Supporting Information

Photoinduced Electron Transfer of Zinc Porphyrin-Oligo(Thienylenevinylene)-Fullerene[60] Triads; Thienylenevinylenes as Efficient Molecular Wires

Frédéric Oswald,[a] D.-M. Shafiqul Islam,[b,c] Mohamed E. El-Khouly,[d] Yasuyuki Araki,[c] Rubén Caballero,[a] Pilar de la Cruz,[a] Osamu Ito*[e] and Fernando Langa*[a]

[a]*Instituto de Nanociencia Nanotecnología y Materiales Moleculares (INAMOL), Universidad de Castilla-La Mancha, 45071-Toledo, Spain. E-mail: Fernando.Langa@uclm.es*

[b]*Department of Chemistry, Jahangirnagar University, Savar, Dhaka, Bangladesh.*

[c]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira, Sendai, 980-8577, Japan.*

[d]*Department of Chemistry, Faculty of Science, Kafr El-Sheikh University, Kafr ElSheikh 33516, Egypt*

[e]*PRESTO, JST, Kitanakayama 2-1-6, Izumi-ku, Sendai, 981-3215, Japan. E-mail: ito@tagen.tohoku.ac.jp*

Contents

Experimental Section

Chemicals: Buckminsterfullerene, C_{60} (+99.95%) was purchased from BuckyUSA (Bellaire, TX). Toluene, PhCN and *o*-dichlorobenzene (*o*-DCB) were purchased from Aldrich Chemicals (Milwaukee, WI). Tetrabutylammonium perchloride, *n*-Bu_4NClO_4 used in electrochemical studies was from Fluka Chemicals. All other chemicals were used as received.

***Electrochemical Measurements*:** Reduction potentials E_{red} and oxidation potentials E_{ox} were measured by cyclic voltammetry with a potentiostat BAS CV50W in a conventional three-electrode cell equipped with glassy carbon working electrode Platinum wire counter electrodes and an Ag/AgCl reference electrode at scan rate of 100 mV/s. The E_{red} and E_{ox} were expressed vs. Fc/Fc^+ used as internal reference. In each case, a solution containing 0.2 mM of a sample with 0.05 M of $(n\text{-}Bu)_4NClO_4$ Fluka purest quality was deaerated with argon bubbling before measurements.

***Steady-state Measurements*:** Steady-state absorption spectra in the visible and near-IR regions were measured on a Jasco V570 DS spectrophotometer. Steady-state fluorescence spectra were measured on a Shimadzu RF-5300 PC spectrofluorophotometer equipped with photomultiplier tube having high sensitivity in the 700-800 nm region.

***Time-Resolved Fluorescence Measurements*:** The time-resolved fluorescence spectra were measured by single photon counting method using a streak-scope Hamamatsu Photonics, C4334-01 as a detector and the laser light second harmonic generation SHG, 410 nm of a Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, fwhm = 1.5 ps) as an excitation source. Lifetime were evaluated with software provided with the equipment.

***Nanosecond Transient Absorption Measurements*:** Nanosecond transient absorption measurements were carried out using the SHG (532 nm) of an Nd:YAG laser (Spectra Physics, Quanta-Ray GCR-130, fwhm 6 ns) as excitation source. For the transient absorption spectra in the near-IR region (600-1600 nm), the monitoring light from a pulsed Xe lamp was detected with a Ge-avalanche photodiode (Hamamatsu Photonics, B2834).[21]

MO calculations. The molecular orbital calculations are performed after optimization of the structures by *ab initio* B3LYP/3-21G method.

General procedure for the synthesis of aldehydes 3a,b: Under argon atmosphere, potassium tert-butoxide (0.22 mmol) was slowly added to a refluxing solution of phosphonateporphyrin **4** (0.16 mmol) and oligomer **2a,b** (0.16 mmol) in dry THF. After 16-20 hours, the crude mixture was cooled to room temperature and a mixture of H_2O/CH_3OH (1:1) was added. The phases were separated and the aqueous phase was extracted with $CHCl_3$. The combined organic phases were washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography using as eluent a mixture toluene/hexane.

Compound 3a: Reaction time: 16 hours. Purified using silica gel and toluene/hexane 7:3 as eluent. Yield: 42% (93 mg, 0.07 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 9.98 (s, 1H), 8.94 (d, 2H, J = 4.6 Hz), 8.77 (d, 2H, J = 4.6 Hz), 8.71 (s, 4H), 8.22 (d, 2H, J = 8.0 Hz), 7.85 (d, 2H, *J* = 8.0 Hz), 7.56 (d, 1H, *J* = 16.0 Hz), 7.29 (d, 1H, *J* = 15.0 Hz), 7.26 (s, 6H), 7.23 (d, 1H, *J* = 16.0 Hz), 7.09 (s, 2H), 6.98 (d, 1H, *J* = 15.0 Hz), 2.87 (t, 2H, *J* = 7.7 Hz), 2.74 (t, 2H, *J* = 7.7 Hz), 2.66 (m, 8H), 2.63 (s, 9H), 1.85 (s, 18H), 1.42-1.26 (m, 48H), 0.93-0.85 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 181.8, 153.0, 149.9, 149.7, 147.4, 144.1, 142.3, 142.2, 142.1, 141.9, 141.4, 139.3, 139.1, 137.4, 137.1, 136.4, 135.5, 134.9, 134.6, 134.0, 132.0, 131.1, 130.6, 127.6, 124.4, 120.4, 119.7,

118.8, 118.6, 32.3, 31.7, 31.61, 31.5, 31.3, 31.1, 29.7, 29.5, 29.4, 29.2, 27.2, 27.1, 26.4, 22.7, 22.6, 21.7, 21.5, 14.2, 14.1.3; FT-IR (ATR) ν/cm^{-1}: 3405, 3022, 2953, 2855, 2359, 1652, 1615, 1522, 1459, 1399, 1334, 1285, 1253, 1203, 1061, 927, 852, 829, 797, 722, 671; UV-Vis (CH_2Cl_2) λ_{max}/nm (log ε): 422 (6.69), 512 (5.99), 552 (5.84); MS (MALDI-TOF) *m/z*: calculated for $C_{108}H_{130}N_4OS_3Zn$: 1658.87; found:1659.20 (M^+).

Compound 3b: Reaction time: 20 hours. Purified using silica gel and toluene/hexane 7:3 as eluent. Yield: 54 % (167 mg, 0.08 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 9.94 (s, 1H), 8.93 (d, 2H, *J* = 4.5 Hz), 8.76 (d, 2H, *J* = 4.5 Hz), 8.70 (s, 4H), 8.20 (d, 2H, *J* = 8.2 Hz), 7.84 (d, 2H, *J* = 8.2 Hz), 7.53 (m, 1H), 7.37-7.28 (m, 7H) 7.01 (m, 14H), 2.86 (m, 2H), 2.64 (m, 39H), 1.84 (s, 18H), 1.70-1.20 (m, 128H), 0.95 (m, 48H); ^{13}C NMR (50 MHz, $CDCl_3$) δ/ppm: 183.2, 154.5, 151.3, 148.8, 145.6, 143.7, 140.7, 140.5, 138.8, 136.4, 135.4, 132.6, 132.1, 129.1, 125.9, 121.2, 89.8, 55.7, 38.8, 33.0, 31.1, 30.8, 28.6, 24.1, 23.1, 22.9, 19.3, 15.6; FT-IR (ATR) ν/cm^{-1}: 2921, 2839, 1732, 1454, 1376, 1254, 996, 918, 800. MS (MALDI-TOF) *m/z*: calculated for $C_{198}H_{270}N_4OS_8Zn$: 3044.2; found: 3044.8 (M).

General procedure for the synthesis of 1a,b: A mixture of the compound **3a** or **3b** (0.04 mmol), C_{60} (0.04 mmol) and sarcosine (0.12 mmol) in dry toluene was refluxed for 15-18 hours. After cooling to room temperature, the crude mixture was purified by column chromatography on silica gel using a mixture of toluene/hexane (1:1) as eluent.

