Supporting Information

Iridium-Complex Modified CdSe/ZnS Quantum Dots; A Conceptual Design for Bifunctionality Toward Imaging and Photosensitization

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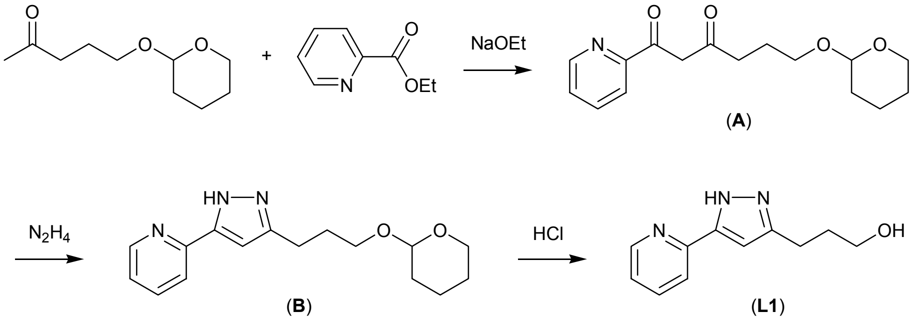
Synthetic Procedures:

General information and Materials. Elemental analyses and mass spectra (operating in FAB mode) were carried out at the NSC Regional Instrument Centre at National Chiao Tung University, Taiwan. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 or an Inova-500 MHz instrument; chemical shifts are quoted with respect to internal standard Me_4Si. All reagents and solvents were used as received, and all synthetic manipulations were performed under N_2 atmosphere. The chloride bridged dimeric iridium reagent, $[(piq)_2IrCl]_2$, (piq)H = 1-phenylisoquinoline, was prepared from treatment of (piq)H with $IrCl_3{\cdot}nH_2O$ in refluxing methoxyethanol,[1] it was then used for subsequent reaction without purification.

*Preparation of pyrazole ligand **L1***. The hydroxyl substituted pyridyl pyrazole, **L1**, was prepared using the following multi-steps synthetic pathway. 5-[(tetrahydr-opyran-2-yl)oxy]-2-pentanone (6.4 g, 34 mmol), prepared from 3-acetyl propanol and dihydropyran in presence of a few drops of conc. HCl solution,[2] was first treated with ethyl picolinate (4.0 g, 26.5 mmol) in presence of excess NaOEt (2.7g, 40 mmol) to give the pyridyl diketone (**A**),1-(pyridin-2-yl)-6-(tetrahydro-2H- pyran-2-yloxy) hexane-1,3-dione, in 72% yield, which was purified using silica gel column chromatography (ethyl acetate : hexane = 2 : 1). Subsequently, treatment of **A** (5.6 g, 19 mmol) with 14 mL of 98% hydrazine hydrate in refluxing ethanol solution (50 mL) for 12 hours gave the respective pyrazole (**B**), 2-(3-(3-(tetrahydro-2H-pyran- 2-yloxy)propyl) -1H-pyrazol-5-yl) pyridine, in 43 % yield. Finally, the de-protected, hydroxyl substituted pyrazole ligand (**L1**), 3-(5-(pyridin-2-yl)-1H-pyrazol-3-yl) propan-1-ol, was prepared by dissolving **B** (2.36 g, 8.2 mmol) into 50 mL of anhydrous methanol; the methanol solution was then acidified with conc. HCl to pH 2 and continuously stirred for 24 hours at room temperature, using method similar to that described in literature,[3] yield: 1.44 g, 7.1 mmol, 86%. The overall reaction sequence is depicted in Scheme 1.

