

Supplementary Materials

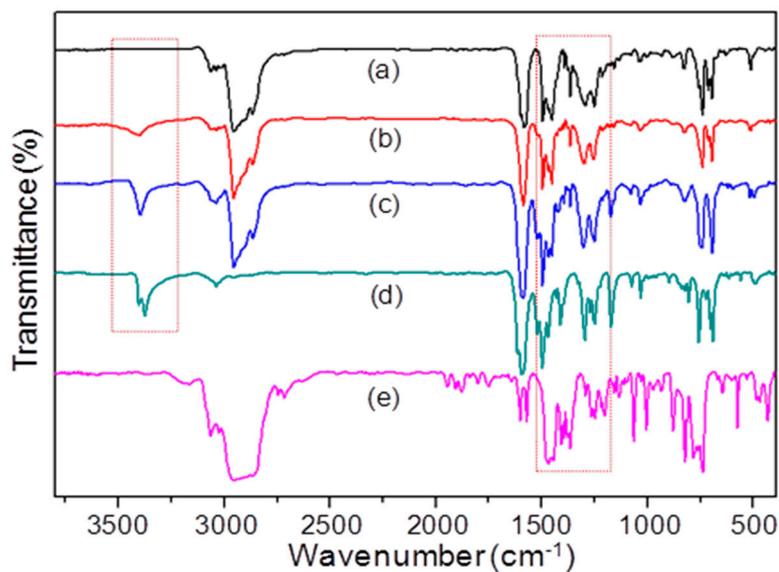


Figure S1. Infrared spectra of (a) tris(DPAF-C₉) **7**, (b) bis(DPAF-C₉) **6**, (c) mono(DPAF-C₉) **5**, (d) TPAB **4**, and (e) BrF-C₉ **2** collected on a KBr pellet.

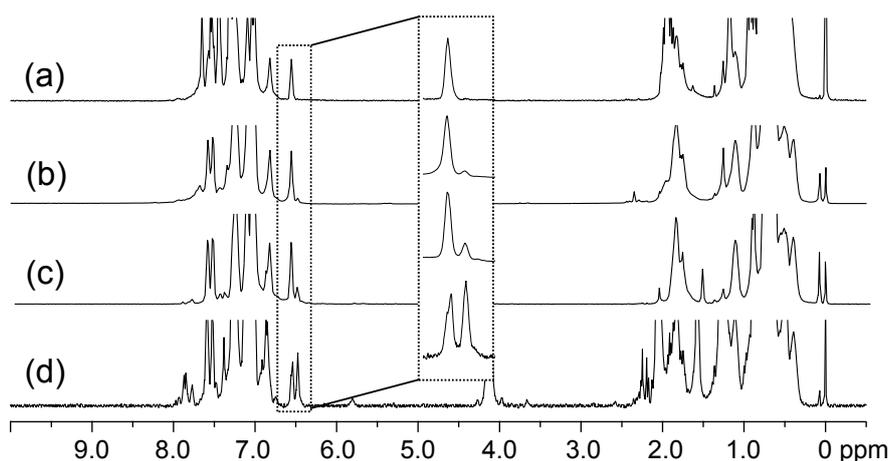


Figure S2. ¹H-NMR spectra of products using a different equivalent starting material ratio (TPAB/BrF-C₉) of (a) 1:6 (excess), (b) 1:4, (c) 1:3, and (d) 1:2.

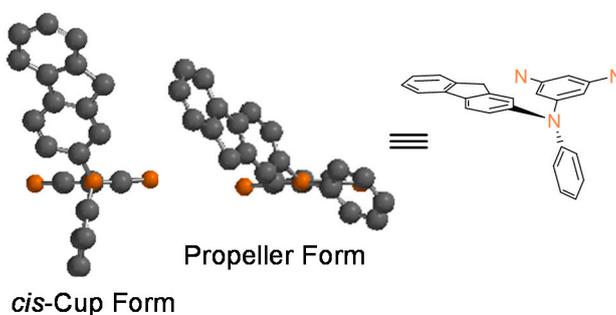


Figure S3. Torsional angle comparison between *cis*-cup and propeller forms showing much higher strain around the central triaminobenzene moiety. Other atoms are omitted for clarity.

