograph of the custom-made DSPEC containing FTO/TiO₂/dye working electrode, Ag/AgCl reference electrode and platinum wire counter electrode that are connected to a potentiostat.

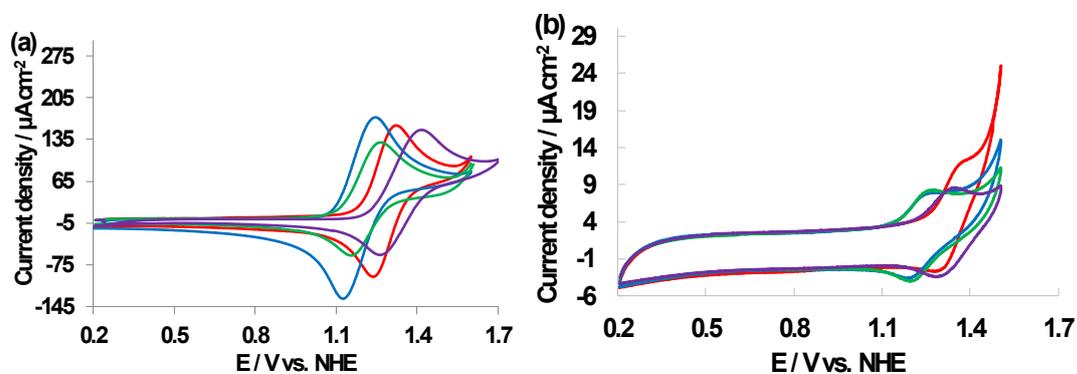


Figure S3 (a) Cyclic voltammograms of **P1** (red), **P2** (blue), **P3** (green), **P4** (purple) immobilized in FTO/TiO₂ electrode using 0.1 M acetate buffer pH 5 containing 0.1 M NaClO₄ electrolyte solution at the scan rate 0.1 V sec⁻¹; (b) The CV of the dye solutions (0.6 mM) in 1:3 methanol/0.1 M acetate buffer pH 5 and methanol containing 0.1 M NaClO₄. The assignments of the redox potentials are presented in Table 1.

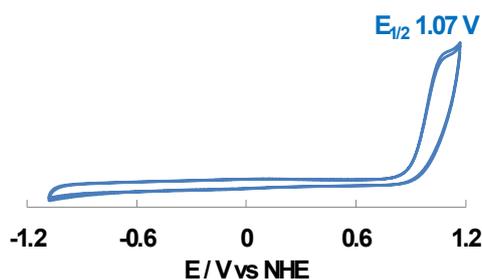


Figure S4 Cyclic voltammogram of EDTA acetate buffer pH 5 solution at the scan rate 0.1 V sec⁻¹. The $E_{1/2}$ was determined from the E_{pa} value.

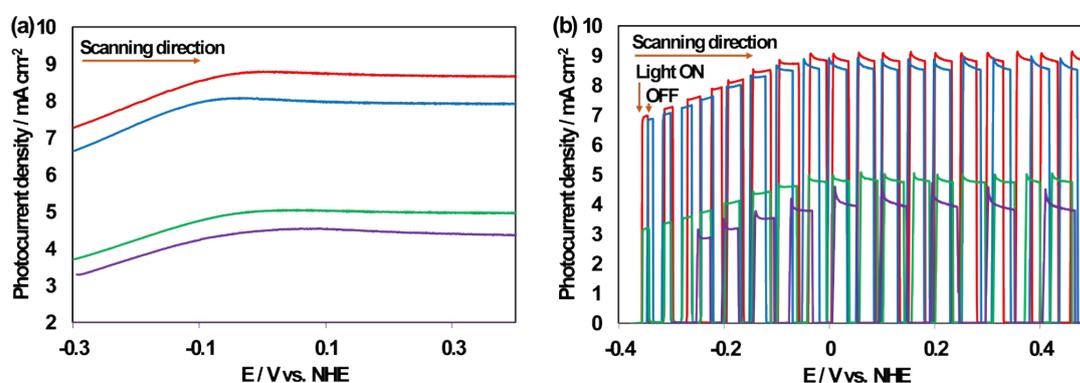


Figure S5 Linear sweep voltammograms of the FTO/TiO₂/P1 (red) FTO/TiO₂/P2 (blue) FTO/TiO₂/P3 (green) FTO/TiO₂/P4 (purple) (a) under continuous photoirradiation (b) under chopped illumination at a scan rate 0.01 V sec⁻¹. Xenon light (160 mW cm⁻²) with 400 nm long pass filter was used to irradiate the electrodes from the FTO side.

Table S1 Reorganization energies of the dyes on TiO₂ measured in acetonitrile

Dye	c_0 [10 ¹⁹ cm ⁻³]	D_{app} at 300 K [10 ⁻¹⁰ cm ² s ⁻¹]	E_{act} [meV]	λ [meV]
P1	13.0 ± 0.5	0.5 ± 0.1	495 ± 28	1916 ± 134
P2	13.0 ± 1.2	1.2 ± 0.2	424 ± 32	1879 ± 183
P3	11.2 ± 0.5	0.2 ± 0.04	548 ± 16	2422 ± 173
P4	8.2 ± 0.2	0.2 ± 0.1	644 ± 24	2874 ± 178