Compound 1a: Reaction time: 15 hours. Yield: 42 % (41 mg, 0.02 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.93 (d, 2H, *J* = 4.5 Hz), 8.77 (d, 2H, *J* = 4.5 Hz), 8.71 (s, 4H), 8.21 (d, 2H, ^{3}*J*=7.8 Hz), 7.84 (d, 2H, *J*=7.8 Hz), 7.55 (d, 1H, *J* = 16.0 Hz), 7.28 (s, 6H), 7.20 (d, 1H, *J* = 16.0 Hz), 7.12-6.95 (m, 4H), 5.36 (s, 1H), 5.03 (d, 1H, *J* = 9.6 Hz), 4.27 (d, 1H, *J* = 9.6 Hz), 2.96 (s, 3H), 2.84-2.58 (m, 12H), 2.64 (s, 9H), 1.85 (s, 18H), 1.65-1.2 (m, 48H), 1-0.85(m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 145.2, 144.6,

144.3, 142.6, 142.1, 141.9, 141.5, 139.8, 139.3, 139.0, 137.4, 137.2, 136.5, 135.0, 134.9, 132.1, 131.1, 130.6, 128.7, 128.2, 127.6, 124.4, 119.8, 118.8, 118.5 ,77.3, 77.2, 70.0, 69.0, 40.6, 31.9, 31.8, 31.7, 31.6, 31.3, 29.7, 29.6, 29.5, 29.3, 29.0, 27.1, 22.7, 22.6, 21.8, 21.7, 21.5, 14.2, 14.1; FT-IR (KBr) ν/cm^{-1}: 2921, 2850, 1456, 1205, 998, 798, 527; UV-Vis (CH_2Cl_2) λ_{max}/nm (log ε): 422 (5.55), 494 (4.93), 594 (4.23). MS (MALDI-TOF) *m/z*: calculated for $C_{170}H_{135}N_5S_3Zn$: 2409.92; found: 2409.12 (M); 720 (C_{60}).

Compound 1b: Reaction time: 18 hours. Yield: 49 % (77 mg, 0.02 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.94 (d, 2H, *J* = 3.8 Hz), 8.77 (d, 2H, *J* = 3.8 Hz), 8.71 (s, 4H), 8.21 (d, 2H, *J* = 7.8 Hz), 7.84 (d, 2H, *J* = 7.8 Hz), 7.53 (d, 1H, *J* = 15.6 Hz), 7.26 (m, 7H), 7.05 (m, 14H), 5.33 (s, 1H), 5.02 (d, 1H, *J* = 9.0 Hz), 4.26 (d, 1H, J = 9.0 Hz), 2.96 (m, 3H), 2.82 (m, 2H), 2.64 (m, 39H), 1.86 (s, 18H), 1.71-1.02 (m, 128H), 1.01-0.67 (m, 48H); FT-IR (KBr) ν/cm^{-1}: 2921, 2839, 1732, 1454, 1376, 996, 918, 522; UV-Vis (CH_2Cl_2) λ_{max}/nm (log ε): 422 (6.20), 557, (5.82), 584, (5.80), 629.5 (5.70). MS (MALDI-TOF) m/z: calculated for $C_{260}H_{275}N_5S_8Zn$: 3792.88; found: 3792.40 (M); 720 (C_{60}).

