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A cationic iridium complex meets an electron-transporting counter-anion: enhanced performances for solution-processed phosphorescent light-emitting diodes

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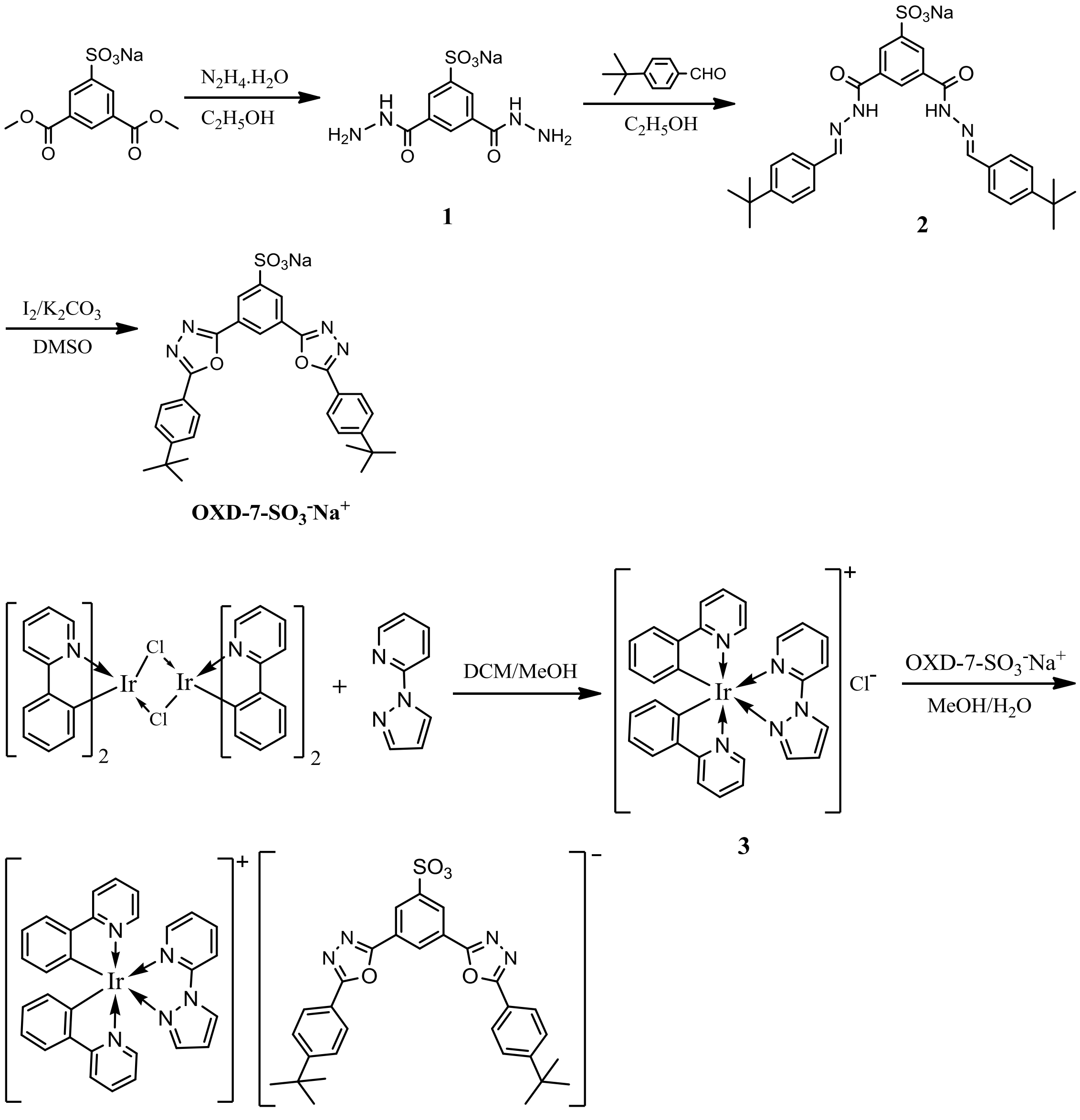
General Experiments. All reactants and solvents, unless otherwise stated, were purchased from commercial sources and used as received. ^{1}H and ^{13}C-NMR spectra were recorded on a Bruker 500 NMR spectrometer or a JOEL JNM-ECA600 NMR spectrometer with $Si(CH_3)_4$ as the internal standards. Mass spectrometry was performed with a LTQ-ORBITRAP-ETD mass spectrometer. Elemental analysis was determined on an EA3000 elemental analyzer (Eurovector, Italy). Absorption spectra were recorded with a UV-vis spectrophotometer (Shimadzu UV-2450). PL spectra were recorded with a fluorospectrophotometer (Hitachi F-4600). The PL transient lifetimes were measured on a transient spectrofluorimeter (Edinburgh Instruments, FLSP920) with a time-correlated single-photon counting technique. The PLQY of the complex (excited at 390 nm) was measured in degassed CH_3CN solutions with quinine sulfate ($\Phi_p = 0.545$ in 1 M H_2SO_4) as the standard. The PLQYs in thin films were measured on an absolute PLQY measurement system (Hamamatsu C11347) equipped with an integrating sphere. Cyclic voltammetry was performed on a LK1100 voltammetric analyzer in DMF solutions (10^{-3} M) at a scan rate of 100 mV/s, with a glass-carbon working electrode, a Ag wire pseudo-reference electrode and a Pt wire counter electrode. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.1 M) and ferrocene was selected as the internal standard. The solutions were degassed with argon before measurements.



Complex 1

Scheme S1. Synthetic routes to OXD-7-SO_3Na and complex 1.

Synthesis of OXD-7-$SO_3^-Na^+$

*S*odium 3,5-di(hydrazinecarbonyl)benzenesulfonate was synthesized according to a reported procedure [1].

Synthesis of sodium 3,5-bis(2-(4-(tert-butyl)benzylidene)hydrazinecarbonyl) benzenesulfonate (2). Sodium 3,5-di(hydrazinecarbonyl)benzenesulfonate (889 mg, 3 mmol) was suspended in ethanol (30 mL) and heated up to 90 ℃. To the mixture, 4-tertbutyl-benzaldehyde (704 μL, 6.6 mmol) in ethanol (10 mL) was dropped slowly. The reaction mixture was refluxed overnight under a nitrogen atmosphere and was filtered after cooling to room temperature. The precipitate was collected and dried under vacuum. The crude product was recrystallized from ethanol, yielding a white powder (1.47 g, 2.6 mmol). Yield: 86%. Mp > 270 ℃ (dec.). ^{1}H-NMR (600 MHz, d^6-DMSO, δ[ppm]) 12.13 (s, 2H), 8.50 (s, 2H), 8.44 (s, 1H), 8.38 (s, 2H), 7.68 (d, J = 7.8 Hz, 4H), 7.51 (d, J = 7.8 Hz, 4H), 1.32 (s, 18H). HRMS (ESI, *m/z*): 561.2112 $[M - Na]^-$ (calc. 561.2177). ^{13}C-NMR (150 MHz, d^6-DMSO, δ[ppm]): 162.14, 152.96, 149.05, 148.32, 133.37, 131.57, 127.66, 127.23, 127.03, 125.64, 34.61, 30.96. Anal. Calcd. (%) for $C_{30}H_{33}N_4NaO_5S$: C, 61.63; H, 5.69; N, 9.58. Found: C, 61.49; H, 5.81; N, 9.50.

