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# Coumarin phosphorescence observed with *N^N* Pt(II) bisacetylide complex and its applications for luminescent oxygen sensing and triplet-triplet-annihilation based upconversion

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## Experimental section

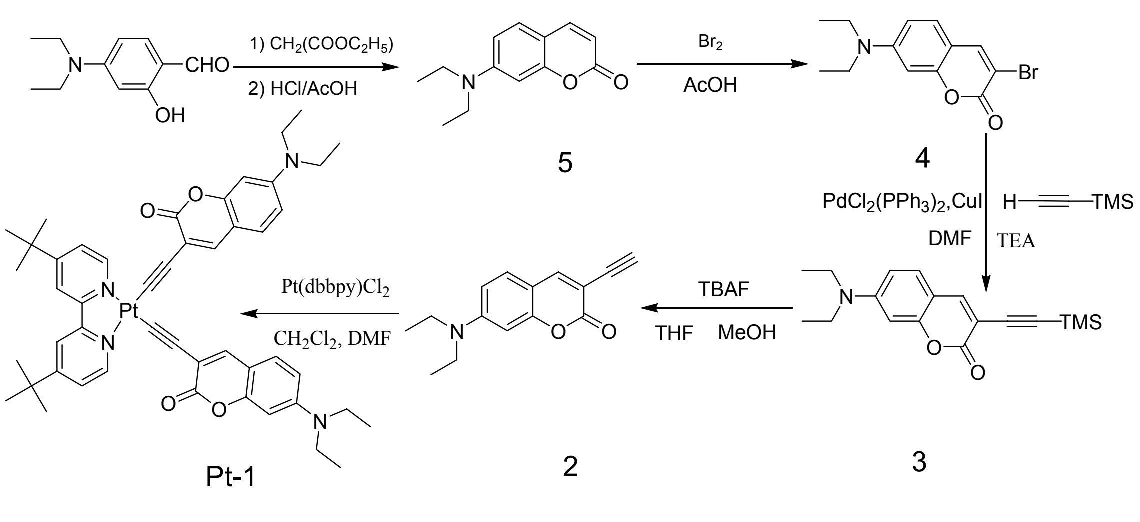
### General information

NMR spectra were taken on a 400 MHz Varian Unity Inova spectrophotometer. Mass spectra were recorded with a Q-TOF Micro MS spectrometer. UV-Vis spectra were taken on a HP8453 UV-visible spectrophotometer. Fluorescence spectra were recorded on a JASCO FP-6500 or a Sanco 970 CRT spectrofluorometer. Luminescence quantum yields were measured with $[Ru(bpy)_2(Phen)][PF_6]_2$ as the reference ($\Phi$ = 6.0 % in actonitrile).

Diode pumped solid state laser (DPSSL) with 473 nm or 532 nm were used as excitation soruce for the upconversion experiments. The diameter of the laser spot is ca. 3 mm. The output power of the DPSS laser can be adjusted continuously. The laser power was measured with phototube. For 532 nm laser, the variation of the power is less than ±5% over eight hours. The noise of the 532 nm DPSS laser is 20%-25% in the range of 1 kHz- 1 MHz. The noise of the 473 nm DPSS laser is 20%-25% in the range of 1 kHz- 1MHz. For the upconversion experiments, the mixed solution of the complex (triplet sensitizer) and perylene (triplet acceptor) was degassed for at least 15 min with $N_2$ or Ar. Then the solution was excited with laser. The upconverted fluorescence of perylene was observed with fluorospectrometer. In order to repress the scattered laser, a black box with a small hole on it was put behind the fluorescent cell to trap the laser beam behind the vial (the small hole as the entrance of the laser into the black box). The upconversion quantum yields were calculated with a reported method.[1]

In the two-site model for the oxygen sensing (please refer to the Fig. 13 in the main text), the $O_2$-sensitive dyes are treated as two different portions. Fraction of the two portions are defined as $f_1$ and $f_2$, respectively ($f_1 + f_2 = 1$), the two portions show different quenching constants ($K_{SV1}$ and $K_{SV2}$, Eq. 1).

$$\frac{I_0}{I} = \frac{1}{\dfrac{f_1}{1+K_{SV1}p_{O_2}} + \dfrac{f_2}{1+K_{SV2}p_{O_2}}} \qquad \textbf{(Eq. 1)}$$




