

Electronic Supplementary Information for:

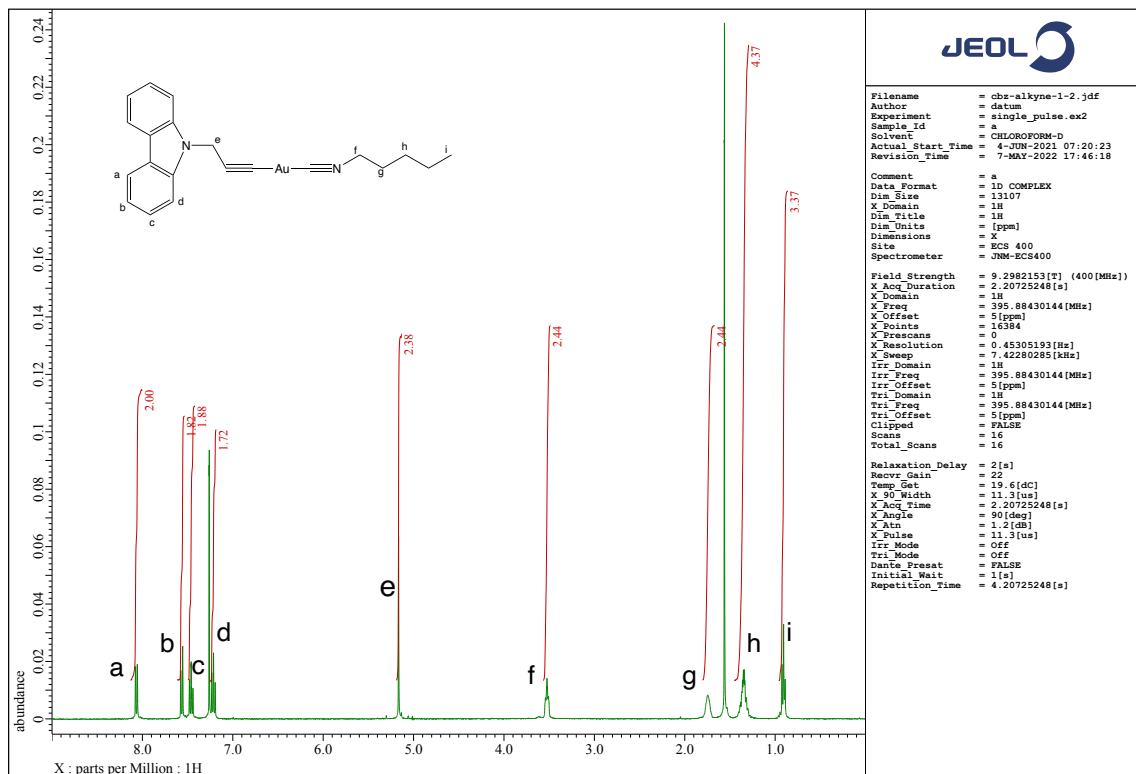
# **Luminescent Behavior of Liquid-Crystalline Gold(I) Complexes Bearing a Carbazole Moiety: Effects of Substituent Bulkiness**