Synthesis of OXD-7-$SO_3^-Na^+$. Sodium 3,5-bis(2-(4-(tert-butyl)benzylidene)-hydrazinecarbonyl)benzenesulfonate (1.3 g, 2.3 mmol), iodine (1.8 g, 5.4 mmol) and potassium carbonate (1.7 g, 9 mmol) were dissolved in dry DMSO (12 mL). The mixture was stirred under nitrogen atmosphere at 100 ℃ for 5 h. After cooling to room temperature, a solution of $Na_2S_2O_3$ (5%) was dropped into the reaction mixture until the brown color disappeared. Brine solution was further added into the reaction mixture to precipitate the product. After filtration, the precipitate was collected and dried under vacuum. The crude product was purified by column chromatography on silica gel (200–300 mesh) with CH_2Cl_2/methanol (20: 1) as the eluent and recrystallized from ethanol, yielding a white powder (1.1 g, 1.86 mmol). Yield: 82%. Mp: 304−306 ℃. ^{1}H-NMR (500 MHz, *d*^{6}-DMSO, δ[ppm]) 8.72 (s, 1H), 8.52 (s, 2H), 8.13 (d, J = 8.3 Hz, 4H), 7.69 (d, J = 8.3 Hz, 4H), 1.36 (s, 18H). ^{13}C-NMR (125 MHz, *d*^{6}-DMSO, δ[ppm]) 164.59, 162.97, 155.24, 150.74, 126.85, 126.38, 126.34, 124.54, 124.25, 120.57, 34.93, 30.89. HRMS (ESI, *m/z*): 557.1794 [M -Na]$^-$ (calc. 557.1864). Anal. Calcd. (%) for $C_{30}H_{29}N_4NaO_5S$: C, 62.06; H, 5.03; N, 9.65. Found: C, 61.94; H, 5.20; N, 9.72.

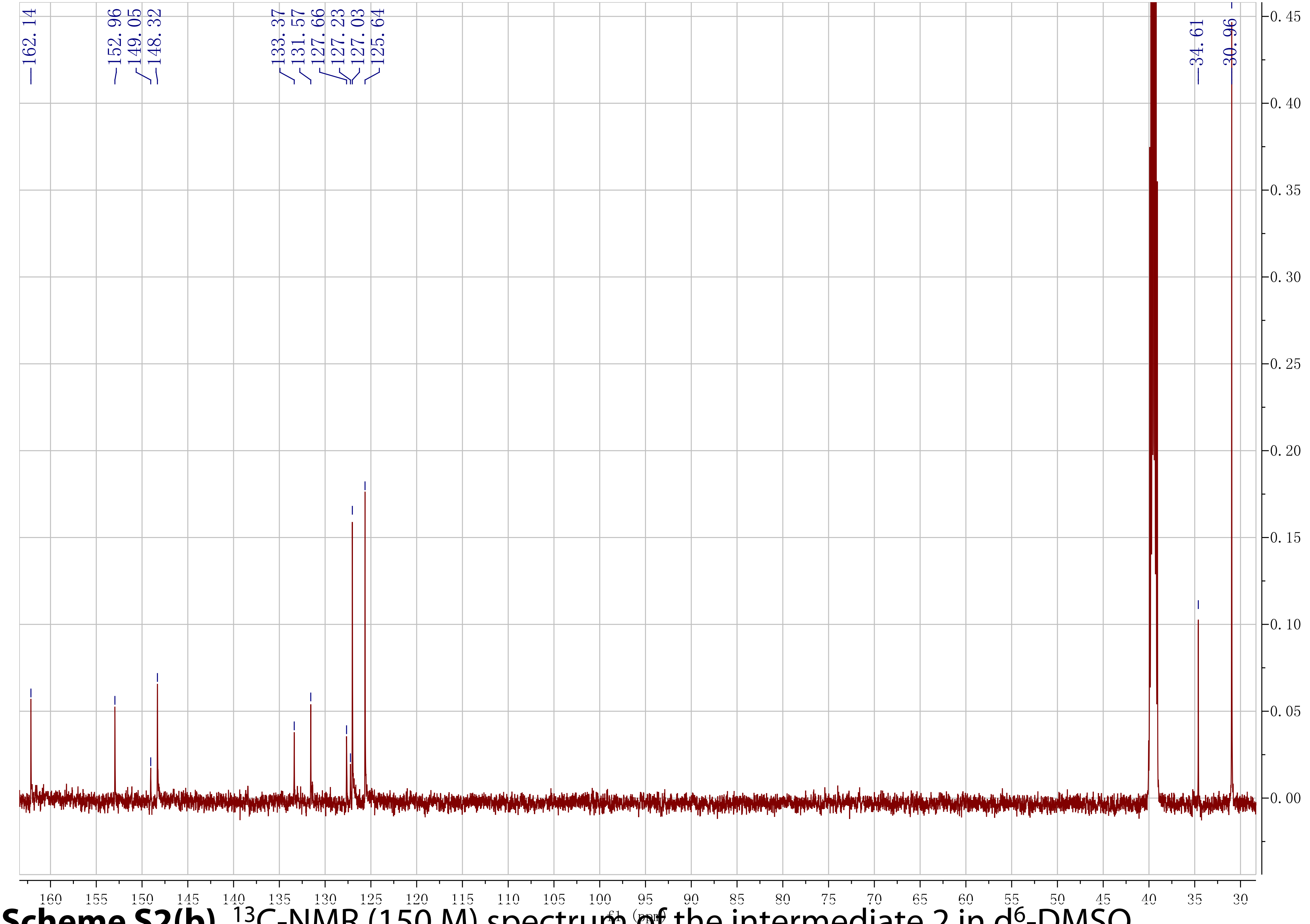
Synthesis of complex 1

Synthesis of $[Ir(ppy)_2(pzpy)]^+Cl^-$ *(3).* $[Ir(ppy)_2Cl]_2$ and pzpy were synthesized following the literature procedures [2,3]. $[Ir(ppy)_2Cl]_2$ (210 mg, 0.2 mmol) and pzpy (64 mg, 0.44 mmol) were suspended in CH_2Cl_2/CH_3OH (20/20 mL). The mixture was refluxed overnight under a nitrogen atmosphere. After cooling to room temperature, the solution was evaporated to dryness. The remaining solid was purified by column chromatography on silica gel (200–300 mesh) with CH_2Cl_2/methanol (20: 1) as the eluent, affording a yellow powder (251 mg, 0.37 mmol). Yield: 92%.

