

Supplementary Material for:

Fundamental guidelines on active control of the molecular orientation of heteroleptic iridium complexes enabled by carbazole-based host materials

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Experimental

General Considerations: mCP2CN^[1], mCBP^[2], mCBPCN^[3], Ir(piq)₂acac were prepared according to the literature procedure. Ir(ppy)₂acac, PO-01-TB, mCP and mCPCN was purchased from Luminescence technology corp. Ir(pq)₂acac was purchased from Chemipro Kasei Kaisha, Ltd. All organics were used after train sublimation. DSC was performed using a Perkin-Elmer Diamond DSC Pyris instrument under nitrogen atmosphere at a heating rate of 10 °C min⁻¹. TGA was undertaken using a SEIKO EXSTAR 6000 TG/DTA 6200 unit under nitrogen atmosphere at a heating rate of 10 °C min⁻¹. UV-vis spectra was measured using a Shimadzu UV-3150 UV-vis-NIR spectrophotometer. Photoluminescence spectra were measured using a FluoroMax-2 (Jobin-Yvon-Spex) luminescence spectrometer. PL quantum efficiencies were measured on a Hamamatsu photonics C9920-01 integral sphere system. Quantum chemistry calculations were performed using the Gaussian 09 suite of programs^[4]. The averaged permanent dipole moment (PDM) values of host materials were calculated by the Boltzmann weighting of conformers those existence ratios estimated using their calculated energies at B3LYP/6-31G(d) level of theory^[5]. The structures of Ir complexes were optimized by Gaussian 09 at B3LYP/6-31G(d)/LANL2DZ level of theory. The transition dipole moment (TDM) of the triplet states of Ir-complex were calculated using the Dalton 2011 programme with a quadratic response function and the 6-31G(d,p) basis set for H, C, N, O; the ecp-sdd-DZ basis set for Ir^[6] according to the literature method^[7]. The aspect ratio and surface area were calculated using the Winmostar program^[8,9] from the optimized structures. The I_p was determined by a PYS under the vacuum ($=10^{-3}$ Pa). The experiments of VASE were performed by using a fast spectroscopic ellipsometer (M-2000U, J. A. Woollam Co., Inc.). Measurements were taken at seven multiple angles of the incident light from 45° to 75° in a step of 5°. The analysis of the data was performed via using the software “WVASE32” (J. A. Woollam Co., Inc.), which can perform an analysis of all the data at all the different incident angles and wavelengths. Doped films of emitters in hosts with 30 nm thickness were prepared

for angle-dependent photoluminescence intensities experiment. The samples were fixed on a stage with adjustable axis and attached to a cylindrical lens. The wavelength of the excited light was set to 340 nm, and the PL intensities at different adjusted angles were via a p-wave polarizer and collected by a Konica Minolta CS-2000.

Device Fabrication and Characterization: The substrates were cleaned with ultrapurified water and organic solvents, and then dry-cleaned for 30 minutes by exposure to UV–ozone. The organic layers were deposited onto the ITO substrates under the vacuum ($=10^{-5}$ Pa), successively. Al was patterned using a shadow mask with an array of $2\text{ mm} \times 2\text{ mm}$ openings without breaking the vacuum ($=10^{-5}$ Pa). The electroluminescent (EL) were taken using an optical multichannel analyzer Hamamatsu Photonics PMA-11. The current density–voltage and luminance–voltage characteristics were measured by using a Keithley source measure unit 2400 and a Minolta CS200 luminance meter, respectively.

References

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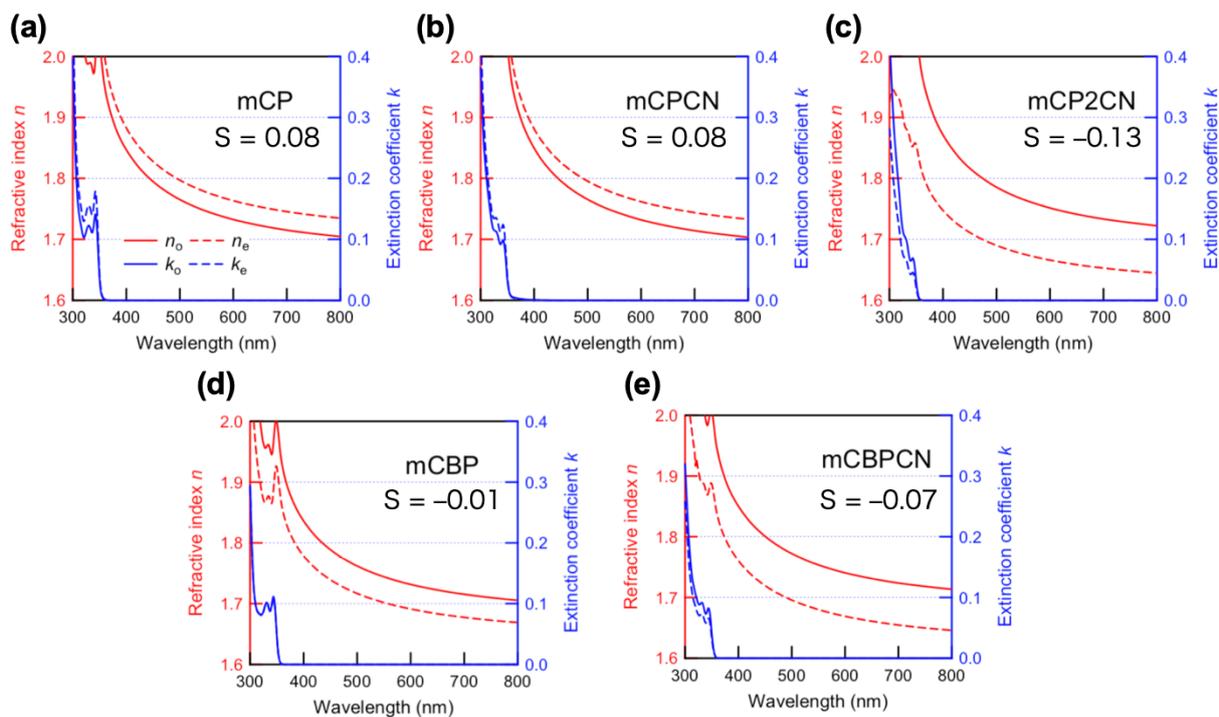


Figure S1. Ordinary (horizontal direction) and extraordinary (vertical direction) refractive indices and extinction coefficients obtained from neat films of (a) **mCP**, (b) **mCPCN**, (c) **mCP2CN**, (d) **mCBP**, (e) **mCBPCN**. Note that the determined values of the orientation order parameter (S) would include an analytical error of ± 0.10 because of the small peak values of extinction coefficients (k_o and k_e) at the long-wavelength absorption bands.

