Electronic Supplementary Information for:

# Accessing the long-lived emissive $^3$IL triplet excited states of coumarin fluorophores by direct cyclometallation and its application for oxygen sensing and upconversion

Wenting Wu, Wanhua Wu, Shaomin Ji, Huimin Guo and Jianzhang Zhao*

*State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, 2 Ling-gong Road, Dalian 116024, P. R. China.*

E-mail: zhaojzh@dlut.edu.cn (J. Zhao)      Phone/Fax: +86 411 8498 6236

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# Experimental Section

## General

Typical film preparation was undertaken by dissolving 10.0 mg of IMPEK-C polymer in 0.3 mL acetone to which was added 0.4 mL of **Pt-1** complex solution in $CH_2Cl_2$ ($5\times10^{-4}$ M). After thorough mixing, about 0.3 mL of the solution was applied to a quartz glass disk (diameter: 1.6 cm) and the solvent was evaporated at room temperature to realize a transparent film. The thickness of the film of **Pt-1** was estimated as 16.8 µm, according to the mass of the film (3.9 mg), the density of the polymer (1.14 g $cm^{-3}$) and the size of the film. Similarly the thickness of the film of **Pt-2**, and **Pt-3** were estimated as 17.6 µm and 12.5 µm, respectively.

The ground state structure of complexes were optimized using density functional theory (DFT)[1] with B3LYP functional and 6-31G(d)/ LanL2DZ basis set. The excited state related calculations were carried out with the Time dependent density functional theory (TD-DFT) with the optimized structure of the ground state (DFT 6-31G(d)/ LanL2DZ) There are no imaginary frequencies in frequency analysis of all calculated structures, therefore each calculated structure express an energy minimum. All these calculations were performed in Gaussian 09.[2]

### Reference:

1. Hohenberg P, Kohn W. *Phys. Rev.* 1964; **136**: B864.

2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al. Gaussian 09 Revision A.1, Gaussian Inc., Wallingford CT, 2009.