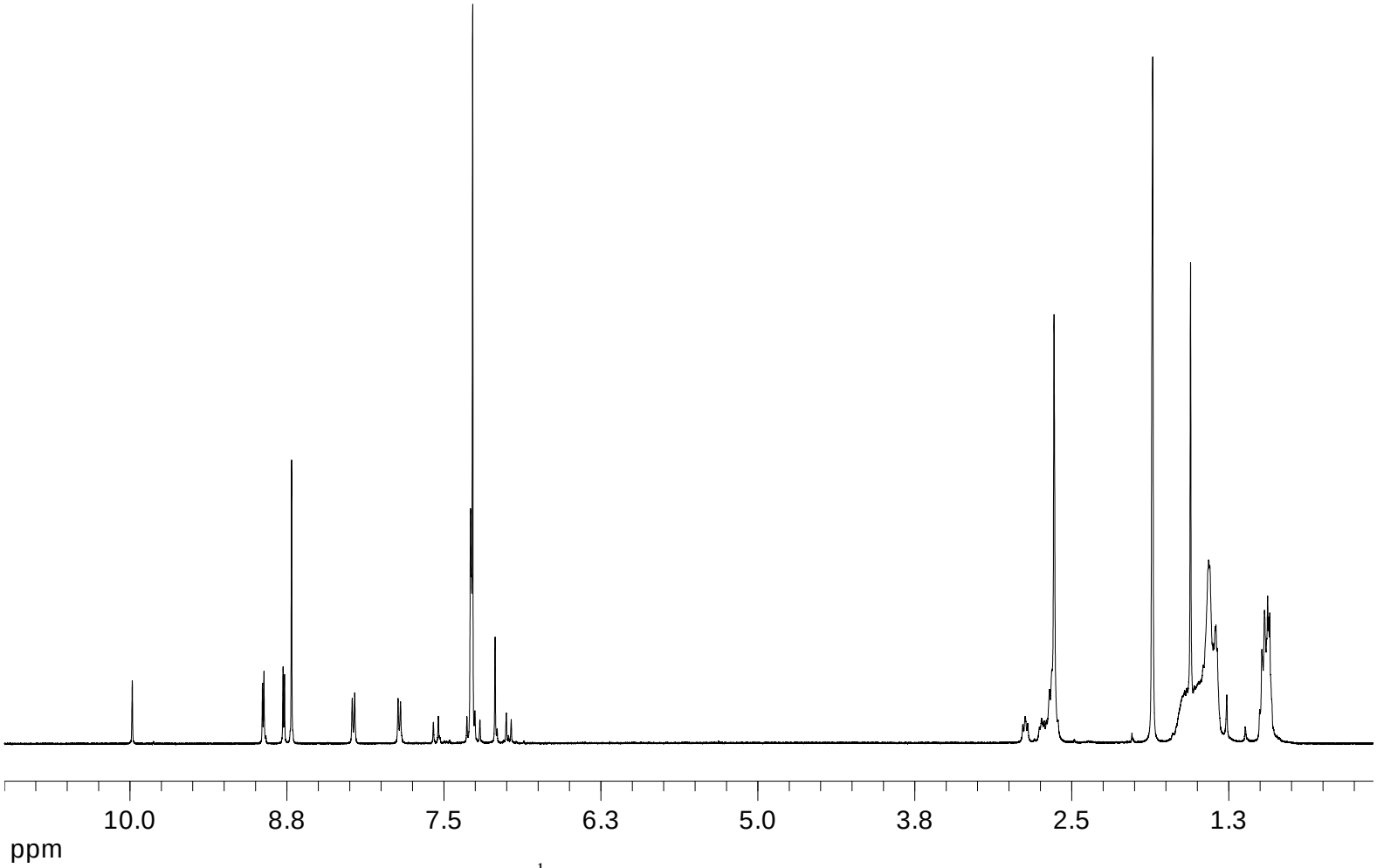

Fig. S1. ^{1}H-NMR spectrum of compound **3a**

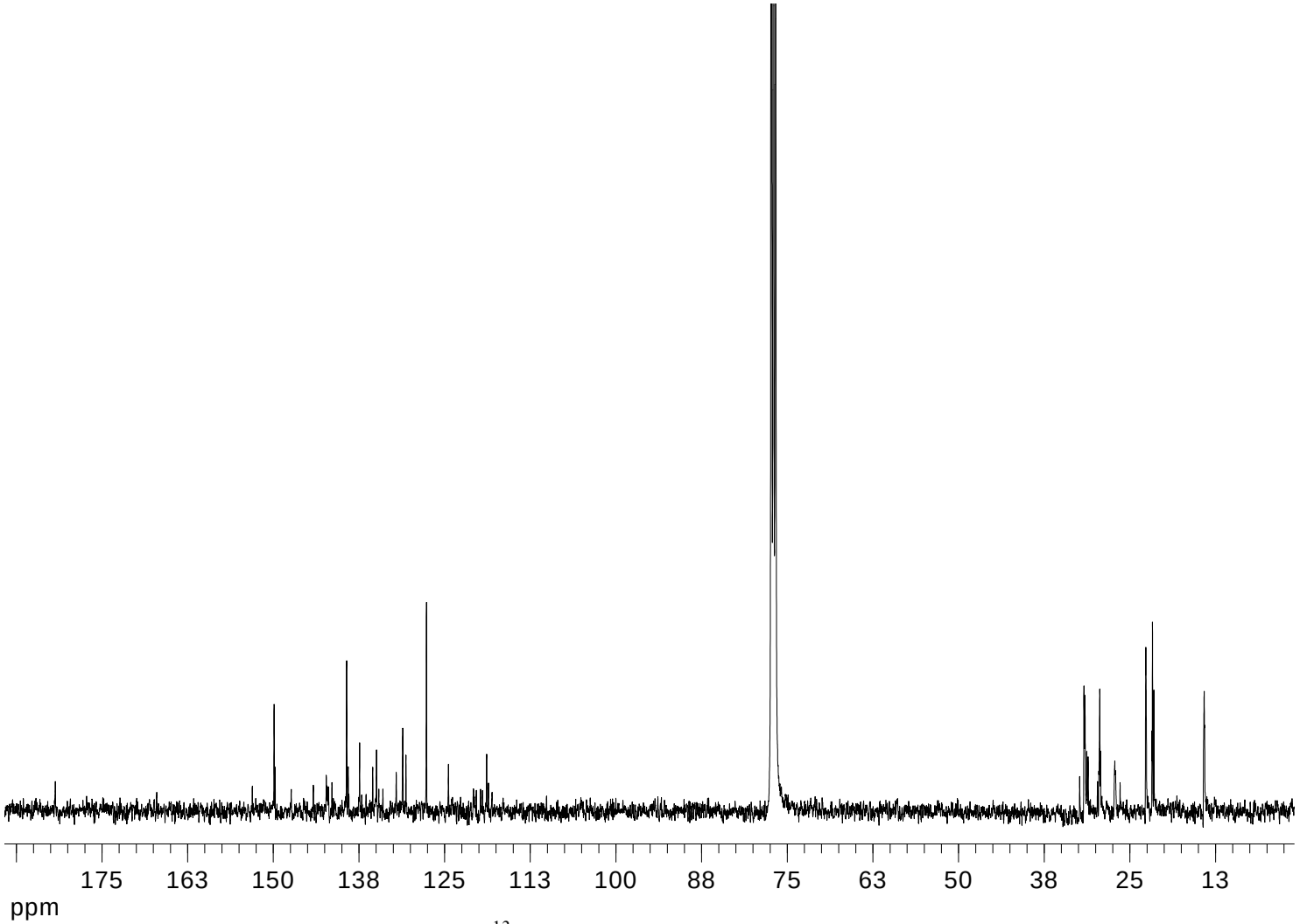

Fig. S2. ^{13}C-NMR spectrum of compound **3a**

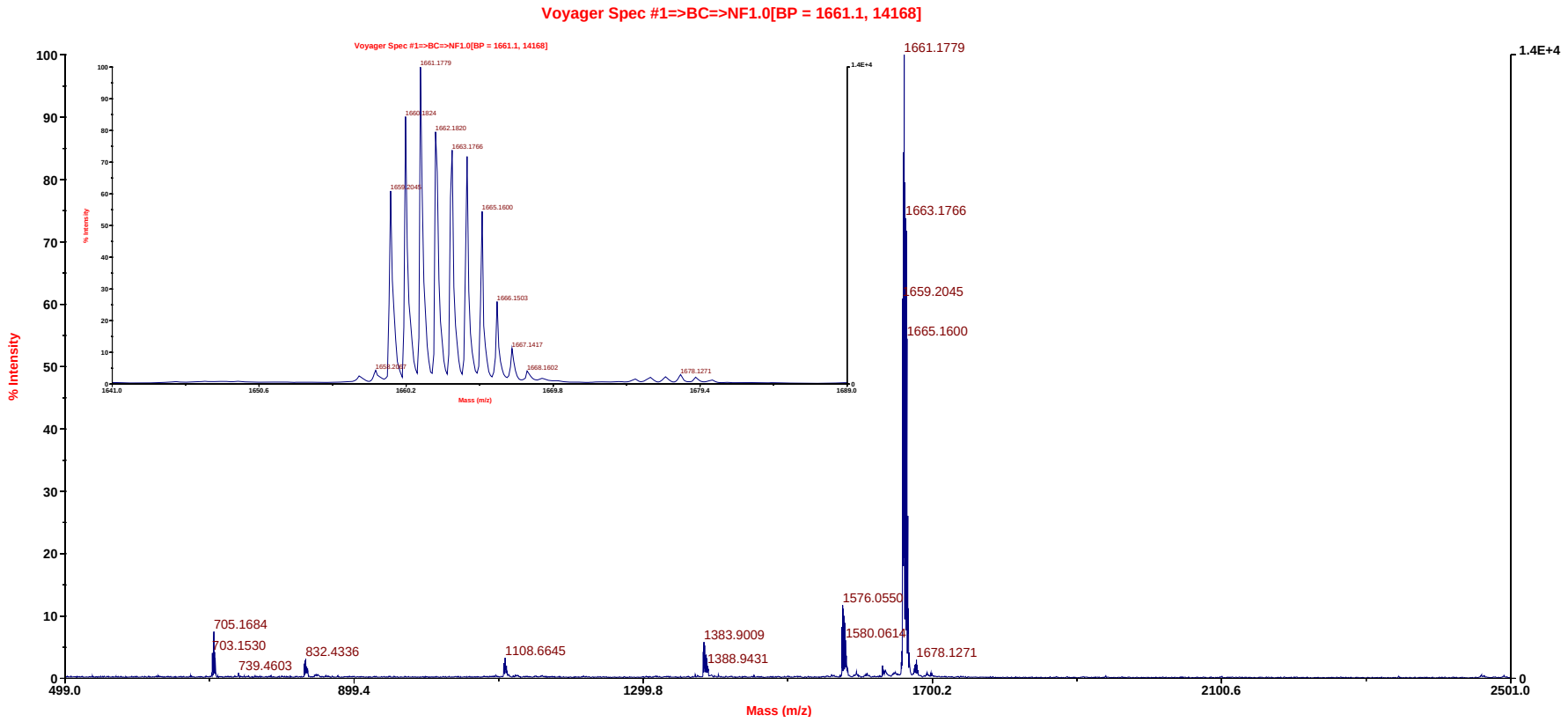

Fig. S3. Mass spectrum of compound **3a**