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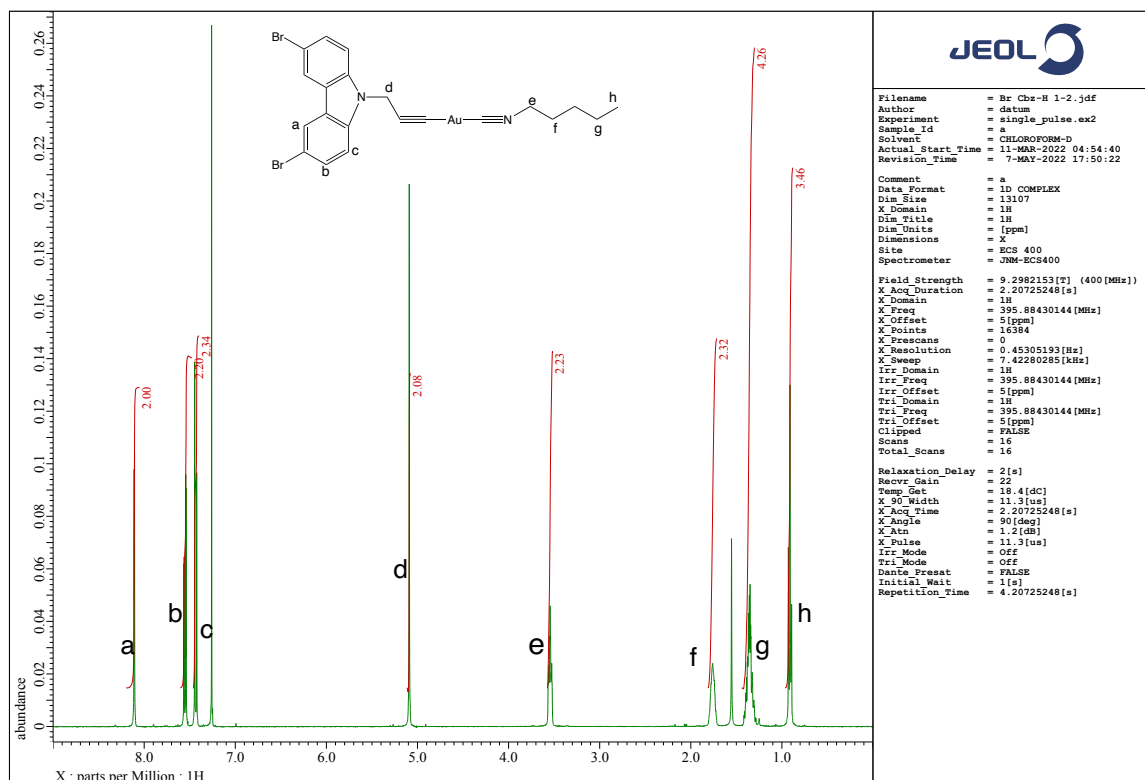
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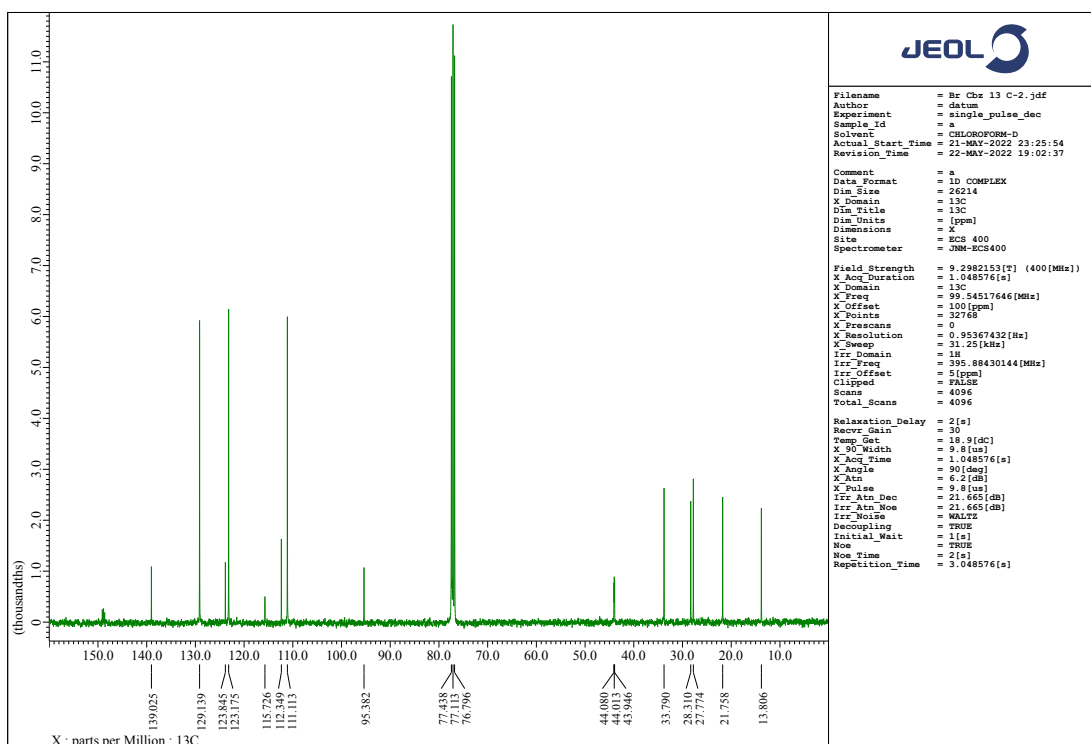


