- Supporting Information -

**Organic Light-Emitting Diode (OLED) Employing Metal-Free Organic Phosphor**

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**Figure S1.** Cyclic voltammetry (CV) curve of BrPFL-TFK in acetonitrile solution. The inset is the CV curve of ferrocene as a standard reference at a scan rate of 50 mV/s.
Figure S2. Comparison of Electroluminescence spectra (red) and thin film steady state emission spectra of BrPFL-TFK doped in each host (blue). (a) CBP based D1 and related films; (b) mCP based D2 and related films; (c) PPT based D3 and related films.
Figure S3. UV-Vis absorption spectrum of BrPFL-TFK compared with the steady state (fluorescence emission) of CBP, mCP, and PPT. Measurements were conducted in toluene at 298 K.
Figure S4. Steady state emission of CBP (a), mCP (b), and PPT (c) films doped with 2 vol% BrPFL-PFK at different temperatures. Measurements were carried out under vacuum and spectra were recorded in the order of low to high temperature. Please notice that the spectral shape or relative peak intensity within the same spectrum is not well-trustable due to the following reasons: 1) Photostability of 50 nm vacuum deposited host-guest films studied here is not good, and thus spectral shape or relative peak intensity might have changed from one trace to another even when all other measurement conditions are the same; 2) Film degradation might have happened during storage even under nitrogen atmosphere and the data in Figure S4 were not recorded directly after the fabrication of films. However, PL traces in Figure S2 or Figure 3a-c were recorded directly after the films were fabricated without any addition photoirradiation processes on the films in between.

Nevertheless, it’s shown here that for doped CBP films, phosphorescence emission intensity has decreased, while the exciplex emission intensity has increased with rising temperature. On the other hand, for doped mCP films, with 298 K as the exception, both phosphorescence and exciplex emission intensity has increased while normal fluorescence intensity has decreased with rising temperature. Such trends were difficult to understand...
but might shine the light on temperature dependency of host-to-guest energy transfer or exciplex formation process.

Because of the reasons stated above, we did not study the temperature dependency of phosphorescence emission. Generally speaking, phosphorescence emission intensity or lifetime would decrease with increasing temperature due to the emerging non-radiative decay processes. However, the complicated photophysical processes here in the host-guest systems have imposed difficulty in extracting such dependency from emission intensity. On the other hand, through the dependency of phosphorescence lifetime on temperature, a clear picture regarding host-dependent non-radiative decay has been demonstrated in Figure 3d.
Figure S5. 

$^1$H NMR spectrum of BrPFL-TFK in DMSO-d6 with suggested proton assignments
Figure S6. Mass spectra (⁺ESI) showing [M+H]⁺ peaks for BrPFL-TFK.