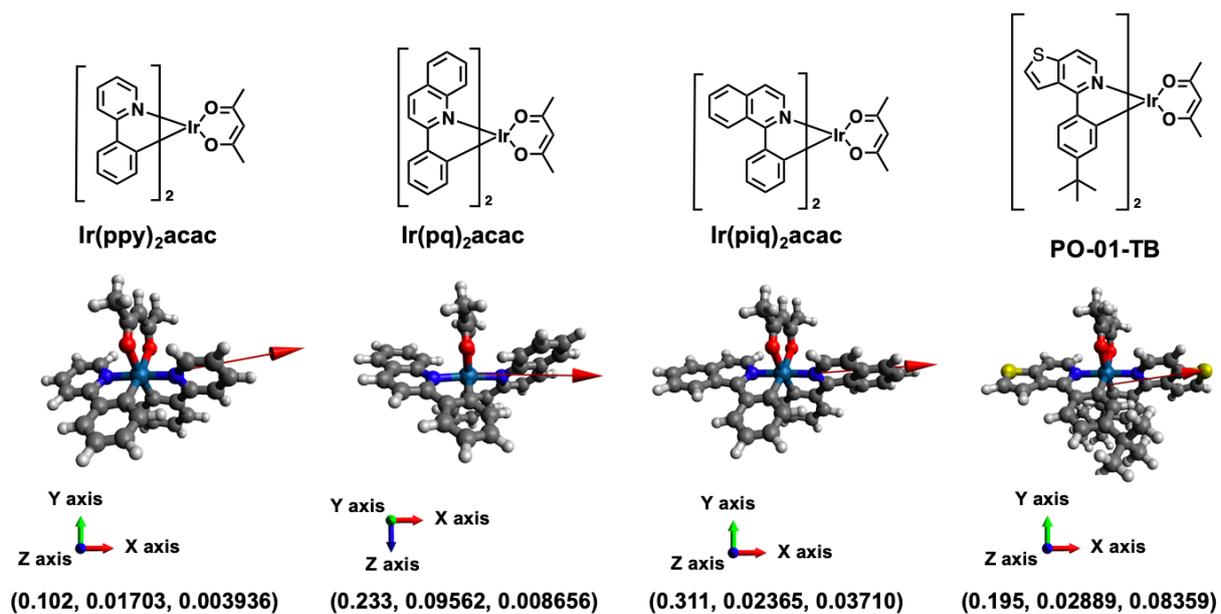


Figure S2. Chemical structures of emitters and the transition dipole moment (TDM).

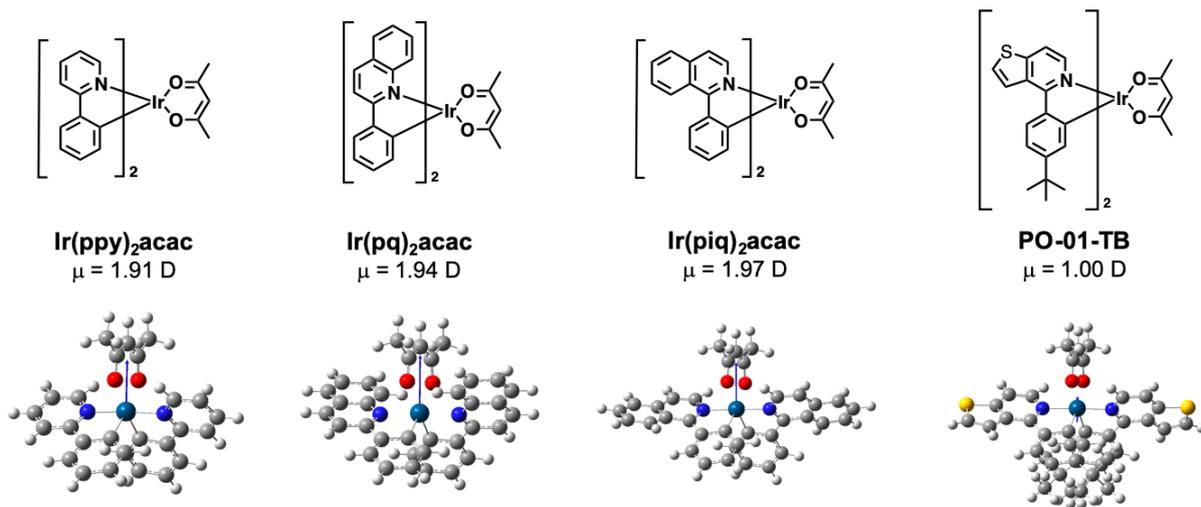


Figure S3. Permanent dipole moment (PDM) of **Ir(ppy)₂acac**, **Ir(pq)₂acac**, **Ir(piq)₂acac**, **PO-01-TB**.

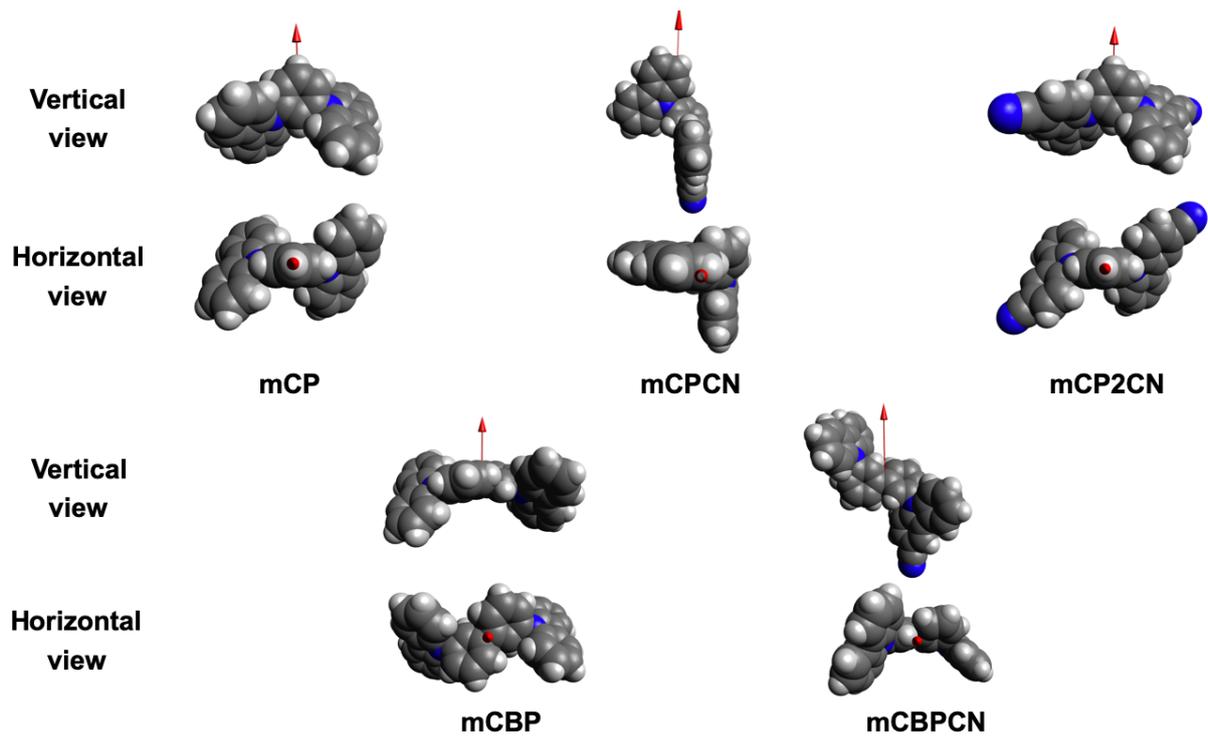


Figure S4. The transition dipole moment (TDM) of host molecules.