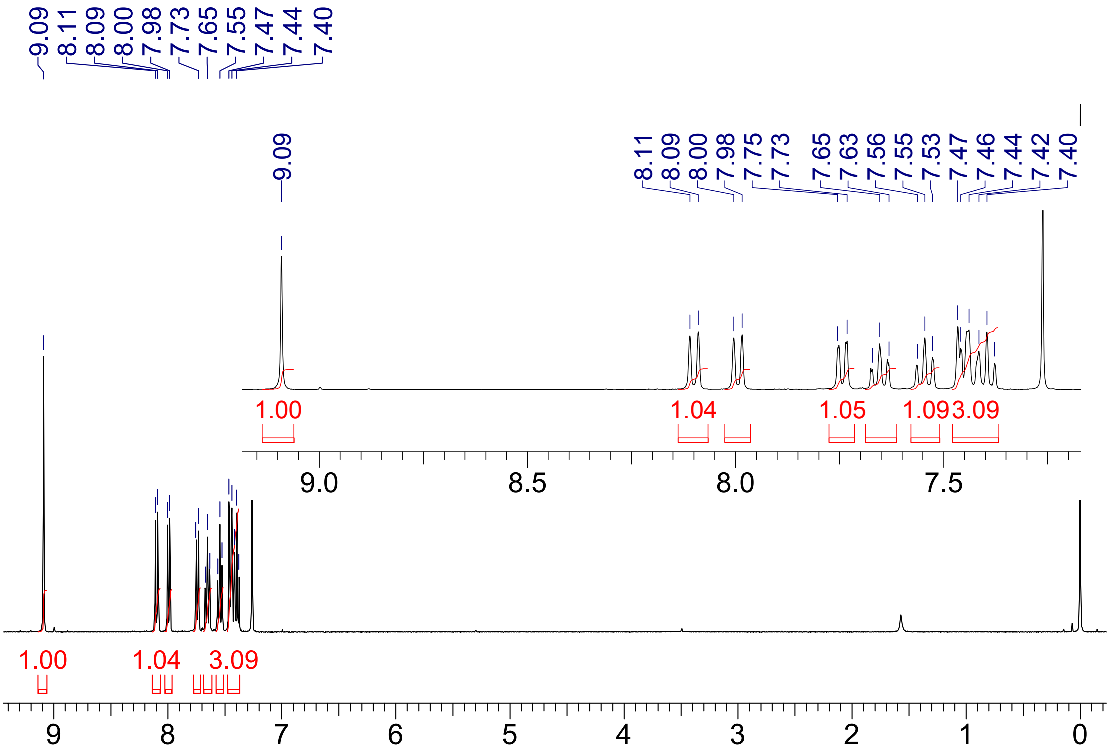


**Figure S1.** $^1$H NMR of **L-3** ($CDCl_3$, 400 MHz)

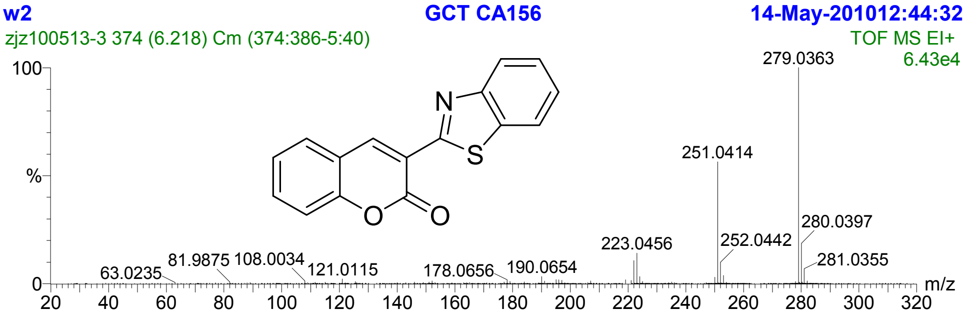


**Figure S2.** EI MS of **L-3.**

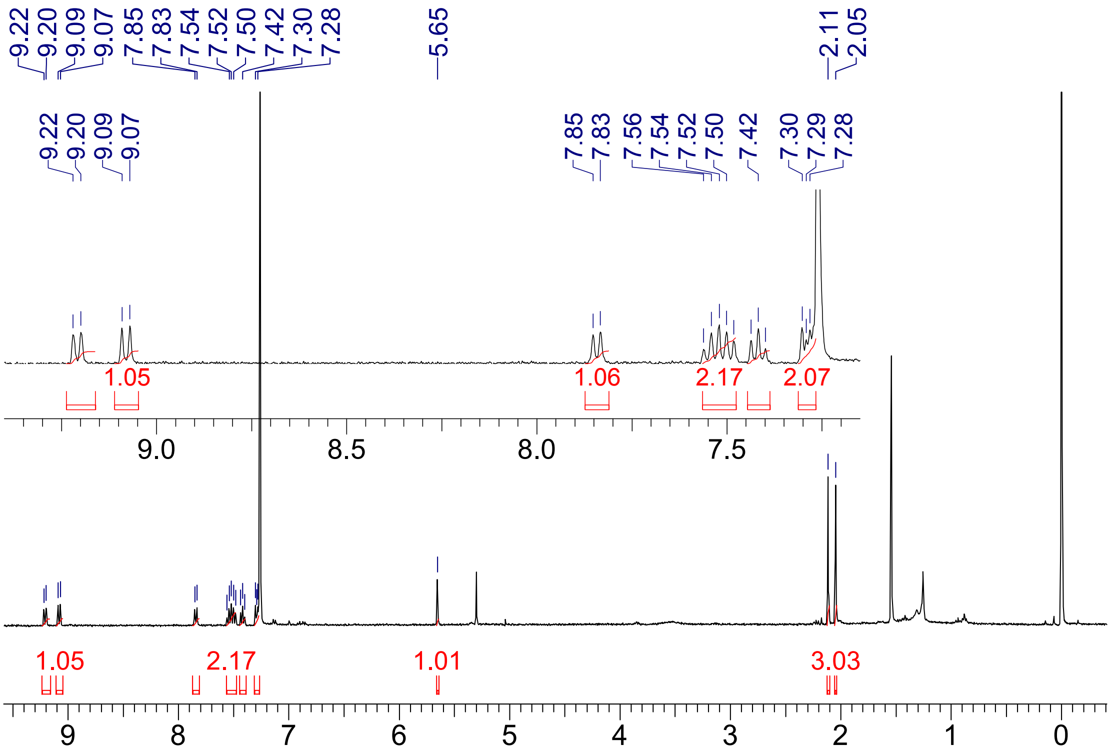


**Figure S3.** $^1$H NMR of **Pt-3** ($CDCl_3$, 400 MHz)

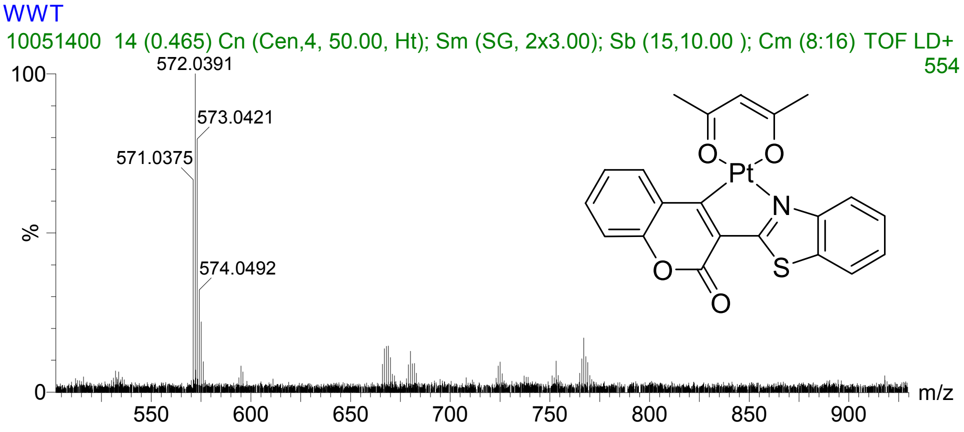


**Figure S4.** MALDI MS of **Pt-3.**

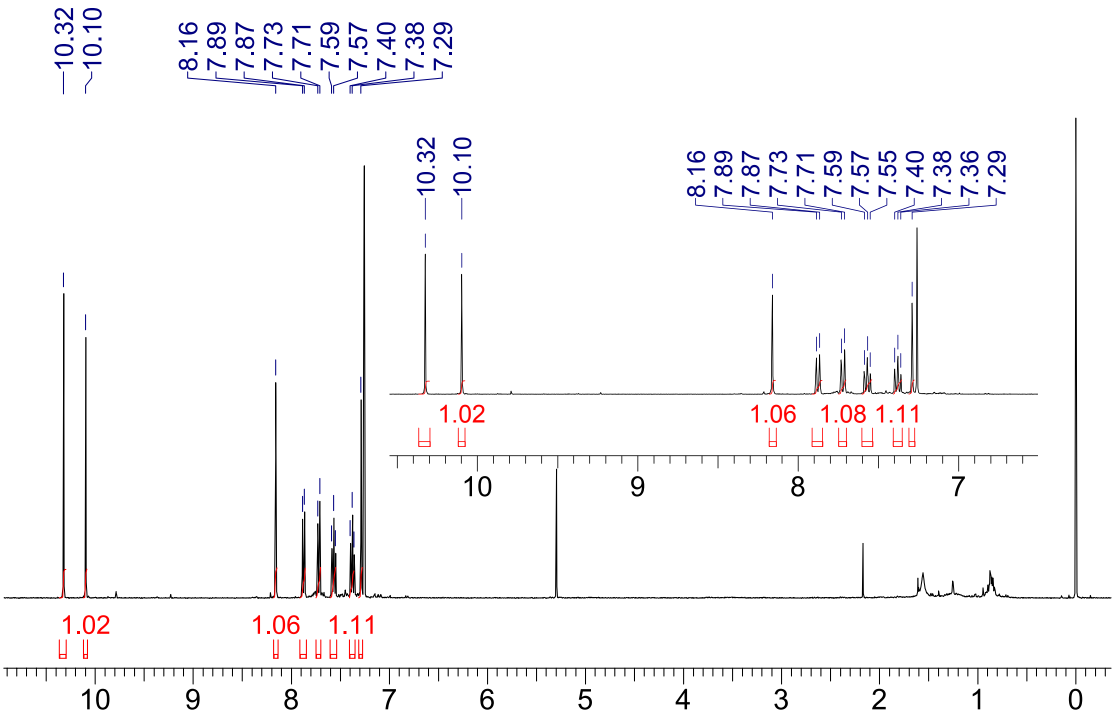


**Figure S5.** $^1$H NMR of **2-Hydroxy-3-naphthaldehyd** ($CDCl_3$, 400 MHz).

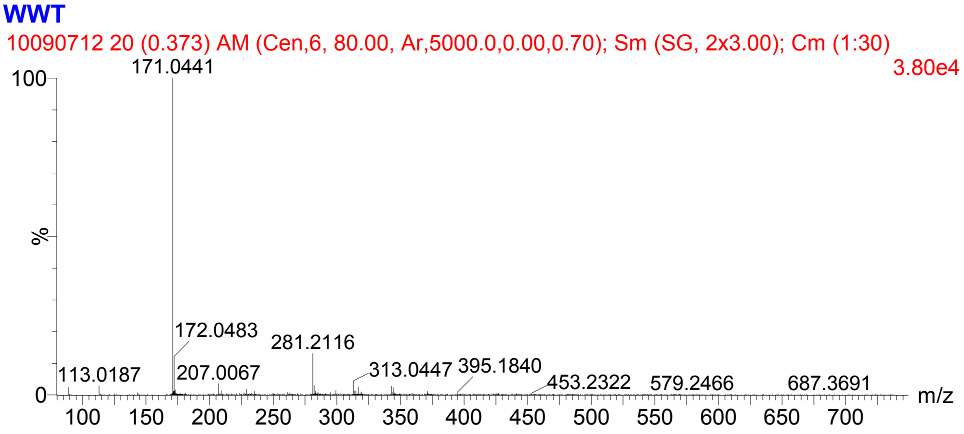


**Figure S6.** TOF MS of **2-Hydroxy-3-naphthaldehyd.**

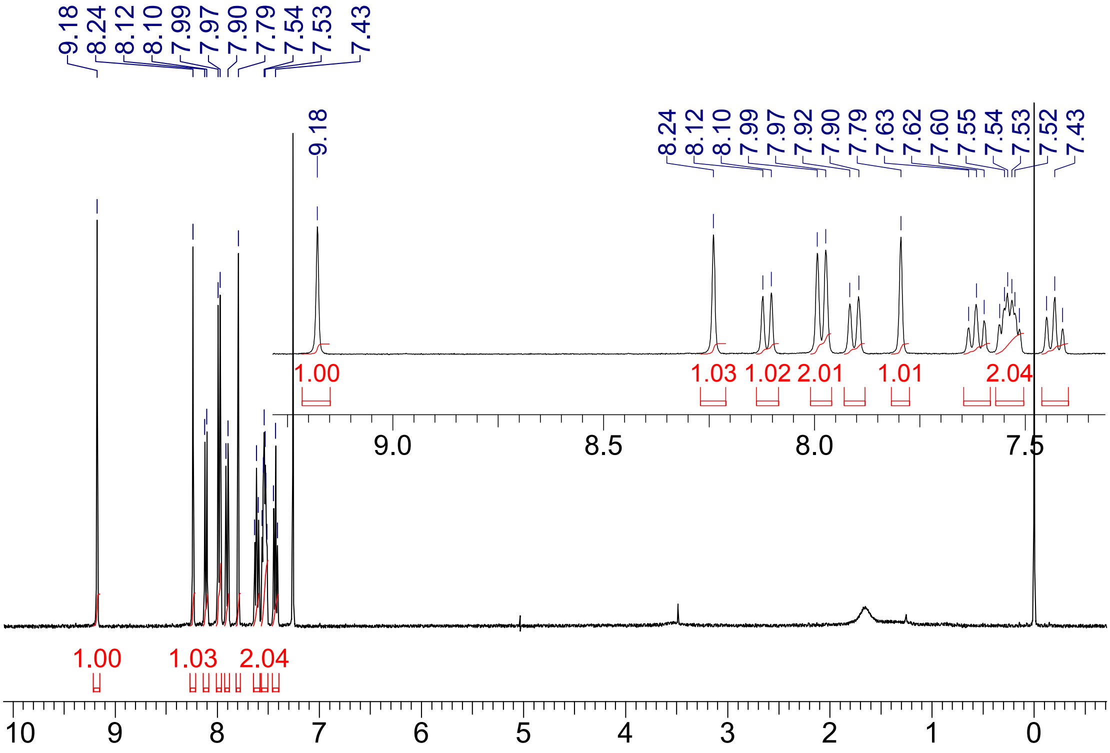