**Figure S1.**  $^1\text{H}$  NMR spectrum of complex **Cbz-H** in  $\text{CDCl}_3$ .

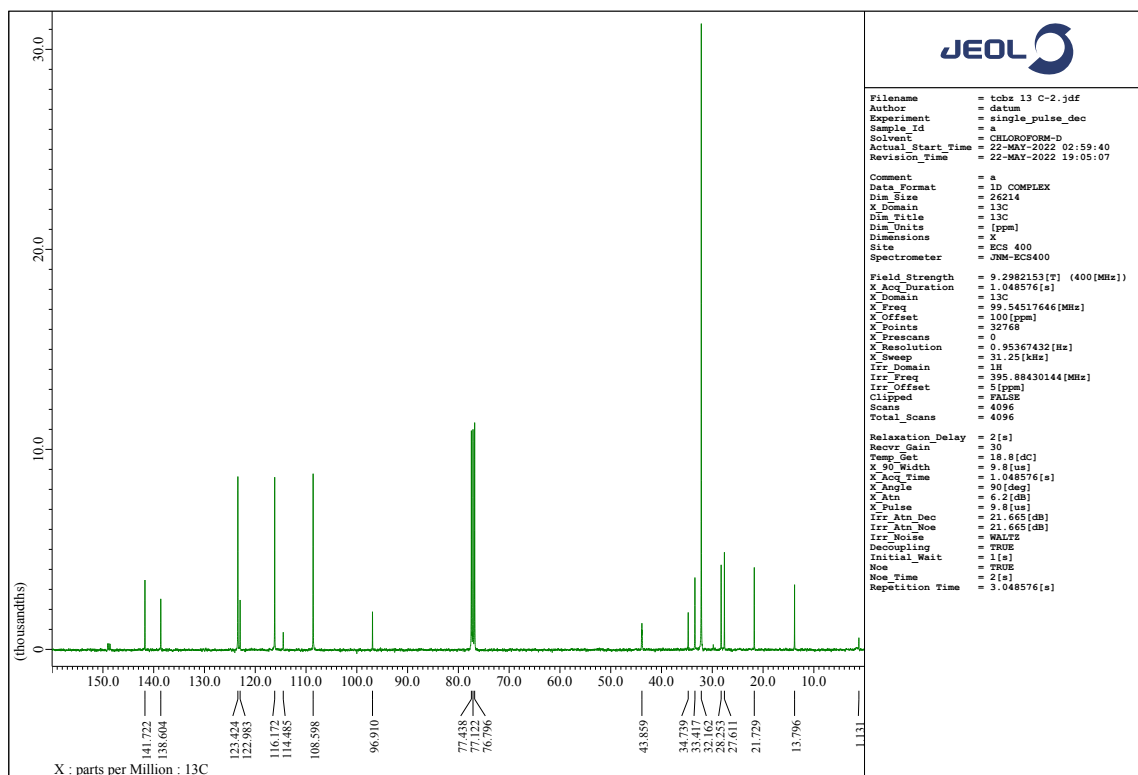


**Figure S2.**  $^1\text{H}$  NMR spectrum of complex **Cbz-Br** in  $\text{CDCl}_3$ .





**Figure S5.**  $^{13}\text{C}$  NMR spectrum of complex **Cbz-Br** in  $\text{CDCl}_3$ .



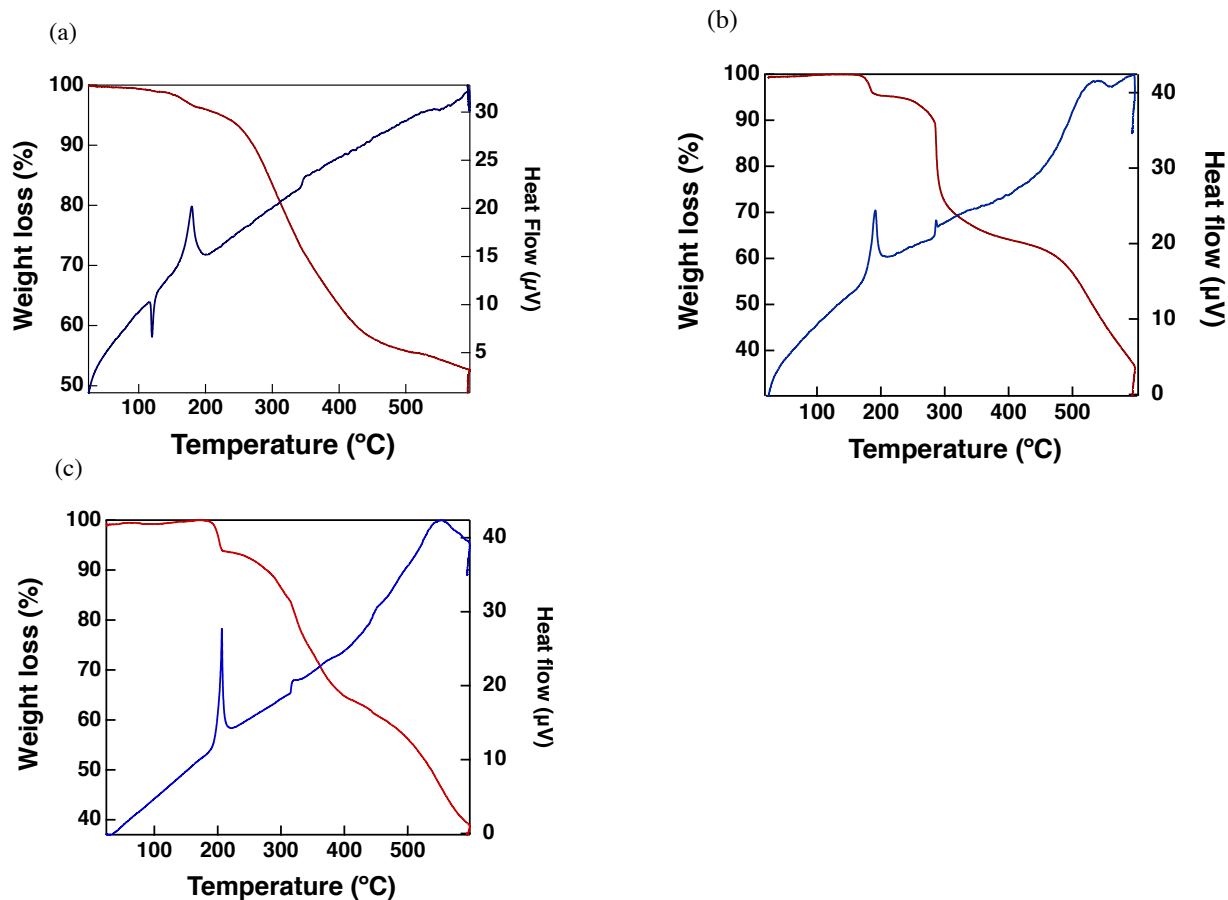
**Figure S6.**  $^{13}\text{C}$  NMR spectrum of complex **Cbz-*t*-Bu** in  $\text{CDCl}_3$ .