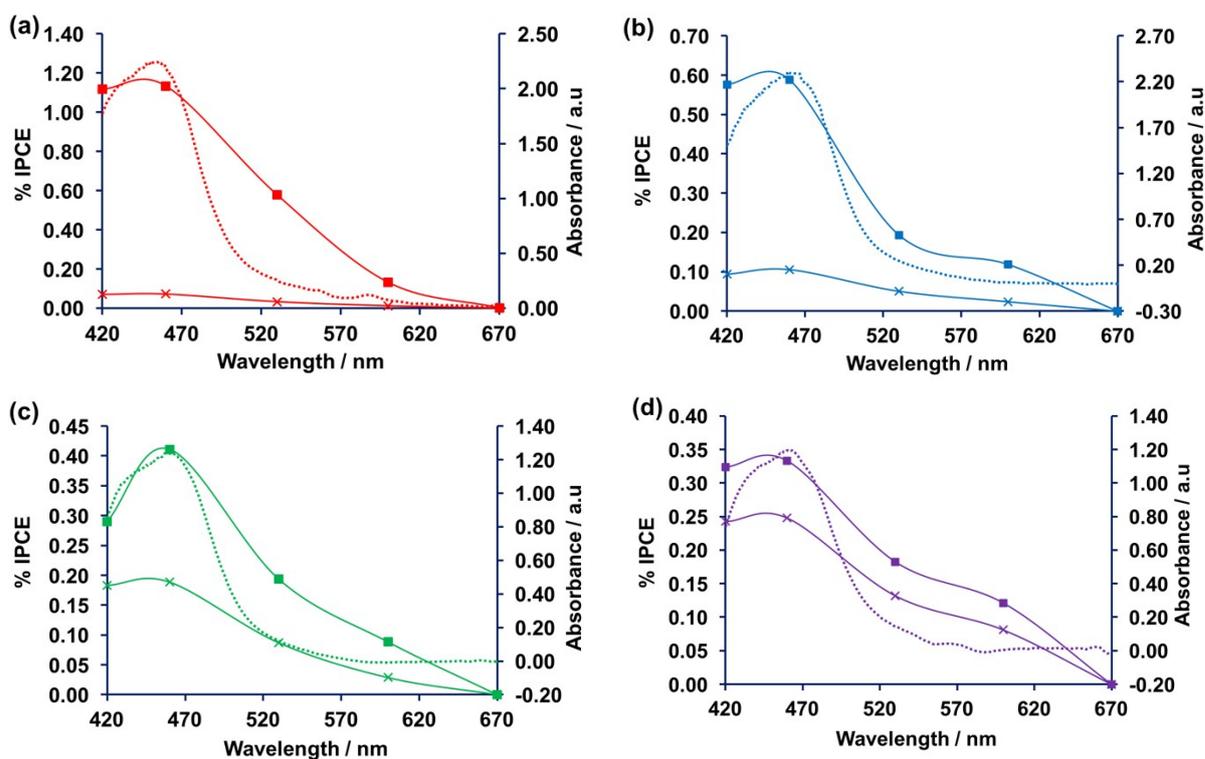
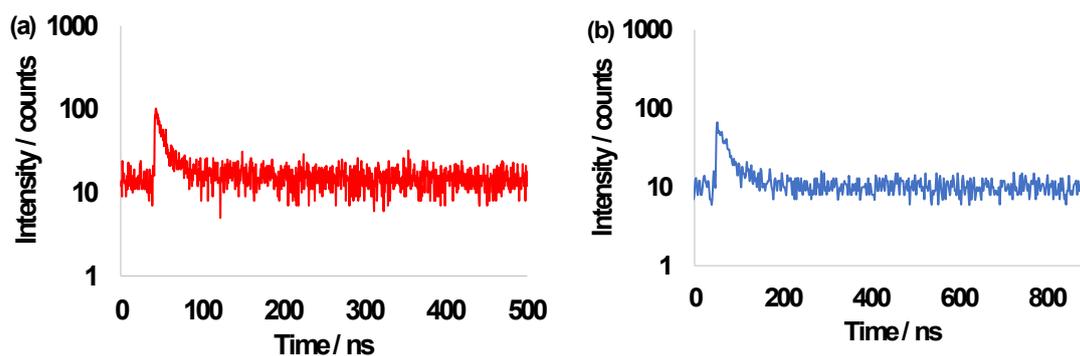


Figure S6 The IPCE value of (a) FTO/TiO₂/P1 (b) FTO/TiO₂/P2 (c) FTO/TiO₂/P3 (d) FTO/TiO₂/P4 in absence of EDTA (x) and presence of EDTA (■) in comparison with their absorption spectra given as dotted lines.



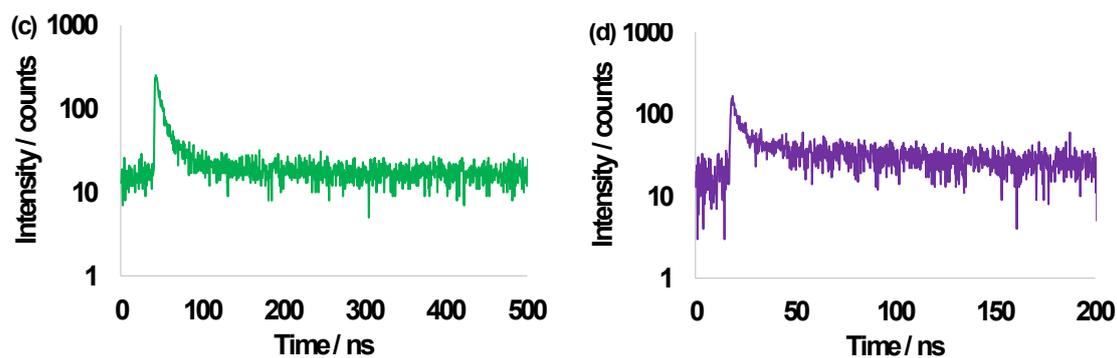


Figure S7 Lifetime decay profiles of (a) P1 (b) P2 (c) P3 and (d) P4 in FTO/TiO₂ film

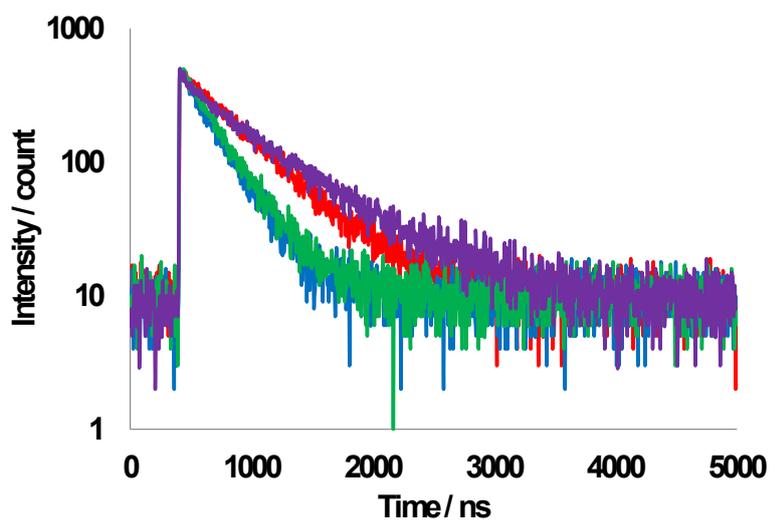


Figure S8 Lifetime decay profiles of P1 (red) P2 (blue) P3 (green) and P4 (purple) in solution