**Figure S7.** $^{1}$H NMR of **L-4** ($CDCl_3$, 400 MHz)

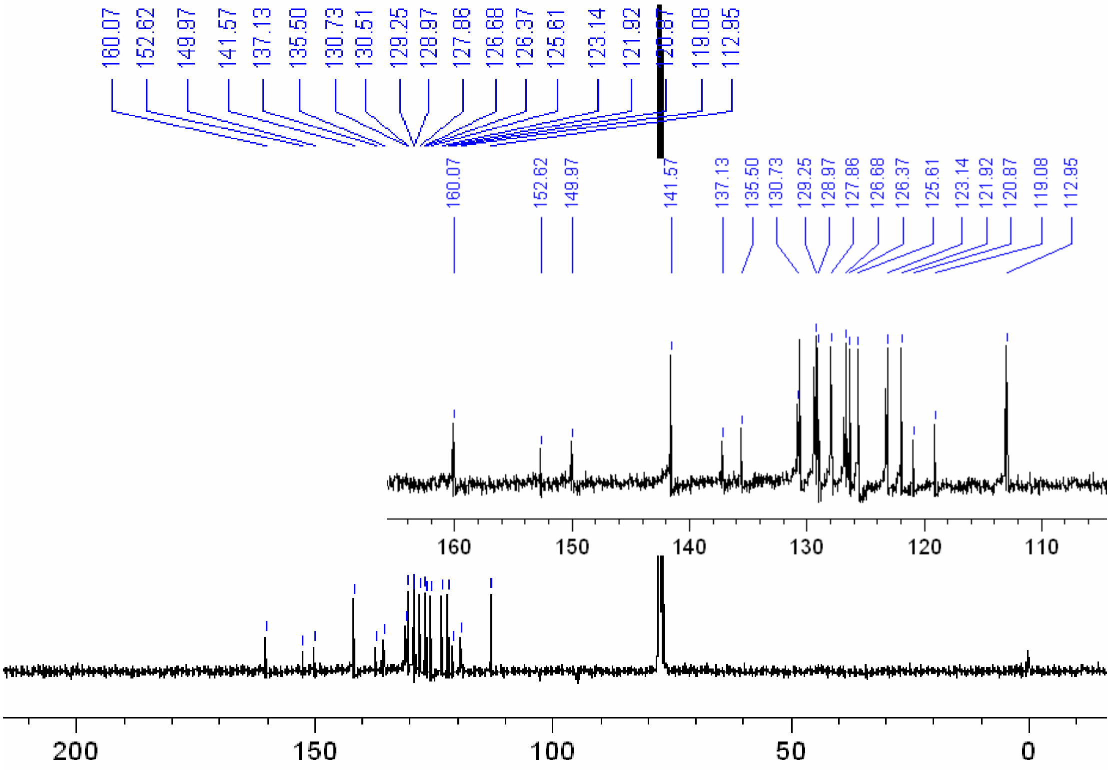


**Figure S8.** $^{13}$C NMR of **L-4** ($CDCl_3$, 100 MHz).

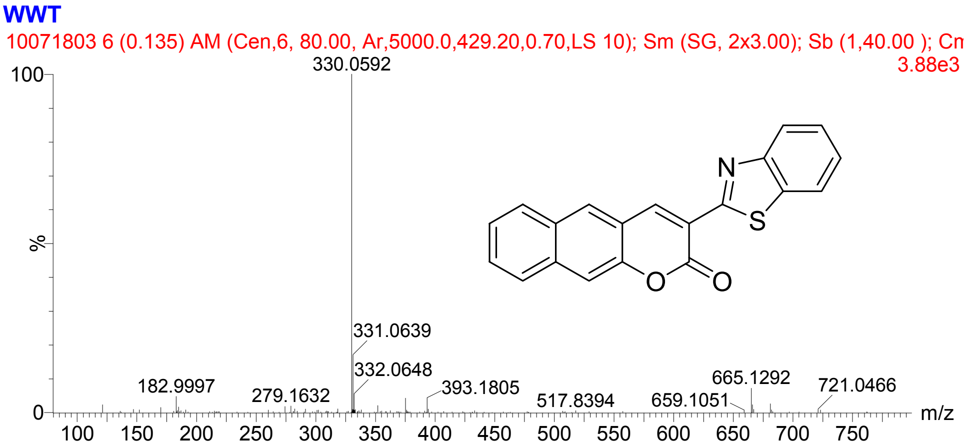


**Figure S9.** EI MS of **L-4.**

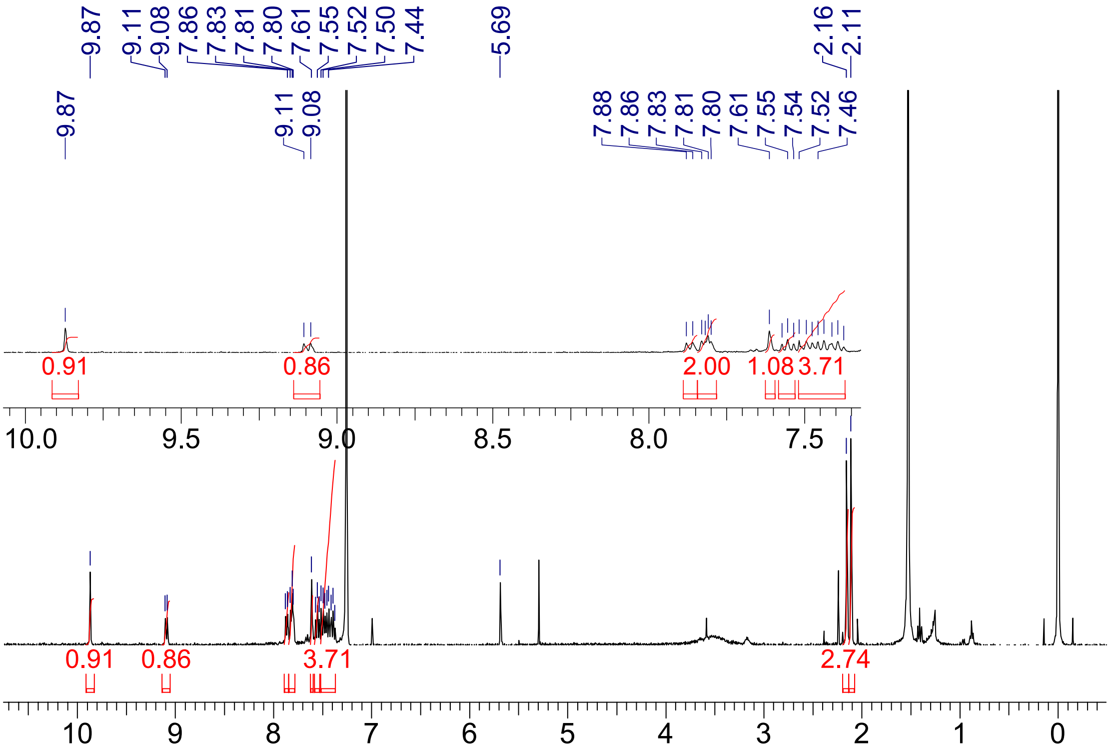


**Figure S10.** $^1$H NMR of **Pt-4** ($CDCl_3$, 400 MHz)

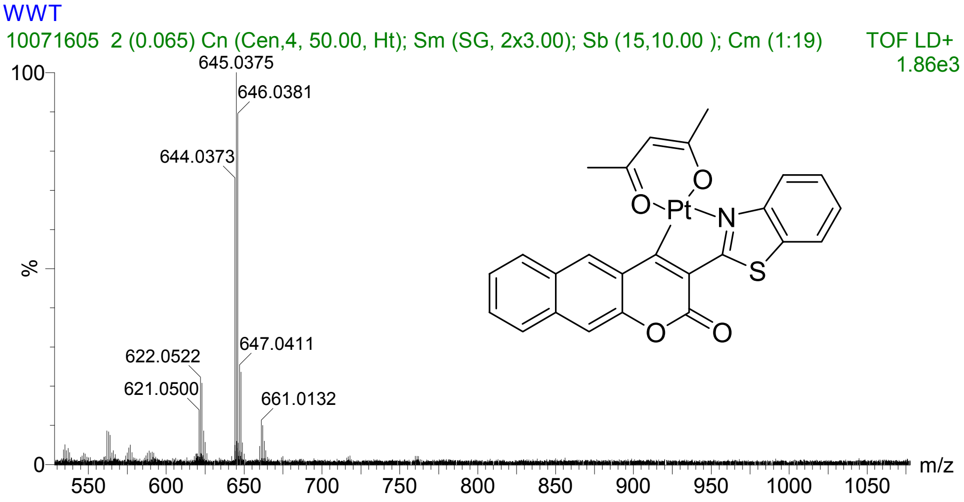
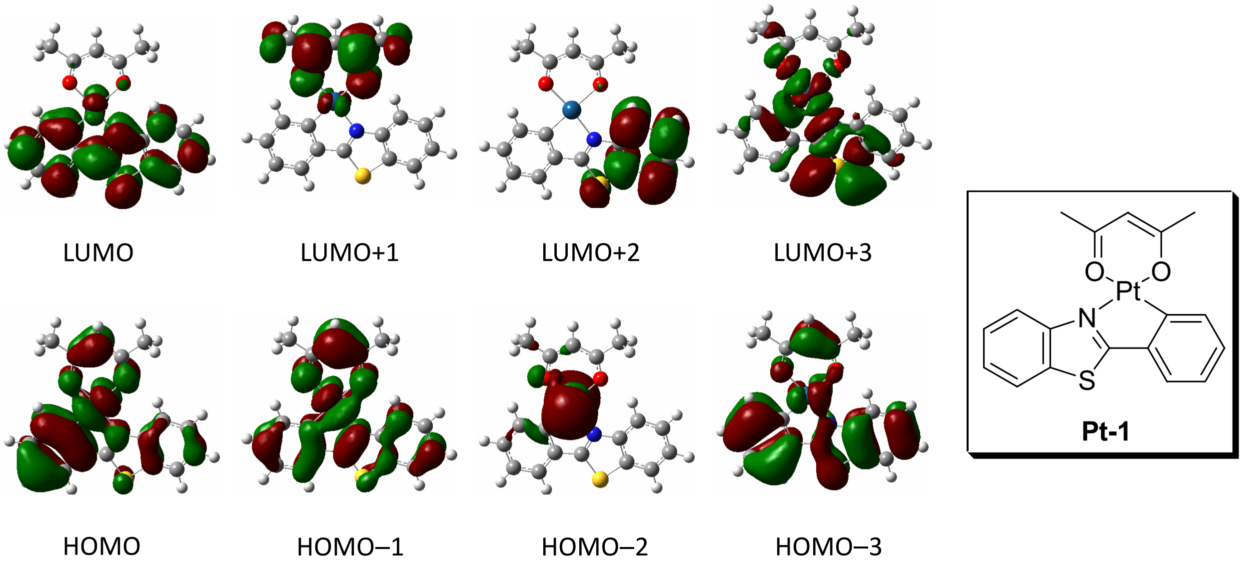


**Figure S11.** MALDI MS of **Pt-4.**

**Table S1.** Electronic Excitation Energies (eV) and corresponding Oscillator Strengths (*f*), main configurations and CI coefficients of the Low-lying Electronically Excited States of