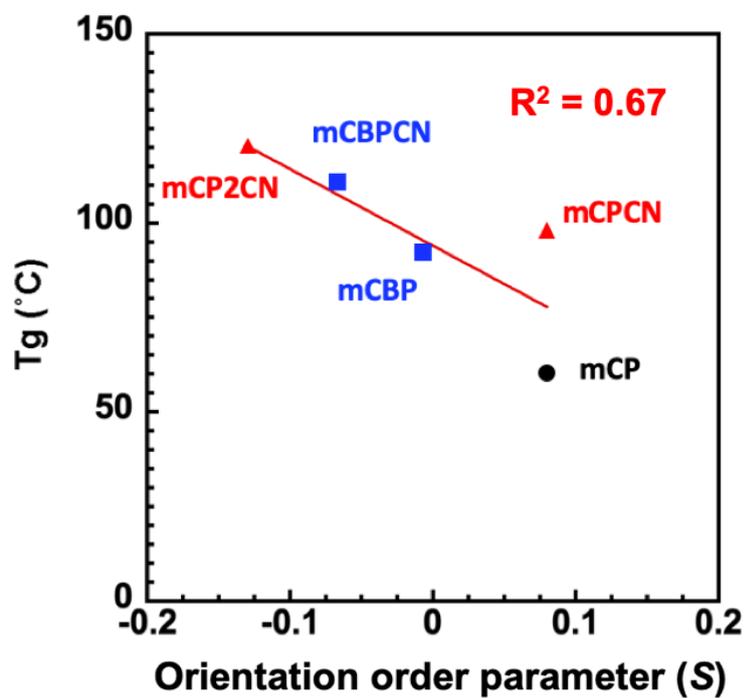


Figure S5. Relationship between orientation order parameter (S) and T_g of host molecules.

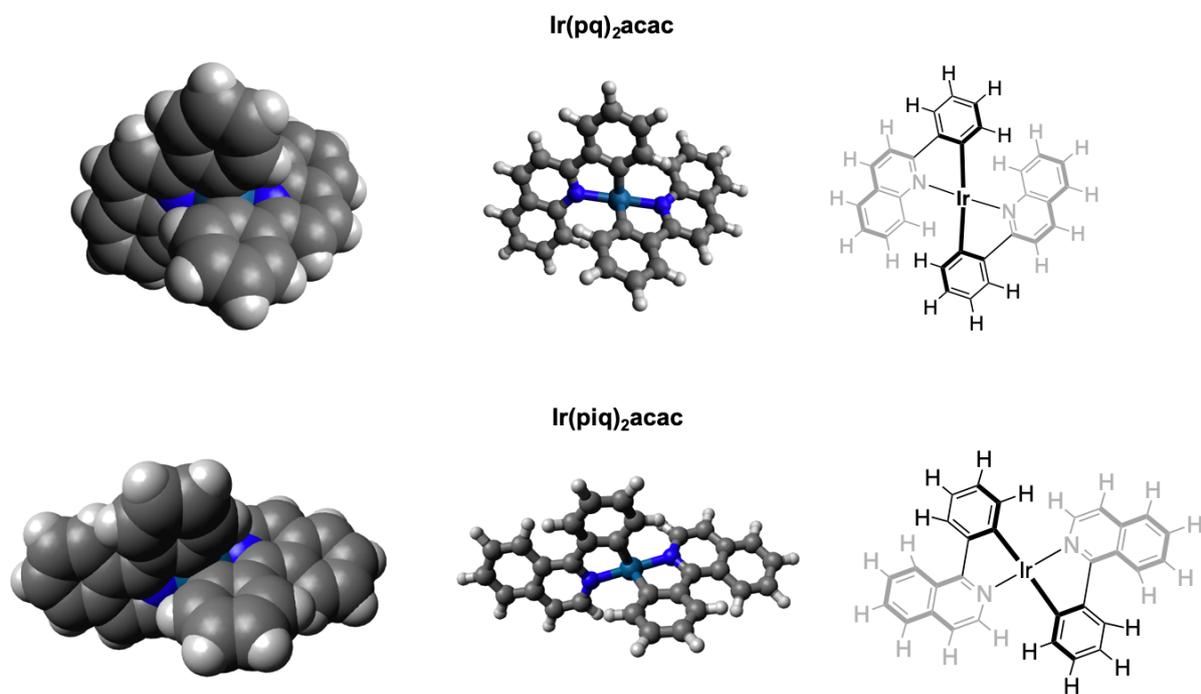


Figure S6. Bottom view of the aromatic main ligand in **Ir(pq)₂acac** and **Ir(piq)₂acac**.

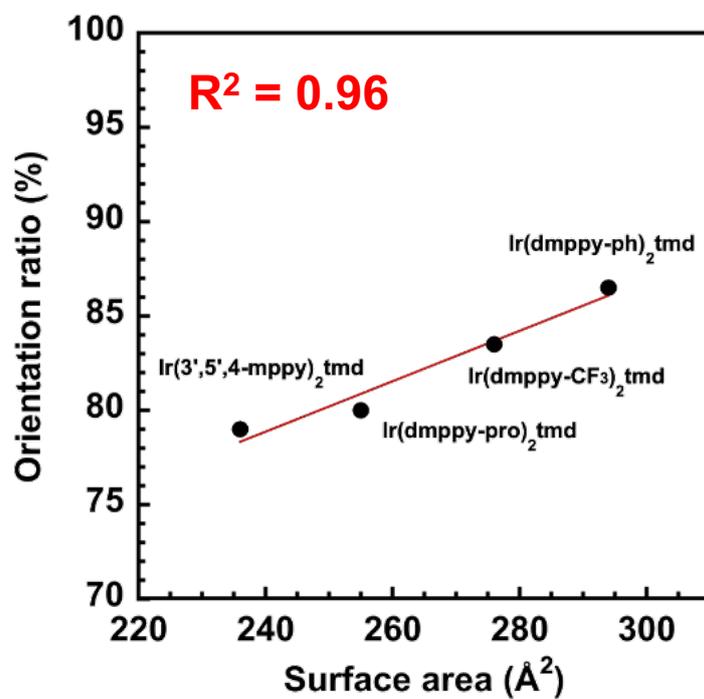
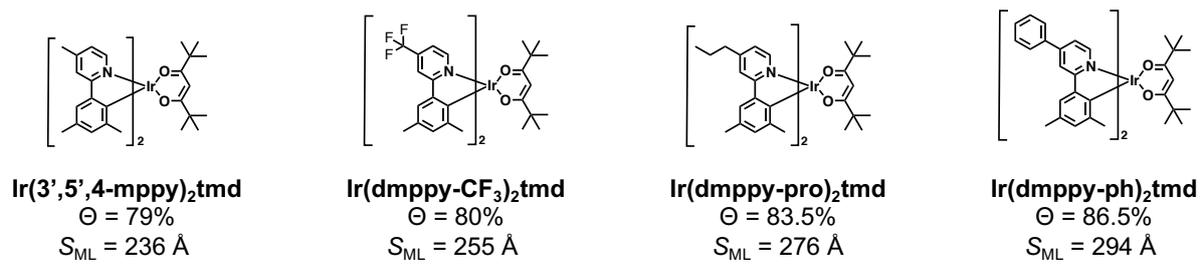


Figure S7. Relationship between Θ values and surface area of the main ligand in HICs.