**Scheme S1**. Synthesis of **Pt-1**.

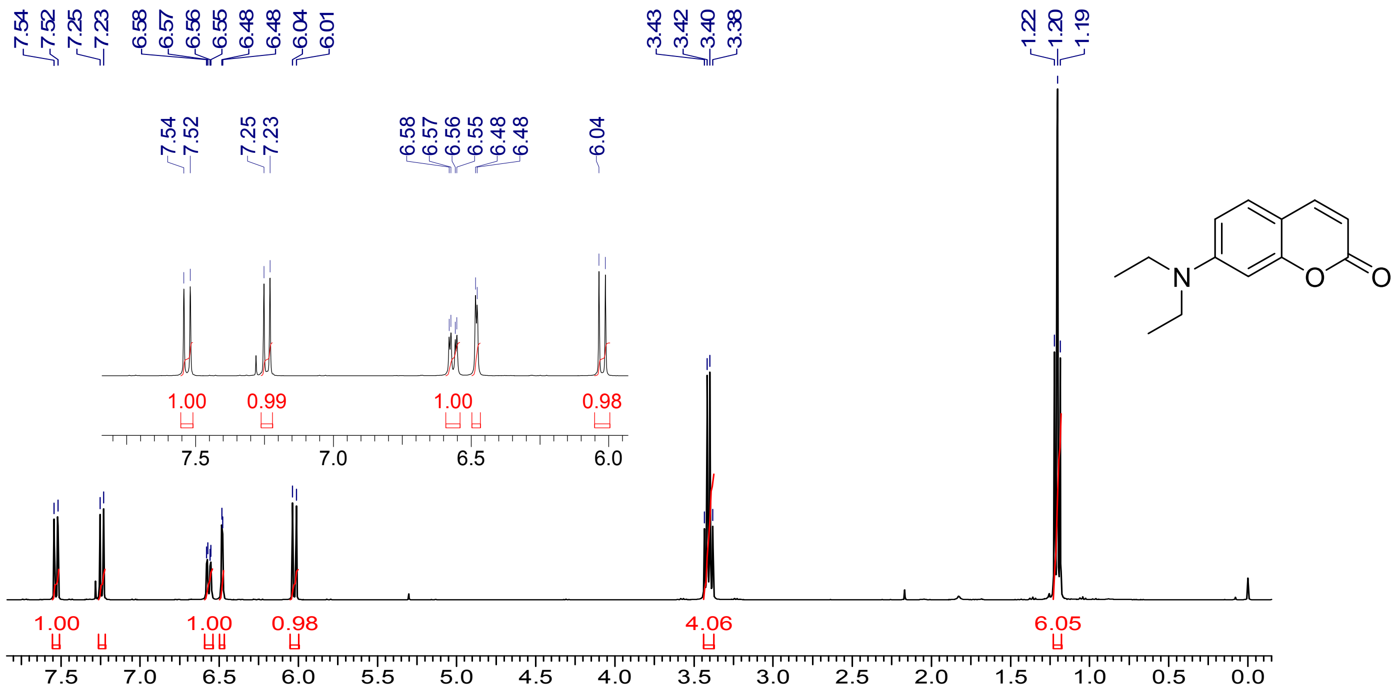


**Figure S1.** $^{1}$H NMR of **5** ($CDCl_3$, 400 MHz).

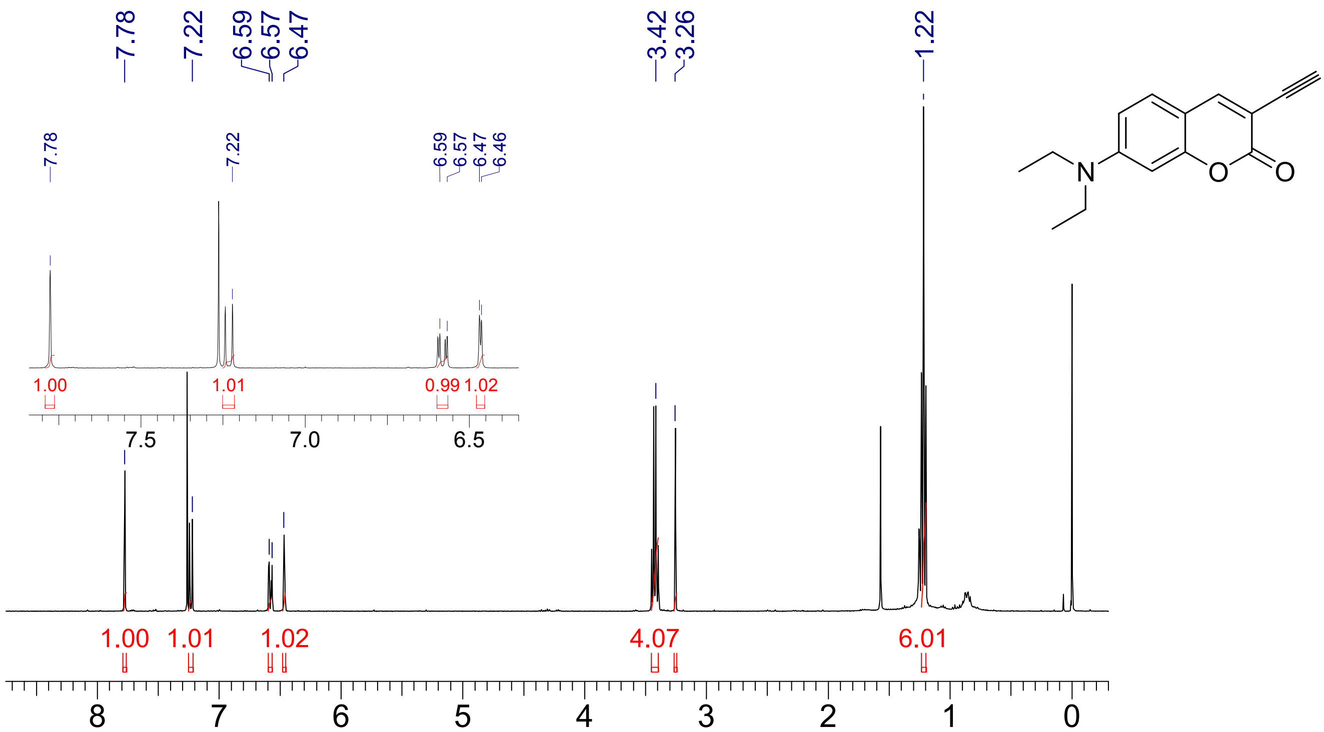


**Figure S2.** $^{1}$H NMR of **2** ($CDCl_3$, 400 MHz).

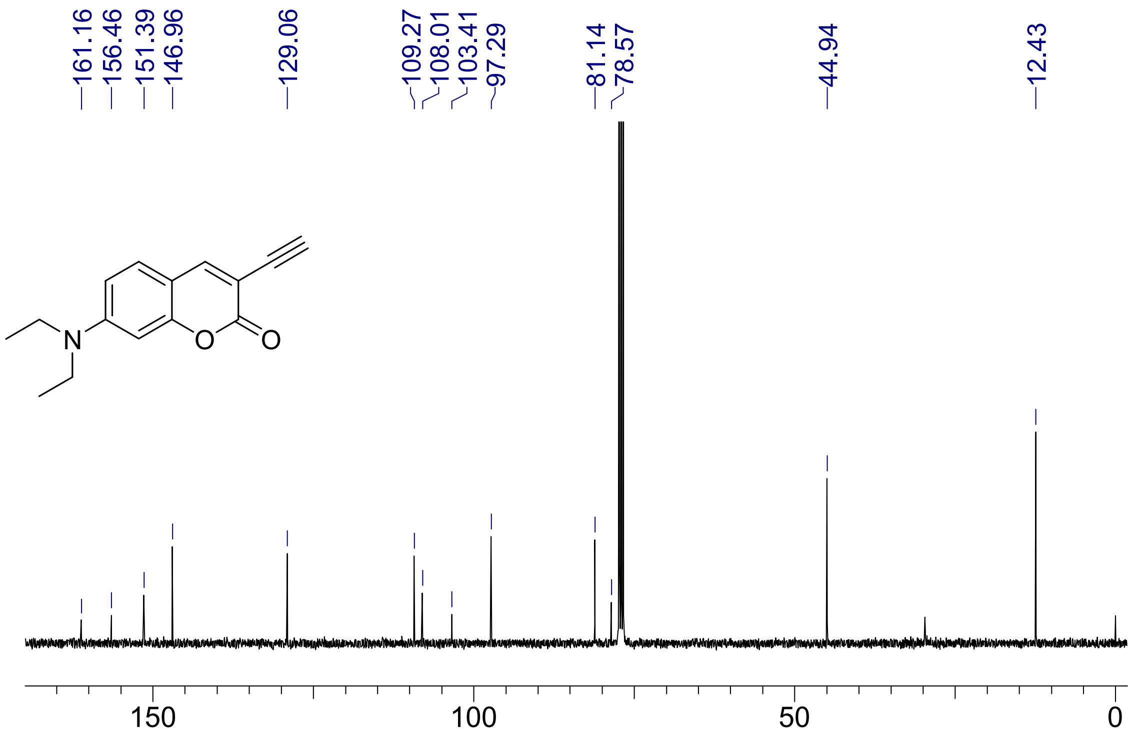