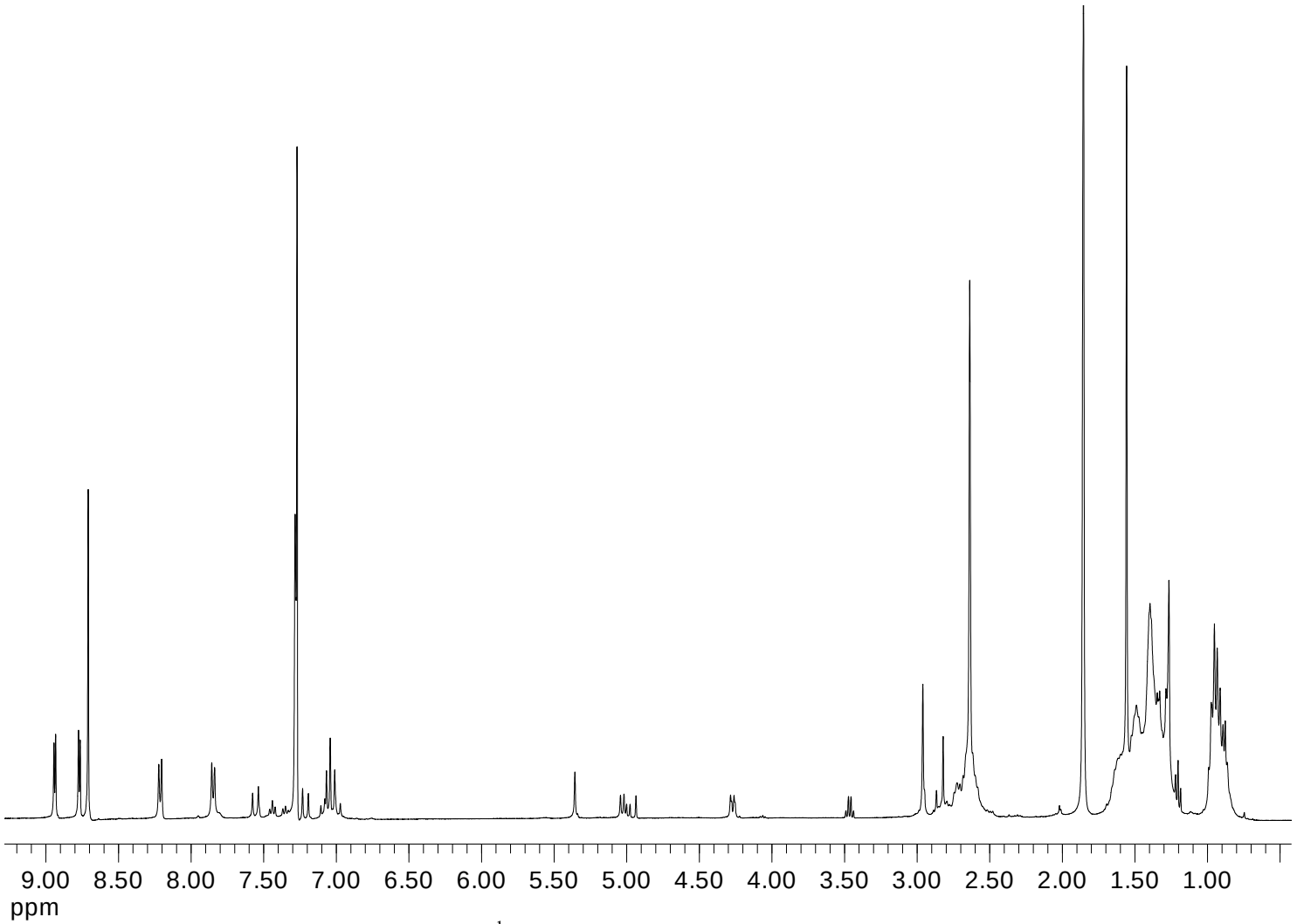

Fig. S4. ^{1}H-NMR spectrum of compound **1a**

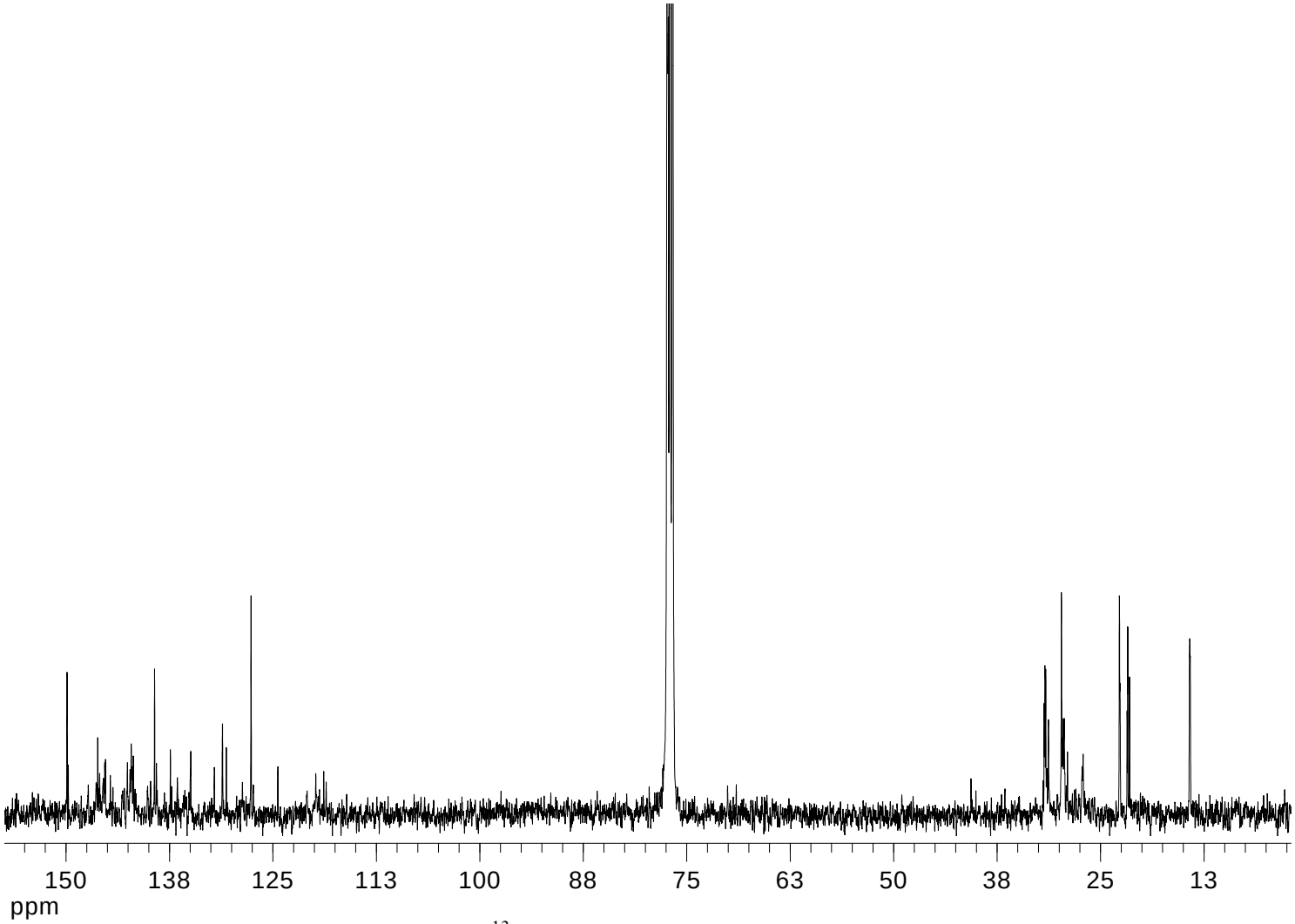

Fig. S5. ^{13}C-NMR spectrum of compound **1a**

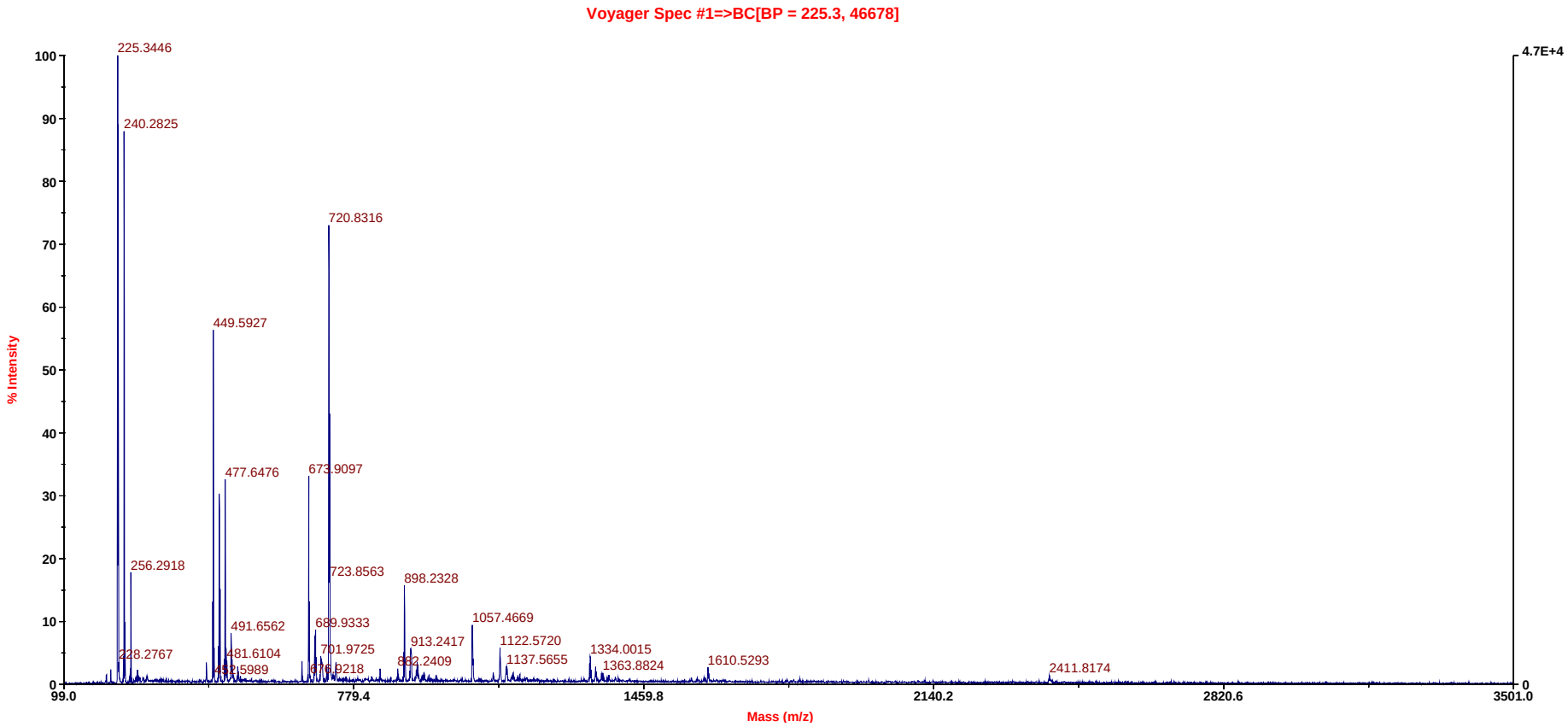

Fig. S6. Mass spectrum of compound **1a**