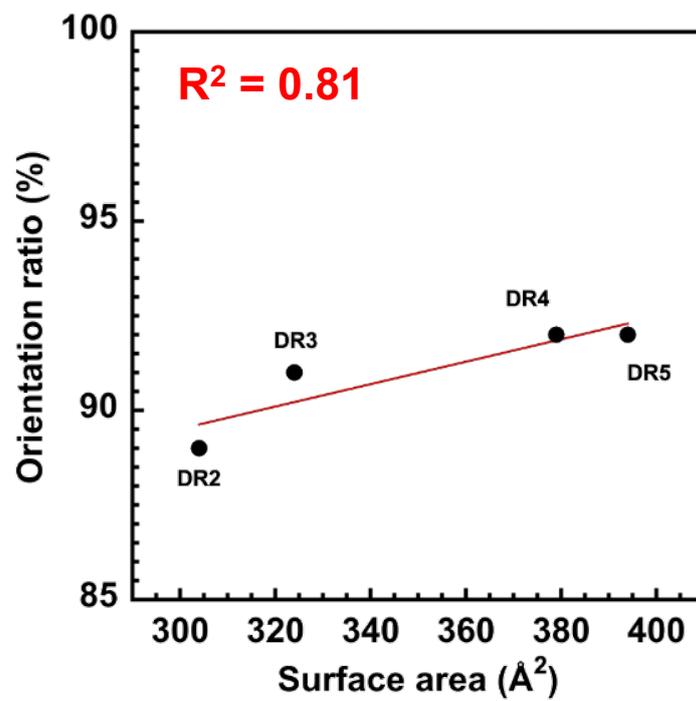
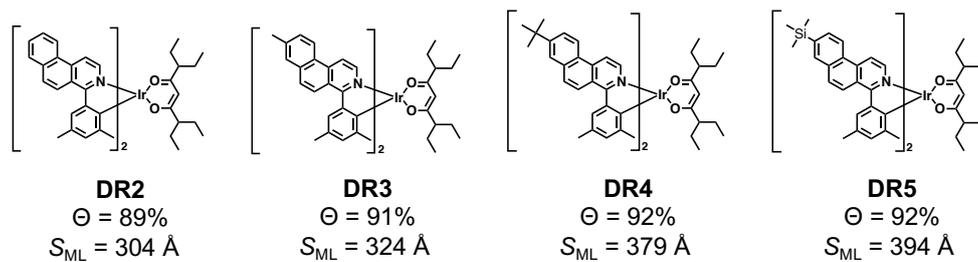


Figure S8. Relationship between Θ values and surface area of the main ligand in HICs.

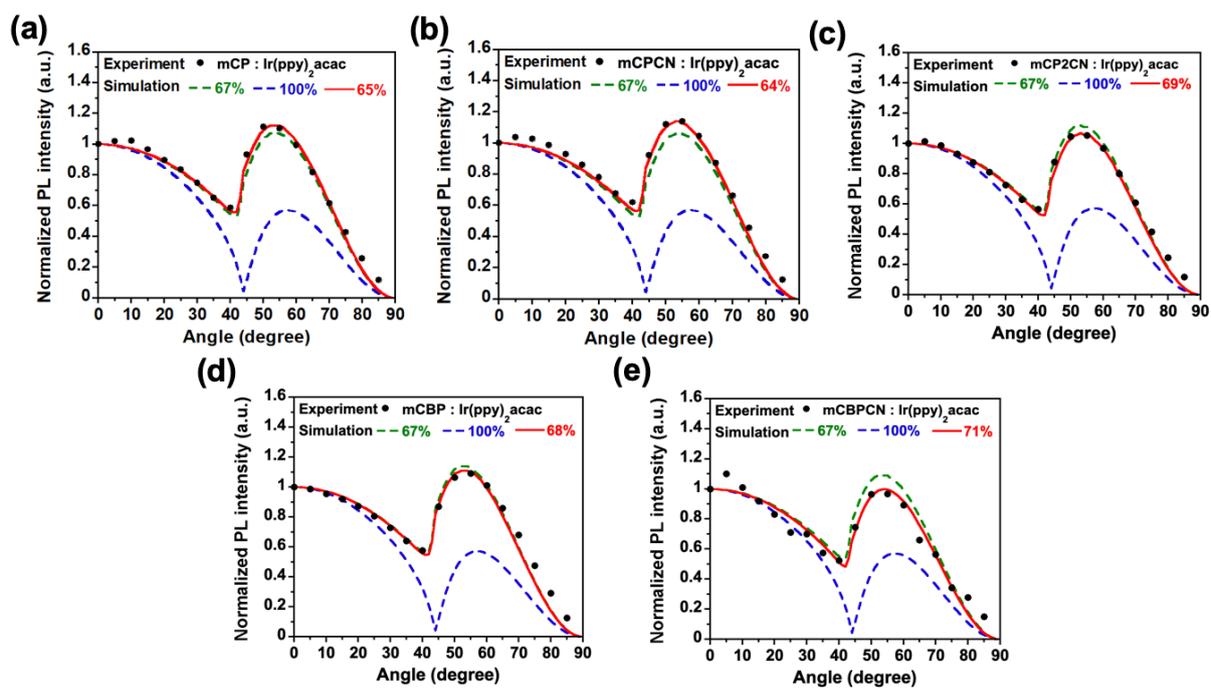


Figure S9. PL intensities of 3 wt% Ir(ppy)₂acac doped in a) mCP, b) mCPCN, c) mCP2CN, (d) mCBP, (e) mCBPCN at different angles. The experimental data are compared with the fitting curve for different horizontal dipole orientations (Θ).