**Figure S3.** $^{13}$C NMR of **2** ($CDCl_3$, 100 MHz).

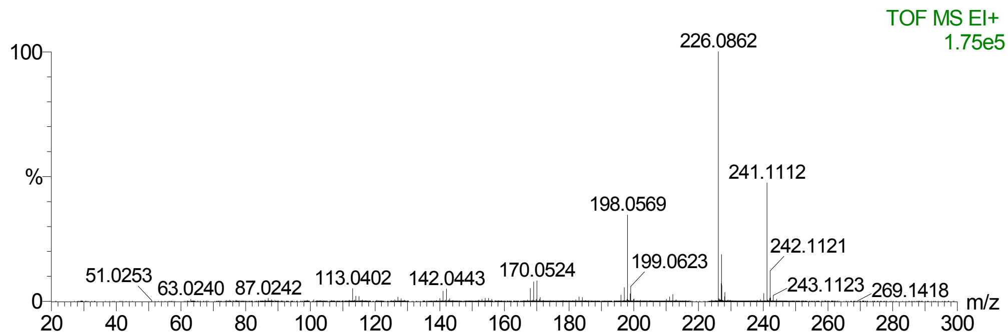



**Figure S4.** TOF MS of **2**.

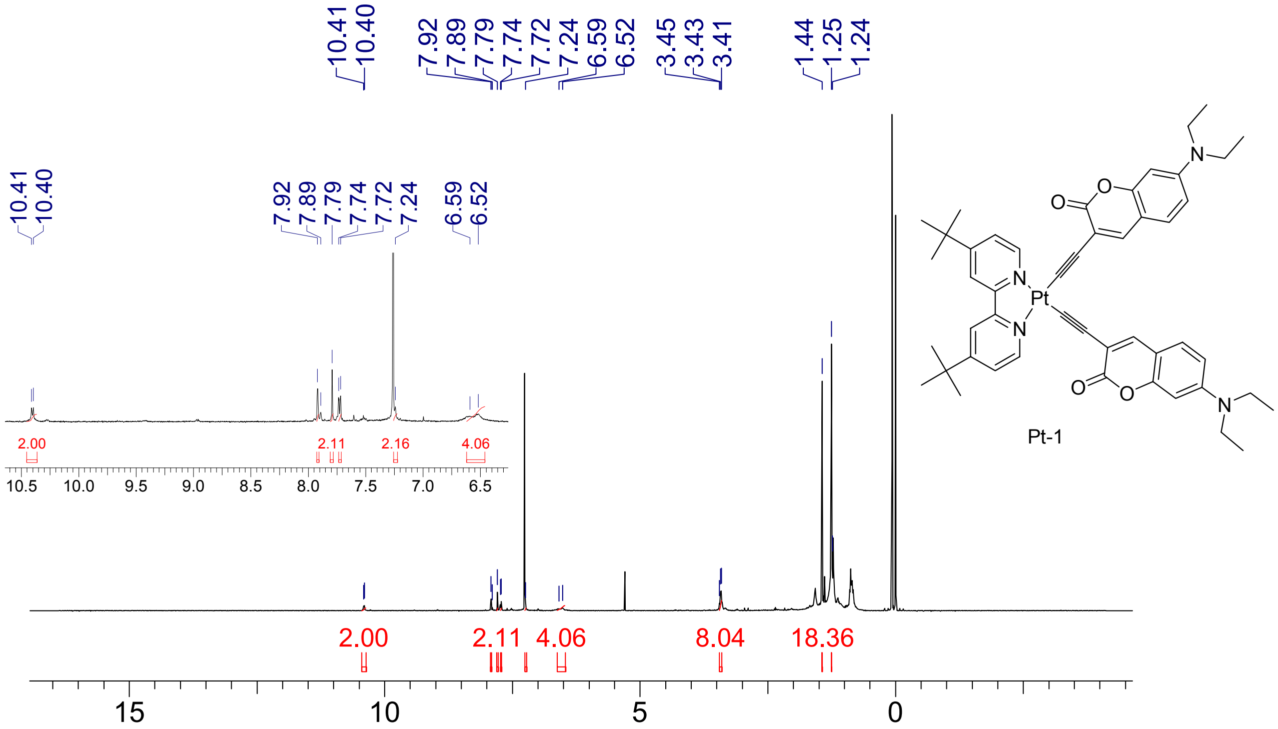


**Figure S5.** $^{1}H$ NMR of **Pt-1** ($CDCl_3$, 400 MHz).

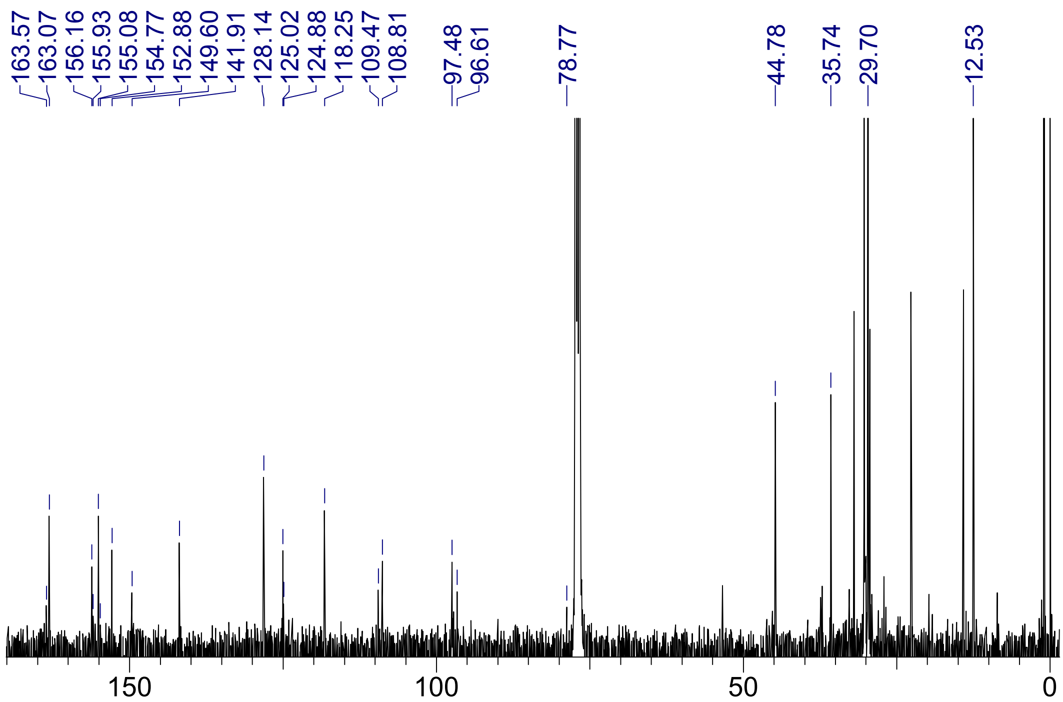


**Figure S6.** $^{13}C$ NMR of Pt-**1** ($CDCl_3$, 100 MHz).