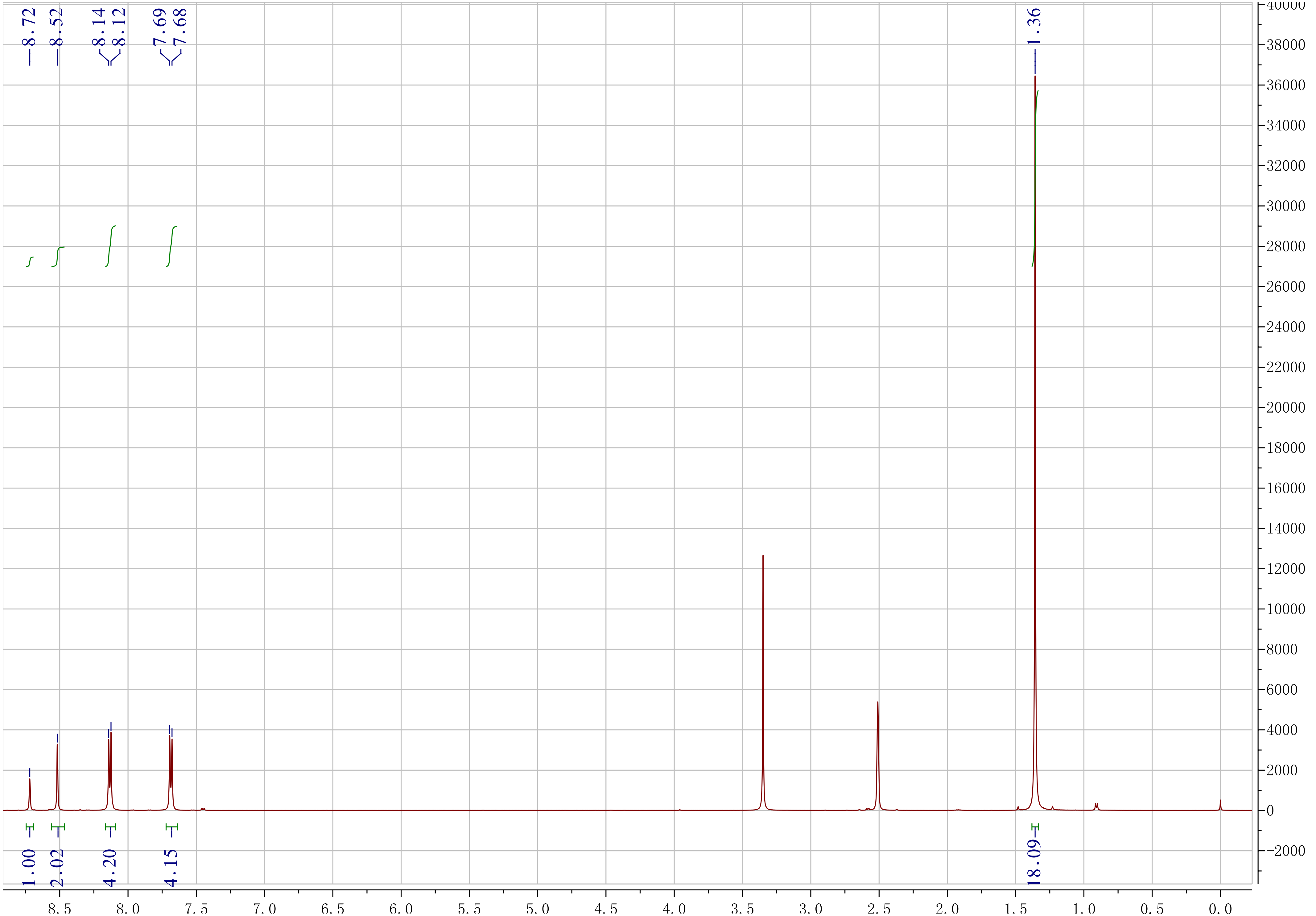
Synthesis of complex 1. $[Ir(ppy)_2(pzpy)]^+Cl^-$ (204 mg, 0.3 mmol) was dissolved in deionized water/CH_3OH (10/10 ml) and to the solution, OXD-7-SO_3Na (174 mg, 0.3 mmol) dissolved in water/CH_3OH (15/15 ml) was dropped slowly under stirring. The mixture was further stirred at room temperature for 1 h and then filtered. The precipitate was collected, dried under vacuum and further purified by recrystallization from CH_2Cl_2/hexane, yielding a yellow powder (317 mg, 0.26 mmol). Yield: 87%. ^{1}H-NMR (500 MHz, d^6-DMSO, δ[ppm]) 9.31 (d, J = 3.0 Hz, 1H), 8.72 (t, J = 1.5 Hz, 1H), 8.55 – 8.49 (m, 3H), 8.34 (dt, J= 8.0, 1.5 Hz, 1H), 8.27 (dd, J = 8.0, 3.0 Hz, 2H), 8.13 (d, J = 8.4 Hz, 4H), 7.97 (t, J=8.0 Hz, 2H), 7.89 (t, J = 8.9 Hz, 2H), 7.77 (d, J = 5.5 Hz, 1H), 7.74 – 7.62 (m, 6H), 7.54 (t, J=6.5 Hz, 1H), 7.29 (d, J = 1.9 Hz, 1H), 7.26 – 7.17 (m, 2H), 7.05 – 6.95 (m, 2H), 6.94 – 6.82 (m, 3H), 6.19 (t, J = 7.8 Hz, 2H), 1.36 (s, 18H). ^{13}C-NMR (125 MHz, d^6-DMSO, δ[ppm]) 166.89, 166.75, 164.59, 162.98, 155.23, 150.83, 149.26, 149.18, 149.13, 148.76, 148.23, 146.17, 144.15, 144.10, 143.30, 141.79, 138.96, 138.83, 132.80, 131.34, 131.16, 130.19, 129.76, 126.85, 126.38, 126.34, 125.34, 125.11, 124.75, 124.54, 124.22, 123.96, 123.83, 122.41, 122.19, 120.58, 120.02, 119.97, 113.61, 111.59, 34.92, 30.88. HRMS (ESI, *m/z*): 557.1805 $[OXD\text{-}7\text{-}SO_3]^-$ (calc. 557.1864); 646.1603 $[Ir(ppy)_2(pzpy)]^+$ (calc. 646.1577). Anal. Calcd. (%) for $C_{60}H_{52}IrN_9O_5S$: C, 59.88; H, 4.36; N, 10.48. Found: C, 59.71; H, 4.47; N, 10.32.