**Table S1:** Crystallographic data of **Cbz-H** obtained at room temperature

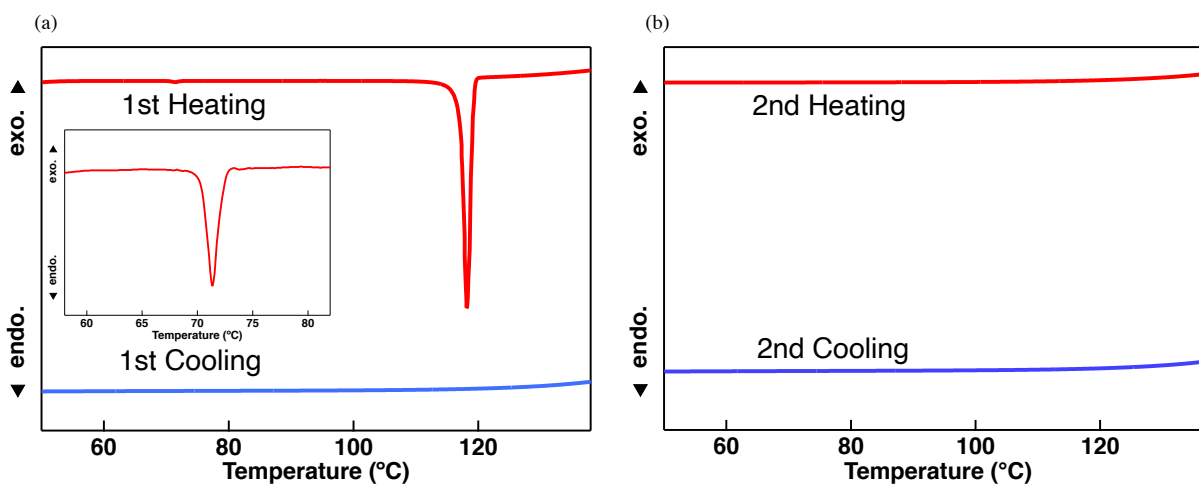
| Identification code         | Cbz-H   |
|-----------------------------|---|
| Empirical formula           | C <sub>21</sub> H <sub>21</sub> AuN <sub>2</sub>  |
| Formula weight              | 498.36  |
| Temperature/K               | 566   |
| Color, Habit                | Colorless, needle                                 |
| Crystal system              | Triclinic   |
| Final R indexes [I > 2σ(I)] | R <sub>1</sub> = 0.0424, wR <sub>2</sub> = 0.1398 |
| Space group                 | P $\bar{1}$                                       |
| Z                           | 2   |
| a (Å)                       | 5.1775(2)   |
| b (Å)                       | 10.8664(5)  |
| c (Å)                       | 16.9535(7)  |
| α (°)                       | 73.258  |
| β (°)                       | 84.479  |
| γ (°)                       | 84.820  |
| d (g cm <sup>-3</sup> )     | 1.821   |
| Volume (Å <sup>3</sup> )    | 908.86  |
| Radiation                   | Mo Kα (λ = 0.71)                                  |
| CCDC NO.                    | 2160379   |

**Table S2:** Key structural parameters of **Cbz-H** determined by the single-crystal X-ray structural analysis.

|          | Bond angles (°) | Bond Distances (Å) |
|----------|-----------------|--------------------|
| N1–C4–C5 | 112.2           |                    |
| C9–Au–C8 | 179.1           |                    |
| Au–Au    |                 | 6.4                |
| N1–C4    |                 | 1.448              |
| C1–Au    |                 | 1.956              |
| C2–Au    |                 | 1.953              |
| N2–C6    |                 | 1.454              |
| C5–C1    |                 | 1.227              |
| C4–C5    |                 | 1.465              |
| N2–C2    |                 | 1.148              |



**Figure S7.** TG/DTA analysis of complexes in air (heating rate =  $5.0^{\circ}\text{C min}^{-1}$ ).  
a) Cbz-H, b) Cbz-Br, c) Cbz-*t*-Bu