Scheme 1



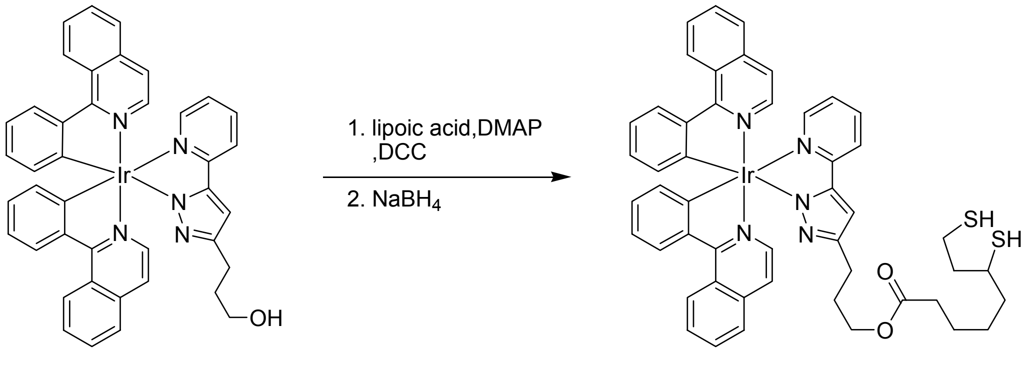
Spectral data of **L1**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.66 (dd, 1H, J_{HH} = 3.6, 1.2 Hz), 7.73 ~ 7.70 (m, 2H), 7.23 ~ 7.17 (m, 1H), 7.20 (br, 2H, NH + OH), 6.57 (s, 1H), 3.68 (t, 2H, J_{HH} = 6 Hz), 2.83 (t, 2H, J_{HH} = 7.2 Hz), 1.97 ~ 1.90 (m, 2H).

Preparation of [(piq)$_2$Ir(L1)]. A mixture of [(piq)$_2$IrCl]$_2$ (350 mg, 0.28 mmol), pyridyl pyrazole ligand **L1** (140 mg, 0.7 mmol) and Na$_2$CO$_3$ (292 mg, 2.8 mmol) in 2-methoxyethanol (50 mL) was heated to reflux for 2 hours. Excess of water was added after cooling the solution to RT. The precipitate was collected by filtration, followed by washing with deionized water and then diethyl ether. Red crystalline solid of [$(piq)_2$Ir(L1)] were obtained from repeated recrystallization using a mixture of THF, methanol and hexane (1 : 1 : 1) at room temperature (280 mg, 0.35 mmol, 63%).

Spectral data of **[$(piq)_2$Ir(L1)]**: MS (FAB, ^{193}Ir): m/z 803 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.93 (ddd, 2H, J_{HH} = 16.6, 9.6, 3.6 Hz), 8.23 (dd, 2H, J_{HH} = 14.4, 8.0 Hz), 7.81 ~ 7.75 (m, 2H), 7.68 ~ 7.57 (m, 7H), 7.52 (d, 1H, J_{HH} = 6 Hz), 7.48 (d, 1H, J_{HH} = 5.6 Hz), 7.25 (d, 1H, J_{HH} = 4.8 Hz), 7.14 (d, 1H, J_{HH} = 6.8 Hz), 7.01 (q, 2H, J_{HH} = 5.6 Hz), 6.85 ~ 6.78 (m, 3H), 6.46 (d, 1H, J_{HH} = 7.6 Hz), 6.45 (s, 1H), 6.39 (d, 1H, J_{HH} = 7.2 Hz) , 3.45 ~ 3.40 (m, 1H), 3.33 ~ 3.27 (m, 1H), 3.20 (br, 1H), 2.81 ~ 2.69 (m, 2H), 1.76 ~ 1.66 (m, 2H). Anal. Calcd. for $C_{46}H_{51}IrN_8O_4$: C, 56.83; H, 5.29; N, 11.53. Found: C, 57.01; H, 5.13; N, 11.73.

Preparation of [$(piq)_2$Ir(L2)]. A mixture of [$(piq)_2$Ir(L1)] (100 mg, 0.125 mmol), thiotic acid (26mg, 0.125 mmol), N,N'-dicyclohexylcarbidiimide (52 mg, 0.262 mmol) and N,N'-dimethylamino pyridine (5 mg, 0.037 mmol) in dichloromethane (20 mL) was stirred at room temperature for 72 hours. Then the mixture was extracted with water (30 mL × 3), and the solvent was removed in vacuo. The crude product was just dissolved in methanol (20 mL), and 4eq of $NaBH_4$ (19 mg, 0.5 mmol) was added, the reaction mixture was stirred at room temperature for 4 hours, and the solvent was removed in vacuo. For further purification, the product was washed by DI-water several times. The overall reaction sequence is schematically as Scheme2.