complex **Pt-1**, Calculated by TDDFT//B3LYP/6-31G(d)/ LanL2DZ , based on the DFT//B3LYP/6-31G(d)/ LanL2DZ Optimized Ground State Geometries.

| | Electronic | TDDFT//B3LYP/6-31G(d) | | | | |
|---|---|---|---|---|---|---|
| | transition | Energy [a] | *f* [b] | Composition [c] | CI [d] | Character [e] |
| Singlet | $S_0 \rightarrow S_1$ | 3.07 eV 404 nm | 0.0773 | H−3→L | 0.1137 | LLCT&MLCT |
| | | | | H−1→L | 0.2129 | LLCT&MLCT |
| | | | | H→L | 0.6293 | LLCT&MLCT |
| | $S_0 \rightarrow S_2$ | 3.34 eV 372 nm | 0.0741 | H−1→L | 0.6289 | LLCT&MLCT |
| | | | | H→L | 0.2380 | LLCT&MLCT |
| | $S_0 \rightarrow S_5$ | 4.04 eV 307 nm | 0.2225 | H−3→L | 0.6371 | LLCT&MLCT |
| | | | | H→L+4 | 0.1054 | |
| Triplet | $S_0 \rightarrow T_1$ | 2.45 eV 505 nm | 0.0000 [f] | H−3→L | 0.2037 | LLCT&MLCT |
| | | | | H−1→L | 0.5062 | LLCT&MLCT |
| | | | | H→L | 0.5087 | LLCT&MLCT |

[a] Only the selected low-lying excited states are presented. [b] oscillator strength. [c] H stands for HOMO and L stands for LUMO. Only the main configurations are presented. [d] The CI coefficients are in absolute values. [e] IL: intraligand, LLCT: ligand to ligand charge transfer, MLCT: metal to ligand charge transfer. [f] No spin-orbital coupling effect was considered, thus the *f* values are zero.