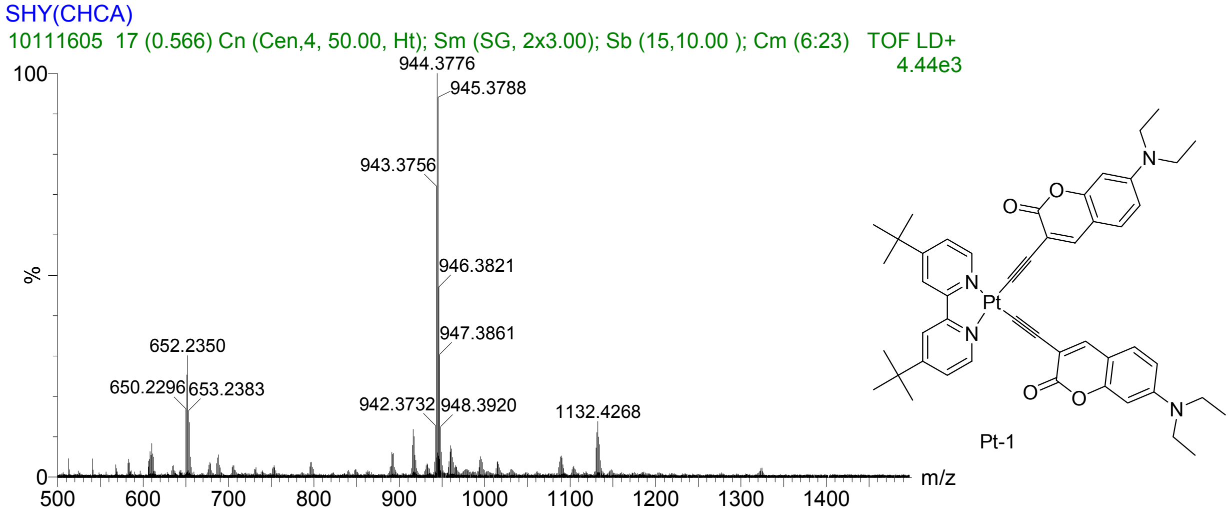



**Figure S7.** HR-MALDI-MS of Pt-**1.**

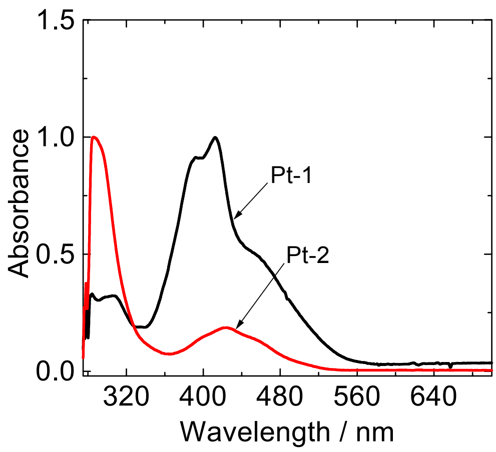



**Figure S8.** Comparison of the UV-Vis absorption spectra of **Pt-1** and **Pt-2** in toluene solution at room temperature. $c = 1.0\times10^{-5}$ mol/L. 20 °C.

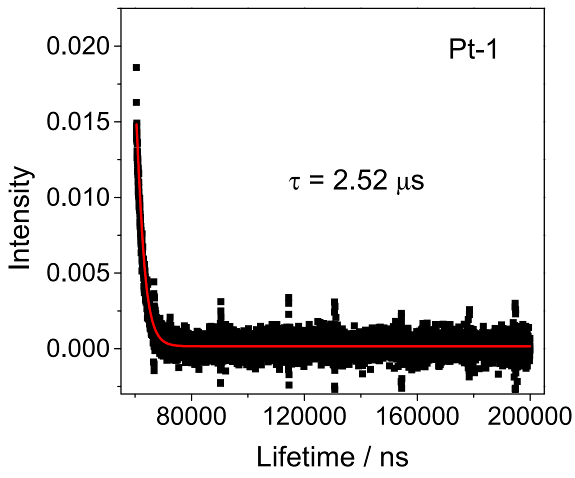