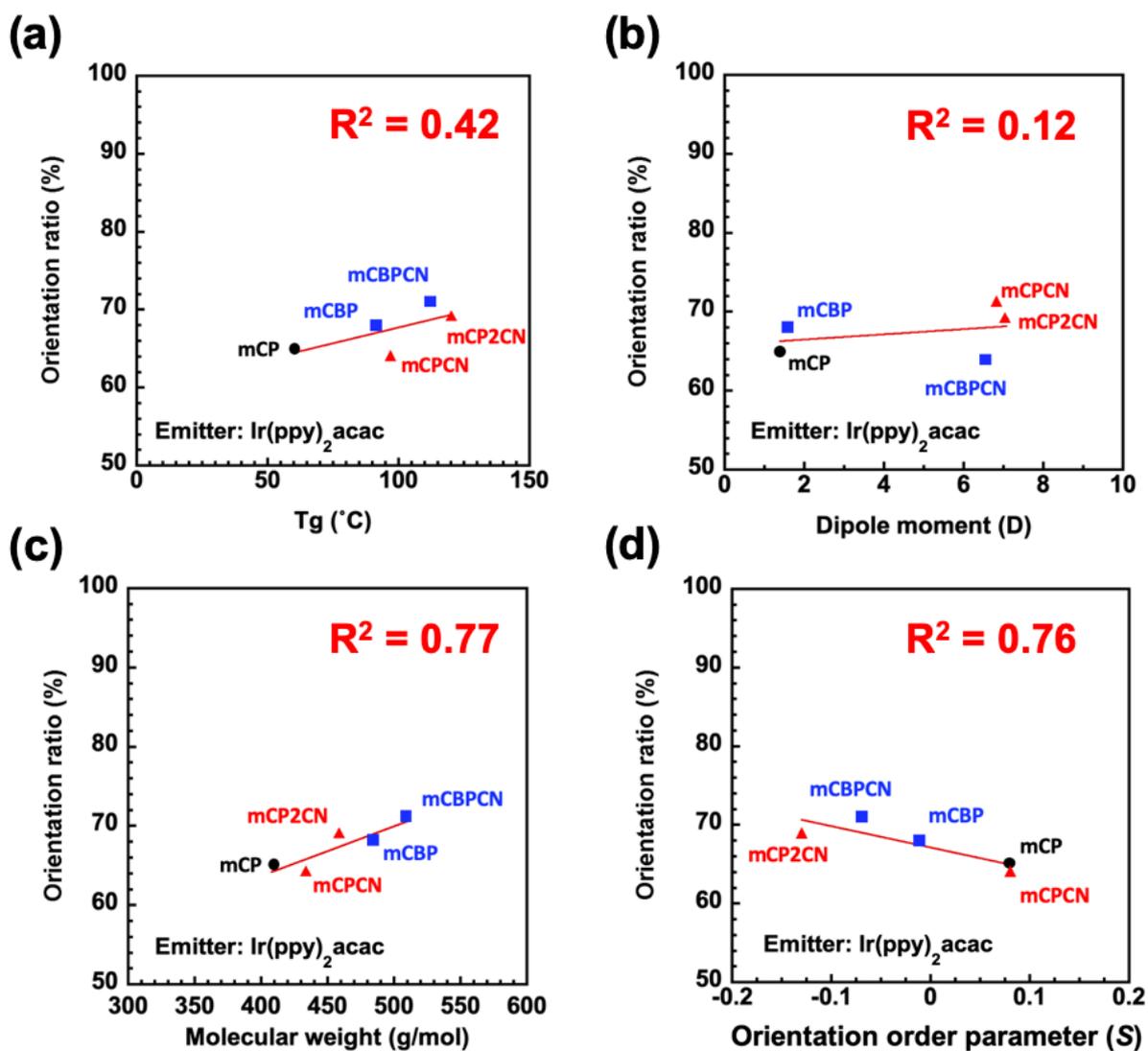


Figure S10. Relationship between Θ value of Ir(ppy)₂acac and a) T_g value, b) dipole moment, c) molecular weight, d) orientation order parameter (S) in different host materials.

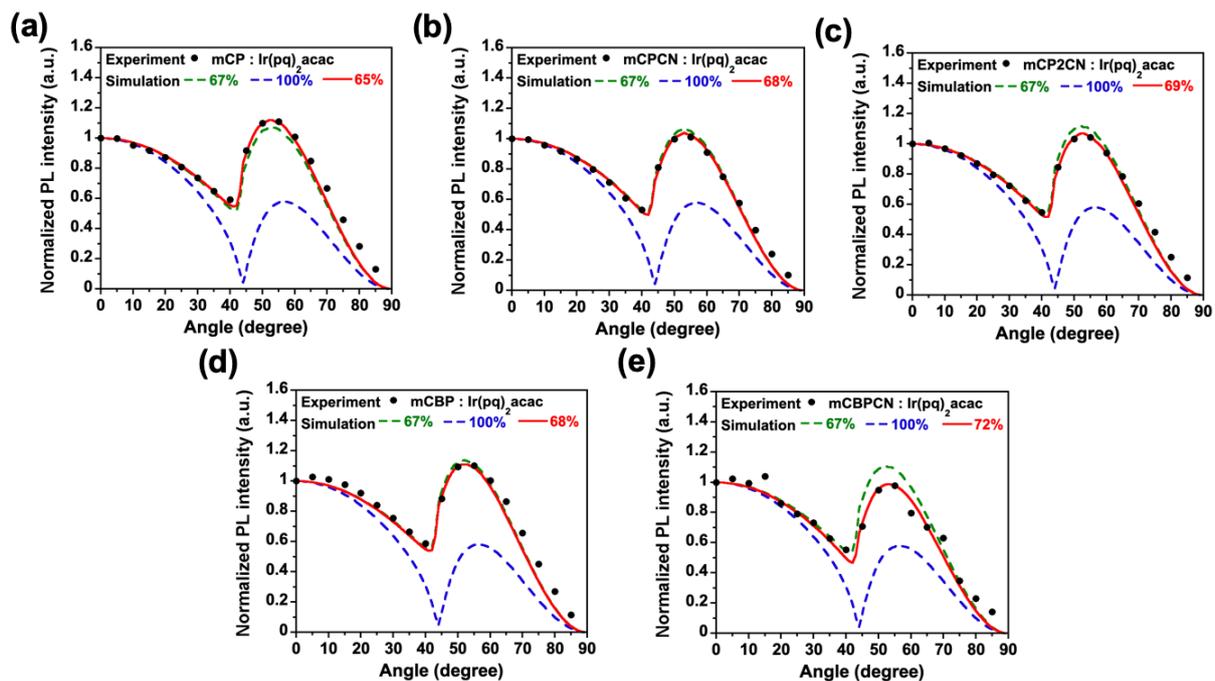


Figure S11. PL intensities of 3 wt% Ir(pq)₂acac doped in a) mCP, b) mCPCN, c) mCP2CN, (d) mCBP, (e) mCBPCN at different angles. The experimental data are compared with the fitting curve for different horizontal dipole orientations (Θ).