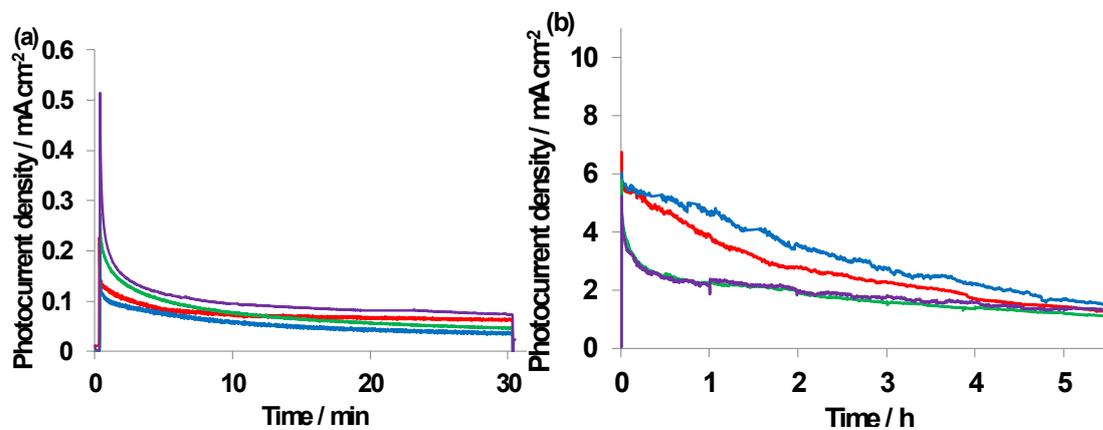


Figure S9 Time-course photocurrent density generated by the FTO/TiO₂/P1 (red)

FTO/TiO₂/P2 (blue) FTO/TiO₂/P3 (green) FTO/TiO₂/P4 (purple) electrodes under continuous irradiation at 0.05 V NHE performed in 0.1 M acetate buffer pH 5 containing 0.1 M NaClO₄ electrolyte solutions (a) in the absence of EDTA for 30 min photolysis; (b) in the presence of 30mM EDTA for 5.5 h photolysis.

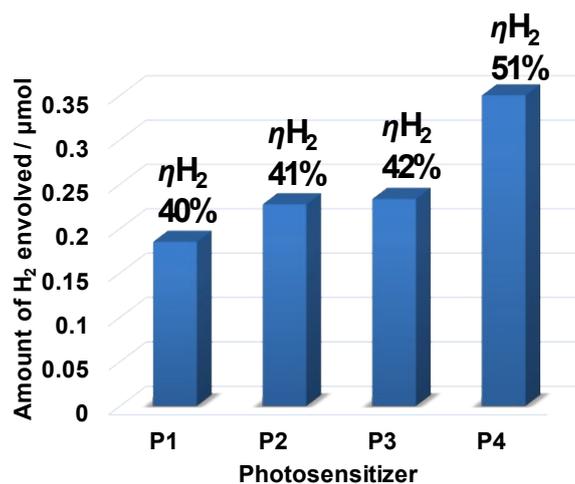


Figure S10 The amount of H₂ evolved after 30 min photolysis under the conditions described in Fig. S7a, where faradaic efficiency were 40, 41, 42, and 51% for P1, P2, P3, and P4 respectively.

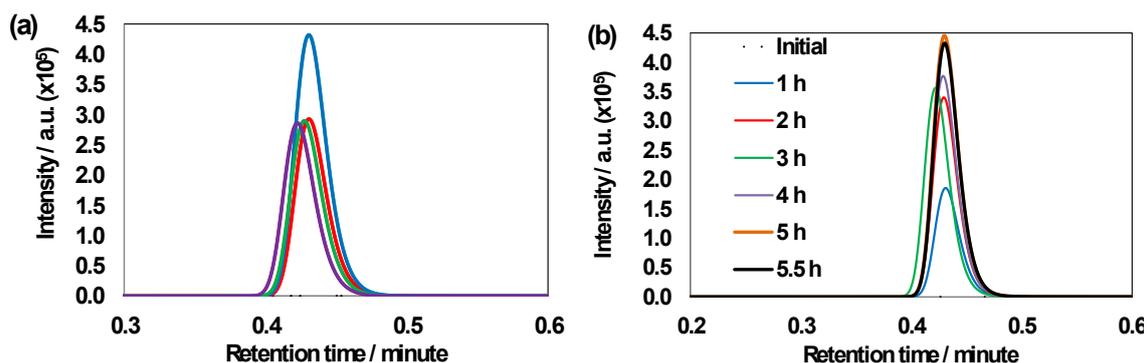


Figure S11 (a) Gas chromatograms showing the hydrogen peak at the retention time 0.42 min for the gas sample taken from FTO/TiO₂/P1 (red), FTO/TiO₂/P2 (blue), FTO/TiO₂/P3 (green), and FTO/TiO₂/P4 (purple) after 5.5 h photolysis; (b) The increase in the hydrogen peak over time is shown for the photolysis of FTO/TiO₂/P2.