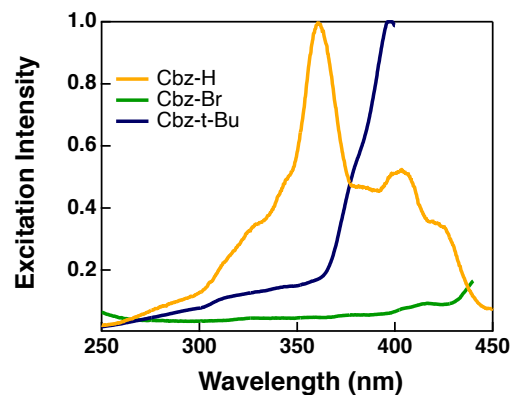


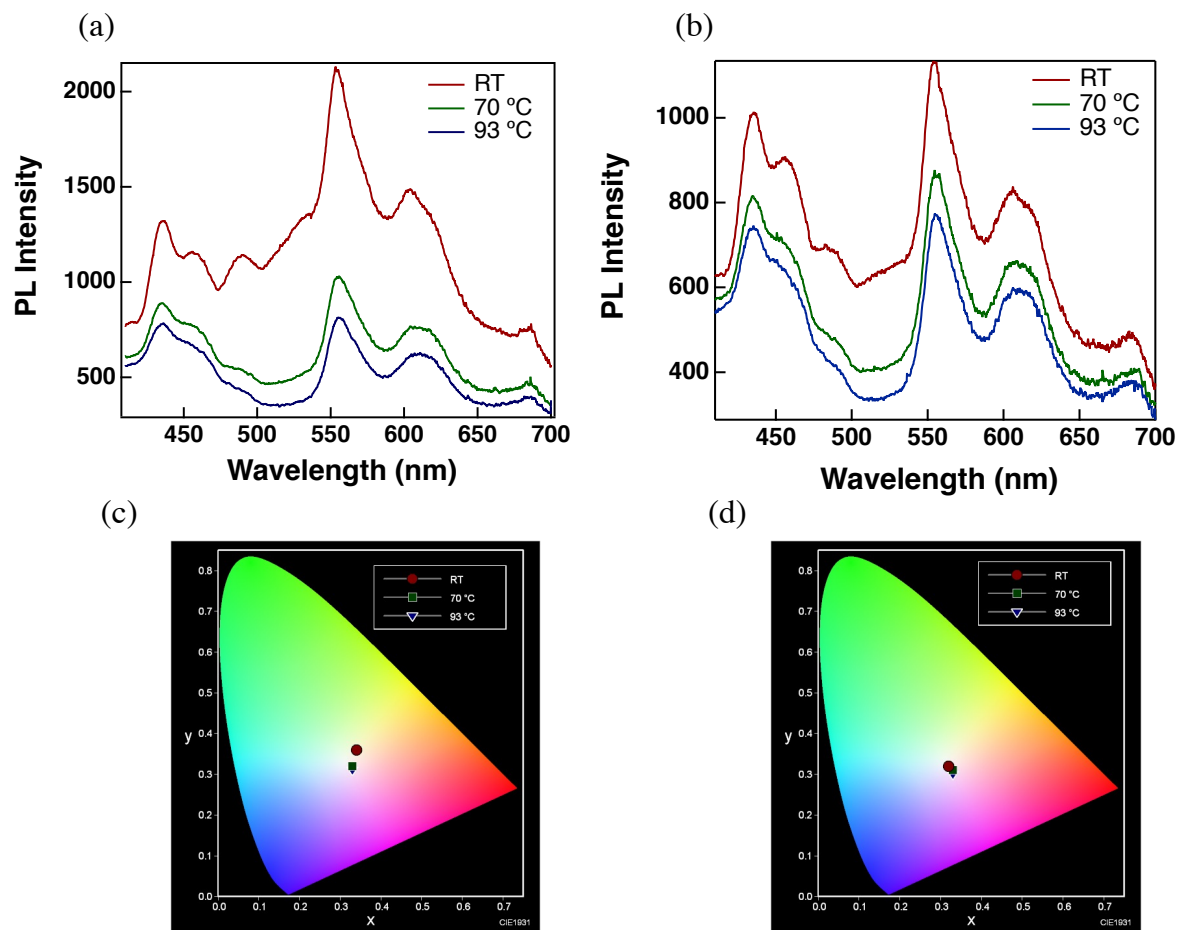
**Figure S8.** DSC thermogram of complex **Cbz-H** (a) 1<sup>st</sup> heating and cooling process; inset: heating process at 73  $^{\circ}\text{C}$ ; (b) 2<sup>nd</sup> heating and cooling process (Scan rate,  $3.0^{\circ}\text{C min}^{-1}$ ).

**Table S3:** Photophysical parameters for complex **Cbz-R** at room temperature.<sup>1</sup>

|                        | $\tau$ at 450 nm ( $\mu$ s)                           | $\tau$ at longer wavelength ( $\mu$ s)               | $\Phi$ (%) |
|------------------------|---|--|------------|
| <b>Cbz-H</b>           | $1.5 \times 10^{-3}$ (94%), $5.1 \times 10^{-3}$ (6%) | $3.6 \times 10^{-3}$ (98%), $3.15$ (2%) <sup>2</sup> | 0.34       |
| <b>Cbz-Br</b>          | 1.93 (43%), 7.1 (57%)                                 | 1.5 (77%), 7.7 (23%) <sup>3</sup>                    | 0.45       |
| <b>Cbz-<i>t</i>-Bu</b> | 6.8 (57%), 25 (43%)                                   | $2.2 \times 10^{-2}$ (96%), 13.13 (4%) <sup>2</sup>  | 2.31       |