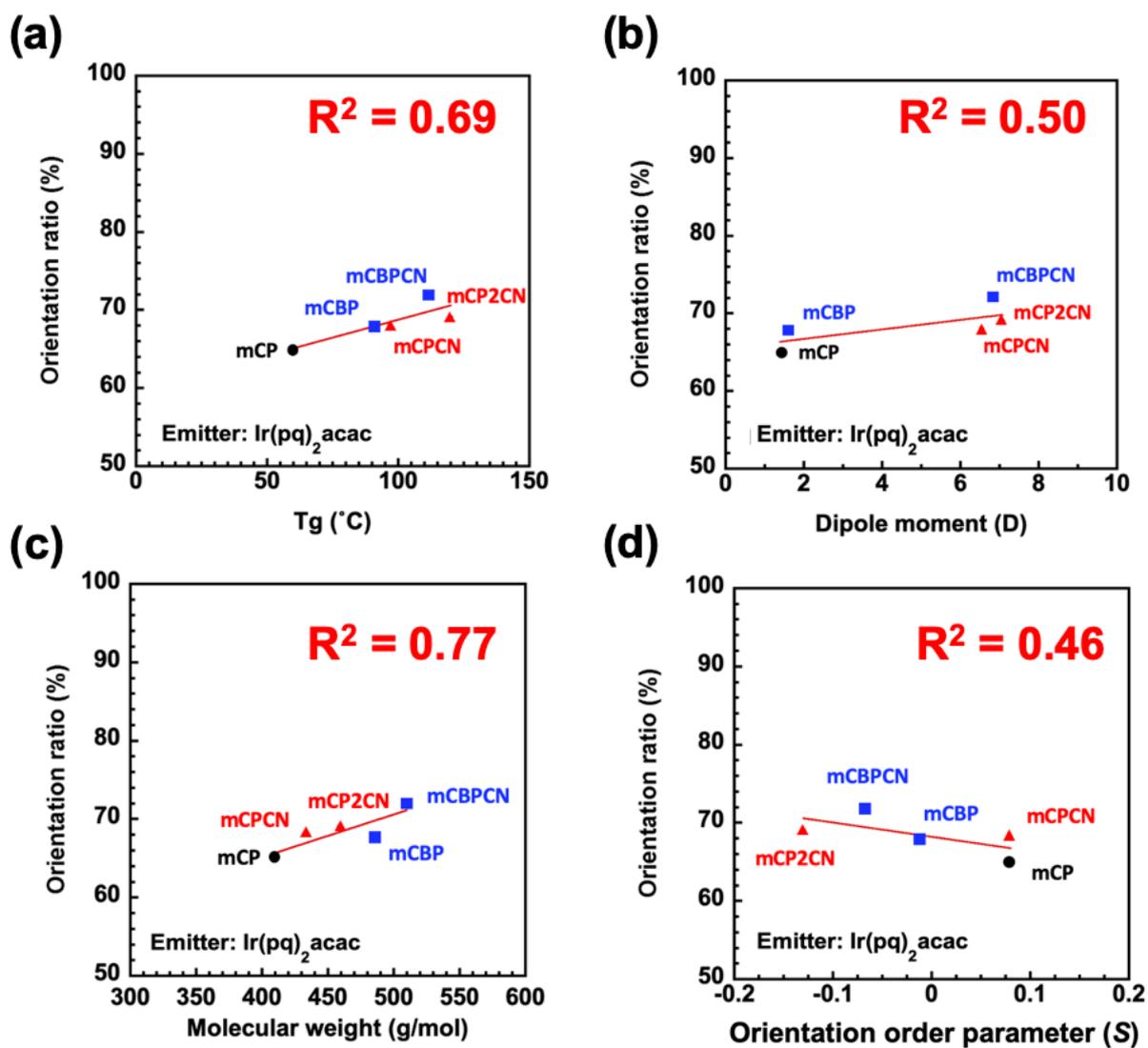


Figure S12. Relationship between Θ value of $\text{Ir}(\text{pq})_2\text{acac}$ and a) T_g value, b) dipole moment, c) molecular weight, d) orientation order parameter (S) in different host materials.

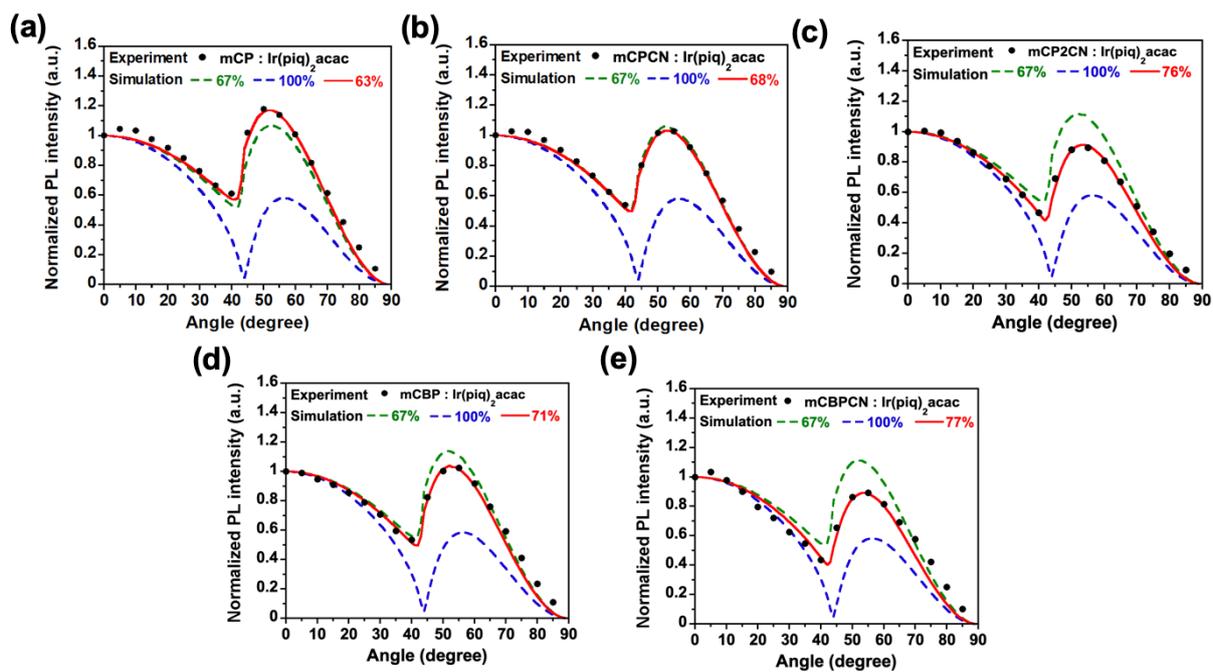


Figure S13. PL intensities of 3 wt% $\text{Ir}(\text{piq})_2\text{acac}$ doped in a) **mCP**, b) **mCPCN**, c) **mCP2CN**, (d) **mCBP**, (e) **mCBPCN** at different angles. The experimental data are compared with the fitting curve for different horizontal dipole orientations (\odot).

