

Supporting Information

**Boosting Organic Room-temperature Phosphorescence Performance through
Joint Luminescence Sensitization**

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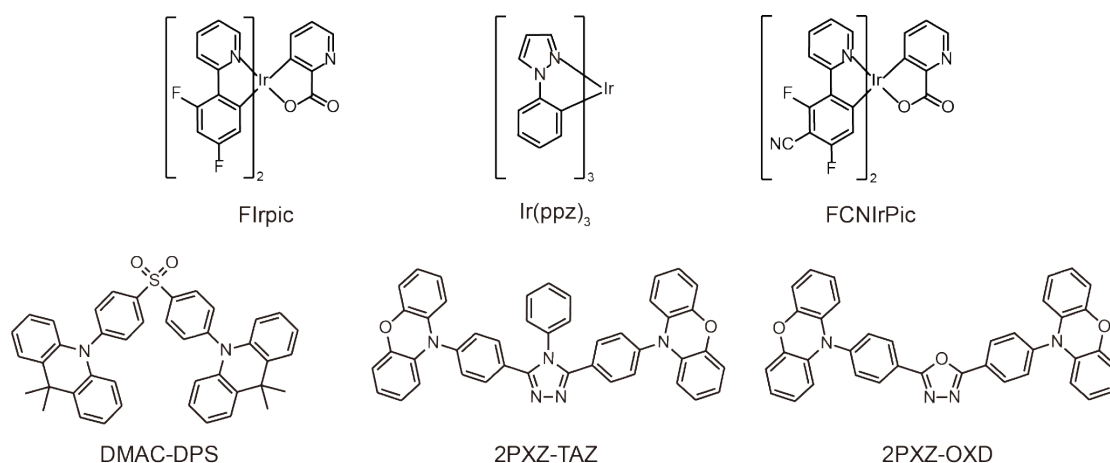
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Preparation and characterization



Scheme S1. Molecule structures of traditional phosphor complexes (Ir(ppy)₃, Ir(ppz)₃, and FCNIrPic) and TADF materials (DMAC-DPS, 2PXZ-TAZ and 2PXZ-OXD) used as guests.

Preparation of Ir(ppy)₃@PhCz crystal: 1 wt% Ir(ppy)₃ and 99 wt% PhCz were dissolved in 1: 1 ratio DCM/hexane solvent in a glass vial. Slow evaporation of the solvent at room temperature for about three days yielded isostructural transparent crystals. The product was isolated prior to total evaporation of the solvent to guarantee the crystal purity.

Preparation of Ir(ppz)₃@PhCz crystal: Ir(ppz)₃@PhCz was prepared in a same procedure to that of Ir(ppy)₃@PhCz crystal, but instead of using 1 wt% Ir(ppz)₃, yielded isostructural colorless crystals.

Preparation of FCNIrPic@PhCz crystal: Similar to the preparation of FCNIrPic@PhCz, FCNIrPic@PhCz was synthesized by using 1 wt% FCNIrPic, resulted in isostructural transparent crystals.

Preparation of DMAC-DPS@PhCz crystal: Similarly, DMAC-DPS@PhCz was prepared from 1 wt% DMAC-DPS, and yielded isostructural colorless crystals.

Preparation of 2PXZ-TAZ@PhCz crystal: Similar operation, 2PXZ-TAZ@PhCz was prepared from 1 wt% 2PXZ-TAZ, and yielded isostructural transparent crystals.

Preparation of 2PXZ-OXD@PhCz crystal: Similarly, 2PXZ-OXD@PhCz was prepared from 1 wt% 2PXZ-OXD, and yielded faint yellow crystals.

Aggregation structure analyses

Time-dependent density functional theory (TD-DFT) calculations were carried out at the B3LYP/6-31G(d) level using on Gaussian 09 package¹. Aggregation structures influence significantly the photophysical properties of organic optoelectronic materials. Especially, H-aggregation plays an important role in stabilizing the triplet excitons to elongate their lifetimes for the realization of organic afterglow at room temperature^{2,3}. To probe the existence of H-aggregation, the aggregation structure analysis was performance on the single crystal structures of these OURTP molecules. According to the molecular exciton theory, the exciton splitting energy ($\Delta\varepsilon$) in dimer is given by⁴:

$$\Delta\varepsilon = \frac{2|M|^2}{r_{uv}^3}(\cos \alpha - 3\cos \theta_1\cos \theta_2) \quad (\text{S1})$$

where M is the electric dipole transition moment, α is the angle between the transition moments of the two molecules in the dimer, and θ_1 and θ_2 are the angles between transition moments of the two molecules and the interconnection of the centers respectively, r_{uv} is the distance between the molecular pair. And, when $\Delta\varepsilon > 0$, it belongs to H-aggregation, and when $\Delta\varepsilon < 0$, it is J-aggregation. Therefore, the **PhCz** crystal forms H-aggregation dominated aggregation structures, results in organic afterglow at room temperature.³