Scheme 2



[(piq)$_2$Ir(L1)]   [(piq)$_2$Ir(L2)]

Spectral data of **[(piq)$_2$Ir(L2)]**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.96 (d, J = 6.0 Hz, 1 H), 8.90 (d, J = 4.2 Hz, 1 H), 8.28 (d, J = 5.9 Hz, 1 H), 8.21 (d, J = 5.7 Hz, 1 H), 7.83 ~ 7.79 (m, 4 H), 7.69 ~ 7.59 (m, 4 H), 7.52 (d, J = 4.5 Hz, 1 H), 7.45 (d, J = 4.2 Hz, 1 H), 7.29 (d, J = 4.8 Hz, 1 H), 7.17 (d, J = 5.1 Hz, 1 H), 7.0 (m, 2 H), 6.80 (m, 4 H), 6.51 (s, 1 H), 6.39 (t, J = 4.7 Hz, 2 H), 2.74 ~ 0.87 (m, 17 H); IR (neat) 3295, 2975, 2720, 2580, 2377, 2104, 1725, 1490, 1060, 1010, 635 cm^{-1}.

*Preparation of CdSe/ZnS-Iridium complex **(Ir-CdSe/ZnS)**.* TBP/TOPO-capped CdSe-ZnS core-shell particles were exchanged with [(piq)$_2$Ir(L2)] (50 mg, 48.8 mmol) placed in a 50 mL of reaction vessel. 15 mL of methanol was added, and the pH value was adjusted to ~12 with tetramethylammonium hydroxide pentahydrate. Under dark conditions, 10 mg of CdSe-ZnS nanocrystals were dissolved in the mixture, and the vessel was placed under regular oxygenflow. The mixture was heated under reflux at 65 ^{o}C overnight, and then the reaction was terminated and allowed to cool to room temperature. The [(piq)$_2$Ir(L2)]-capped nanocrystals were then precipitated with diethyl ether. For further purification, crude solid was washed with CH$_2$Cl$_2$ for several times.

Spectral data of **Ir-CdSe/ZnS**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.96 (d, J = 6.0 Hz, 1 H), 8.91 (d, J = 4.2 Hz, 1 H), 8.28 (d, J = 6.0 Hz, 1 H), 8.21 (d, J = 5.7 Hz, 1 H), 7.84 ~ 7.79 (m, 4 H), 7.69 ~ 7.59 (m, 4 H), 7.52 (d, J = 4.5 Hz, 1 H), 7.45 (d, J = 4.2 Hz, 1 H), 7.29 (d, *J* = 4.8 Hz, 1 H), 7.17 (d, *J* = 5.1 Hz, 1 H), 7.0 (m, 2 H), 6.80 (m, 4 H), 6.50 (s, 1 H), 6.40 (t, *J* = 4.8 Hz, 2 H), 2.24 ~ 0.82 (m, 17 H); IR (neat): 3300, 2980, 2730, 2253, 2080, 1715, 1480, 1056, 1020, 650 cm^{-1}.

Figure S1. ^{1}H NMR spectrum for $[(piq)_2Ir(L1)]$ in $CDCl_3$.