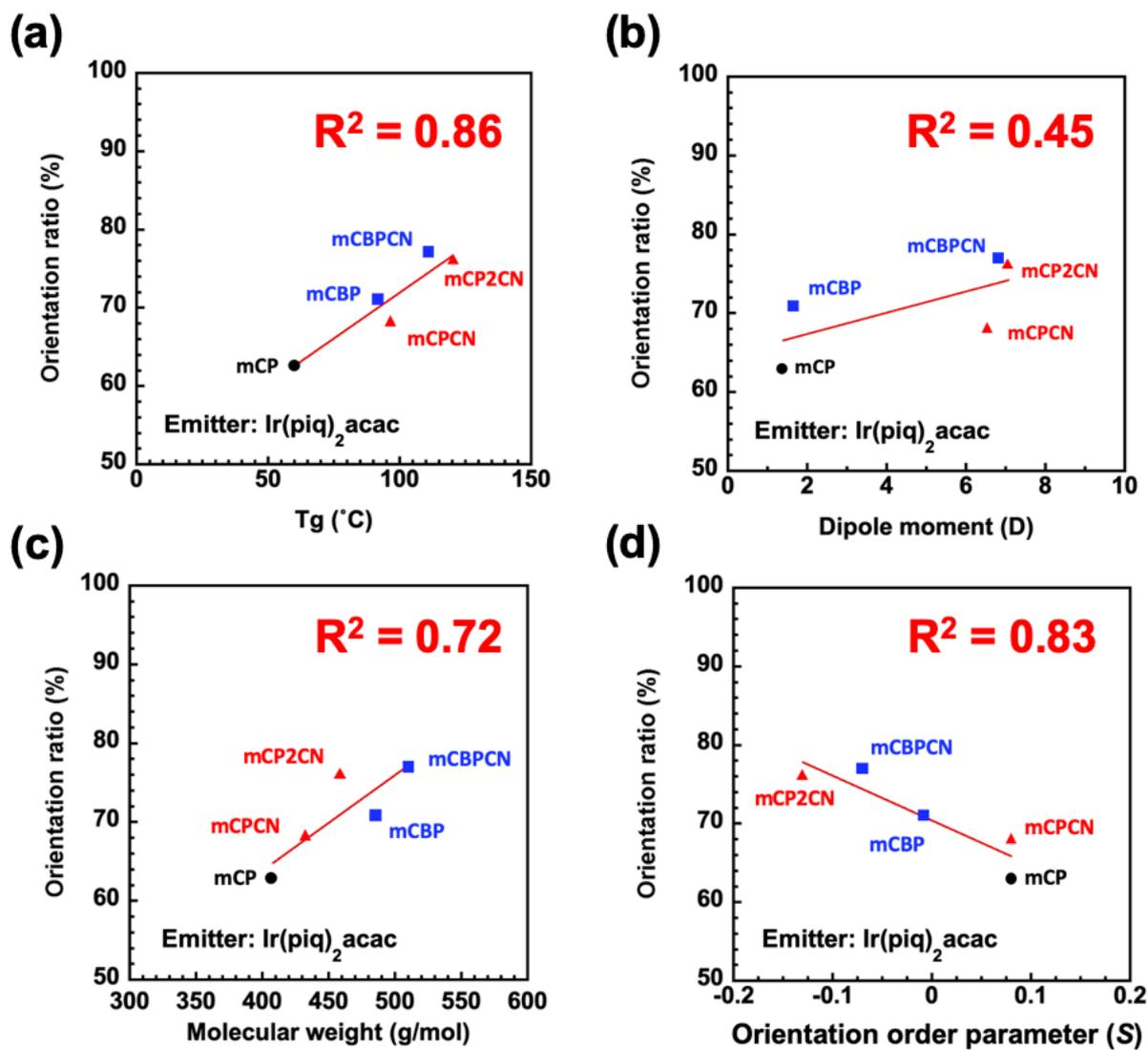


Figure S14. Relationship between Θ value of $\text{Ir}(\text{piq})_2\text{acac}$ and a) T_g value, b) dipole moment, c) molecular weight, d) orientation order parameter (S) in different host materials.

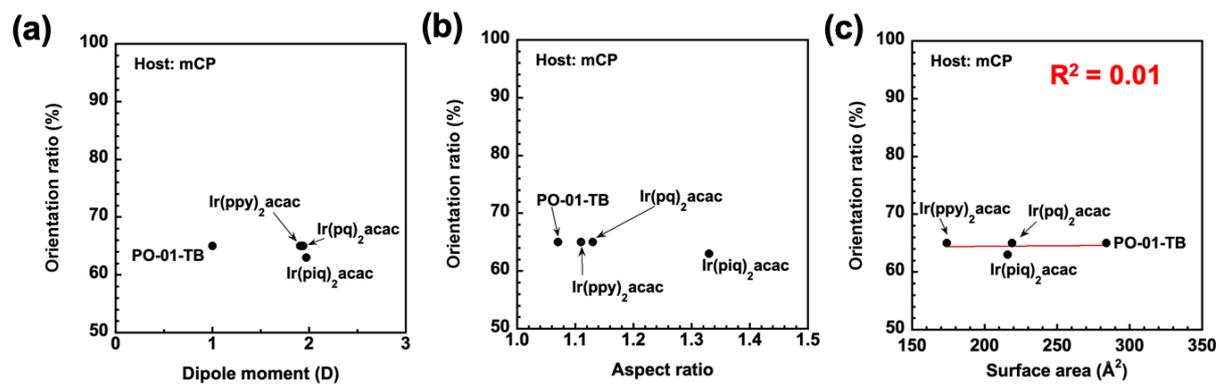


Figure S15. Relationship between Θ values of the emitters and a) dipole moment, b) aspect ratio, c) surface area of the aromatic main ligand in HICs of the emitters dispersed in **mCP** host material.

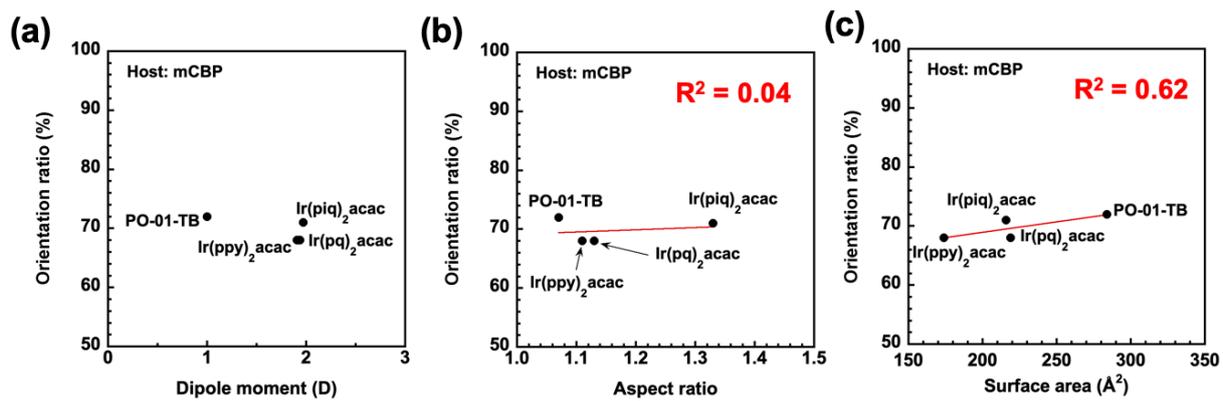


Figure S16. Relationship between Θ values of the emitters and a) dipole moment, b) aspect ratio, c) surface area of the aromatic main ligand in HICs of the emitters dispersed in **mCBP** host material.

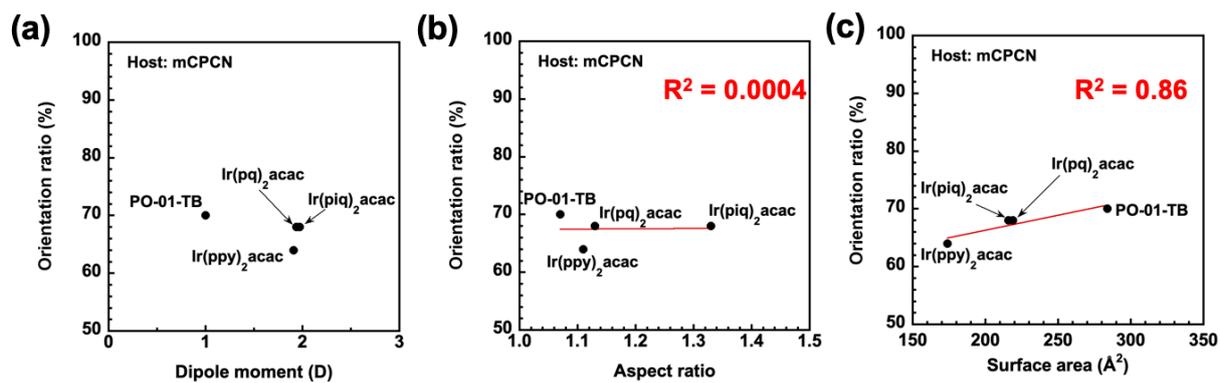


Figure S17. Relationship between Θ values of the emitters and a) dipole moment, b) aspect ratio, c) surface area of the aromatic main ligand in HICs of the emitters dispersed in **mCPCN** host material.

