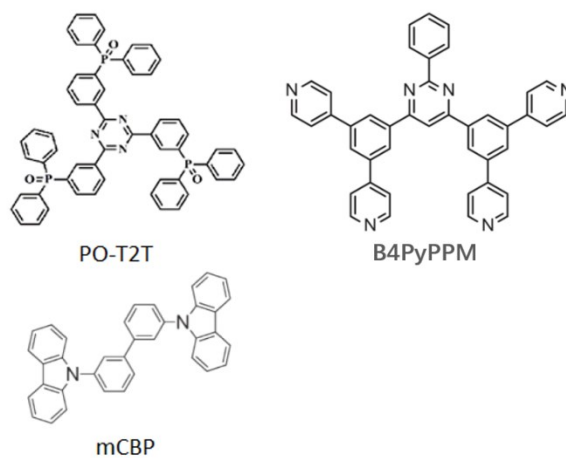


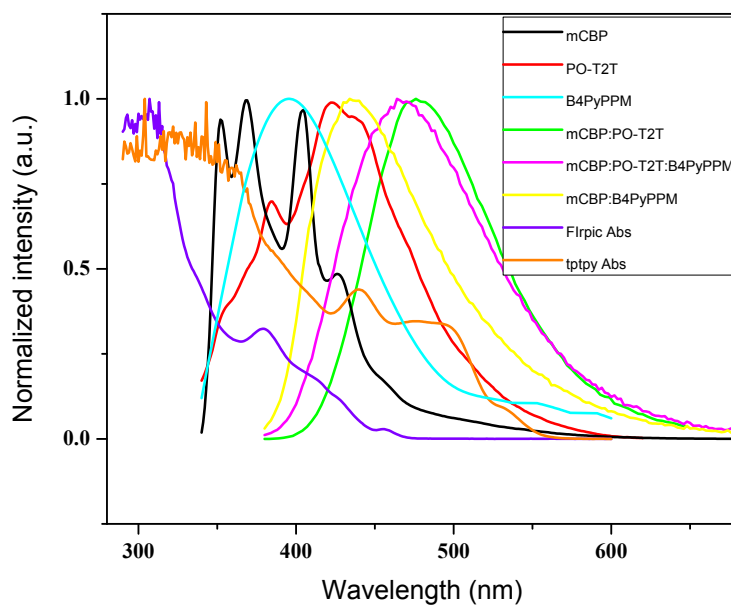
## Supporting Information

1.



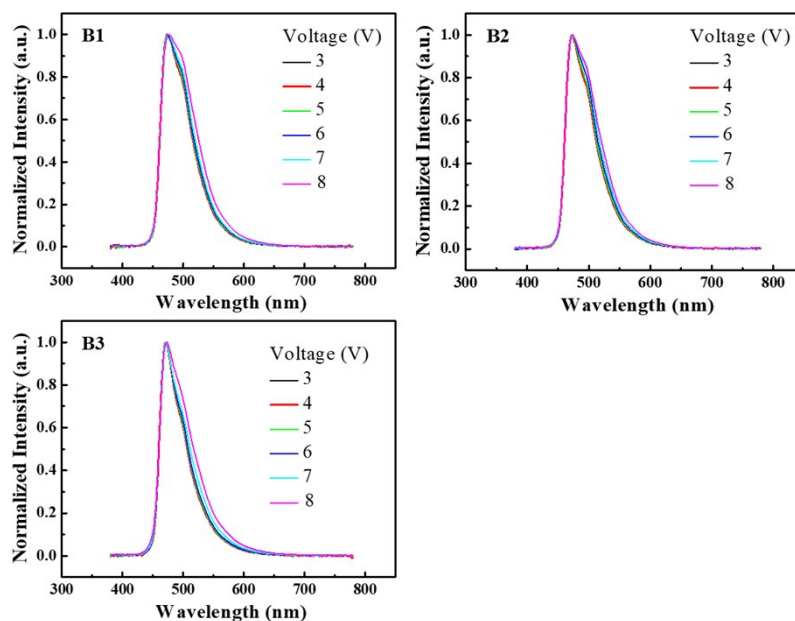
**Figure S1** Structures of the materials within the forming exciplexes.

2.