**Figure S9.** The lifetime of **Pt-1** by following decay at the bleaching wavelength. 20 °C.

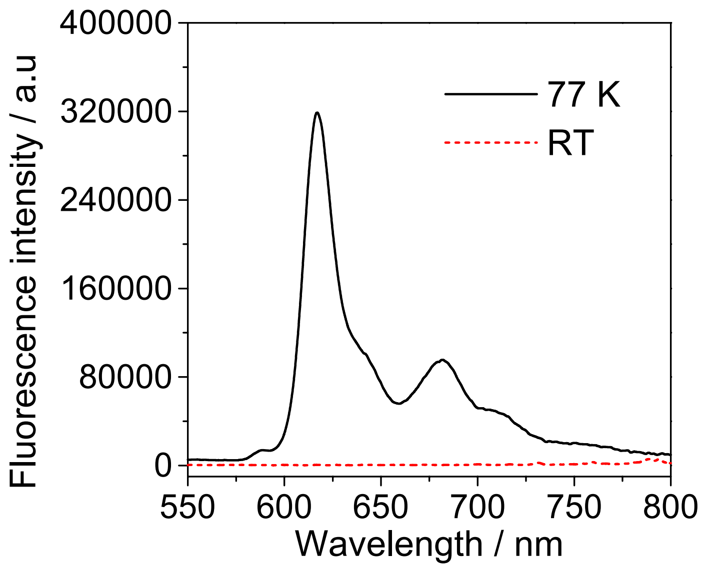



**Figure S10.** Emission spectra of **Pt-1** in the solution of EtOH:MeOH (v/v= 4:1) in 77 K and room temperature (RT) , λex = 414 nm.