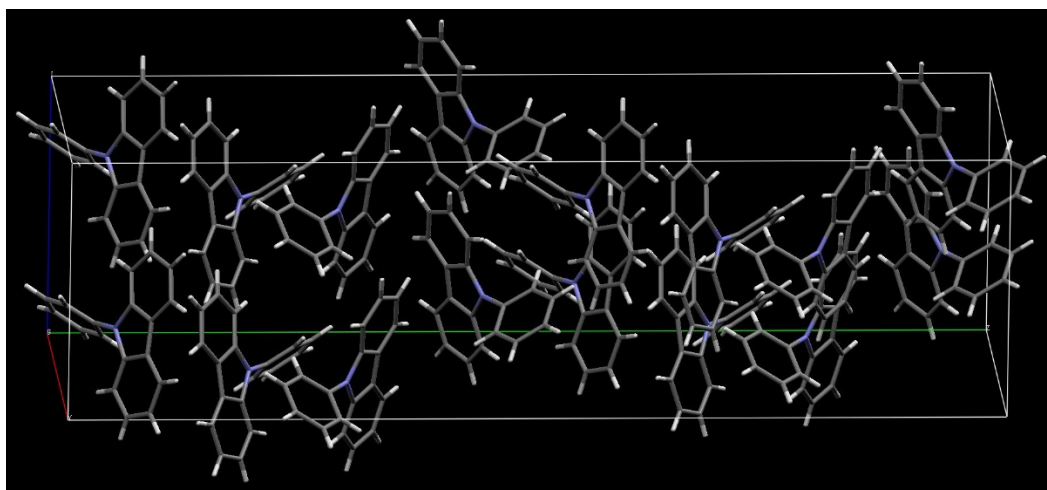


Figure S1. Single-crystal unit cell of **PhCz**.

Table S1. Crystallographic data of **PhCz** single crystal.

Compound	PhCz ⁵
Empirical formula	C ₁₈ H ₁₃ N
Formula weight (g mol ⁻¹)	243.29
Crystal color	colorless
Wavelength (Å)	0.71073
Space Group	Fdd2
<i>a</i> (Å)	12.7887(15)
<i>b</i> (Å)	38.1950(19)
<i>c</i> (Å)	10.8230(15)
α (deg)	90
β (deg)	90
γ (deg)	90
<i>V</i> (Å ³)	5286.6(10)
<i>Z</i>	16
Density (g cm ⁻³)	1.223
μ (mm ⁻¹)	0.071
<i>T</i> _{min} , <i>T</i> _{max}	0.9769, 0.9852
<i>F</i> (000)	2048.0
<i>h</i> _{max} , <i>k</i> _{max} , <i>l</i> _{max}	12, 12, 18
<i>Theta</i> _{max}	24.99
Goof	0.982
Refinement parameters	R ₁ =0.0427 wR ₂ =0.0554

Table S2. H-aggregates (H, in red) and J-aggregates (J, in black) in **PhCz** crystal identified by the positive and negative exciton splitting energy ($\Delta\varepsilon$) respectively.

Compd.	Aggregation	α (°)	θ_1 (°)	θ_2 (°)	M (Debye)	<i>r</i> _{uv} (Å)	$\Delta\varepsilon$ (eV)
PhCz	H1	73.0	95.1	31.7	1.41	6.83	0.0041
	H2	73.0	94.1	56.3	1.41	10.26	0.0001
	H3	178.8	16.1	163.9	1.41	11.90	0.0026
	H4	0.0	89.4	89.4	1.41	10.82	0.0020
	H5	0.0	90.6	90.6	1.41	10.82	0.0020
	H6	73.0	148.3	84.9	1.41	6.83	0.0041
	H7	178.8	40.2	138.6	1.41	8.32	0.0031
	H8	178.8	41.4	139.8	1.41	8.32	0.0031
	J1	178.8	75.0	105.0	1.41	4.47	-0.0200
	J2	0.0	127.3	127.3	1.41	8.38	-0.0004
	J3	0.0	128.4	128.4	1.41	8.38	-0.0007
	J4	0.0	51.6	51.6	1.41	8.38	-0.0007
	J5	0.0	52.7	52.7	1.41	8.38	-0.0004