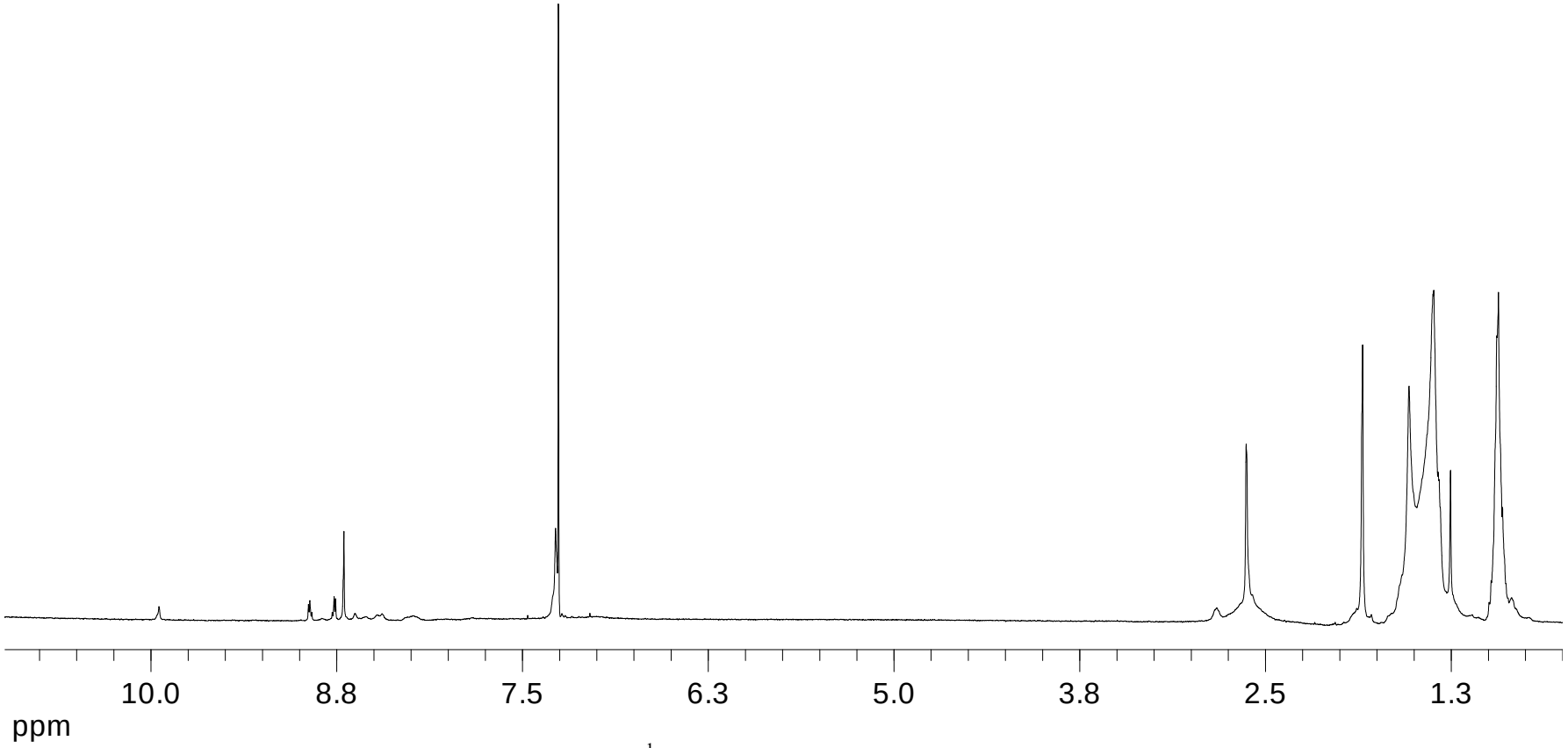

Figure S7. ^{1}H-NMR spectrum of compound **3b**

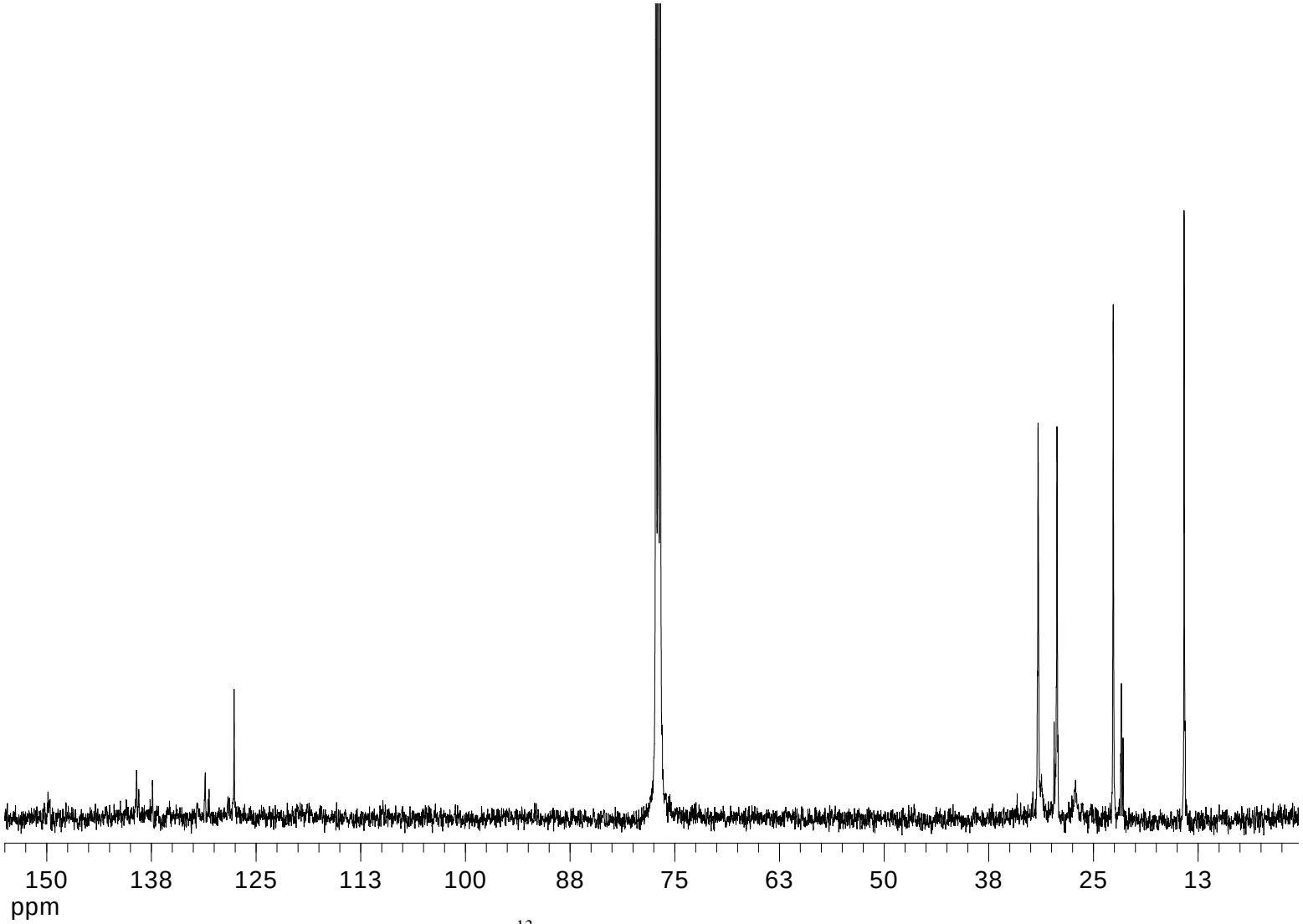

Figure S8. ^{13}C-NMR spectrum of compound **3b**

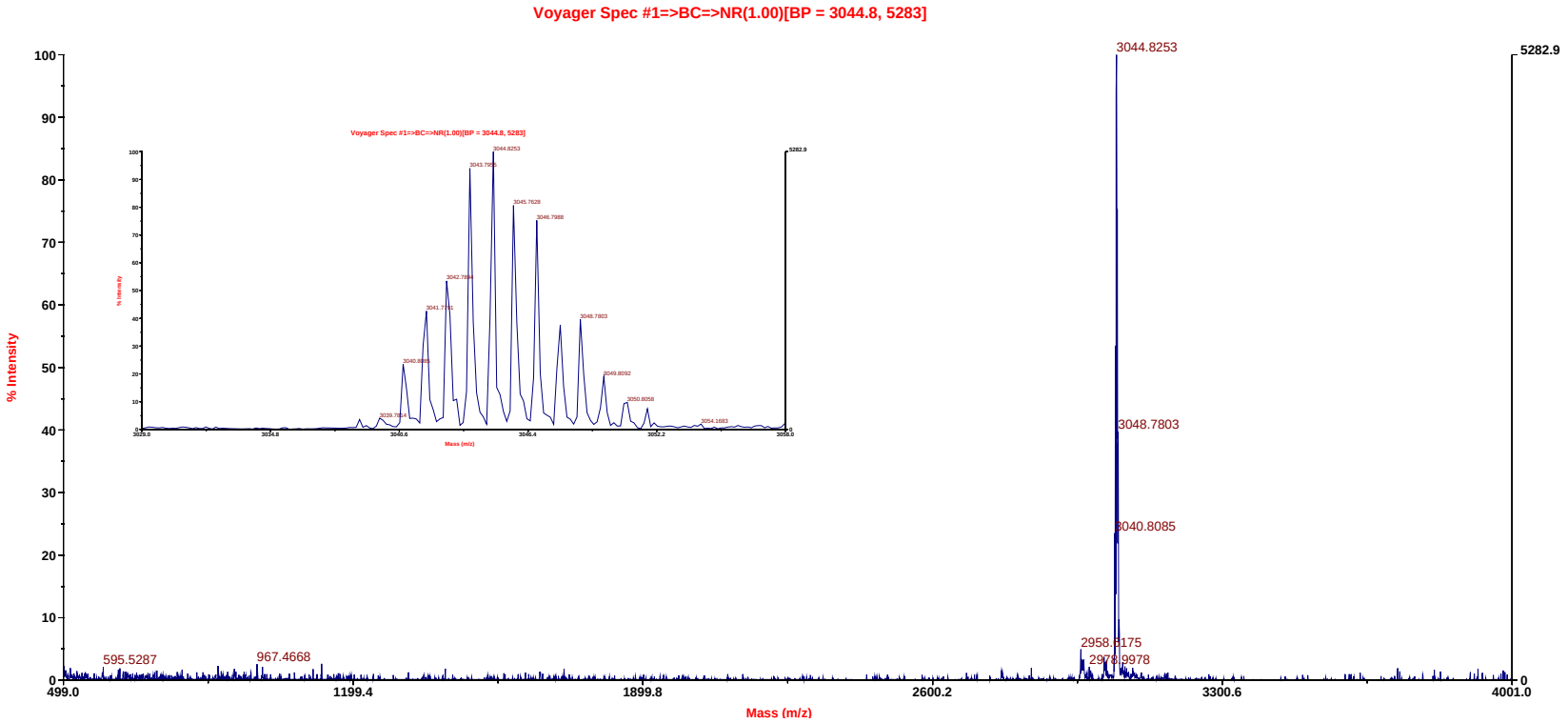

Figure S9. Mass spectrum of compound **3b**