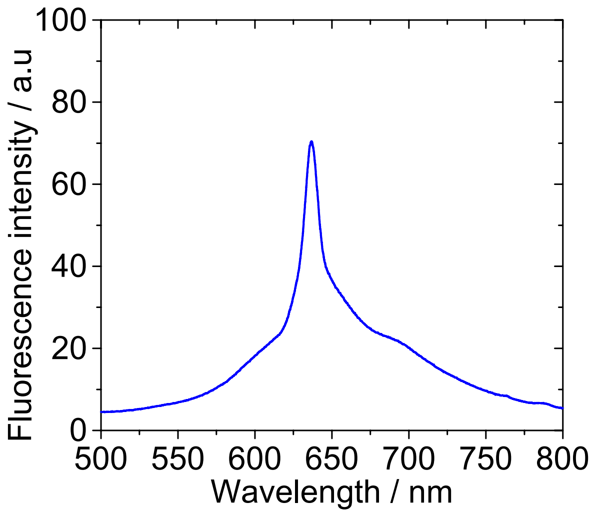



**Figure S11.** Emission spectra of **Pt-1** in solid state, λex = 420 nm, 20 °C.

We performed NBO analysis on the optimized $T_1$ state, as shown in Table S1. We found that the SOMO states of $T^1$ are contributed by C73, C83 and the localized the interaction among C71, C72, C75, C76, O77 C78, C79, C80, C81, C83 and N86. This is consistent with the contour plot of the spin density. Due to the charge transfer involved from the electronic process during the excitation-annealing circle from $S_0$ to $S_1$ and then to $T_1$, and the localization nature of the $\pi$ and $\pi^*$ states of the molecule, *dbbpy* part of the molecule also bear spin. To support this, we also performed population analysis. As the NBO doesn't provide information on spin population, we also studied the population of $T_1$ with respect to $S_0$ within Mulliken scheme. The results are shown in Table S2. It's apparent from Table S2 that the results of NBO and Mulliken analysis show the same trend. And, we show that the overall result of the excitation-annealing on the population is the formation of the localized spin state crossing *dbbpy* and the coumarin acetylide ligand. The IL character of the $T^1$ state is obvious. (In Table S2, the red highlighted items indicate a significant charge transfer).

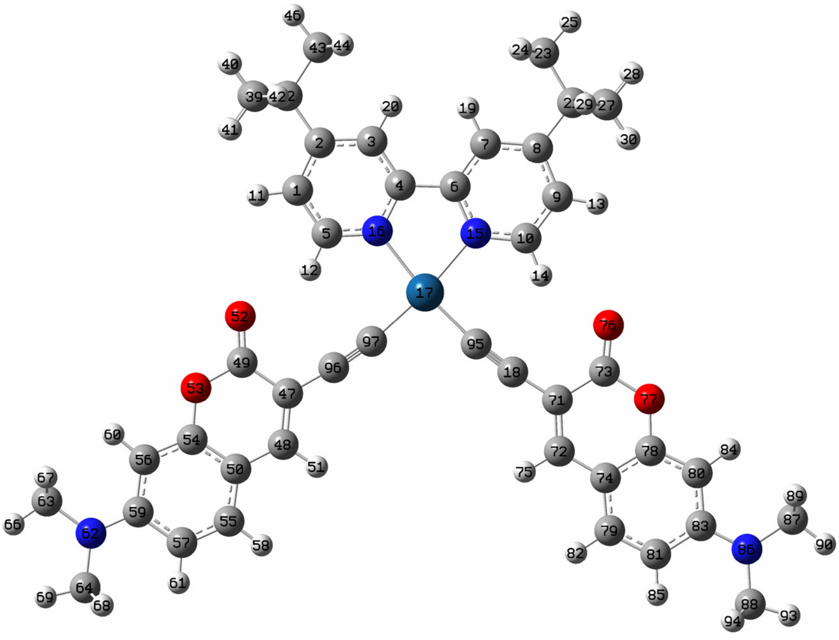


**Figure S12.** Optimzied $T_1$ state geometry of **Pt-1**.

**Table S1.** NBO analysis of SOMOs of $T_1$ state of **Pt-1**.

| NBO No. | Bond Type | Occupation (e) | Energy (a.u.) | Principal Delocalizations[a] (geminal,vicinal,remote) |
|---|---|---|---|---|
| 183 | LP*(1) C 73 | 0.412 | -0.131 | 520[0.668(p)C71-0.744(p)C72](v),<br>336[(p)O76](v),<br>329[(p)C73](g),<br>320[(p)C47] (v),<br>340[(p)O77] (r) |
| 198 | LP*(1) C 83 | 0.420 | -0.093 | 559[0.549(p)O77-0.836($sp^3$)C78](v)<br>561[0.763(p)C79-0.647(p)C81](v),<br>428[(p)C83](g),<br>422[(p)C81](v),<br>419[(p)C80](v),<br>432[(p)N86](v) |

