

# Supplemental file of

## Excited-state dynamics of room-temperature phosphorescent organic materials based on monobenzil and bisbenzil frameworks

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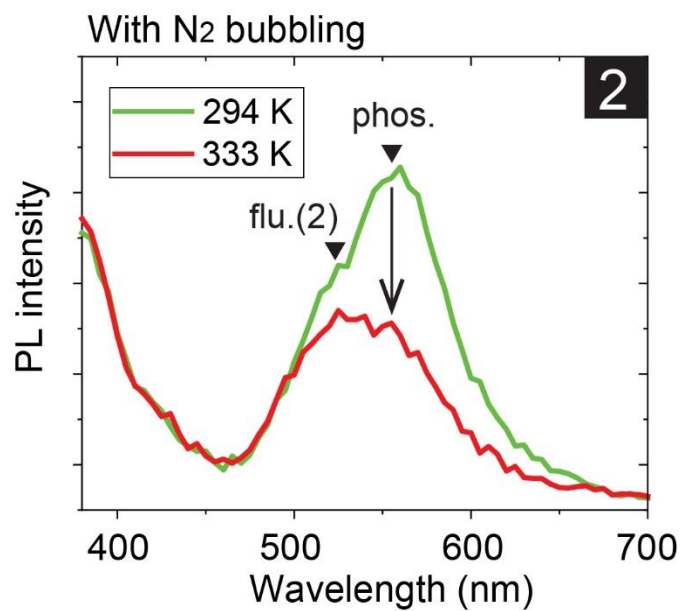
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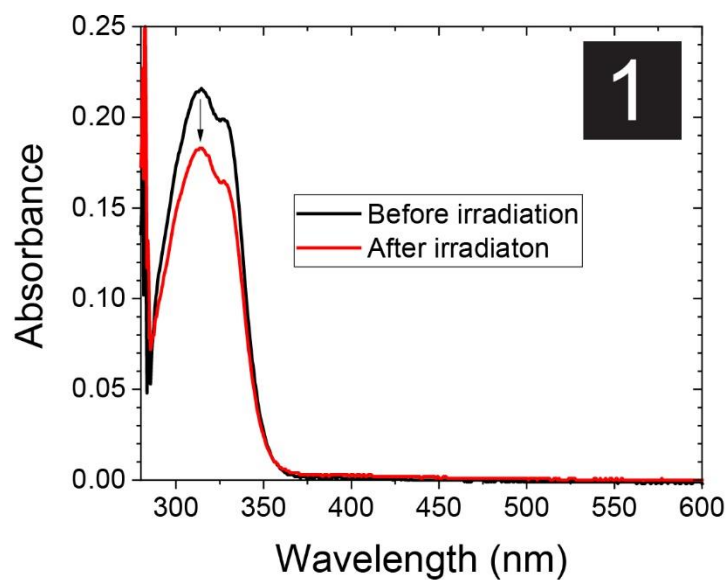
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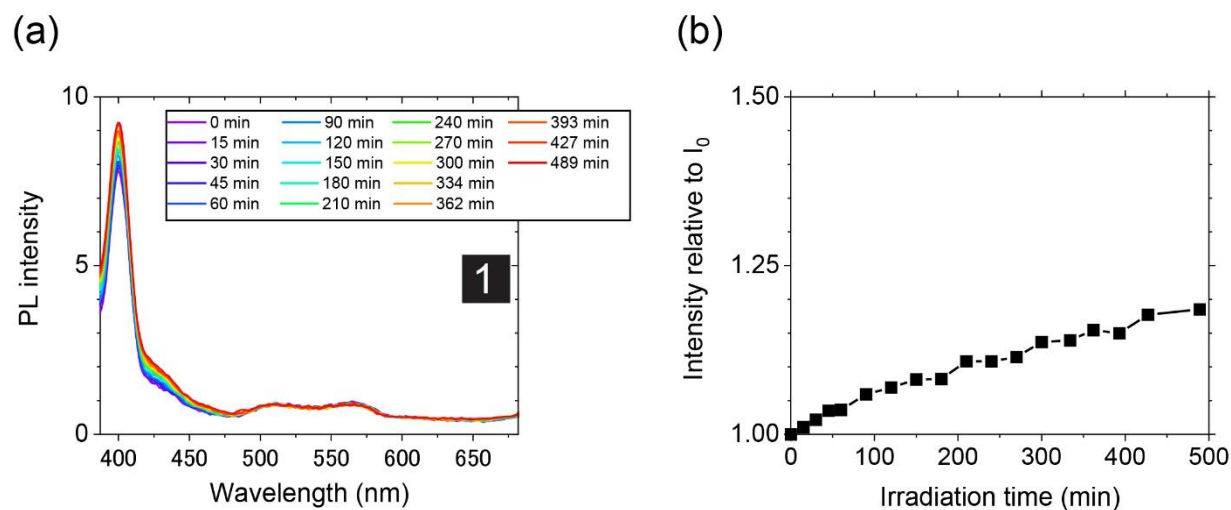