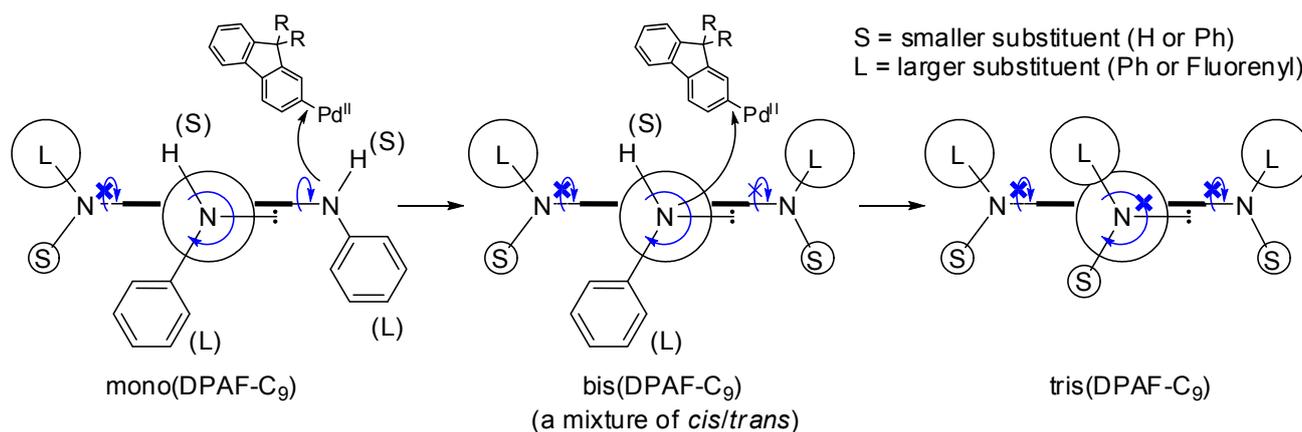


Figure S4. Alternative mechanism for the formation of exclusive *cis*-cup form by the restriction of central phenyl C-N bond rotation and the consideration of steric hindrance effect, leading to a preferred geometrical conformation going from mono(DPAF-C₉) to tris(DPAF-C₉) molecules.

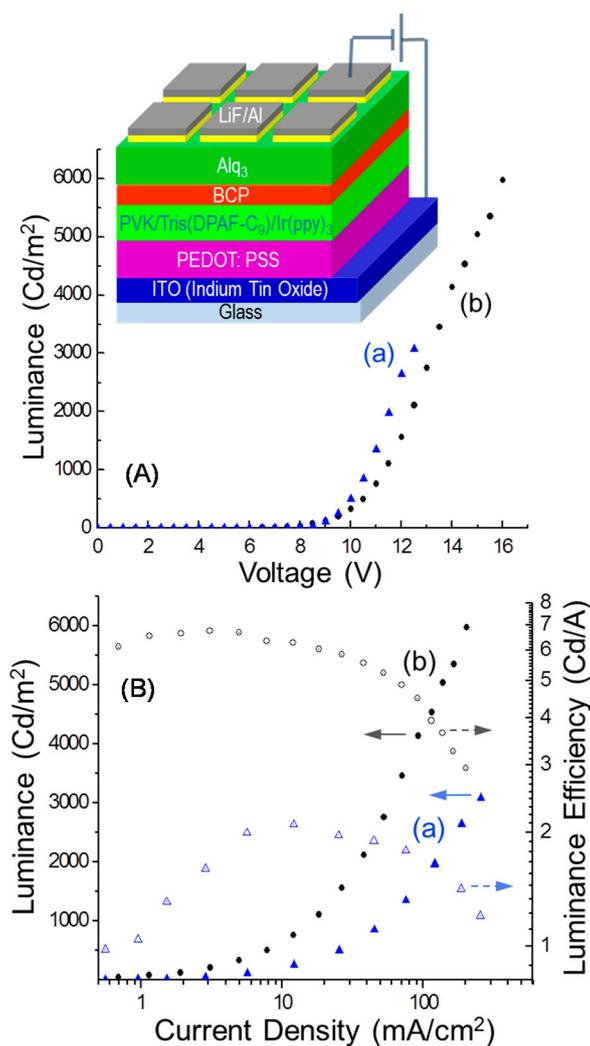


Figure S5. (A) Luminance (L)–voltage (V) and (B) luminance and luminance efficiency–current density (I) characteristics of multi-layered PVK–tris(DPAF-C₉)–Ir(ppy)₃ devices in a weight ratio of (a) 5:5:0.87 (▲/△) and (b) 10:0:0.87 (●/○).