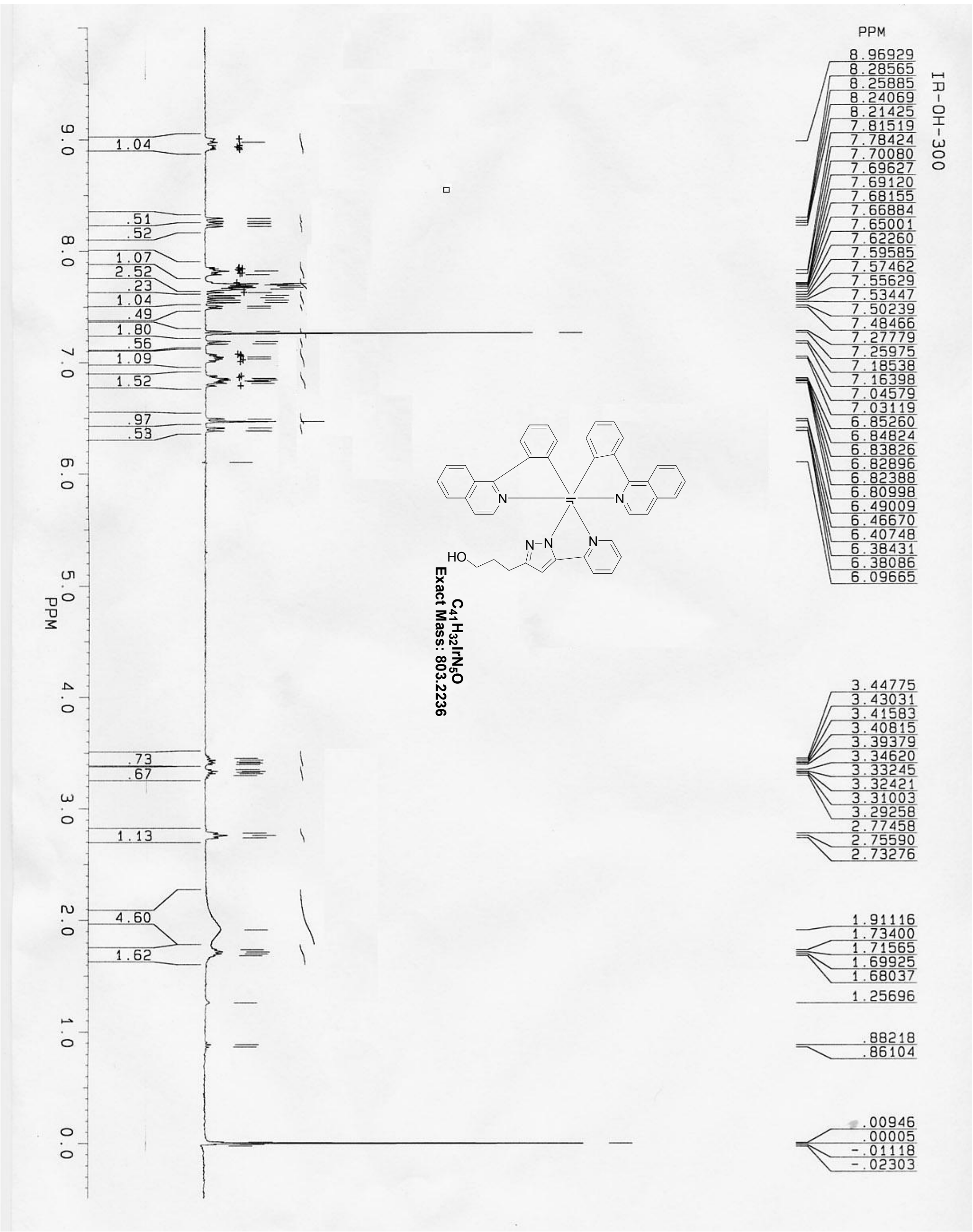


Figure S2. ^{1}H NMR spectrum for [(piq)$_2$Ir(L2)] in CDCl$_3$.