Fabrication and characterization of PhOLEDs. ITO substrates with a sheet resistance of 15 Ω/□ were cleaned in detergent and then in deionized water. The ITO substrates were treated with UV-zone before use. The PEDOT: PSS layers were spin coated onto the ITO substrates in air and baked at 200 ℃ for 10 minutes. The PEDOT: PSS-coated substrates were transferred into a nitrogen-filled glove box, where the emissive layers composed of [PVK: complex 1 or 2] or [PVK: OXD-7: complex 2] were spin coated on top of PEDOT:PSS from the 1,2-dichloroethane solution and baked at 80 ℃ for 30 minutes. The film-coated substrates were then transferred into a vacuum chamber, where the TPBI, LiF and Al layers were consecutively evaporated at the evaporation rates of 1-2, 0.1-0.2 and 2-3 Ǻ/s, respectively. The devices were characterized with Keithley 4200 semiconductor characterization systems. The EL spectra were collected with a Photo Research PR705 spectrophotometer in ambient conditions.

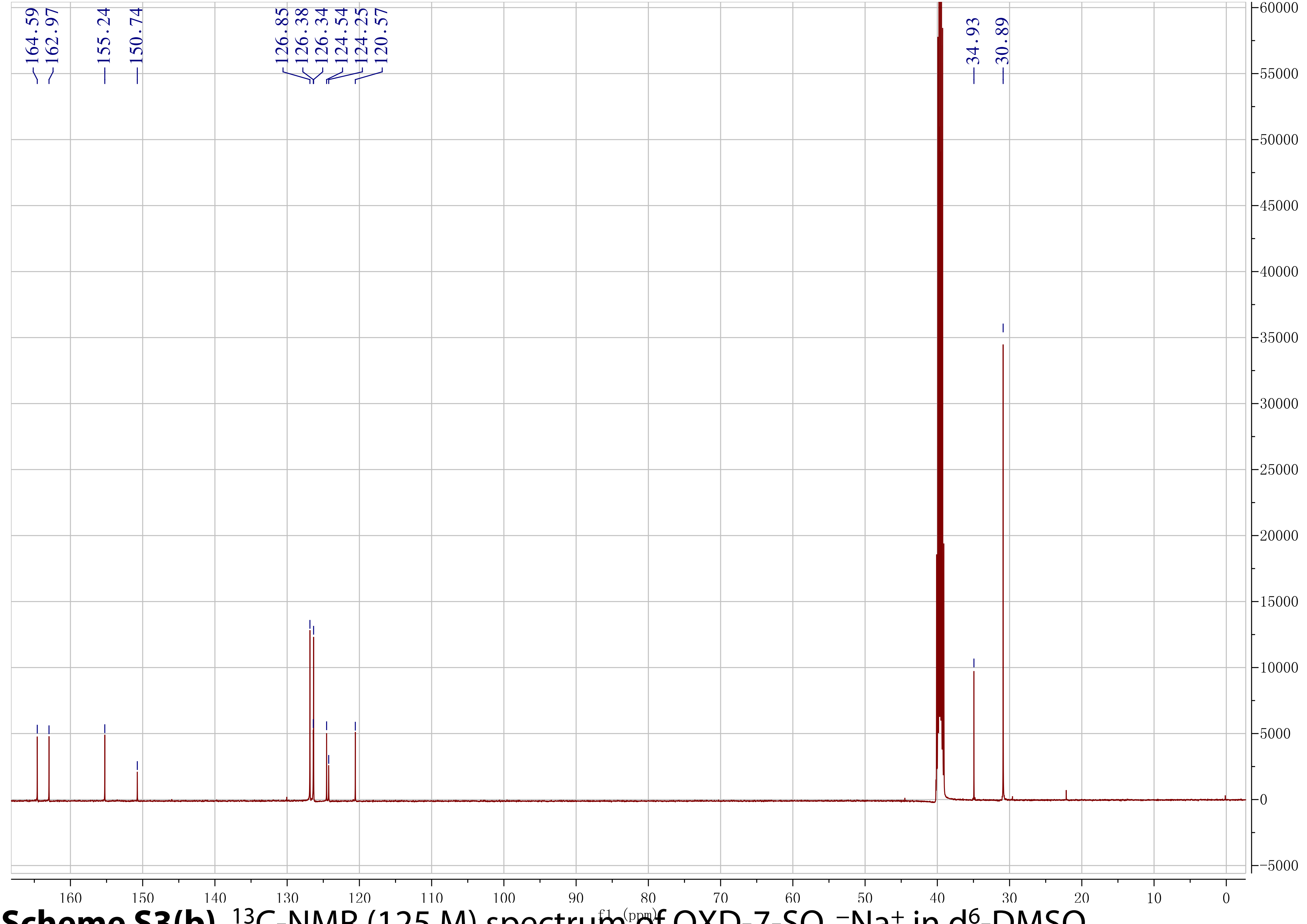
Scheme S2(a). ^{1}H-NMR (600 M) spectrum of the intermediate 2 in d^6-DMSO.



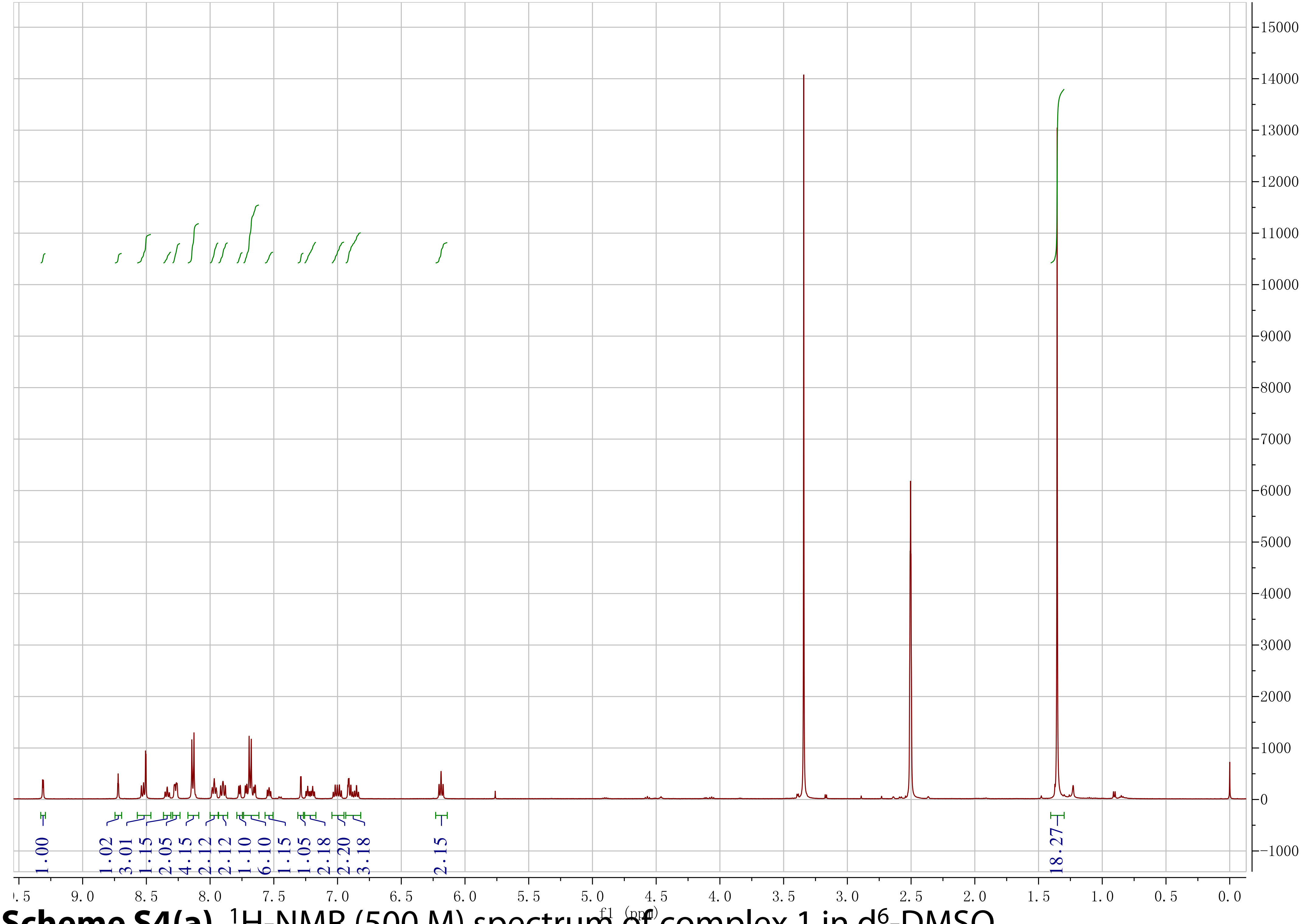
Scheme S2(b). ^{13}C-NMR (150 M) spectrum of the intermediate 2 in d^6-DMSO.