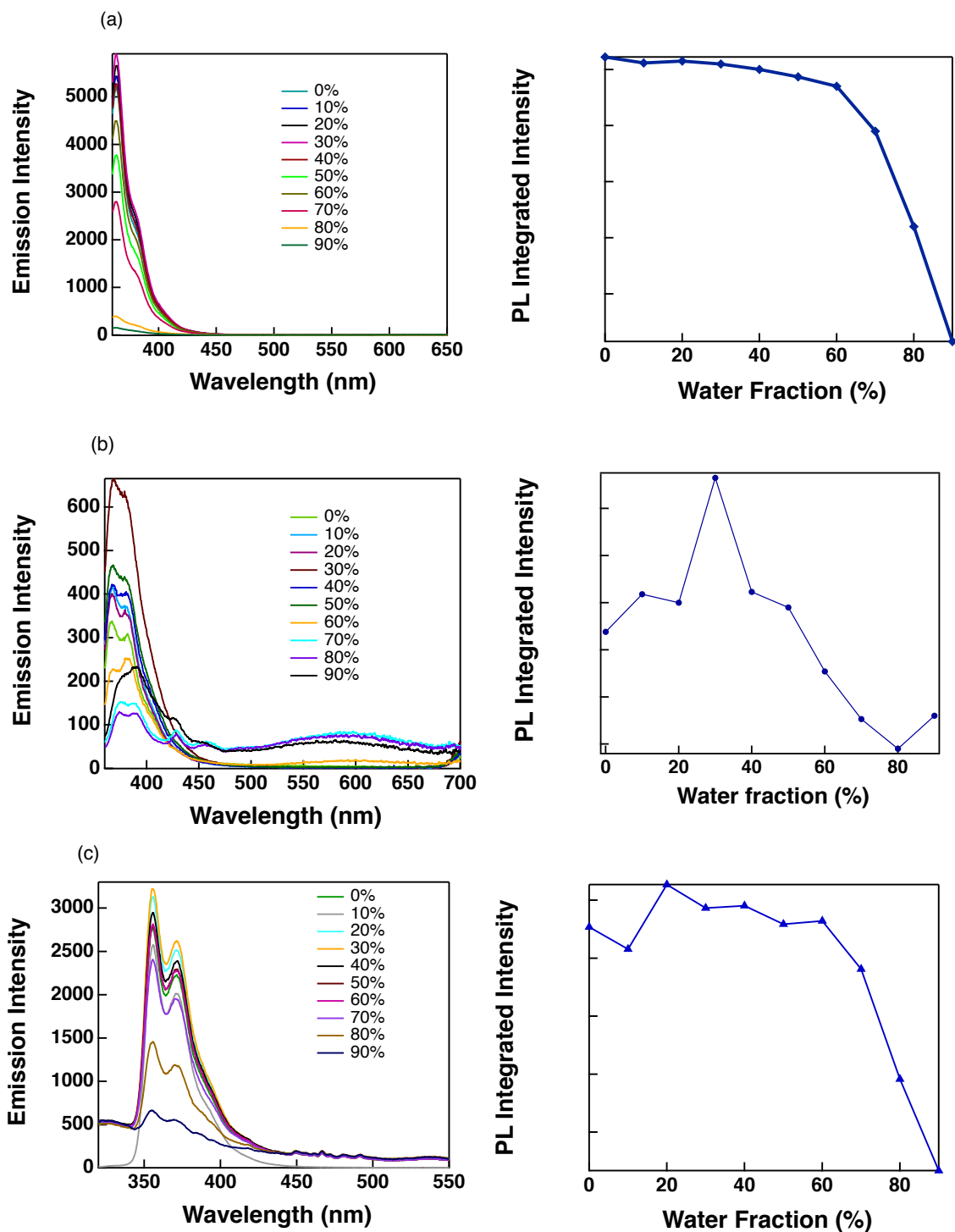
- 1)  $\lambda_{\text{ex}} = 280$  nm for all measurement.
- 2) The lifetimes were monitored at 550 nm.
- 3) The lifetimes were monitored at 565 nm.

**Figure S9.** Solid state excitation spectra of complexes: orange, **Cbz-H**,  $\lambda_{\text{em}} = 554$  nm; green, **Cbz-Br**,  $\lambda_{\text{em}} = 467$  nm; blue, **Cbz-*t*-Bu**,  $\lambda_{\text{em}} = 451$  nm.