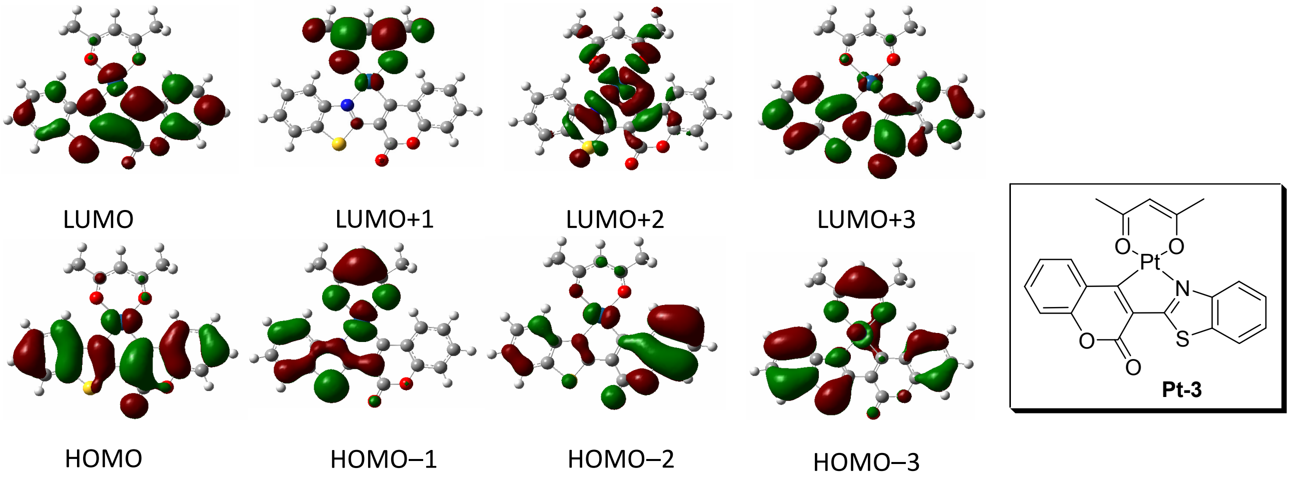


**Scheme S1.** Qualitative scheme of frontier molecular orbitals of **Pt-1** calculated by DFT/TDDFT at the B3LYP/6-31G((d)/ LanL2DZ level using Gaussian 09.

**Table S2.** Electronic Excitation Energies (eV) and corresponding Oscillator Strengths (*f*), main configurations and CI coefficients of the Low-lying Electronically Excited States of complex **Pt-3**, Calculated by TDDFT//B3LYP/6-31G(d)/ LanL2DZ , based on the DFT//B3LYP/6-31G(d)/LanL2DZ Optimized Ground State Geometries.

| | Electronic | TDDFT//B3LYP/6-31G(d) | | | | |
|---|---|---|---|---|---|---|
| | transition | Energy [a] | *f* [b] | Composition [c] | CI [d] | Character [e] |
| Singlet | $S_0 \rightarrow S_1$ | 3.00 eV 412 nm | 0.2014 | H−5→L | 0.1420 | |
| | | | | H−1→L | 0.1275 | LLCT |
| | | | | H→L | 0.6312 | IL |
| | $S_0 \rightarrow S_2$ | 3.38 eV 367 nm | 0.1224 | H−1→L | 0.6625 | LLCT |
| | | | | H→L | 0.1146 | IL |
| | $S_0 \rightarrow S_4$ | 3.67 eV 338 nm | 0.0454 | H−2→L | 0.6670 | IL |
| | $S_0 \rightarrow S_{10}$ | 4.10 eV 302 nm | 0.1311 | H−5→L | 0.3799 | |
| | | | | H−4→L+2 | 0.3935 | |
| | | | | H−1→L+1 | 0.3416 | LLCT&MLCT |
| Triplet | $S_0 \rightarrow T_1$ | 2.23 eV 556 nm | 0.0000 [f] | H→L | 0.7514 | IL |

[a] Only the selected low-lying excited states are presented. [b] oscillator strength. [c] H stands for HOMO and L stands for LUMO. Only the main configurations are presented. [d]The CI coefficients are in absolute values. [e] IL: intraligand, LLCT: ligand to ligand charge transfer, MLCT: metal to ligand charge transfer. [f] No spin-orbital coupling effect was considered, thus the *f* values are zero.



**Scheme S2.** Qualitative scheme of frontier molecular orbitals of **Pt-3** calculated by DFT/TDDFT at the B3LYP/6-31G((d)/ LanL2DZ level using Gaussian 09.

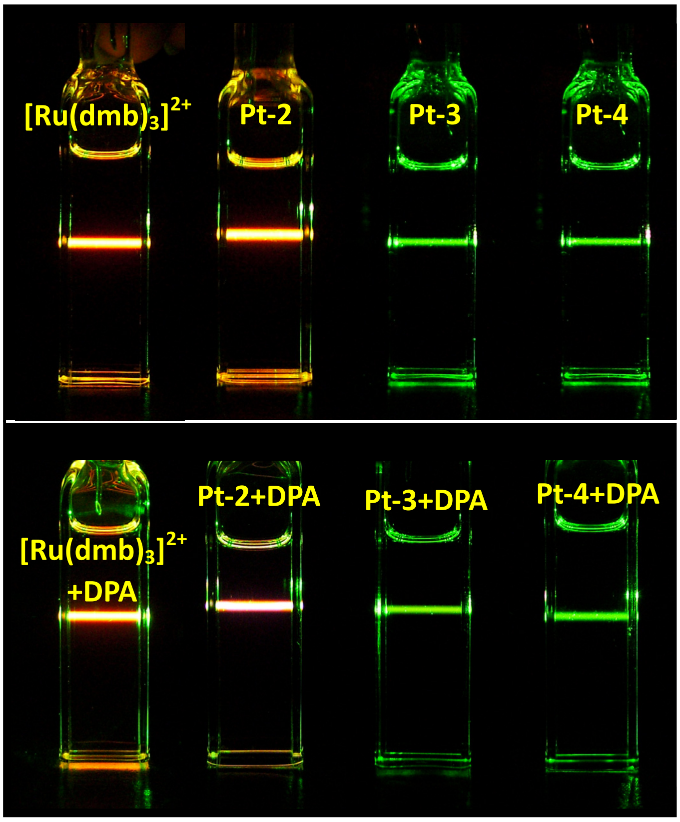
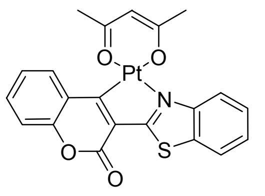
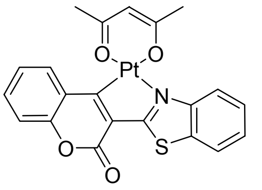