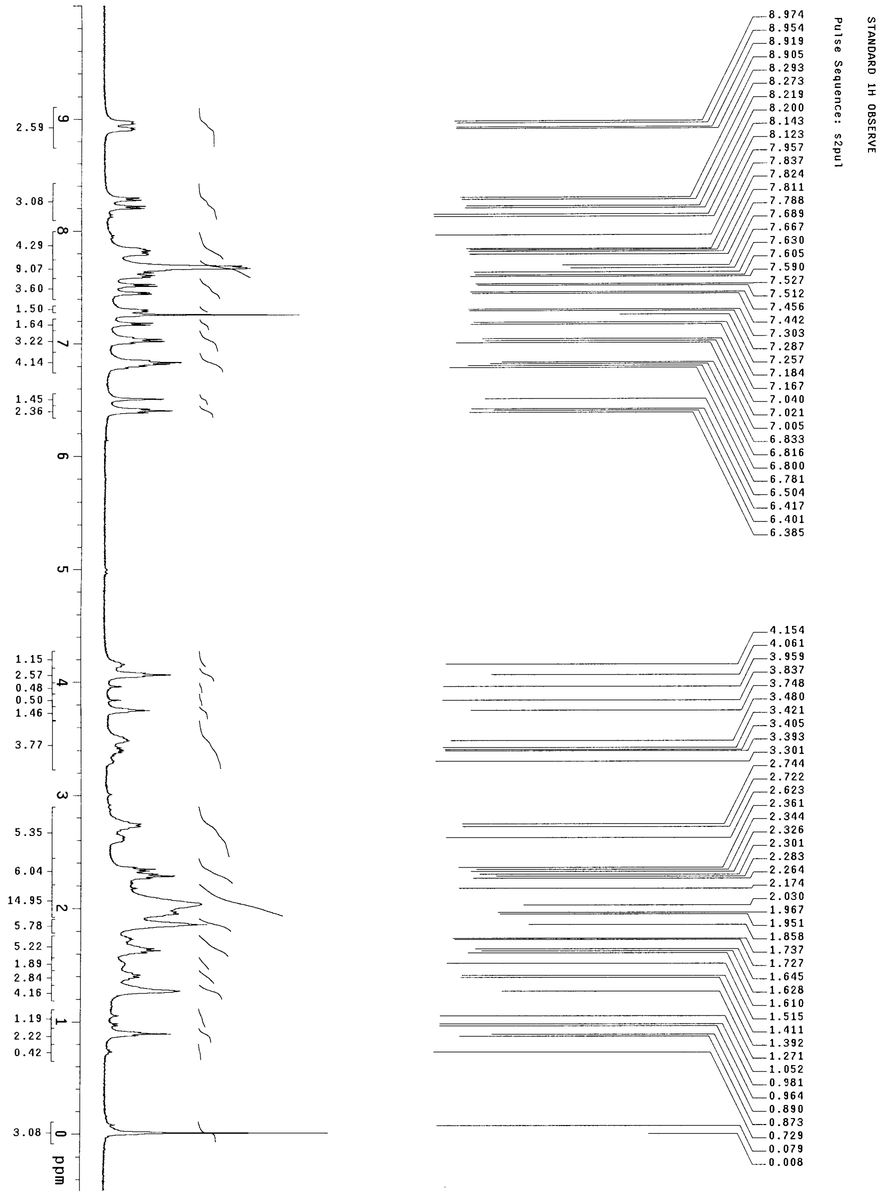


Figure S3. ^{1}H NMR spectrum for **Ir-CdSe/ZnS** in $CDCl_3$