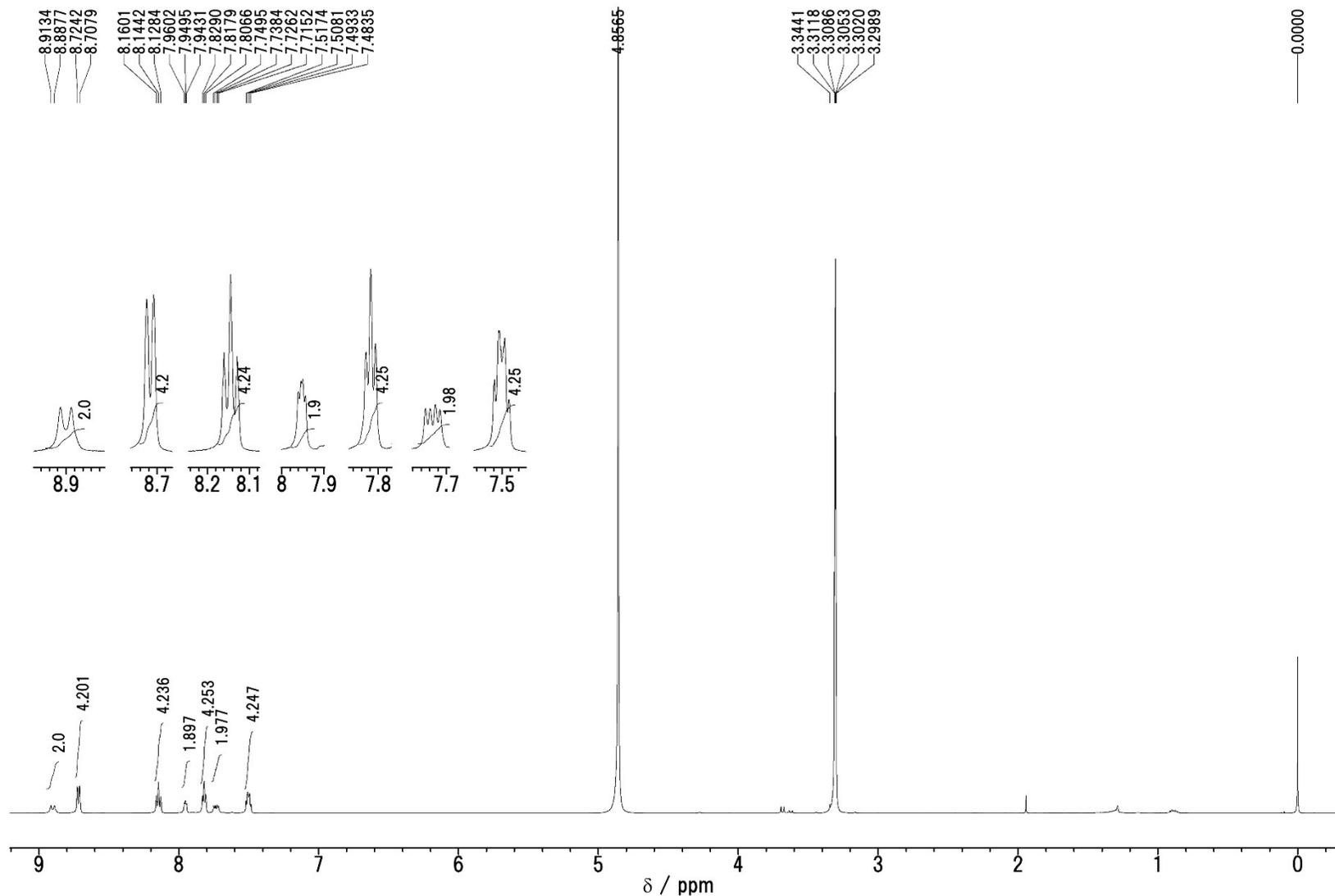


Figure S12 ¹H NMR spectrum of P1 in Methanol-d₄

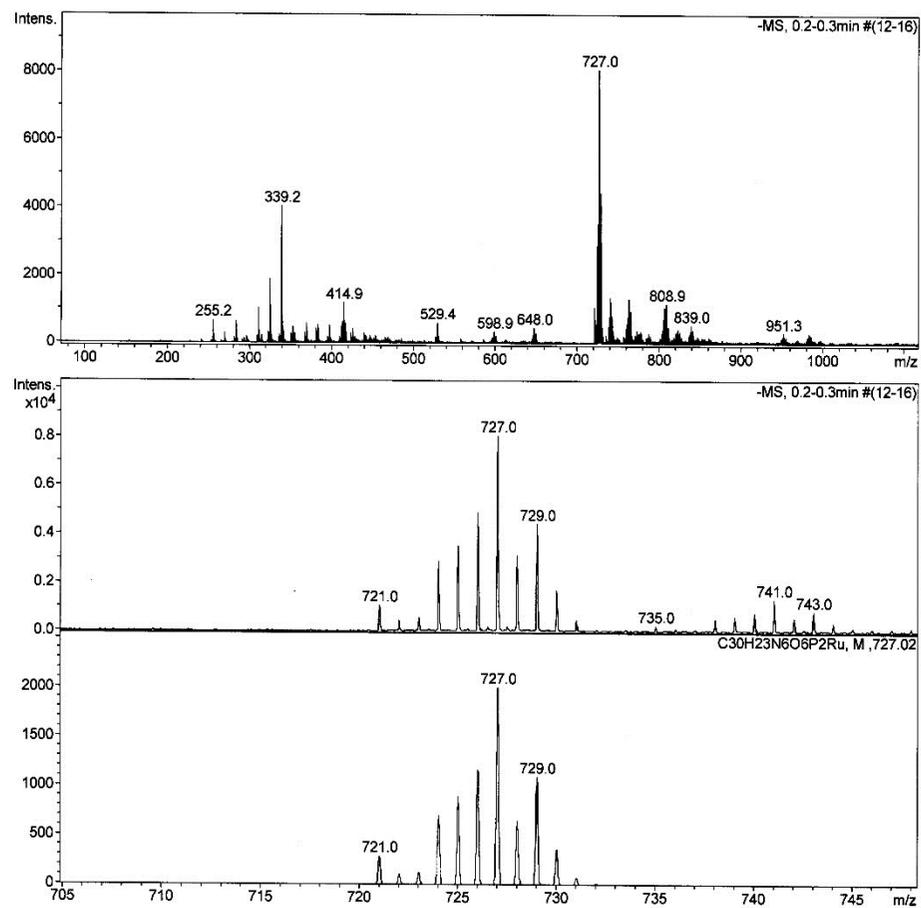


Figure S13 ESI-MS spectrum (negative mode) of P1, showing m/z 727.0 ([M-3H]⁻)