**Figure S1.** Temperature dependence of PL spectra of **2** after N<sub>2</sub> bubbling.

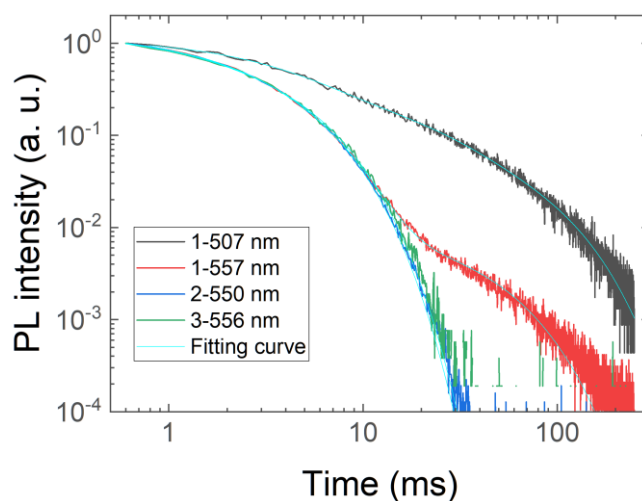
Khara et al. has reported that benzil in imidazolium ionic liquids showed two bands peaks at 505 nm and 560 nm, and an increase of the intensity for the 505 nm band measured at 10  $\mu$ sec at high temperatures [1]. They mentioned the high energy band is thermally activated delayed fluorescence (TADF) band, since TADF can be observed at the delay time over  $\mu$ sec and the intensity is increased at higher temperature due to increase of the rate of reverse intersystem crossing. To investigate this point for our benzil molecules, we have also measured PL spectra at 294 and 333 K for **2** in toluene solution with N<sub>2</sub> bubbling. As shown in Figure S1, the flu.(2) band at around 505 nm does not increase at the higher temperature and instead phos. band decreases. This can be the indication of the high energy band for **2** not to be TADF. The decrease in the phos. band is caused by the increase of non-radiative decay rate from T<sub>1</sub> to S<sub>0</sub>. Note that we confirm that such the intensity change was reversible when the temperature is returned to 294 K, which implies no deterioration due to the measurement at the higher temperature.



**Figure S2.** Absorptions spectra of **1** in toluene solution with N<sub>2</sub> bubbling: Before and after irradiation of Xe-290 nm light shown in Figure 3(a) in the main text.



**Figure S3.** (a) Photostability of **1** in toluene solutions with N<sub>2</sub> bubbling using Xe-355 nm lamp. (b) The ratio of peak intensity of flu.(1) band ( $I_t$ ) to the initial peak intensity ( $I_0$ ).