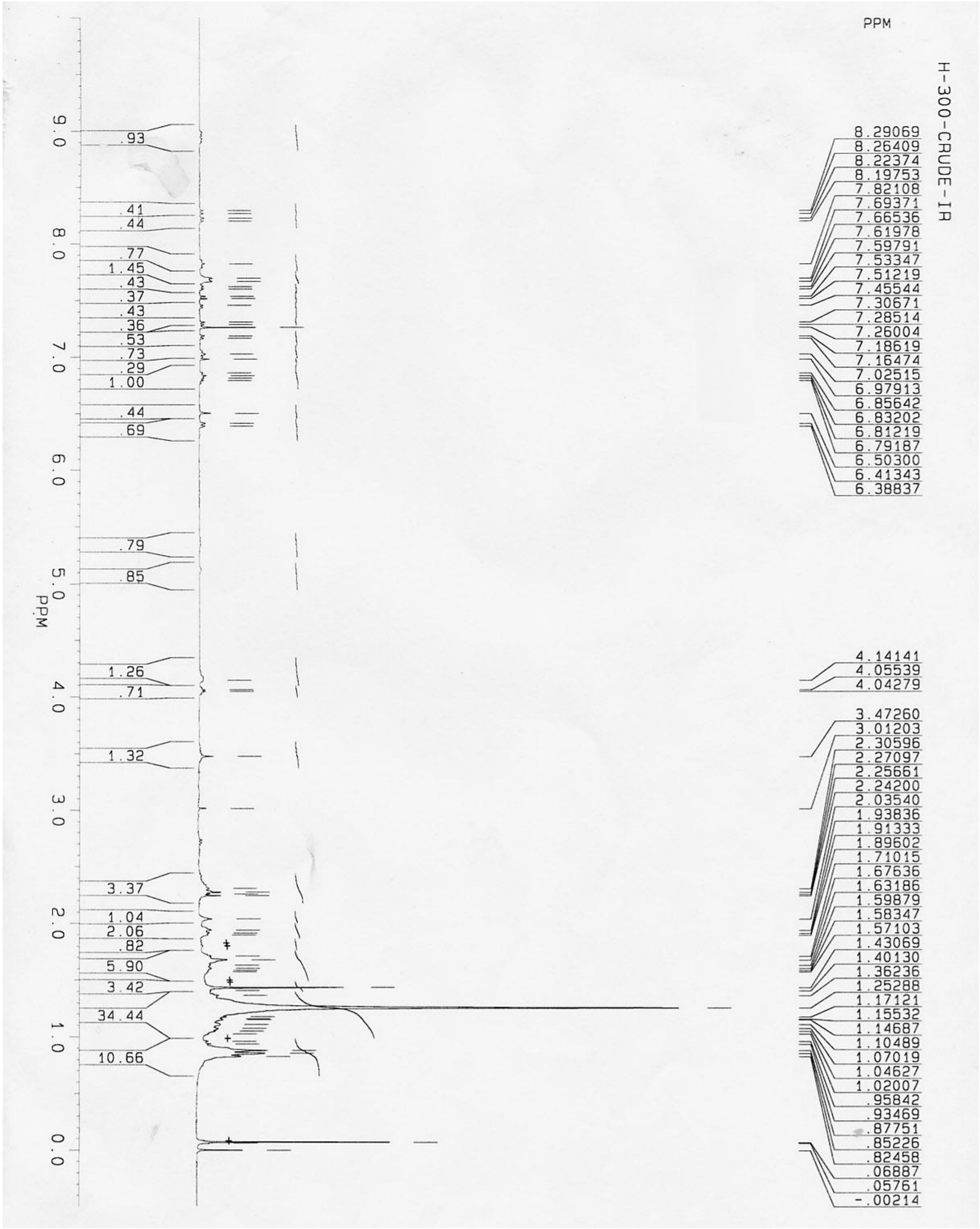


Figure S4. ^{1}H NMR spectrum for **Ir-CdSe/ZnS** in $CDCl_3$ (detailed expansion).