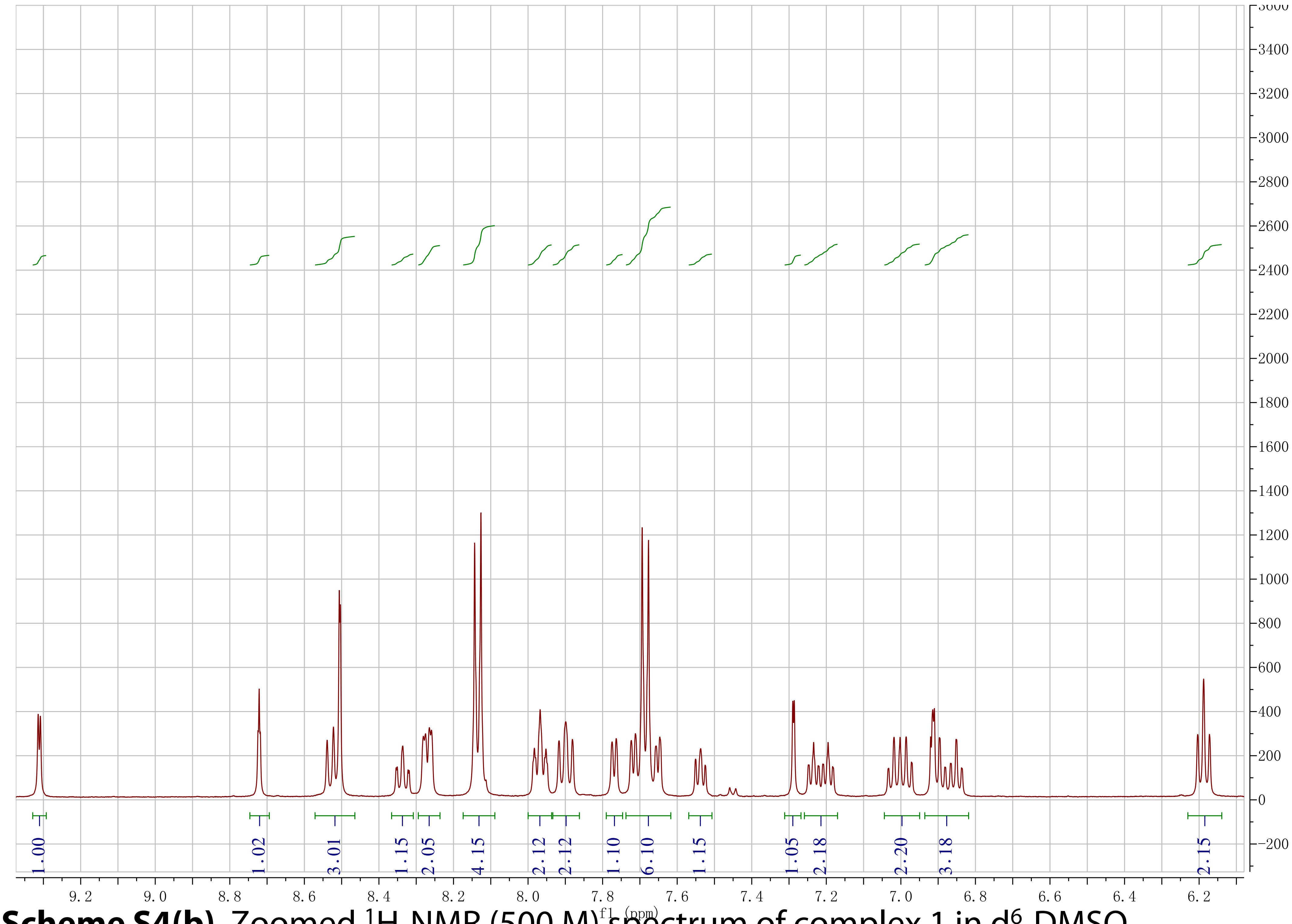
Scheme S3(a). ^{1}H-NMR (500 M) spectrum of OXD-7-$SO_3^-Na^+$ in d^6-DMSO.