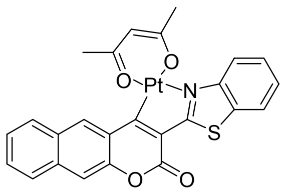
**Figure S12.** The digital photographs of (a) the emission of the complexes alone, with 532 nm laser excitation (5 mW) and (b) the upconversion, i.e. the excitation of the mixed solution of the complex with DPA. For **Pt-2**, **Pt-3** and **Pt-4**, the upconverted blue fluorescence of DPA were observed, among which the **Pt-2** shows the most intensive emission. In deaerated $CH_2Cl_2$ solution. The complexes solution are at $1.0 \times 10^{-5}$ M and the DPA concentration is at $2.3 \times 10^{-4}$ M. 25°C.



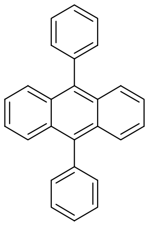
**Pt-2**



**Pt-3**



**Pt-4**



**DPA**

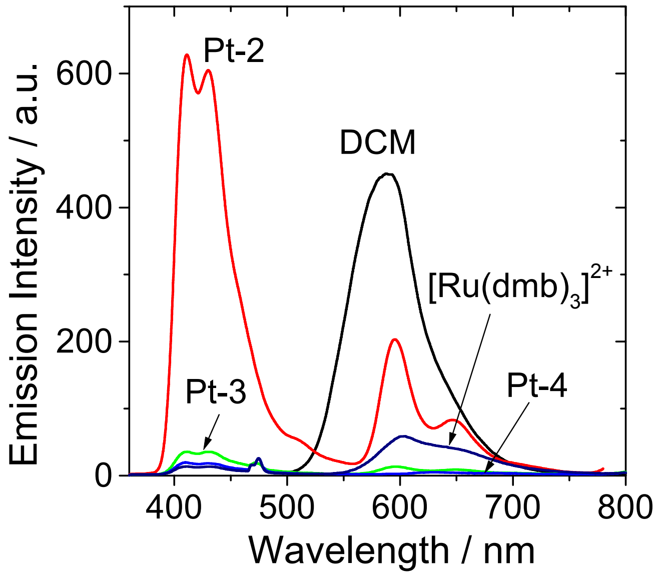
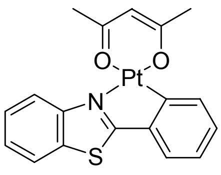
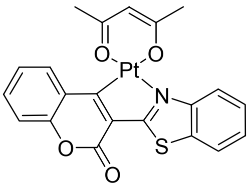


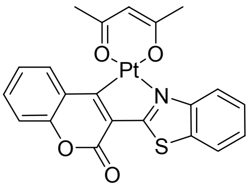
**Figure S13.** Emission of the fluorescence of DCM ($1.0\times10^{-5}$ M) and the upconverted fluorescence of 9,10-diphenylanthracene (DPA, $4.3\times10^{-5}$ M) and the residual photoluminescence of the complex of **Pt-2**, **Pt-3**, **Pt-4** and $[Ru(dmb)^3]^{2+}$ ($1.0\times10^{-5}$ M) in the upconversion experiments. Excitation by diode pumped solid state blue laser (λex = 473 nm, 5 mW). 25 °C.



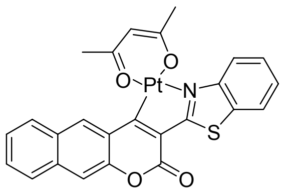
**Pt-1**



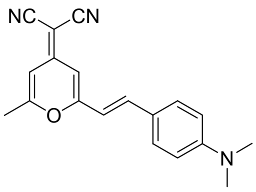
**Pt-2**



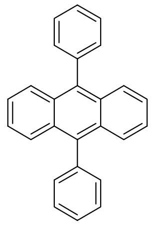
**Pt-3**



**Pt-4**



DCM



**DPA**

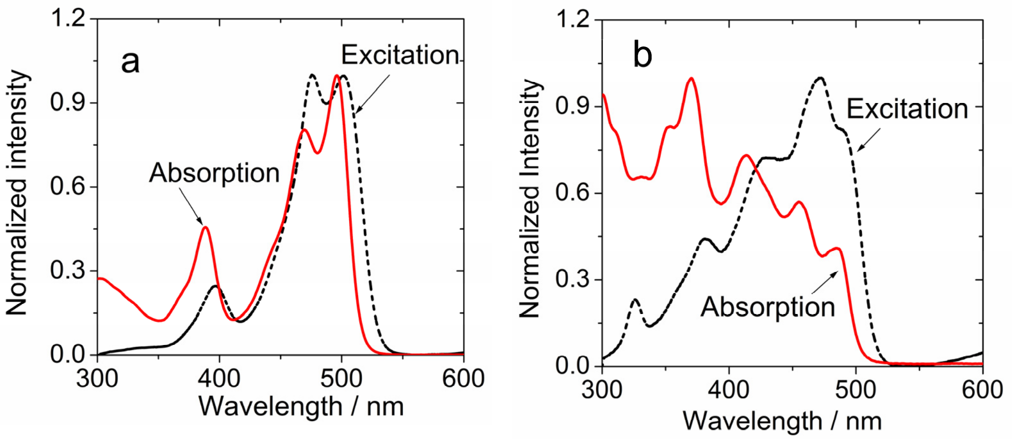


**Figure S14.** Comparison of the UV-Vis absorption and the excitation spectra of the complex (a) **Pt-2**. The excitation spectra were recorded with λem = 597 nm. (b) **Pt-4**. The excitation spectra were recorded with λem = 629 nm $c$ = 1.0× $10^{-5}$ mol $dm^{-3}$ of the compounds in dichloromethane. 25 °C.