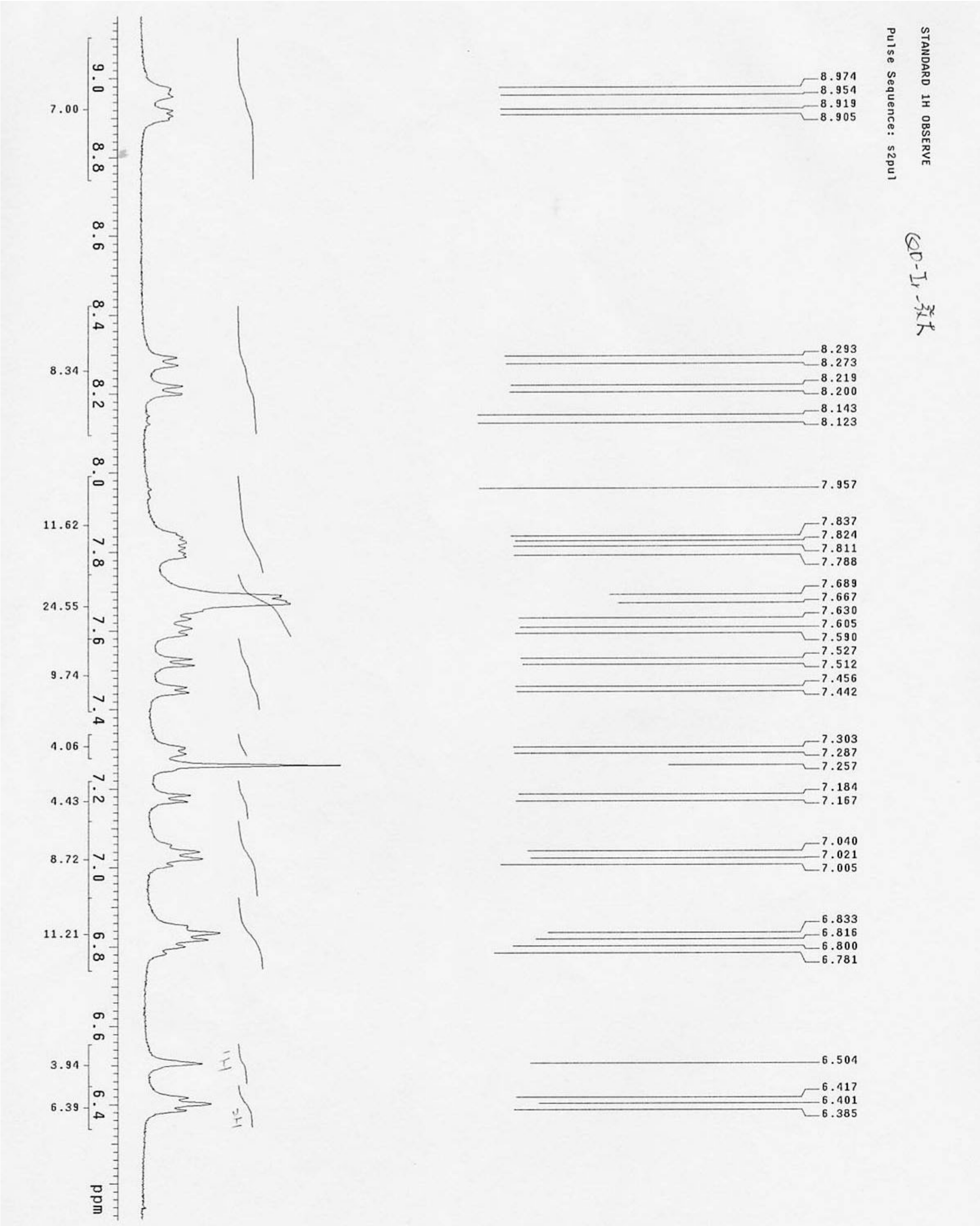


Figure S5. The absorption extinction coefficient as a function of wavelength for $[(piq)_2Ir(L1)]$ in MeOH solution.

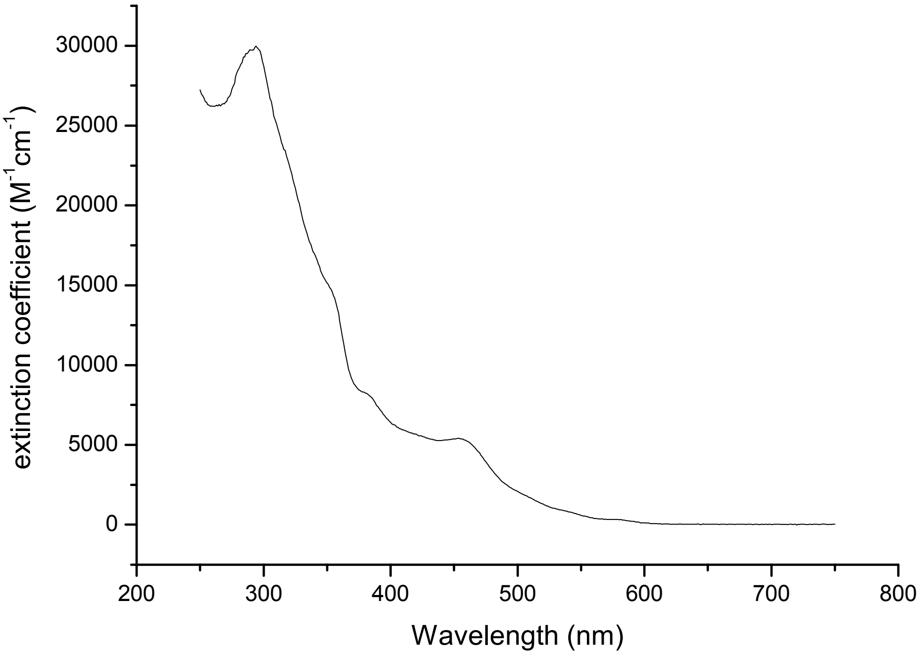


Figure S6. The TEM image of TOPO capped CdSe/ZnS. Counting the an average of > 300 particles, the size (diameter) was determined to be 6.8 ± 0.7 nm.