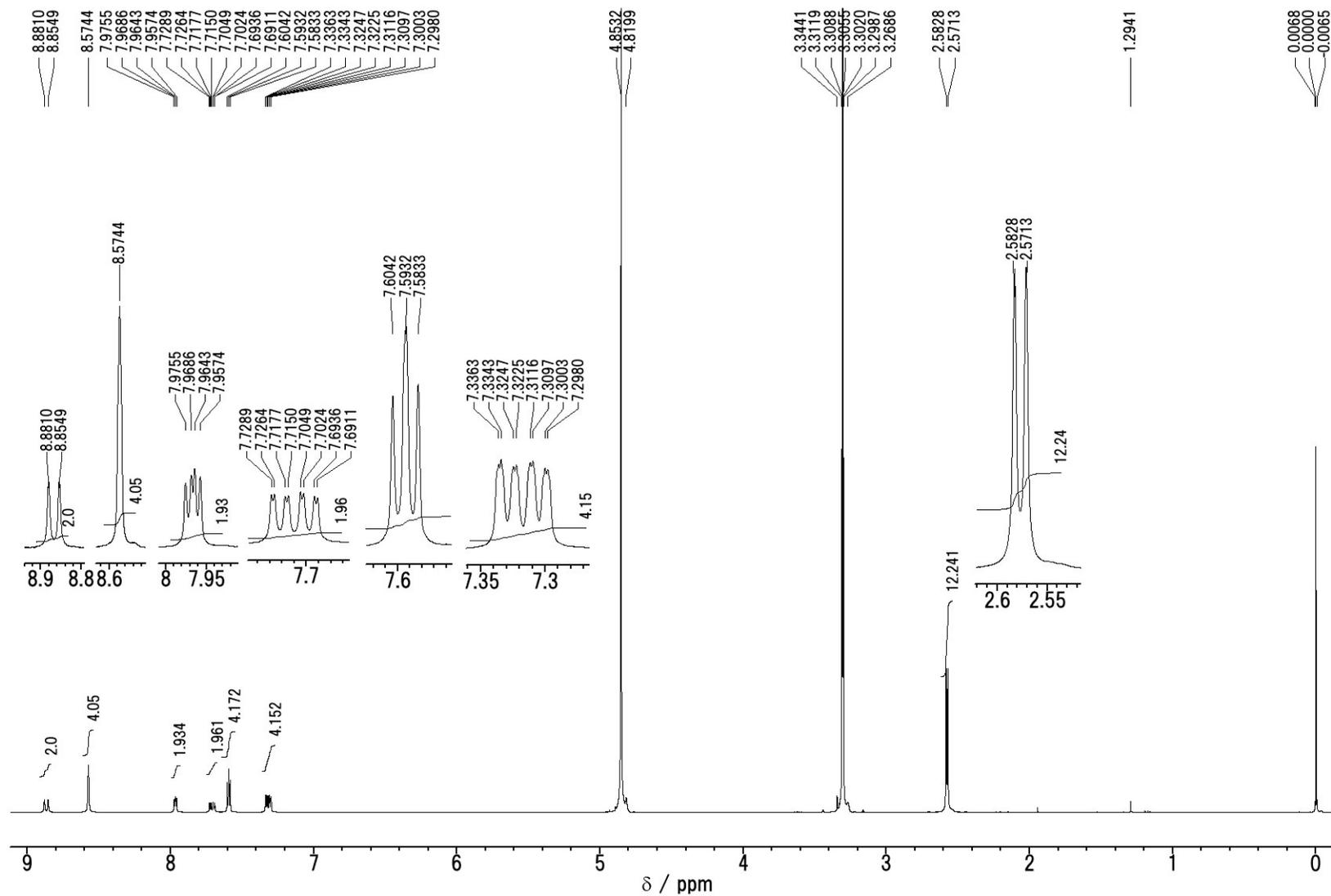


Figure S14 ¹H NMR spectrum of P2 in Methanol-d₄

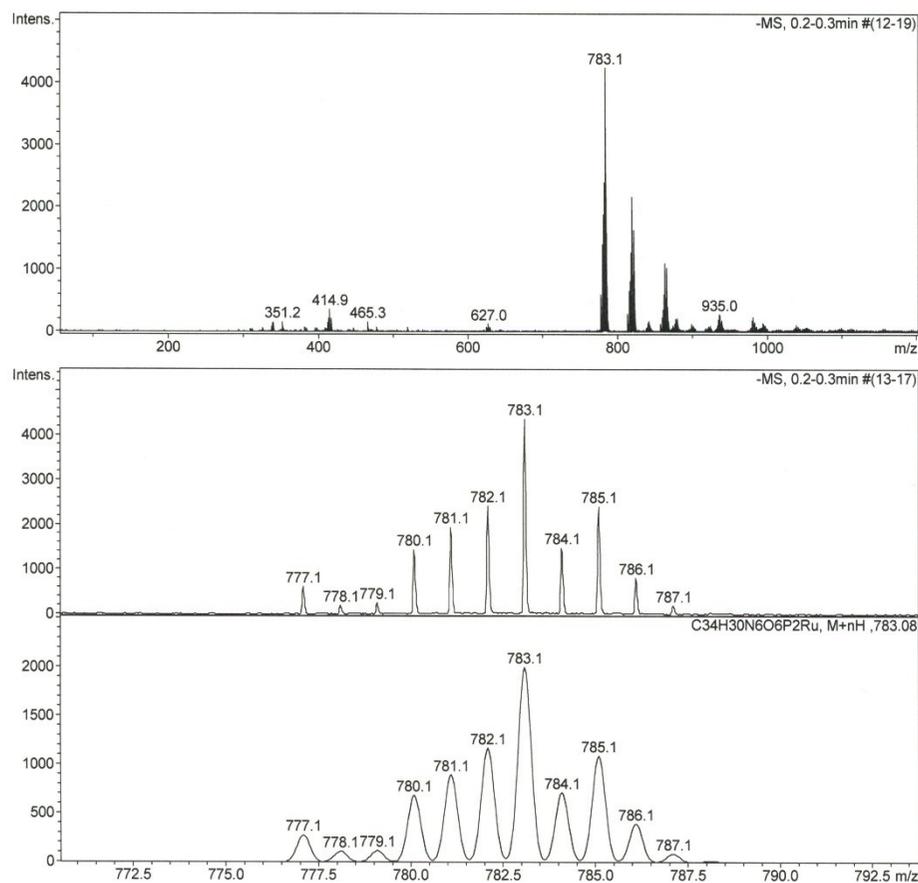


Figure S15 ESI-MS spectrum (negative mode) of P2 showing m/z 783.1 ($[M-3H]^-$)