Photophysical properties measurements

Ultraviolet-visible (UV-Vis) spectra were measured using a SHIMADZU UV-3600 UV-VIS-NIR spectrophotometer. Steady-state photoluminescence, phosphorescence spectra, time-resolved excitation spectra, kinetic measurement and quantum yields were performed on an Edinburgh FLSP920 fluorescence spectrophotometer. For steady-state photoluminescence, time-resolved excitation spectra and quantum yield measurements, a xenon arc lamp (Xe900) was used; Xe900 provides excellent steady state excitation source. For getting phosphorescence spectra, a microsecond flash-lamp (uF900) was used, since the uF900 flash lamp produces short, typically a few μs , and high irradiance optical pulses for phosphorescence measurements in the range from microseconds to seconds. The LED flash lamp provides subnanosecond optical pulses over the UV-to-vis spectral range for fluorescence decay measurements. The microsecond flash lamp produces short, typically a few microsecond (μs), and high irradiance optical pulses for the organic ultralong room temperature phosphorescence (OURTP) decay measurements. The lifetime (τ) of the luminescence was obtained by fitting the decay curve with a multi-exponential decay function⁶ of

$$I(t) = \sum_i A_i e^{-\frac{t}{\tau_i}} \quad (\text{S1})$$

where A_i and τ_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively. The photographs were recorded by a Nikon D90 camera.

The quantum yield (η) of the emission was the absolute one done by photons counting from the excitation source into an integration sphere with the ratio of photons emitted, as described in the following equation⁷.

$$\eta = \frac{N^{em}}{N^{abs}} \quad (\text{S2})$$

In the equation, N^{em} is the number of emitted photons and N^{abs} is the number of absorbed photons. The quantum efficiency (QE) of OURTP is determined through peak-

differentiation-imitating analysis from the steady-state PL spectrum.

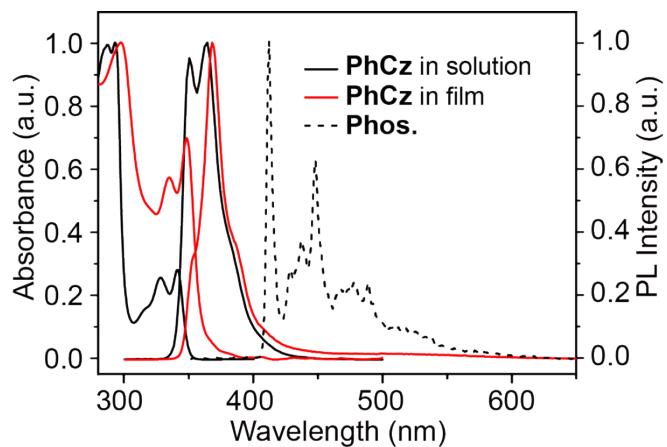


Figure S2. UV-vis absorption (left) and fluorescence (right) spectra of **PhCz** in dilute CH_2Cl_2 ($\sim 10^{-5}$ mol L^{-1}) and thin film at room temperature, and corresponding phosphorescence spectrum in 2-methyltetrahydrofuran excited by 295 nm UV-light at 77 K with a delay time of 10 ms.

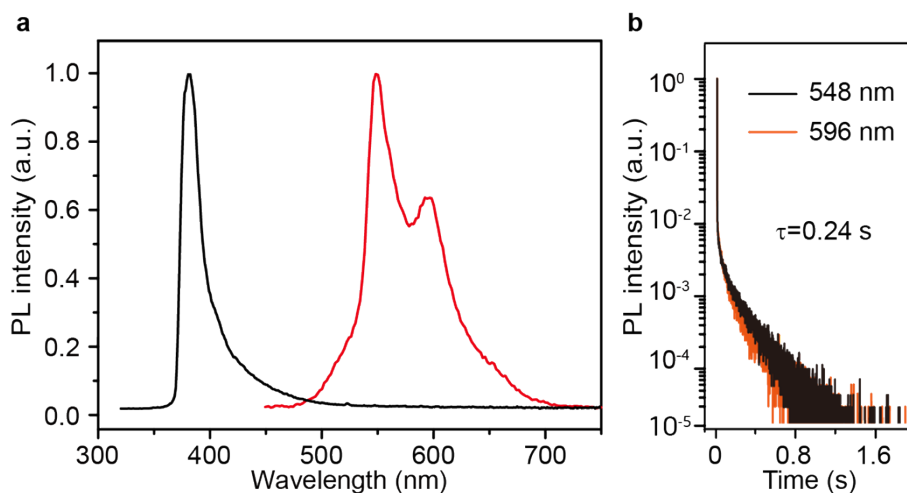


Figure S3. (a) Steady-state and OURTP emission spectra of PhCz crystal. OURTP was collected with a delay time of 40 ms. (b) Lifetime decay profiles of PhCz crystal excited at 400 nm.