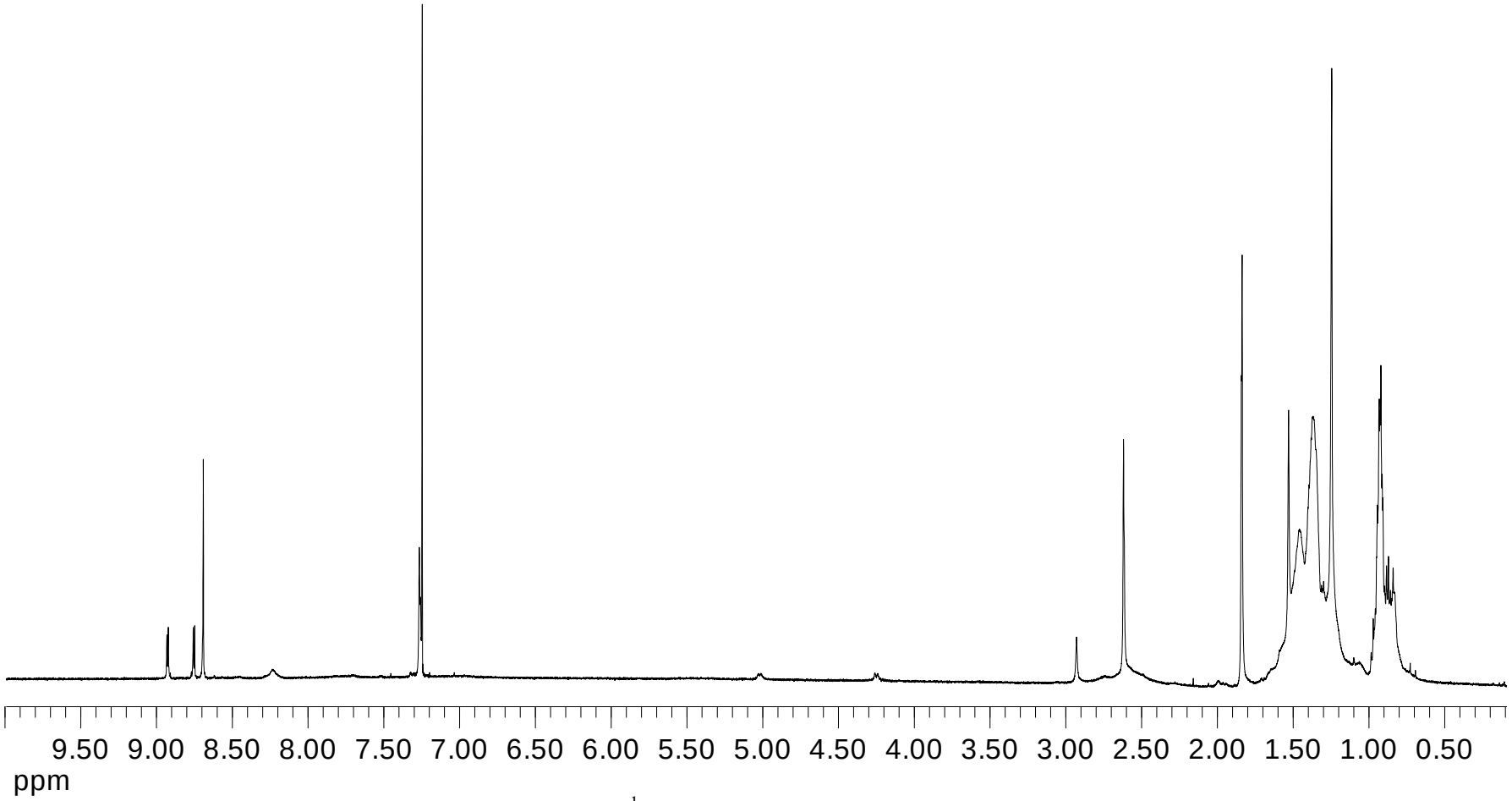

Figure S10. ^{1}H-NMR spectrum of compound **1b**

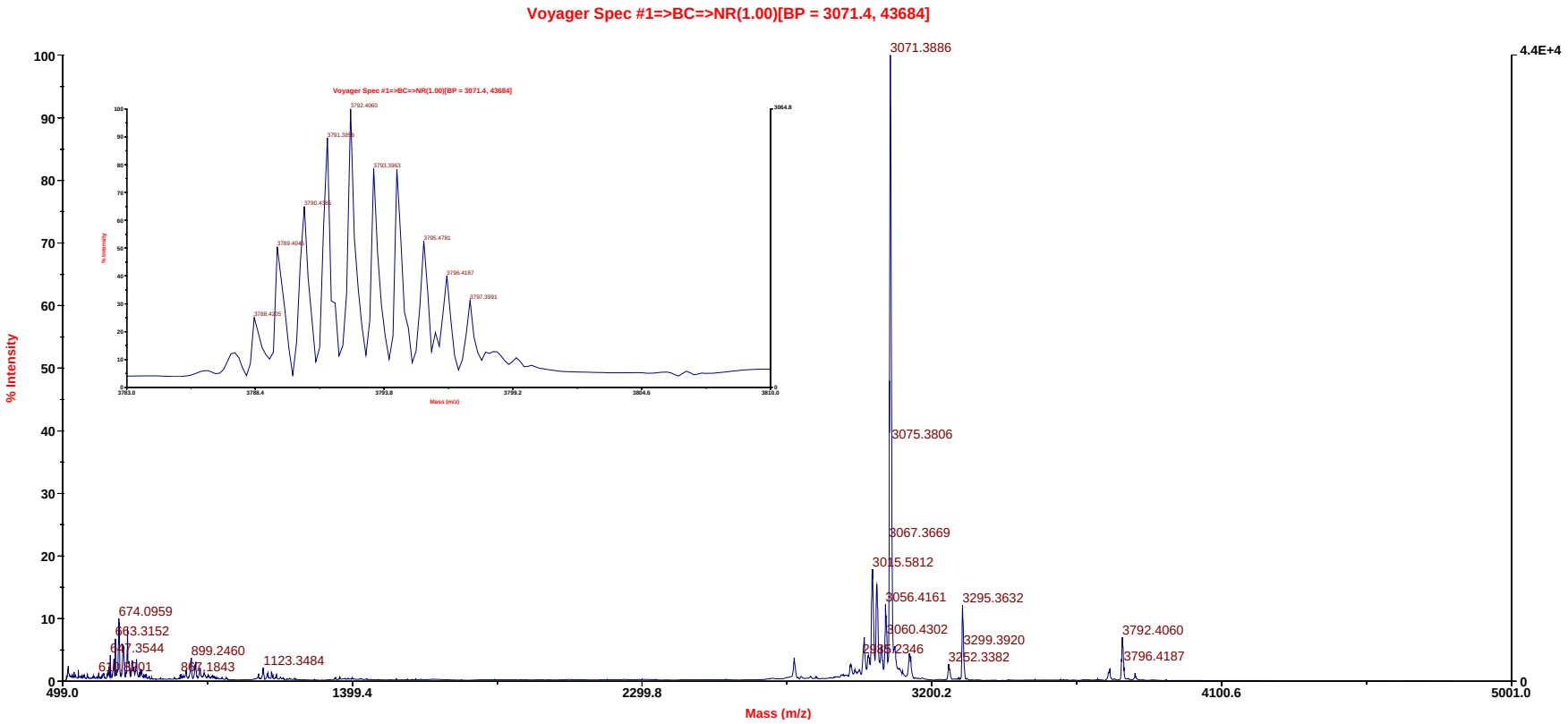

Figure S11. Mass Spectrum of compound **1b**

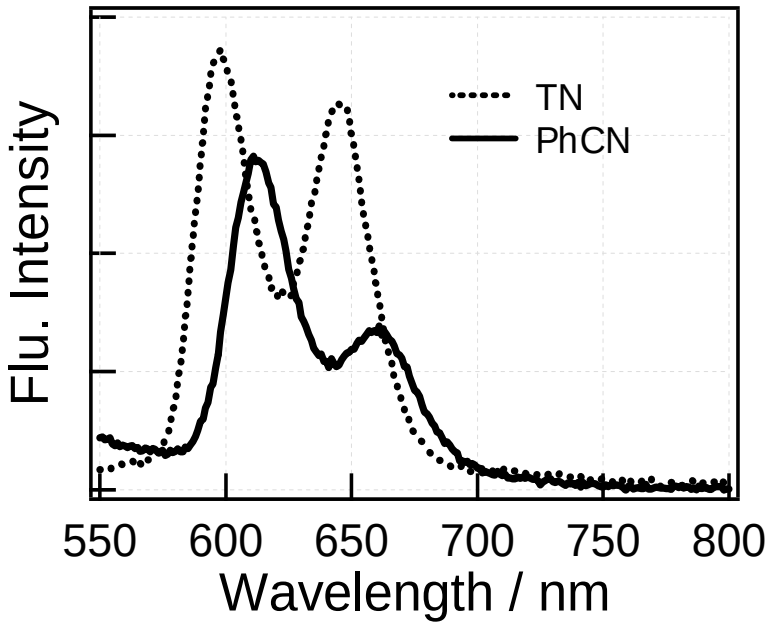

Fig. S12. Steady-state fluorescence spectra of ZnP-3TV-C_{60} (**1a**) in toluene and benzonitrile. The concentrations kept at 2.2 μM; λ_{ex} = 420 nm. The ZnP-fluorescence intensity of the ZnP-CH_2Br model (**4**) is almost the same as ZnP-3TV-C_{60} (**1a**) in each solvent.