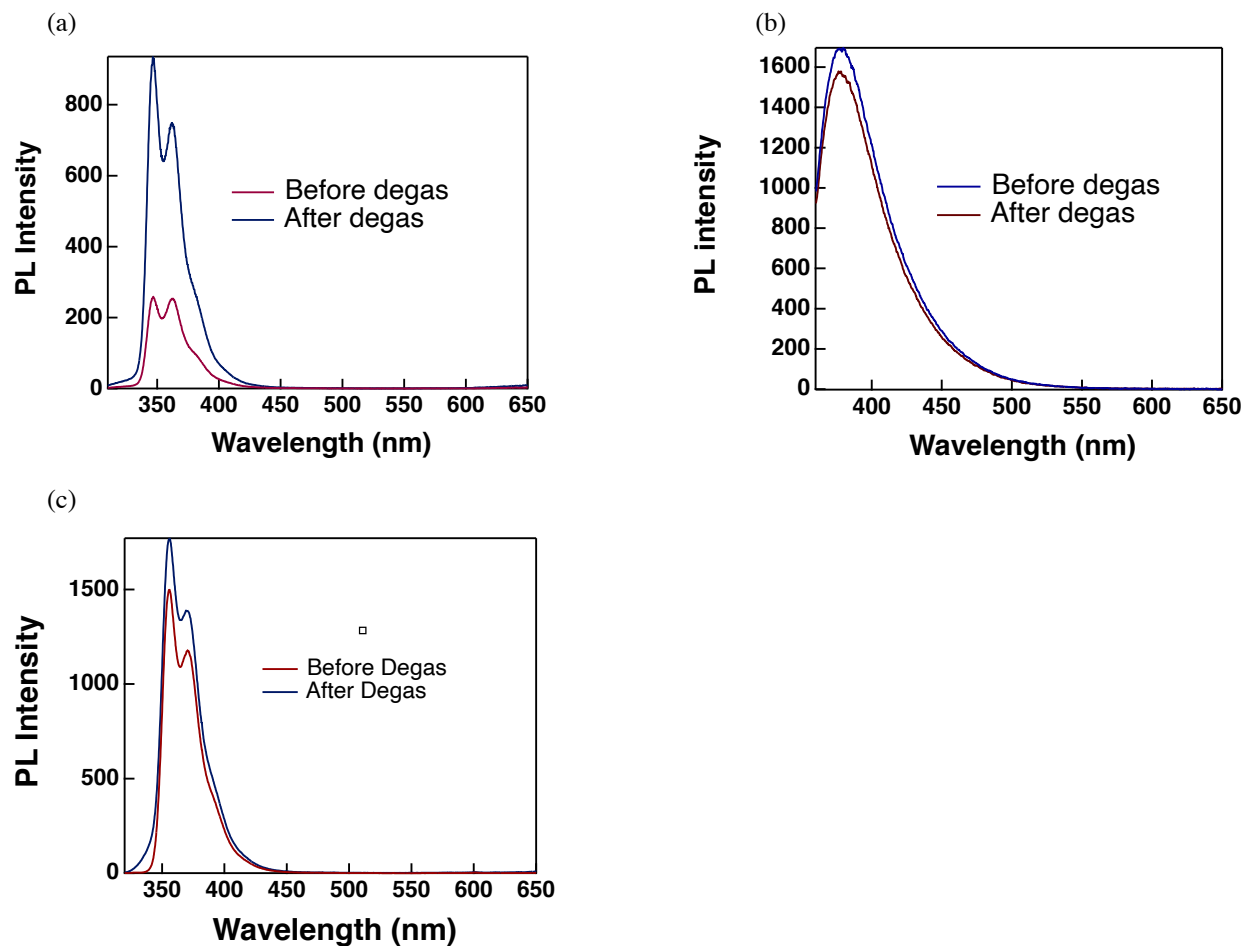


**Figure S10.** Solid state emission spectra of complex **Cbz-H** at excitation wavelength of 293 nm using filter L–39 after (a) 1<sup>st</sup> heating; (b) 1<sup>st</sup> cooling; CIE plot of complex **Cbz-H** at excitation wavelength of 293 nm at different temperatures (c) 1<sup>st</sup> heating; (d) 1<sup>st</sup> cooling; red, RT; green, 70 °C; blue, 93 °C.