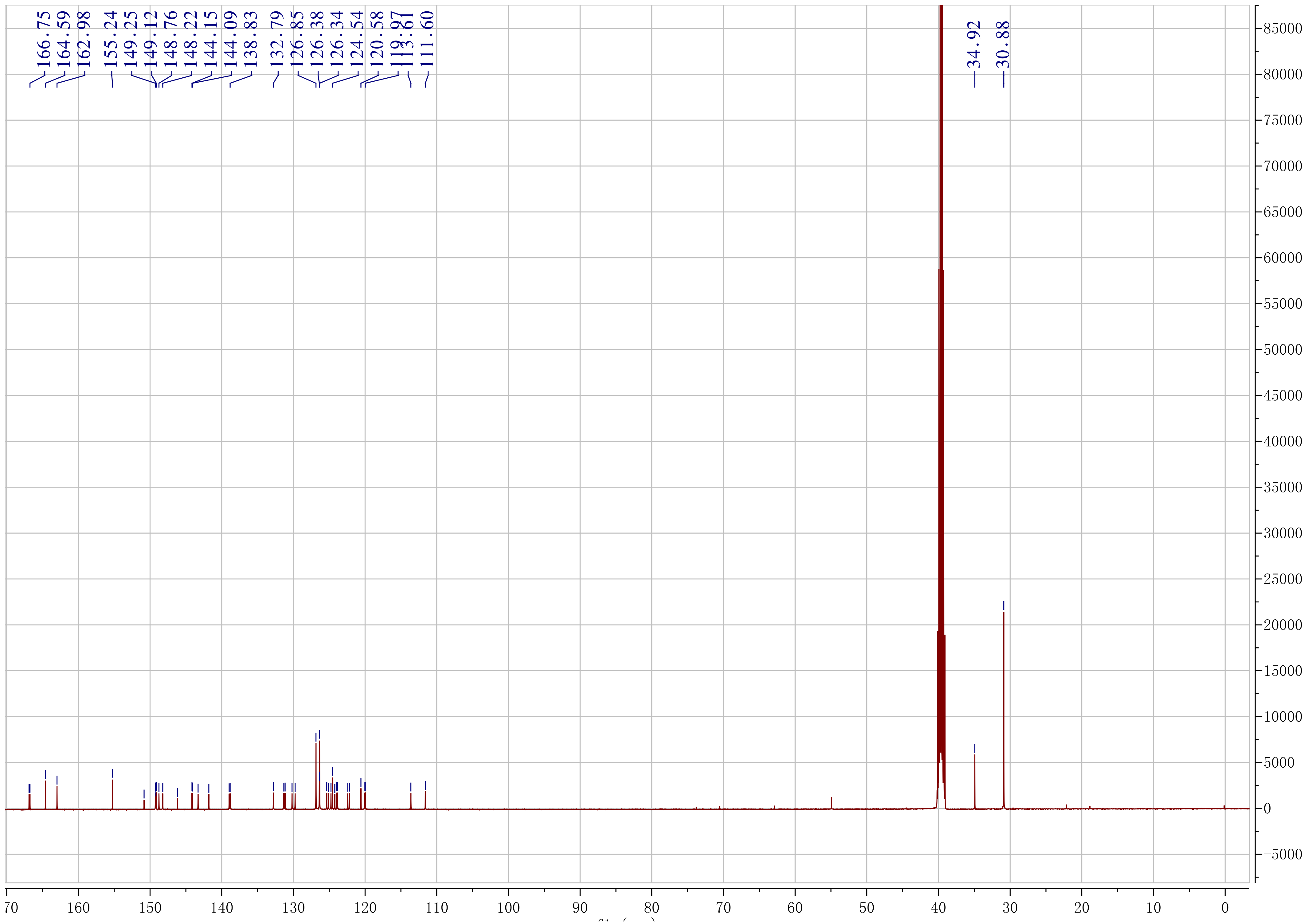
Scheme S3(b). ^{13}C-NMR (125 M) spectrum of OXD-7-$SO_3^-Na^+$ in d^6-DMSO.



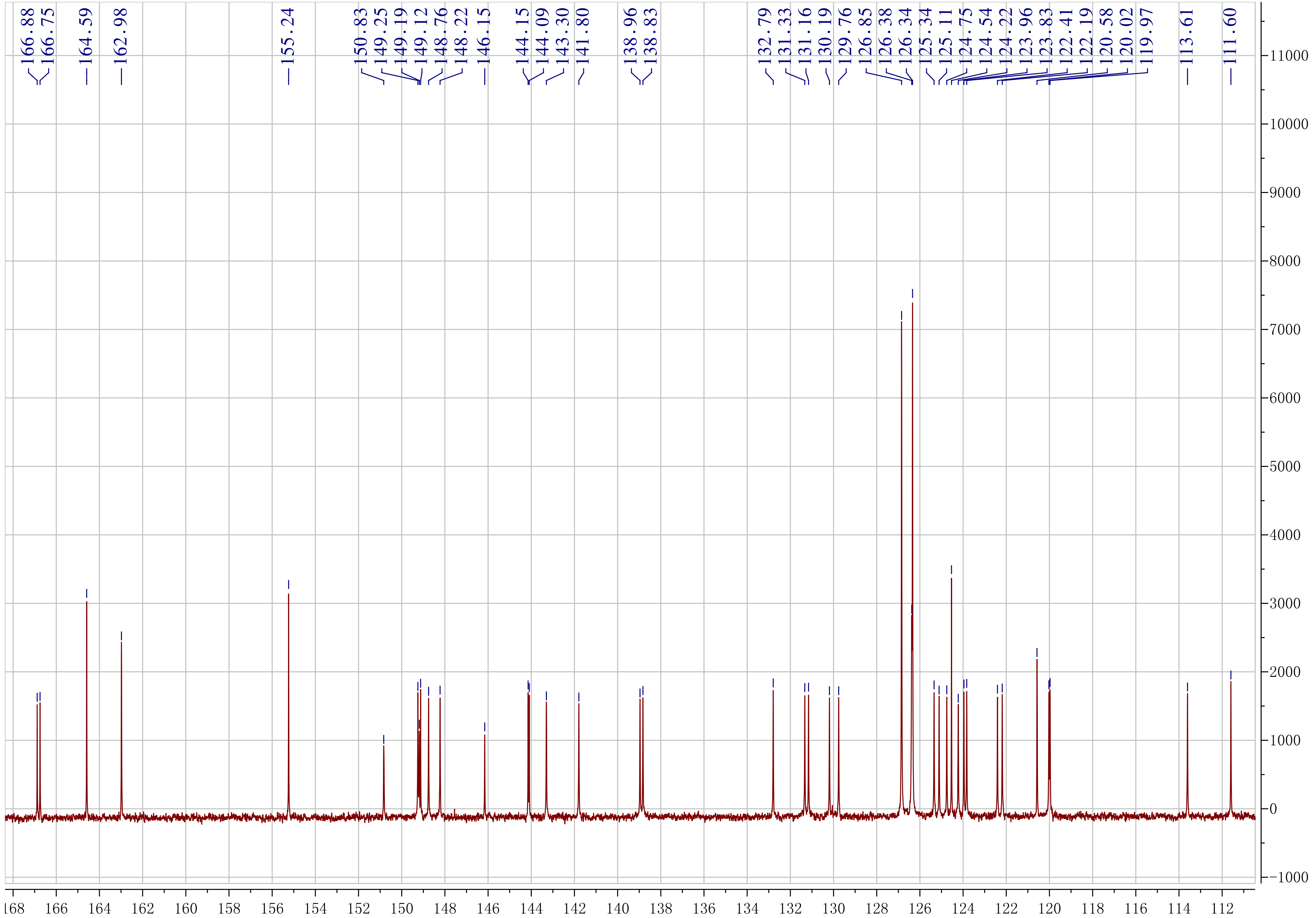
Scheme S4(a). ^{1}H-NMR (500 M) spectrum of complex 1 in d^{6}-DMSO.