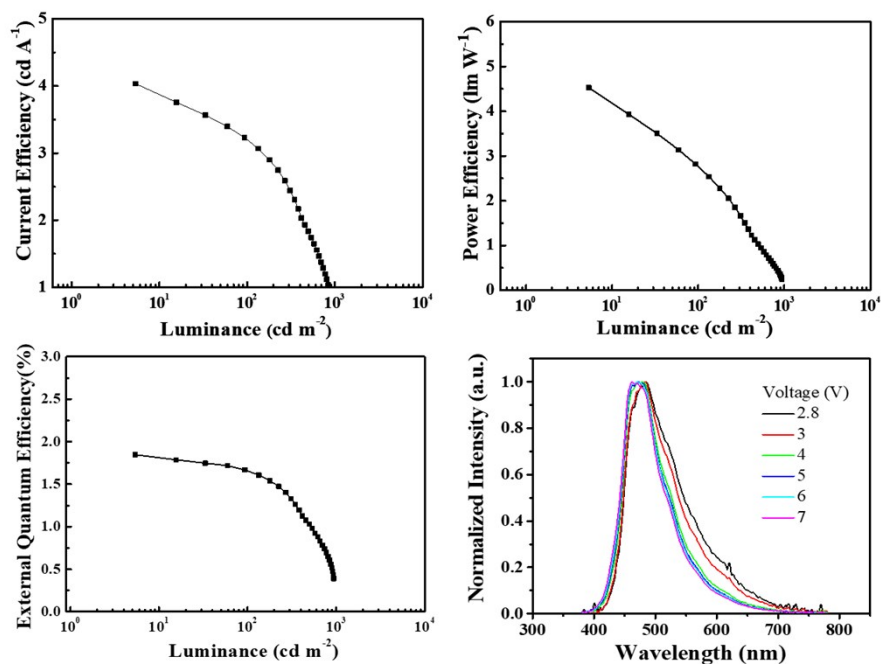
**Figure S2** Normalized photoluminescence (PL) and absorption spectra of the related materials. Excitation wavelength: 305 nm.

3.



**Figure S3** Normalized electroluminescence (EL) spectra of the devices B1, B2 and B3.

4.

