Supplementary Figure 1: FIrpic Emission in t-Bu-PBD or MCP Host

The t-Bu-PBD host significantly quenches the triplet emission from FIrpic, demonstrating a lower energy triplet state in t-Bu-PBD.

Supplementary Figure 2: Steady State Photoluminescence of m-MTDATA:t-Bu-PBD

Measured m-MTDATA:t-Bu-PBD film steady state PL under pressure. Vertical line indicates the peak wavelength for each PL spectrum.
Supplementary Figure 3: Time Resolved Photoluminescence of m-MTDATA:3TPYMB
Transient PL for the m-MTDATA:3TPYMB system. Green and purple dashed lines indicate fitted prompt and delay lifetimes, respectively.

Supplementary Note 1 t-Bu-PBD Triplet Energy
We were unable to obtain clean phosphorescent spectra for t-Bu-PBD at low temperature. Previous measurements of the low temperature phosphorescence of t-Bu-PBD derivatives estimated that the t-Bu-PBD triplet is 2.54 eV.\(^1\) We tested this estimation by comparing the triplet energy of t-Bu-PBD to the phosphor FIrpic, which has a triplet energy of 2.65 eV.\(^2\) FIrpic was doped at 5% weight into both N,N'-dicarbazolyl-3,5-benzene (MCP) and t-Bu-PBD; see Supplementary Figure 1. The MCP-doped film phosphoresced brightly (green line) while the t-Bu-PBD doped film (purple line) was less than 2% as bright. Charge transfer state formation is not energetically favorable.\(^3,4\) This demonstrates the triplet energy of t-Bu-PBD is less than that of FIrpic, which is traditionally accepted to be approximately 2.65 eV. We conclude that t-Bu-PBD acts as a triplet exciton acceptor for triplet m-MTDATA:t-Bu-PBD exciplexes.
Supplementary Note 2 Steady State Photoluminescence of m-MTDATA:t-Bu-PBD

Corresponding to m-MTDATA:3TPYMB PL data shown in Fig. 2(d), Supplementary Figure 2 shows steady state PL of m-MTDATA:t-Bu-PBD sample under pressure. We observe similar red shift and slight increase in intensity, suggesting the increase in charge overlap is observed in both material systems under pressure. Note that exciton emission from donor and acceptor material is quenched by the lower CT states and not observed in photoluminescence (PL).\(^4\)

Supplementary Note 3 Time Resolved Photoluminescence of m-MTDATA:3TPYMB

The complementary transient PL for m-MTDATA:3TPYMB system is plotted in Supplementary Figure 3. Similar to the t-Bu-PBD system, the transient is fitted with prompt and delayed lifetime corresponding to direct emission from singlet CT and emission due to reverse intersystem crossing from triplet to singlet CT at much slower rate.

Supplementary References