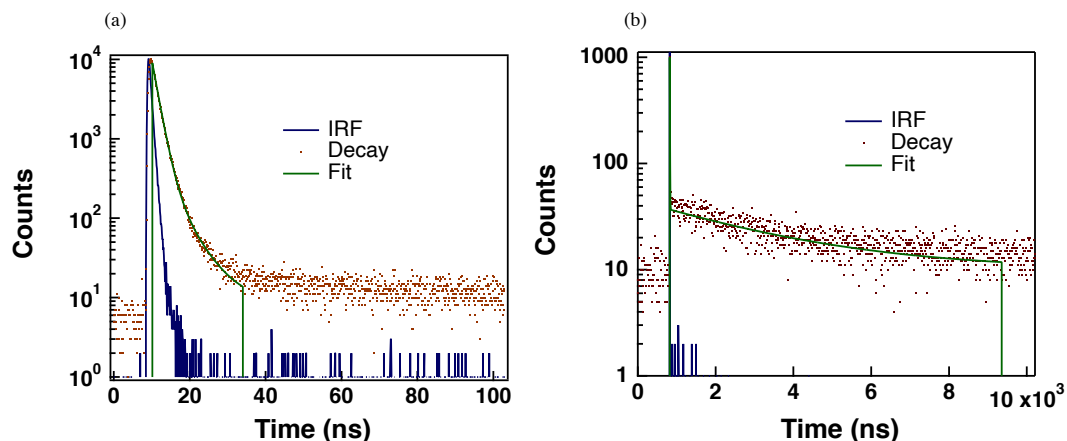




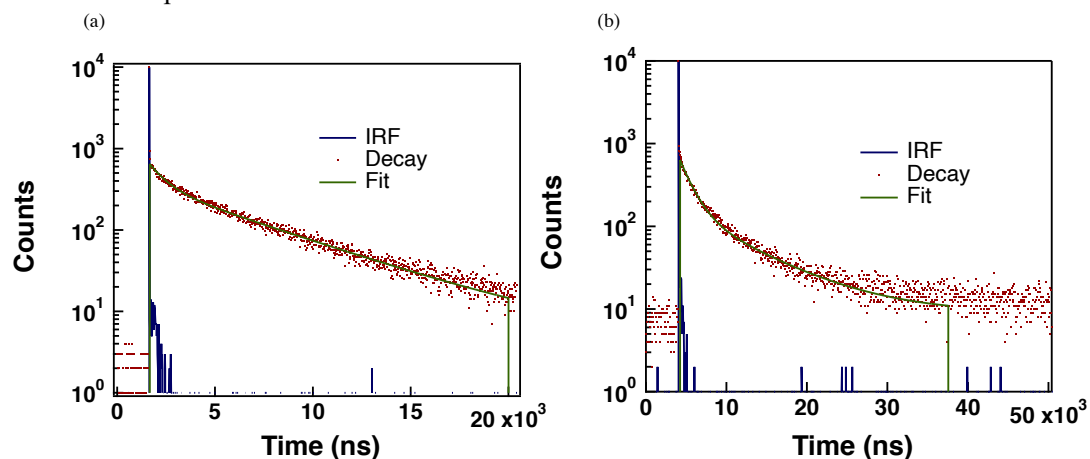
**Figure S11.** Emission spectra of complexes in THF/ H<sub>2</sub>O fraction and plot of PL Integrated Intensity vs water fraction (%) (a) **Cbz-H**,  $\lambda_{ex} = 293$  nm; (b) **Cbz-Br**,  $\lambda_{ex} = 310$  nm; (c) **Cbz-*t*-Bu**,  $\lambda_{ex} = 297$  nm.



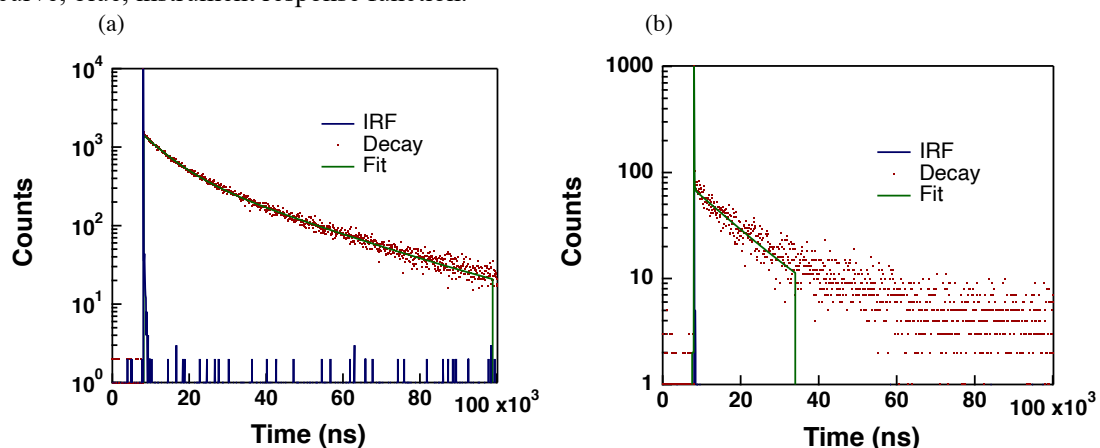
**Figure S12.** Solution state emission spectra of complexes in  $\text{CH}_2\text{Cl}_2$  solution (a) **Cbz-H**; (b) **Cbz-Br**; (c) **Cbz-*t*-Bu**; (before and after degassing (red, before degassing; blue, after degassing)); (**Cbz-H**,  $2.1 \times 10^{-5} \text{ mol L}^{-1}$ ,  $\lambda_{\text{ex}} = 293 \text{ nm}$ , UV-35 filter; **Cbz-Br**,  $4.3 \times 10^{-5} \text{ mol L}^{-1}$ ,  $\lambda_{\text{ex}} = 310 \text{ nm}$ , UV-35 filter; **Cbz-*t*-Bu**,  $3.3 \times 10^{-5} \text{ mol L}^{-1}$ ,  $\lambda_{\text{ex}} = 297 \text{ nm}$ , L-39 filter).



**Figure S13.** Decay profile for room temperature phosphorescence of complex **Cbz-H** in the solid state monitored at emission wavelength (a) 450 nm (b) 565 nm; red, observed luminescence decay; green, fitting curve; blue, instrument response function.



**Figure S14.** Decay profile for room temperature phosphorescence of complex **Cbz-Br** in the solid state monitored at emission wavelength (a) 450 nm (b) 565 nm; red, observed luminescence decay; green, fitting curve; blue, instrument response function.



**Figure S15.** Decay profile for room temperature phosphorescence of complex **Cbz-*t*-Bu** in the solid state monitored at emission wavelength (a) 450 nm (b) 550 nm; red, observed luminescence decay; green, fitting curve; blue, instrument response function.