**Table S2.** Mulliken and NBO population analysis on $T_1$ and $S_0$ of **Pt-1.**

| No. | El. | $T^1$ | | | $S^0$ | | Diff. | |
|---|---|---|---|---|---|---|---|---|
| | | Mulliken | NBO | Spin | Mulliken | NBO | Mulliken | NBO |
| 1 | C | -0.364 | -0.116 | 0.014 | -0.357 | -0.117 | -0.006 | 0.001 |
| 2 | C | 0.506 | 0.026 | 0.043 | 0.509 | 0.010 | -0.002 | 0.016 |
| 3 | C | -0.432 | -0.123 | -0.015 | -0.428 | -0.118 | -0.004 | -0.004 |
| 4 | C | 0.218 | 0.134 | 0.054 | 0.209 | 0.116 | 0.009 | 0.018 |
| 5 | C | -0.218 | 0.072 | 0.011 | -0.228 | 0.068 | 0.010 | 0.004 |
| 6 | C | 0.211 | 0.123 | 0.024 | 0.209 | 0.116 | 0.002 | 0.007 |
| 7 | C | -0.432 | -0.114 | 0.008 | -0.428 | -0.118 | -0.004 | 0.005 |
| 8 | C | 0.508 | 0.014 | 0.012 | 0.509 | 0.010 | -0.001 | 0.004 |
| 9 | C | -0.362 | -0.106 | 0.038 | -0.357 | -0.117 | -0.005 | 0.010 |
| 10 | C | -0.230 | 0.061 | -0.012 | -0.228 | 0.068 | -0.003 | -0.007 |
| 11 | H | 0.254 | 0.119 | -0.001 | 0.257 | 0.121 | -0.003 | -0.001 |
| 12 | H | 0.321 | 0.131 | -0.001 | 0.327 | 0.133 | -0.006 | -0.002 |
| 13 | H | 0.253 | 0.119 | -0.003 | 0.257 | 0.121 | -0.004 | -0.002 |
| 14 | H | 0.316 | 0.129 | -0.001 | 0.327 | 0.133 | -0.011 | -0.004 |
| 15 | N | -0.369 | -0.242 | 0.027 | -0.357 | -0.250 | -0.013 | 0.007 |
| 16 | N | -0.391 | -0.251 | 0.013 | -0.357 | -0.250 | -0.035 | -0.001 |
| 17 | Pt | 0.850 | 0.245 | 0.093 | 0.784 | 0.188 | 0.066 | 0.057 |
| 18 | C | -0.196 | -0.022 | 0.017 | -0.227 | -0.081 | 0.032 | 0.059 |
| 19 | H | 0.237 | 0.110 | -0.001 | 0.238 | 0.110 | -0.001 | -0.001 |
| 20 | H | 0.237 | 0.110 | 0.000 | 0.238 | 0.110 | -0.001 | -0.001 |
| 21 | C | 0.160 | 0.004 | 0.000 | 0.158 | 0.004 | 0.001 | 0.000 |
| 22 | C | 0.160 | 0.003 | -0.003 | 0.158 | 0.004 | 0.002 | -0.001 |
| 23 | C | -0.713 | -0.328 | 0.000 | -0.713 | -0.328 | 0.000 | 0.000 |
| 24 | H | 0.200 | 0.109 | 0.000 | 0.200 | 0.109 | 0.000 | 0.000 |
| 25 | H | 0.210 | 0.114 | 0.000 | 0.211 | 0.114 | -0.001 | 0.000 |
| 26 | H | 0.200 | 0.109 | 0.000 | 0.200 | 0.109 | 0.000 | 0.000 |
| 27 | C | -0.667 | -0.319 | 0.000 | -0.666 | -0.319 | -0.001 | 0.000 |
| 28 | H | 0.198 | 0.110 | 0.000 | 0.199 | 0.110 | -0.001 | 0.000 |
| 29 | H | 0.207 | 0.111 | 0.000 | 0.207 | 0.111 | 0.000 | 0.000 |
| 30 | H | 0.212 | 0.110 | 0.000 | 0.213 | 0.110 | -0.001 | 0.000 |
| 31 | C | -0.667 | -0.319 | 0.000 | -0.666 | -0.319 | -0.001 | 0.000 |
| 32 | H | 0.212 | 0.110 | 0.000 | 0.213 | 0.110 | -0.001 | 0.000 |
| 33 | H | 0.207 | 0.111 | 0.000 | 0.207 | 0.111 | 0.000 | 0.000 |
| 34 | H | 0.198 | 0.110 | 0.000 | 0.199 | 0.110 | -0.001 | 0.000 |
| 35 | C | -0.667 | -0.318 | 0.001 | -0.666 | -0.319 | -0.001 | 0.001 |
| 36 | H | 0.213 | 0.110 | 0.000 | 0.213 | 0.110 | 0.000 | 0.000 |
| 37 | H | 0.198 | 0.109 | 0.000 | 0.199 | 0.110 | -0.001 | 0.000 |
| 38 | H | 0.207 | 0.111 | 0.000 | 0.207 | 0.111 | 0.000 | 0.000 |
| 39 | C | -0.667 | -0.318 | 0.001 | -0.666 | -0.319 | -0.001 | 0.001 |
| 40 | H | 0.198 | 0.109 | 0.000 | 0.199 | 0.110 | -0.001 | 0.000 |
| 41 | H | 0.213 | 0.110 | 0.000 | 0.213 | 0.110 | 0.000 | 0.000 |
| 42 | H | 0.207 | 0.111 | 0.000 | 0.207 | 0.111 | 0.000 | 0.000 |
| 43 | C | -0.713 | -0.328 | 0.000 | -0.713 | -0.328 | -0.001 | 0.000 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 44 | H | 0.199 | 0.109 | 0.000 | 0.200 | 0.109 | 0.000 | 0.000 |
| 45 | H | 0.199 | 0.109 | 0.000 | 0.200 | 0.109 | 0.000 | 0.000 |
| 46 | H | 0.210 | 0.114 | 0.000 | 0.211 | 0.114 | -0.002 | -0.001 |
| 47 | C | 0.195 | -0.099 | -0.009 | 0.195 | -0.095 | 0.000 | -0.004 |