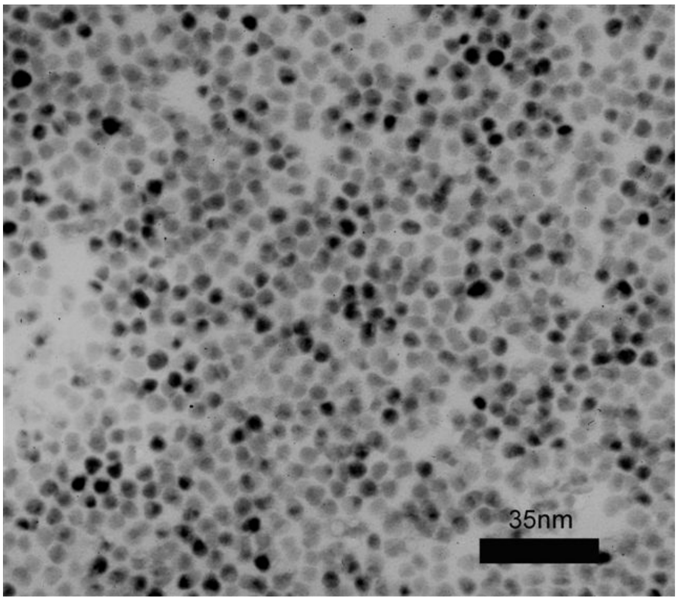
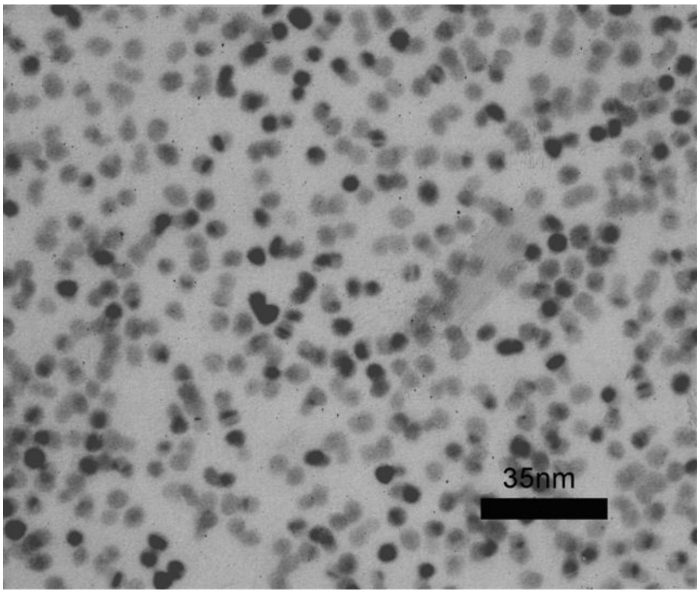


Figure S7. The TEM image of Ir-complex capped CdSe/ZnS. Counting an average of > 300 particles, the size (diameter) was determined to be 7.0 ± 0.6 nm



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Measurements. Steady-state absorption and emission spectra were recorded by a Hitachi (U-3310) spectrophotometer and an Edinburgh (FS920) fluorimeter, respectively. Details of nanosecond and microsecond lifetime measurements have been described previously.[4]

The singlet oxygen emission spectra were obtained by scanning from 1000 nm to 1500 nm with a Ar ion laser (λ_{ex} ~ 514 nm) or a Mercury-Xenon lamp (500 W) coupled with a monochromator and detected with a lock-in amplifier (Stanford Research System model SR830 DSP) coupled with a NIR sensitive photomultiplier (Hamamatsu model R5509 – 72) operated at –80 °C. A chopper was operated at 134 Hz for phase sensitively picking the signal. A long-pass (> 950 nm) optical filter was used to exclude the excitation laser wavelengths.

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