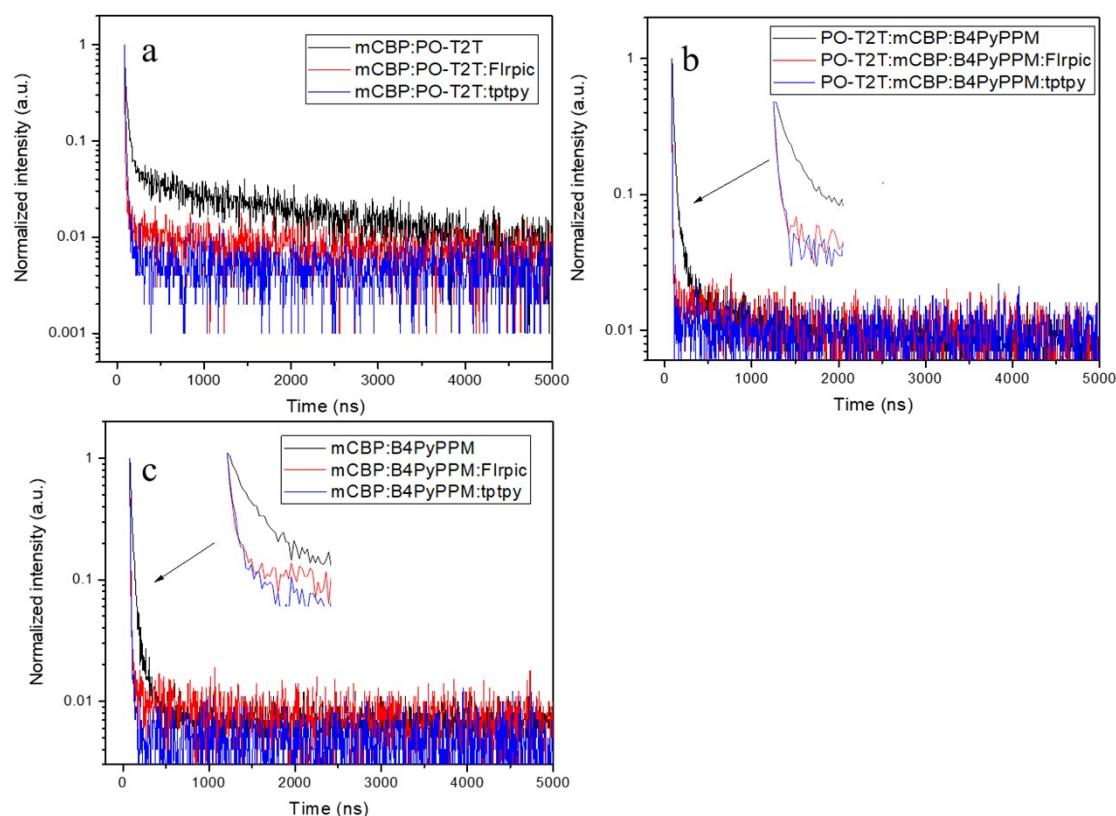


**Figure S4** Normalized EL spectra of the double-excimer mCBP: PO-T2T: B4PyPPM.

The characterization of the fluorescent OLED of double-excimer mCBP: PO-T2T: B4PyPPM.

The structure is illustrated as : ITO (180 nm)/ HAT-CN (10 nm)/ TAPC (60 nm)/ TCTA (5 nm)/ mCBP (5 nm)/ mCBP: PO-T2T: B4PyPPM (2:1:1, 10 nm) / PO-T2T (45 nm)/ LiF (1 nm)/ Al(100 nm)

5.



**Figure S5** PL transient decay curves of the mCBP:PO-T2T, mCBP: PO-T2T: B4PyPPM and mCBP: B4PyPPM mixed films with 15% Flrpic and 6% Ir(tptpy)<sub>2</sub>acac (tptpy) dopants, respectively. (Excitation wavelength: 305 nm; Detection wavelength: 430 nm)

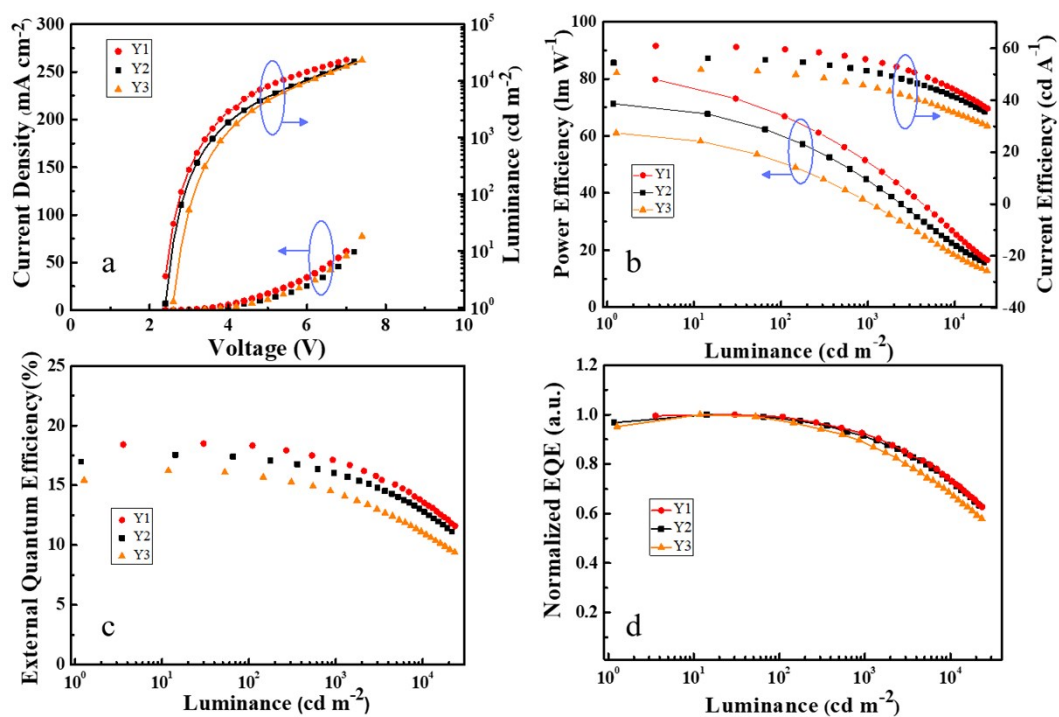
The structures of the yellow phosphorescent OLEDs:

Y1: ITO (180 nm)/ HAT-CN (10 nm)/ TAPC (60 nm)/ TCTA (5 nm)/ mCBP (5 nm)/ mCBP: PO-T2T: B4PyPPM: Ir(tptpy)<sub>2</sub>acac (2:1:1; 6%, 10 nm) / PO-T2T (45 nm)/ LiF (1 nm)/ Al(100 nm)

Y2: ITO (180 nm)/ HAT-CN (10 nm)/ TAPC (60 nm)/ TCTA (5 nm)/ mCBP (5 nm)/ mCBP: PO-T2T: Ir(tptpy)<sub>2</sub>acac (1:1; 6%, 10 nm) / PO-T2T (45 nm)/ LiF (1 nm)/ Al(100 nm)

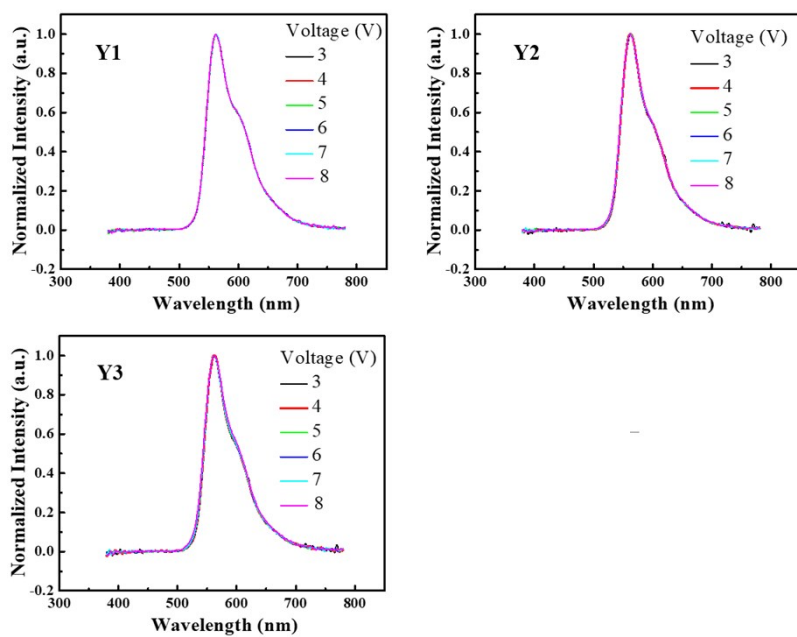
Y3: ITO (180 nm)/ HAT-CN (10 nm)/ TAPC (60 nm)/ TCTA (5 nm)/ mCBP (5 nm)/ mCBP: B4PyPPM: Ir(tptpy)<sub>2</sub>acac (1:1; 6%, 10 nm) / PO-T2T (45 nm)/ LiF (1 nm)/ Al(100 nm)

6.



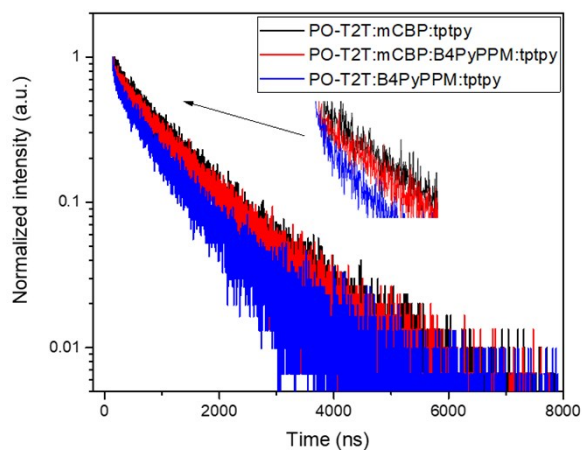
**Figure S6** Performance of the resulting orange ph-OLEDs. a. Current Density-Voltage-Luminance; b. Current Efficiency-Luminance and Power Efficiency-Luminance; c. External Quantum Efficiency-Luminance; d. Normalized External Quantum Efficiency-Luminance.

7.



**Figure S7** Normalized EL spectra of the devices Y1, Y2 and Y3.

8.



**Figure S8** PL decay PL transient decay curves of the mCBP:PO-T2T, mCBP: PO-T2T: B4PyPPM and mCBP: B4PyPPM mixed films with 6% Ir(tptpy)<sub>2</sub>acac dopants, respectively. (Excitation wavelength: 305 nm; Detection wavelength: 450 nm)