| 48 | C | -0.420 | -0.056 | 0.017 | -0.421 | -0.064 | 0.001 | 0.009 |
| 49 | C | 0.071 | 0.407 | 0.001 | 0.071 | 0.407 | 0.000 | 0.000 |
| 50 | C | 0.443 | -0.078 | -0.004 | 0.443 | -0.076 | 0.000 | -0.002 |
| 51 | H | 0.263 | 0.116 | -0.001 | 0.263 | 0.116 | -0.001 | 0.000 |
| 52 | O | -0.262 | -0.309 | -0.001 | -0.267 | -0.311 | 0.005 | 0.002 |
| 53 | O | -0.294 | -0.278 | 0.000 | -0.295 | -0.278 | 0.000 | 0.000 |
| 54 | C | 0.152 | 0.189 | 0.005 | 0.153 | 0.186 | 0.000 | 0.002 |
| 55 | C | -0.430 | -0.078 | 0.005 | -0.431 | -0.081 | 0.001 | 0.002 |
| 56 | C | -0.486 | -0.158 | -0.003 | -0.487 | -0.157 | 0.001 | -0.001 |
| 57 | C | -0.362 | -0.141 | -0.002 | -0.363 | -0.140 | 0.000 | -0.001 |
| 58 | H | 0.231 | 0.111 | 0.000 | 0.231 | 0.111 | 0.000 | 0.000 |
| 59 | C | 0.407 | 0.112 | 0.005 | 0.407 | 0.110 | 0.000 | 0.003 |
| 60 | H | 0.265 | 0.118 | 0.000 | 0.264 | 0.118 | 0.001 | 0.000 |
| 61 | H | 0.231 | 0.110 | 0.000 | 0.230 | 0.109 | 0.001 | 0.000 |
| 62 | N | -0.163 | -0.230 | 0.003 | -0.164 | -0.232 | 0.000 | 0.002 |
| 63 | C | -0.597 | -0.206 | 0.000 | -0.597 | -0.206 | 0.000 | 0.000 |
| 64 | C | -0.595 | -0.206 | 0.000 | -0.595 | -0.206 | 0.000 | 0.000 |
| 65 | H | 0.224 | 0.106 | 0.000 | 0.224 | 0.106 | 0.001 | 0.000 |
| 66 | H | 0.206 | 0.109 | 0.000 | 0.205 | 0.109 | 0.000 | 0.000 |
| 67 | H | 0.224 | 0.106 | 0.000 | 0.224 | 0.106 | 0.001 | 0.000 |
| 68 | H | 0.220 | 0.105 | 0.000 | 0.220 | 0.105 | 0.000 | 0.000 |
| 69 | H | 0.207 | 0.109 | 0.000 | 0.206 | 0.109 | 0.001 | 0.000 |
| 70 | H | 0.220 | 0.105 | 0.000 | 0.220 | 0.105 | 0.000 | 0.000 |
| 71 | C | 0.183 | 0.024 | 0.262 | 0.195 | -0.095 | -0.012 | 0.119 |
| 72 | C | -0.478 | 0.121 | 0.475 | -0.421 | -0.064 | -0.057 | 0.185 |
| 73 | C | 0.072 | 0.405 | -0.001 | 0.071 | 0.407 | 0.001 | -0.003 |
| 74 | C | 0.500 | -0.084 | -0.079 | 0.443 | -0.076 | 0.057 | -0.008 |
| 75 | H | 0.263 | 0.105 | -0.033 | 0.263 | 0.116 | 0.000 | -0.011 |
| 76 | O | -0.267 | -0.243 | 0.128 | -0.267 | -0.311 | 0.001 | 0.068 |
| 77 | O | -0.308 | -0.274 | 0.021 | -0.295 | -0.278 | -0.014 | 0.004 |
| 78 | C | 0.133 | 0.243 | 0.148 | 0.153 | 0.186 | -0.019 | 0.057 |
| 79 | C | -0.440 | -0.001 | 0.202 | -0.431 | -0.081 | -0.009 | 0.080 |
| 80 | C | -0.476 | -0.177 | -0.073 | -0.487 | -0.157 | 0.011 | -0.020 |
| 81 | C | -0.348 | -0.158 | -0.068 | -0.363 | -0.140 | 0.014 | -0.018 |
| 82 | H | 0.230 | 0.107 | -0.013 | 0.231 | 0.111 | -0.001 | -0.004 |
| 83 | C | 0.387 | 0.186 | 0.195 | 0.407 | 0.110 | -0.020 | 0.076 |
| 84 | H | 0.263 | 0.119 | 0.003 | 0.264 | 0.118 | -0.001 | 0.001 |
| 85 | H | 0.228 | 0.110 | 0.002 | 0.230 | 0.109 | -0.002 | 0.000 |
| 86 | N | -0.154 | -0.162 | 0.113 | -0.164 | -0.232 | 0.009 | 0.070 |
| 87 | C | -0.597 | -0.210 | -0.013 | -0.597 | -0.206 | 0.000 | -0.004 |
| 88 | C | -0.595 | -0.210 | -0.013 | -0.595 | -0.206 | 0.000 | -0.004 |
| 89 | H | 0.228 | 0.111 | 0.009 | 0.224 | 0.106 | 0.004 | 0.005 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 90 | H | 0.207 | 0.109 | 0.000 | 0.205 | 0.109 | 0.001 | 0.000 |
| 91 | H | 0.228 | 0.111 | 0.009 | 0.224 | 0.106 | 0.004 | 0.005 |
| 92 | H | 0.223 | 0.110 | 0.009 | 0.220 | 0.105 | 0.004 | 0.005 |
| 93 | H | 0.208 | 0.110 | 0.000 | 0.206 | 0.109 | 0.001 | 0.000 |
| 94 | H | 0.223 | 0.110 | 0.009 | 0.220 | 0.105 | 0.004 | 0.005 |
| 95 | C | -0.229 | 0.138 | 0.363 | -0.233 | -0.070 | 0.004 | 0.208 |
| 96 | C | -0.217 | -0.065 | 0.023 | -0.227 | -0.081 | 0.010 | 0.016 |
| 97 | C | -0.241 | -0.080 | -0.015 | -0.233 | -0.070 | -0.008 | -0.010 |