Scheme S4(b). Zoomed ^{1}H-NMR (500 M) spectrum of complex 1 in d^6-DMSO.



Scheme S4(c). ^{13}C-NMR (125 M) spectrum of complex 1 in d^6-DMSO.



Scheme S4(d). Zoomed ^{13}C-NMR (125 M) spectrum of complex 1 in d^6-DMSO.

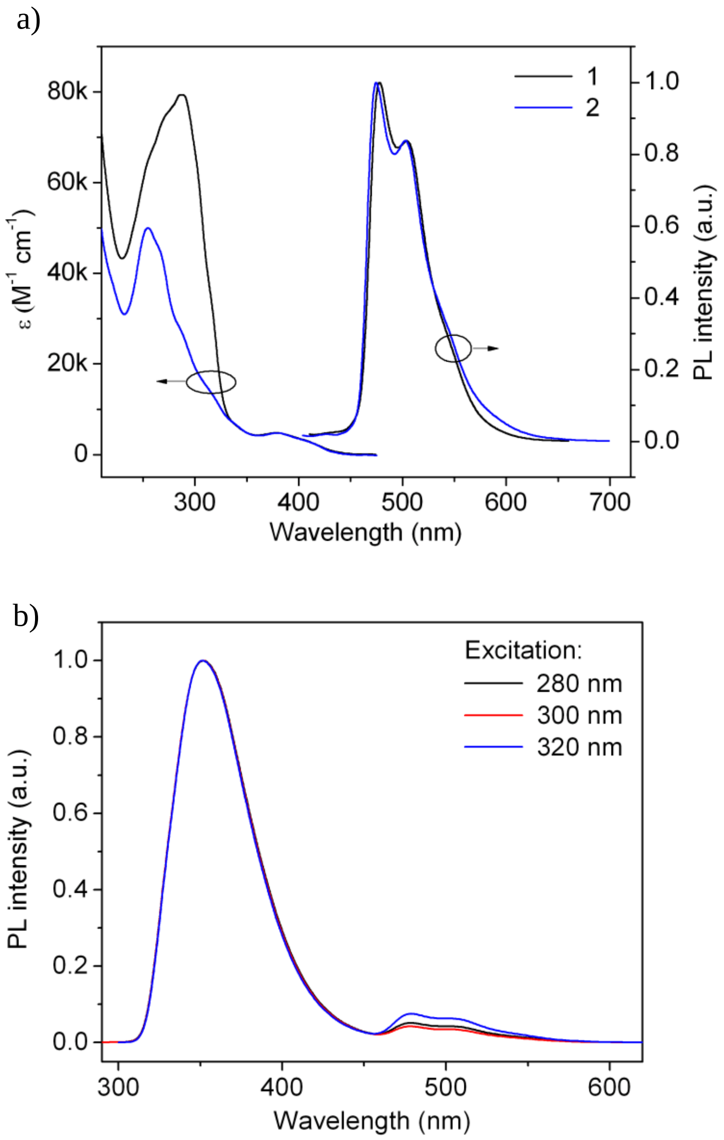


Figure S1. a) Absorption and PL spectra of complexes 1 and 2 in acetonitrile solution; PL was recorded under the excitation at 380 nm. b) PL spectra of complex 1 in acetonitrile solution under different excitations below 340 nm.

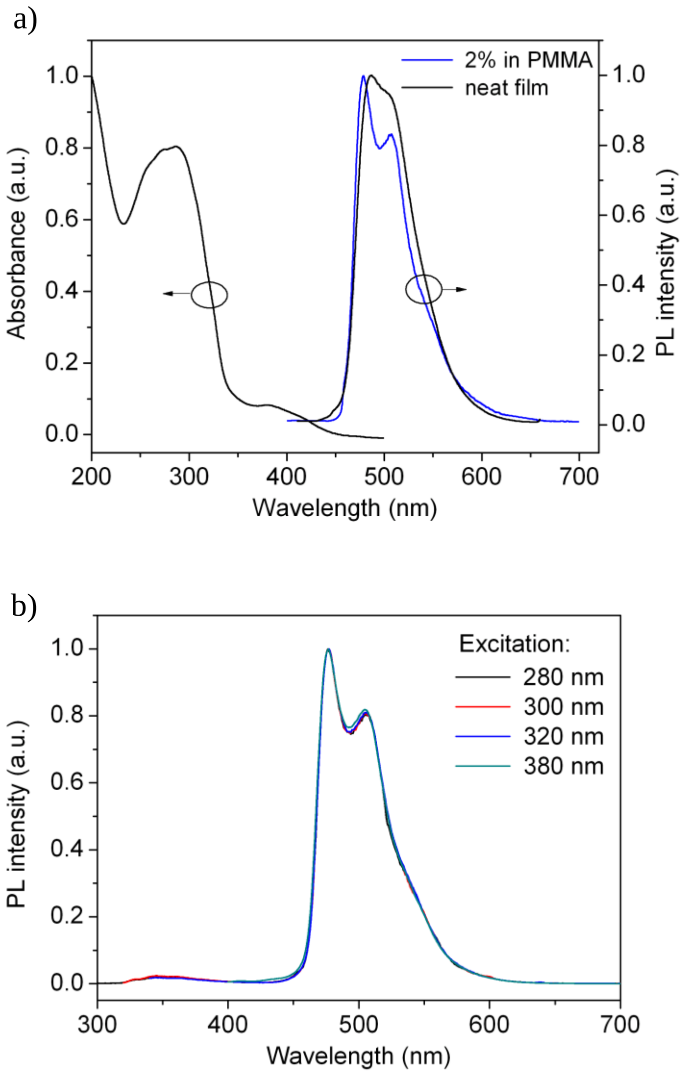


Figure S2. a) Absorption and PL spectra of complex 1 in 2 wt.% doped PMMA film and neat film. PL spectra were measured under the excitation of 380 nm. b) PL spectra of complex 1 in 2 wt.% doped PMMA film under different excitations.