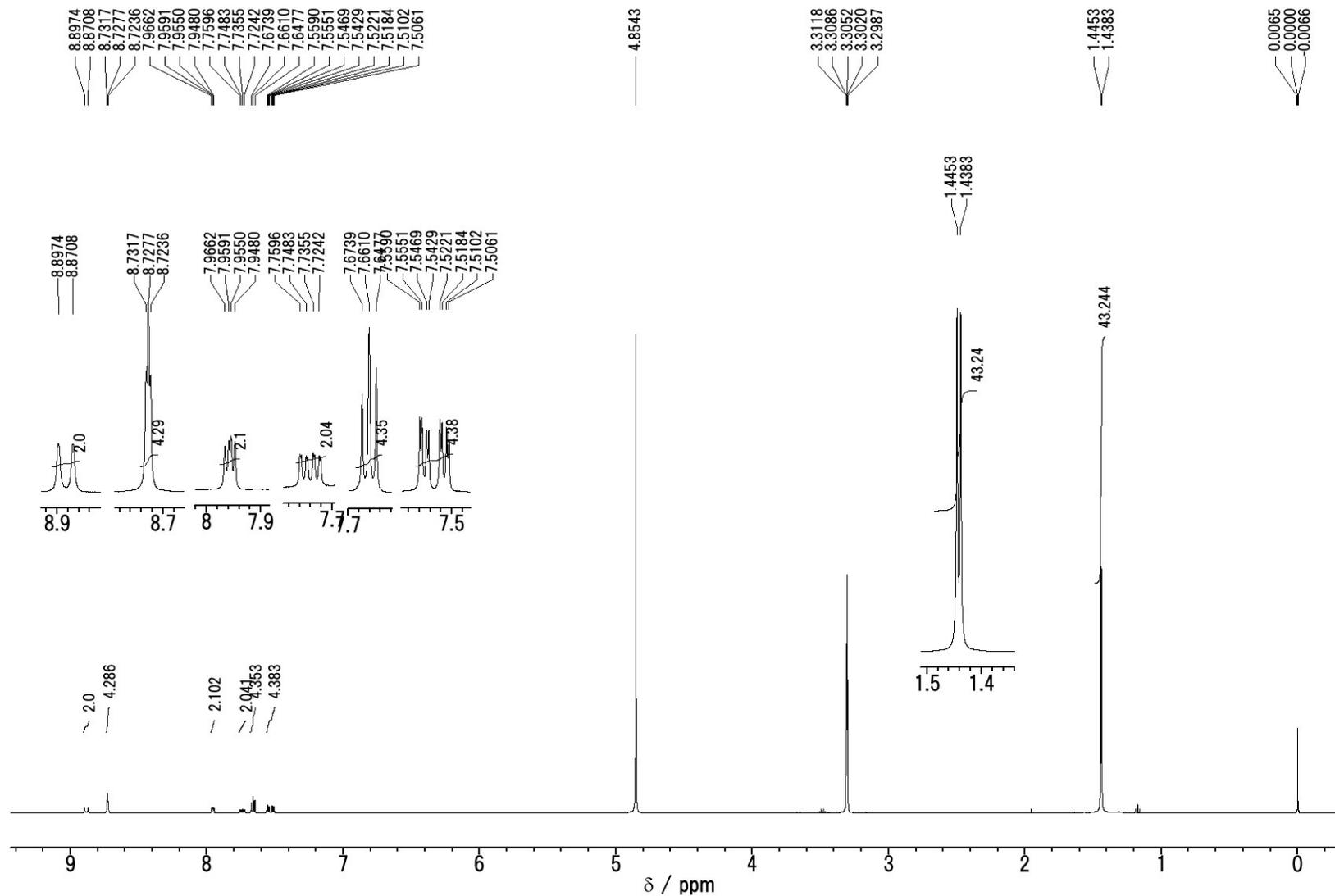


Figure S16 ¹H NMR spectrum of P3 in Methanol-d₄

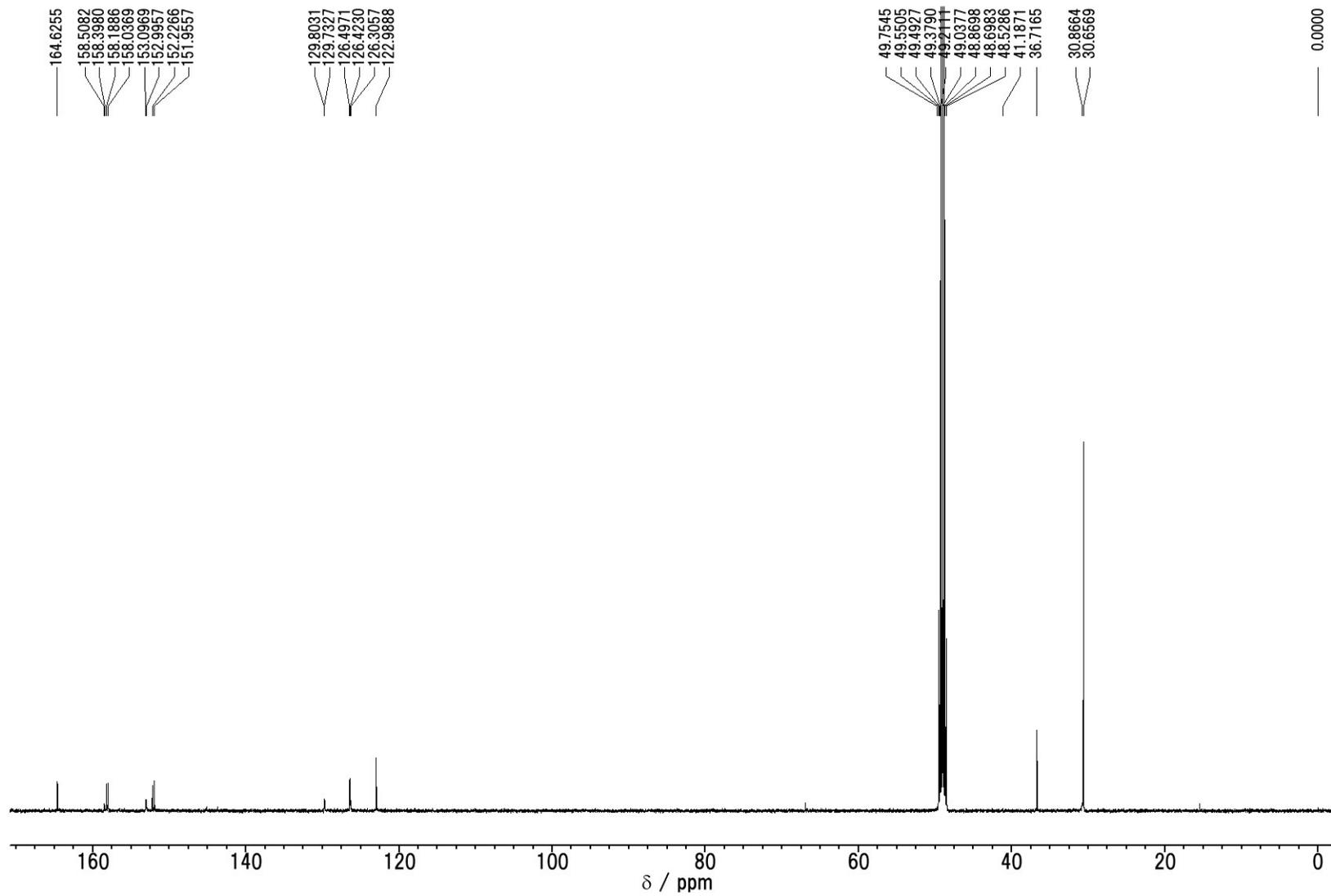