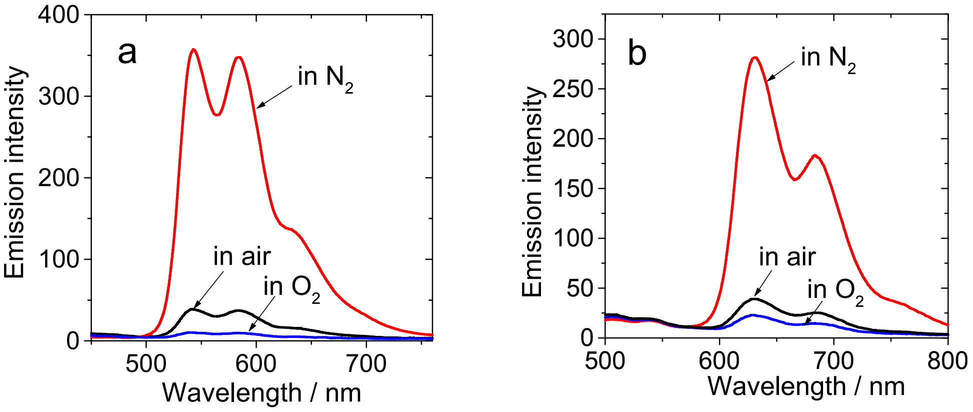


**Figure S15.** Emission spectra of (a) **Pt-1**, λex = 404 nm, (b) **Pt-4**, λex = 472 nm, in $CH_2Cl_2$ solution saturated with air, oxygen and nitrogen. $c$ = $1.0\times10^{-5}$ mol / L, 25 °C.

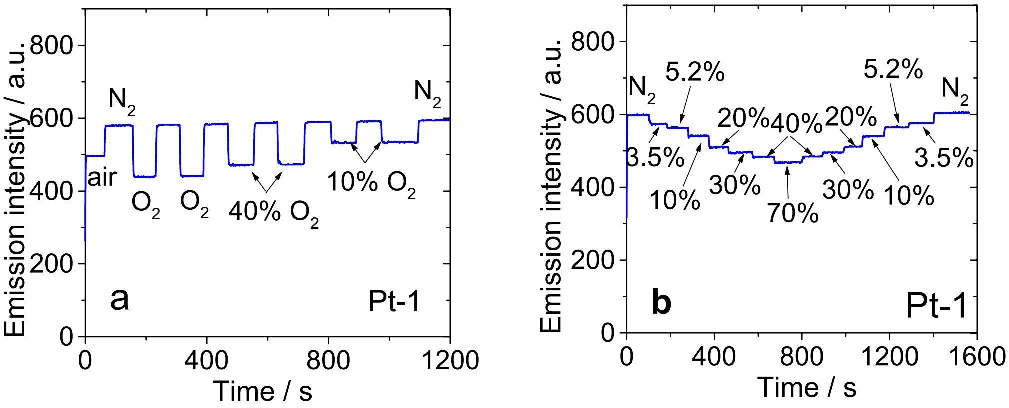
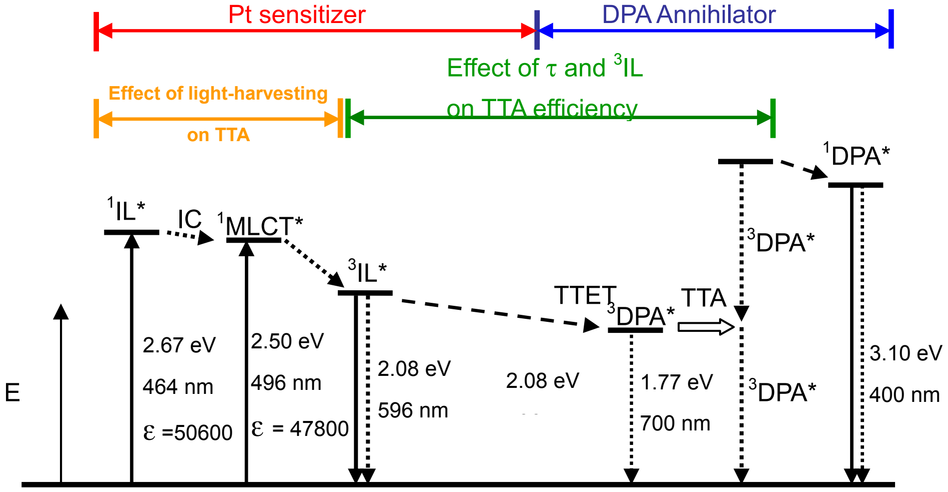


**Figure S16.** Phosphorescent emission intensity response of the complexes to step variations of $O_2$ concentration levels. (a) and (b) **Pt-1**, λex = 404 nm, λem = 543 nm. 25 °C.



**Scheme S3.** Qualitative Jablonski Diagram illustrating the sensitized TTA up-conversion process between Pt(II) complexes and DPA. The effect of the light-harvesting ability and the luminescent lifetime of the Pt(II) sensitizer on the efficiency of the TTA-up-conversion is also shown (please note that the vibration energy levels of each electronic state are omitted for clarity. However, the vibrational energy levels may also be important for the photophysics). E is energy. GS is ground state ($S_0$). $^1$IL* is intraligand singlet excited state (coumarin localized). IC is inner conversion. $^1$MLCT* is the Pt(II) based metal-to-ligand charge transfer singlet excited state. ISC is intersystem crossing. $^3$IL* is intraligand triplet excited state (coumarin localized). TTET is triplet-triplet energy transfer. $^3$DPA* is the triplet excited state of DPA. TTA is triplet-triplet annihilation. $^1$DPA* is the singlet excited state of DPA. The emission bands observed for the sensitizers along is the $^3$MLCT emissive excited state (we propose the $^3$IL* is non-emissive). The emission bands observed in the TTA experiment is the simultaneous $^3$MLCT* emission (phosphorescence) and the $^1$DPA* emission (fluorescence).