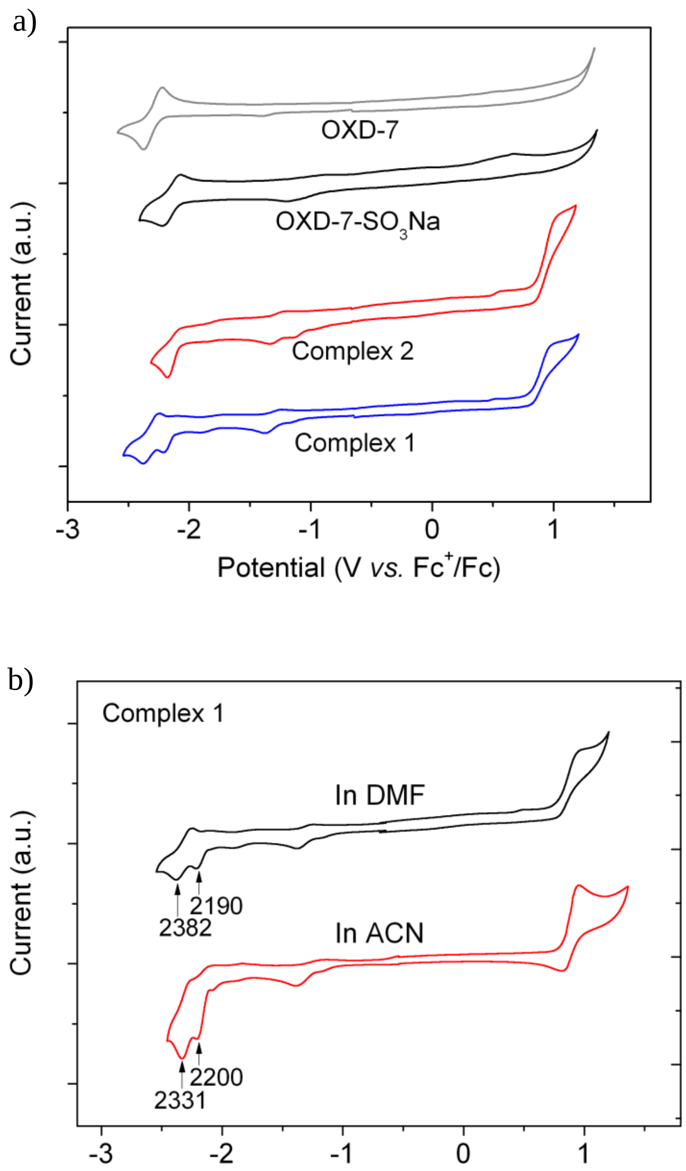


Figure S3. a) Cyclic voltammograms of OXD-7, OXD-7-$SO_3^-Na^+$, complexes 1 and 2 in DMF. b) Comparison between the cyclic voltammograms of complex 1 in DMF and acetonitrile (ACN). The small peaks around −1.35 V arise from some unknown impurities which also appear in the blank test.

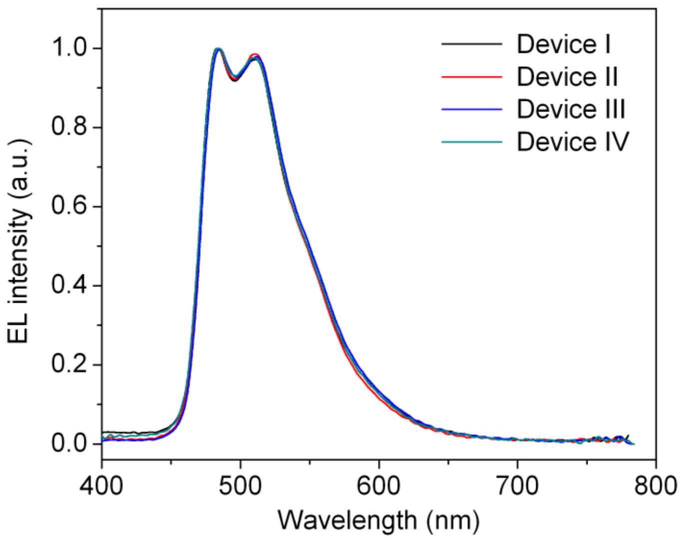
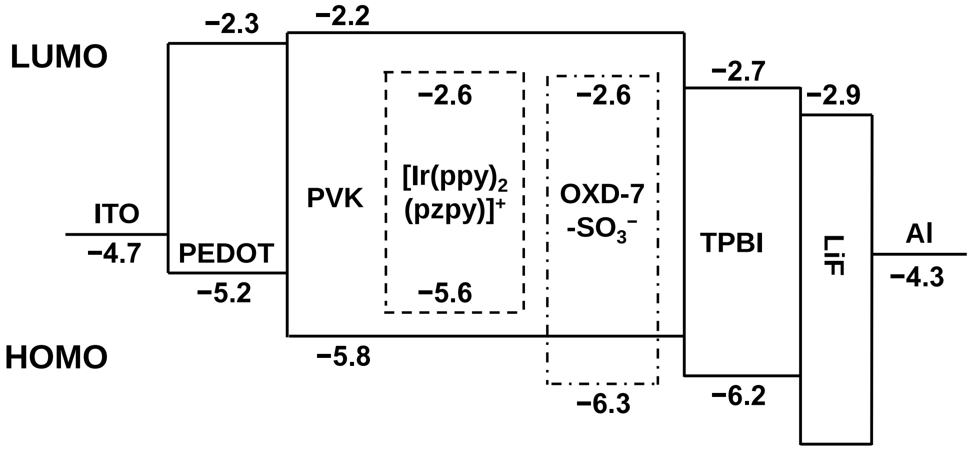


Figure S4. EL spectra of devices I to IV recorded at 10 V.



Scheme S5. Energy level diagram for devices I to IV (unit for the energy level: eV); the HOMO and LUMO levels of $[Ir(ppy)_2(pzpy)]^+$ were calculated from the oxidation and reduction potentials of complex 2; the LUMO level of OXD-7-SO_3^- was calculated from the reduction potential of OXD-7-$SO_3^-Na^+$ and its HOMO level was then calculated on the basis of the LUMO level and the optical band gap estimated from the absorption spectrum of OXD-7-$SO_3^-Na^+$.

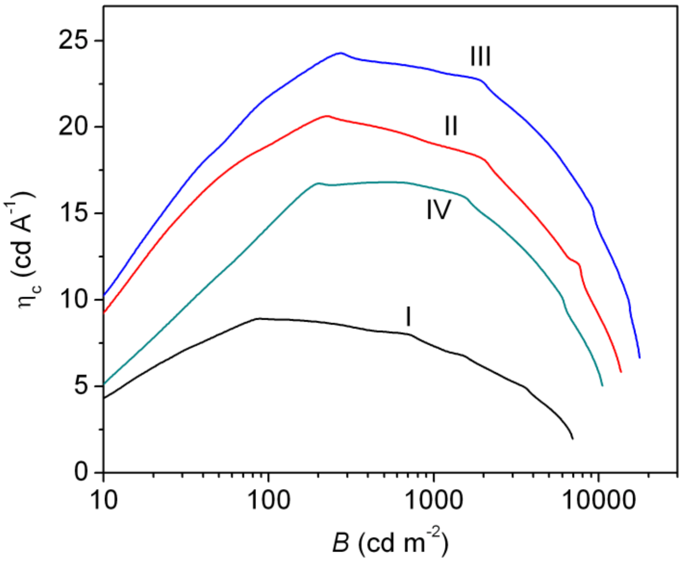


Figure S5. Current efficiency (η_c) *versus* brightness (B) curves for devices I to IV.

References

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