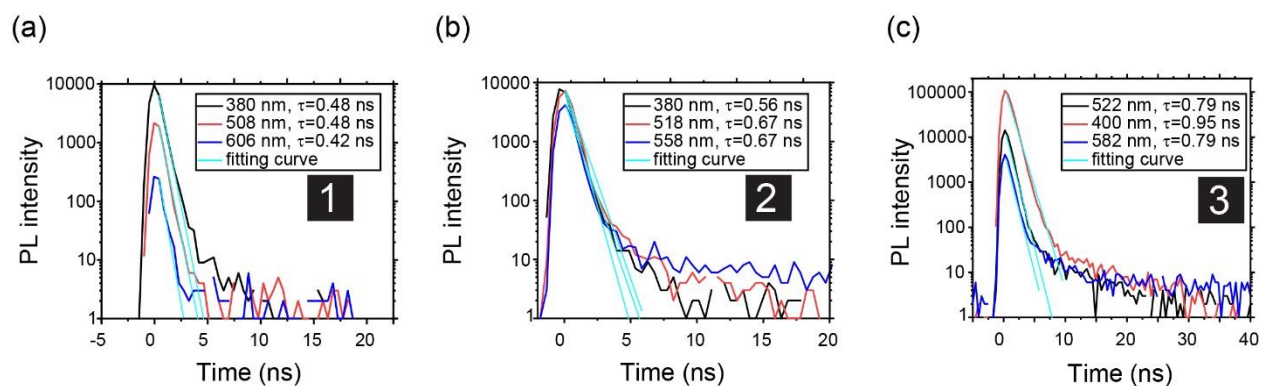


**Figure S4.** Triple decay emission at 77 K of **1–3** in toluene solutions. The peaks are chosen from Figure 4 in the main text.

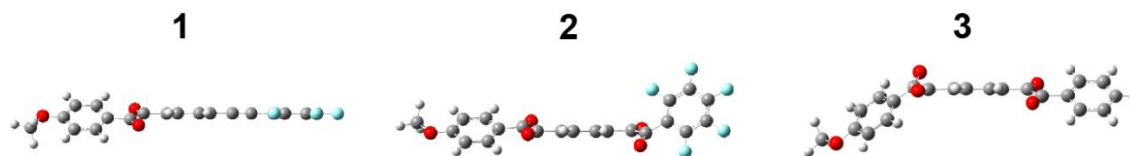
Figure 4(d) show the time profiles and theoretical curve fitting results of the  $T_1$  and  $T_2$  peaks for **1–3** by using multi-exponential decay functions, and the numerical results are summarized in Table S1. The time constant ( $\tau$ ) of phosphorescence from the common  $T_1$  band ( $\tau_1$ ) is nearly the same as for all the **1–3** by 3.2 ~ 3.4 ms with the largest amplitude. For **2** and **3**, the second largest decay constant ( $\tau_2$ ) is shorter as 1.24 and 1.58 ms, is attributed to the initially observed spectral narrowing. For **1**, the double exponential decay function was required to fit the longer component of  $T_2$  band, and the intensity averaged  $\tau$  at 507 nm is estimated to 38.7 ms, one order of magnitude larger than the  $T_1$  band.

**Table S1.** Amplitudes ( $A_n$ ) and time constants ( $\tau_n$ ) estimated by theoretical curve fittings of time-profiles of PL spectra of **1–3** in toluene solutions measured at 77 K.

	$A_1$	$\tau_1$ (ms)	$A_2$	$\tau_2$ (ms)	$A_3$	$\tau_3$ (ms)
<b>1@507 nm</b>	0.792	3.16	0.248	14.66	0.098	54.89
<b>1@557 nm</b>	0.789	3.20	0.482	1.58	0.010	33.67
<b>2@550 nm</b>	0.89	3.23	0.418	1.24	-	-
<b>3@556 nm</b>	0.88	3.37	0.434	1.07	-	-



**Figure S5.** Time profiles of flu. (1), flu. (2) and phos. bands of **1–3** in toluene solutions taken from Fig. 5.: flu. (1) is 380 nm for **1** and **2**, 400 nm for **3**, flu. (2) is 508 nm for **1**, 518 nm for **2**, and 522 nm for **3**, phos. is 606 nm for **1**, 558 nm for **2**, and 582 nm for **3**, respectively.



**Figure S6.** Optimized structure of **1–3** in the ground triplet state obtained by DFT calculations [M06-2X/6-31g(d)]

## References

- [1] D.C. Khara, A. Samanta, Fluorescence, Phosphorescence, and Delayed Fluorescence of Benzil in Imidazolium Ionic Liquids, *Aust. J. Chem.*, 65 (2012) 1291-1297.