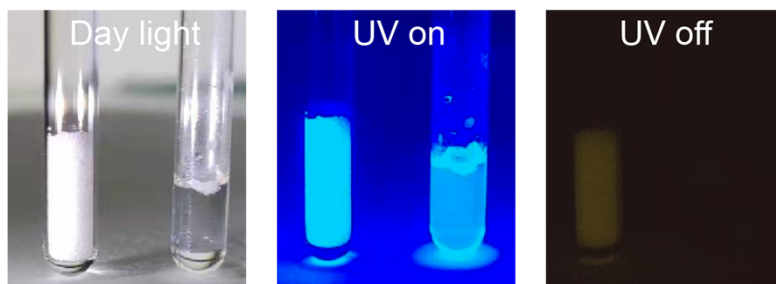


Figure S4. Photographs of the pure **PhCz** crystal (left) and amorphous solid (right) in quartz tubes taken under day light, on (UV-on) and after (UV-off) the 365 nm UV lamp excitation.

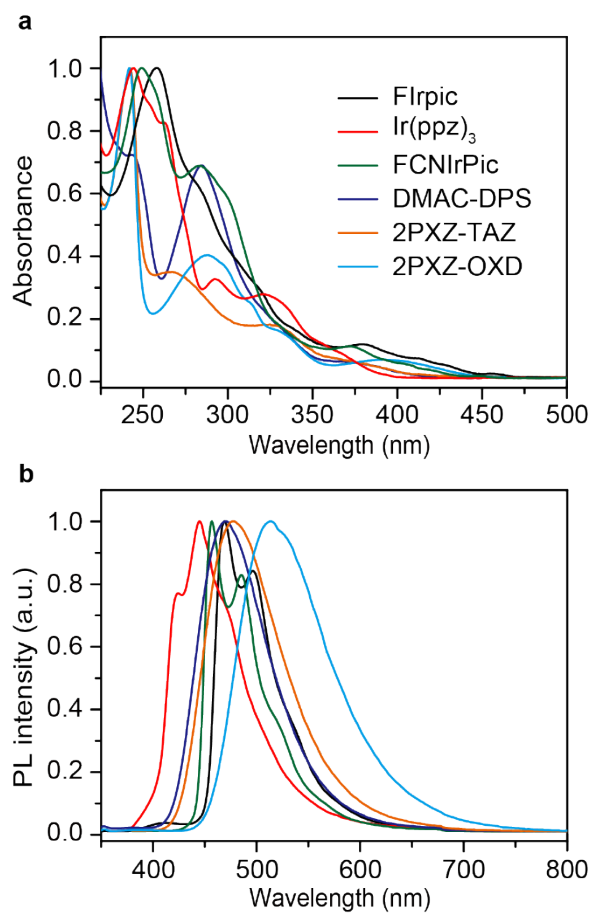


Figure S5. (a) UV-vis absorption and (b) steady-state PL spectra of **FIrpic**, **Ir(ppz)₃**, **FCNIrpic**, **DMAC-DPS**, **2PXZ-TAZ** and **2PXZ-OXD** in dilute CH₂Cl₂ solutions at room temperature.