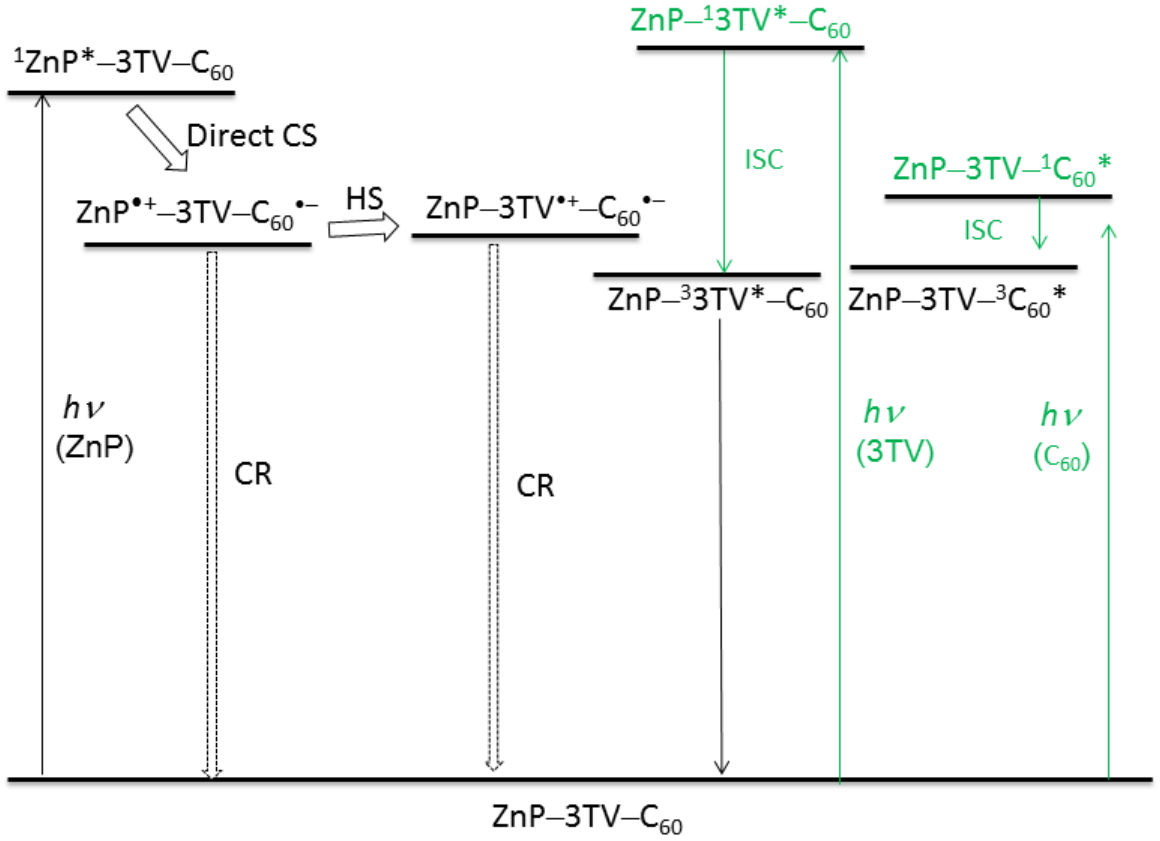

Fig. S13 Schematic energy diagram for the CS and CR processes of ZnP-3TV-C_{60} via ZnP-excitation assuming in non-polar solvents (E_{RIP}'s are larger than those in Table 1 by ca. 0.2 eV). The processes via ^{1}ZnP* are depicted as black color. The CS process via ^{1}3TV* and $^1C_{60}$* as re depicted with green color.

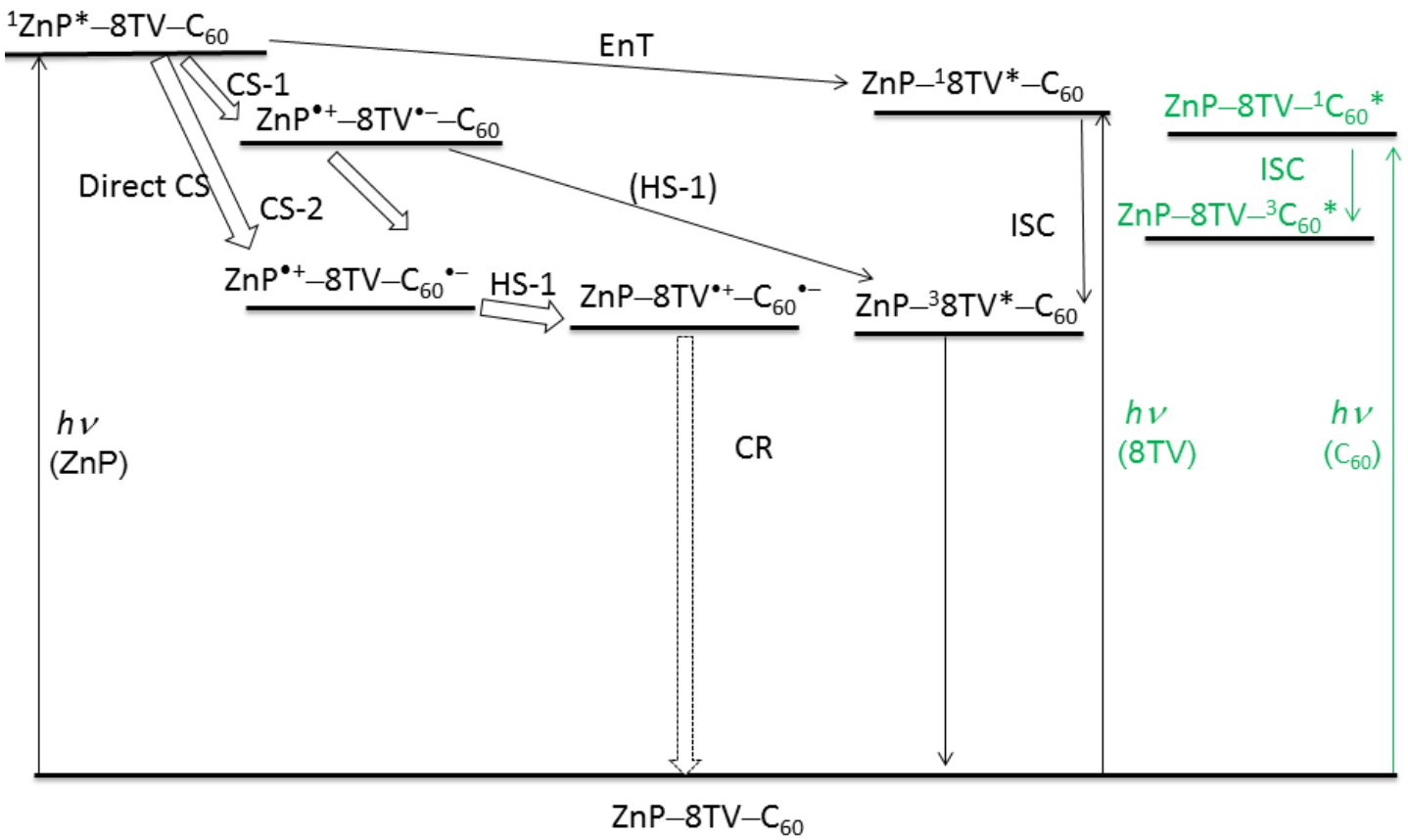

Fig. S14 Schematic energy diagram for the CS and CR processes and EnT process of ZnP-8TV-C_{60} via ZnP-excitation assuming in non-polar solvents. Combination of CS-1 and HS-1 in $ZnP^{\bullet+}$-$8TV^{\bullet-}$-C_{60} induces EnT from ZnP*-8TV-C_{60} to ZnP-8TV*-C_{60}