Figure S17 ¹³C NMR spectrum of P3 in Methanol-d₄

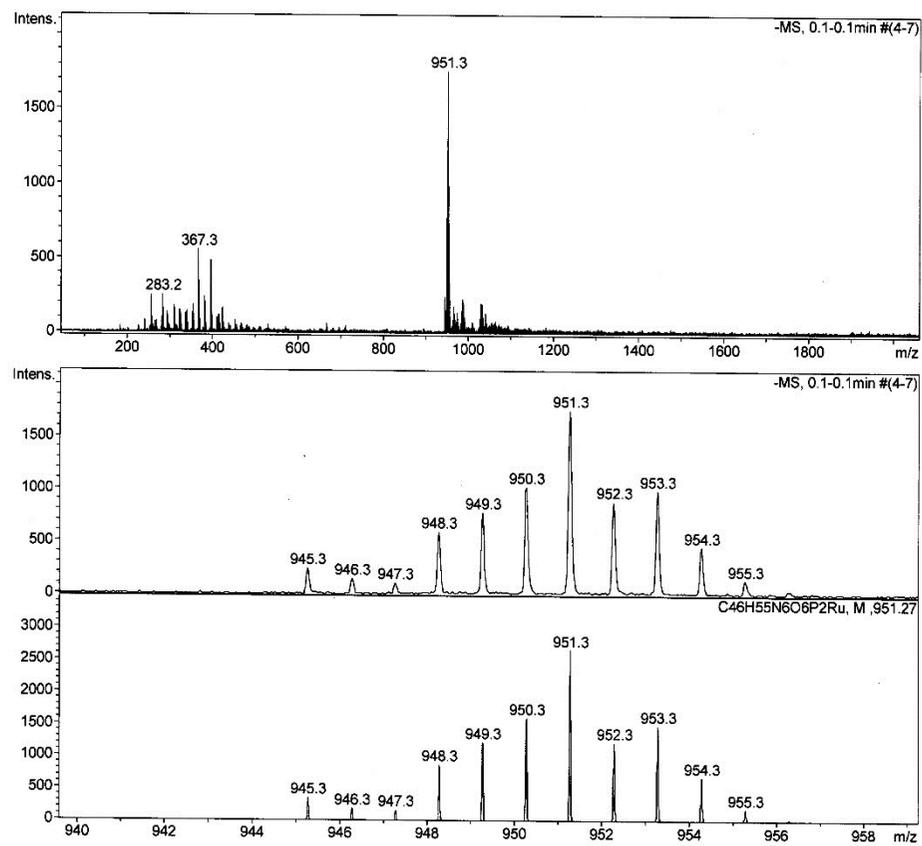


Figure S18 ESI-MS spectrum (negative mode) of P3, showing m/z 951.3 ($[M-3H]^-$)