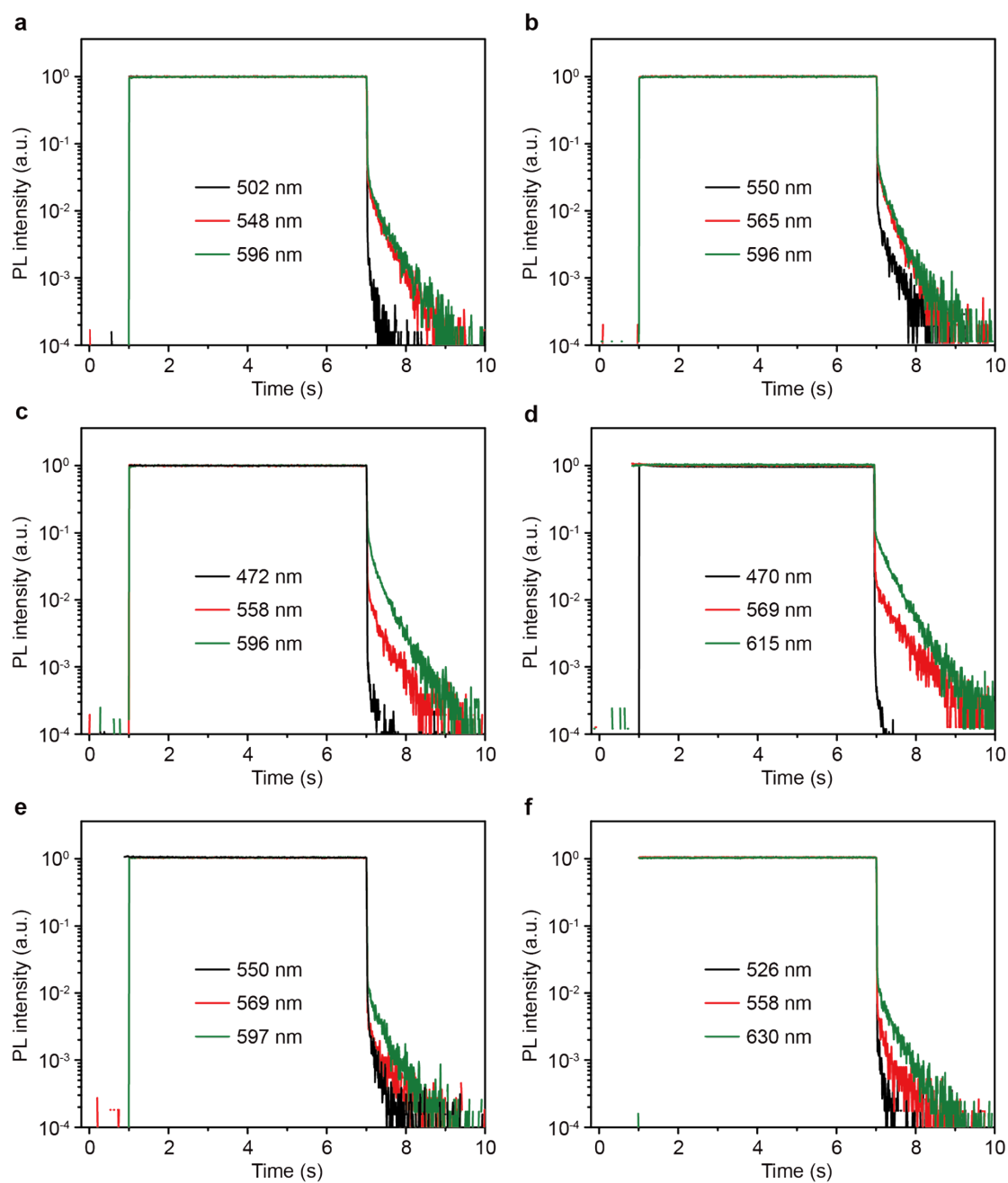


Figure S6. (a) Time-dependent intensity profiles of the OURTP emissions of **FIrpic@PhCz** (471, 552, 596 nm), **Ir(ppz)₃@PhCz** (550, 565, 596 nm), **FCNIrpic@PhCz** (504, 550, 596 nm), **DMAC-DPS@PhCz** (470, 569, 615 nm), **2PXZ-TAZ@PhCz** (450, 569, 597 nm) and **2PXZ-OXD@PhCz** (550, 558, 630nm) crystals excited by 295 nm light under ambient conditions. The excitation is turned on at 1 s and maintained for 6 s at room temperature.

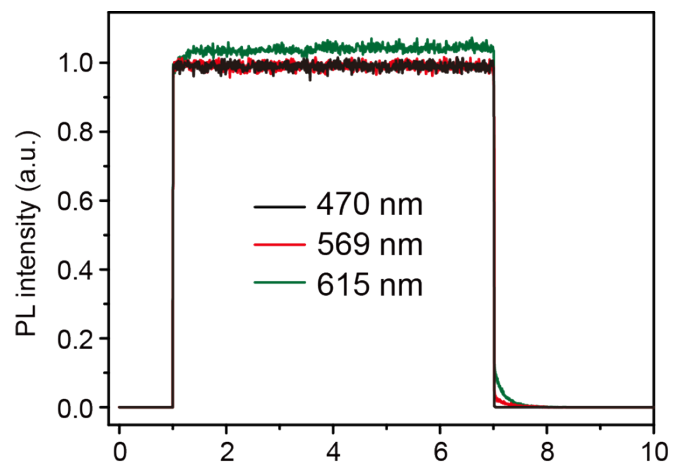


Figure S7. Time-dependent intensity profiles of the phosphorescent (470 nm) /OURTP (569 and 615 nm) emissions of DMAC-DPS@PhCz excited at 295 nm at room temperature in N₂ atmosphere.

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