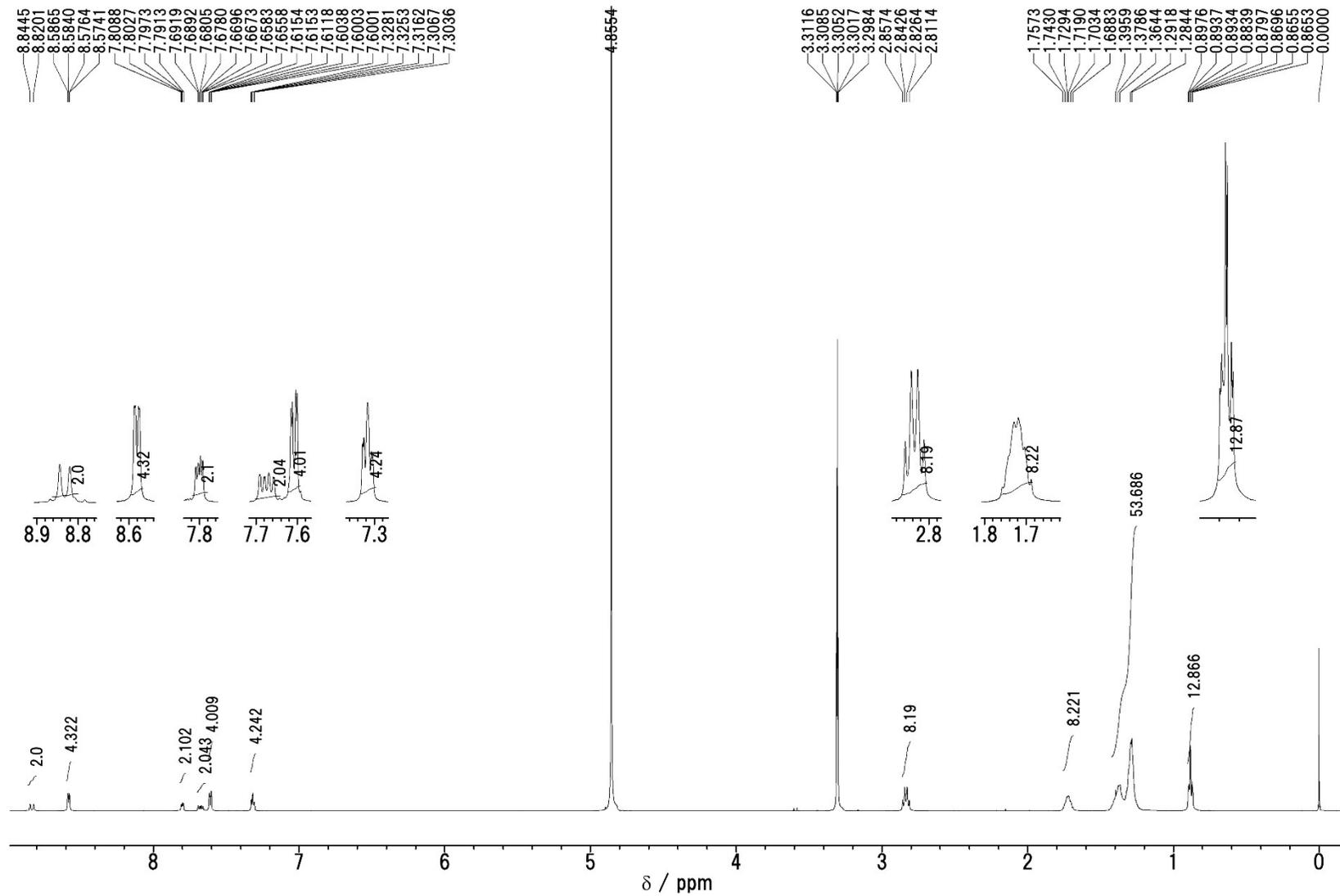


Figure S19 ^1H NMR spectrum of P4 in Methanol- d_4

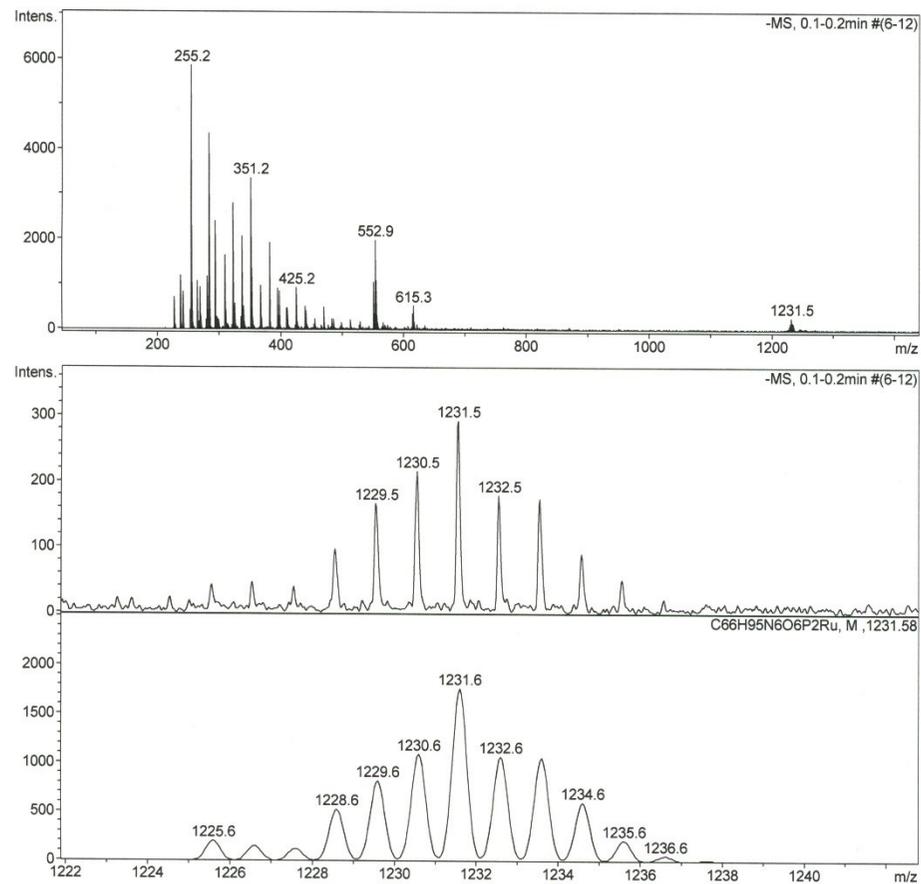


Figure S20 ESI-MS spectrum (negative mode) of **P4**, showing m/z 1230.5 ($[M-3H]^-$)