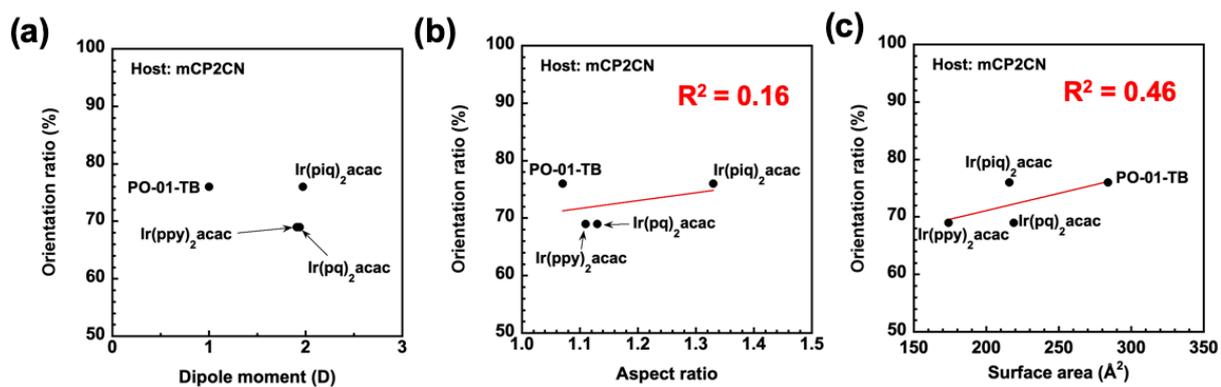


Figure S18. Relationship between Θ values of the emitters and a) dipole moment, b) aspect ratio, c) surface area of the aromatic main ligand in HICs of the emitters dispersed in mCP2CN host material.

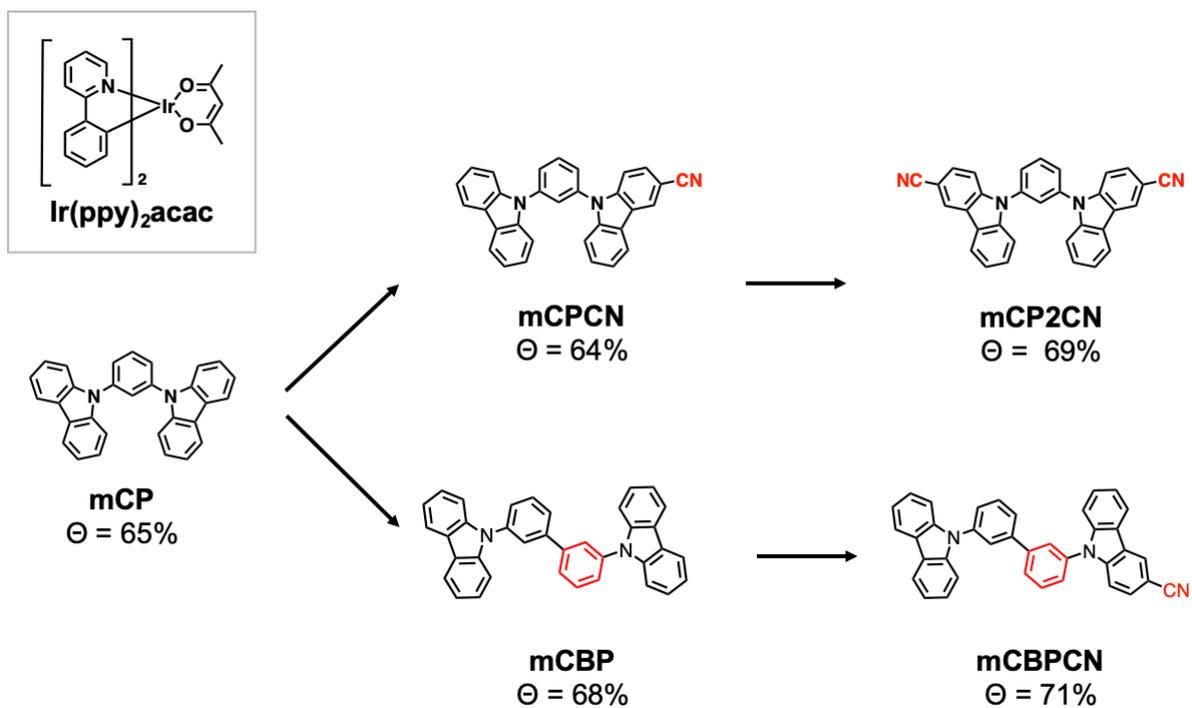


Figure S19. Chemical structures of $\text{Ir}(\text{ppy})_2\text{acac}$ and host molecules with horizontal orientation ratios (Θ).

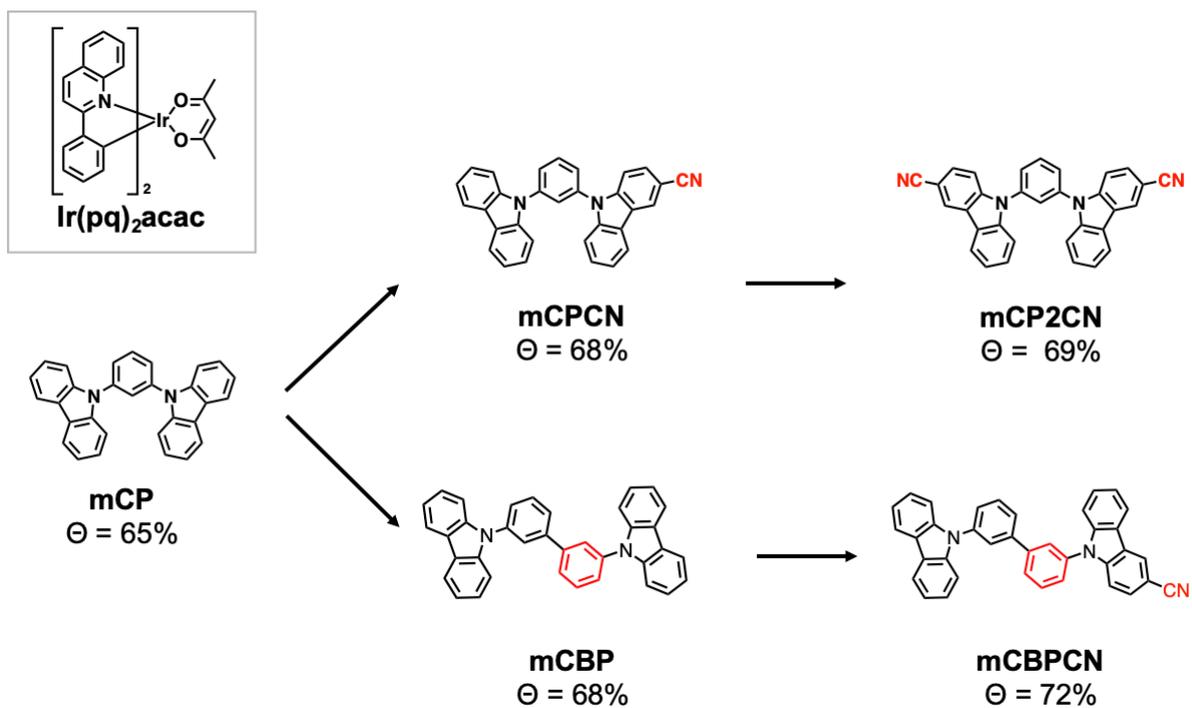


Figure S20. Chemical structures of $\text{Ir}(\text{pq})_2\text{acac}$ and host molecules with horizontal orientation ratios (Θ).

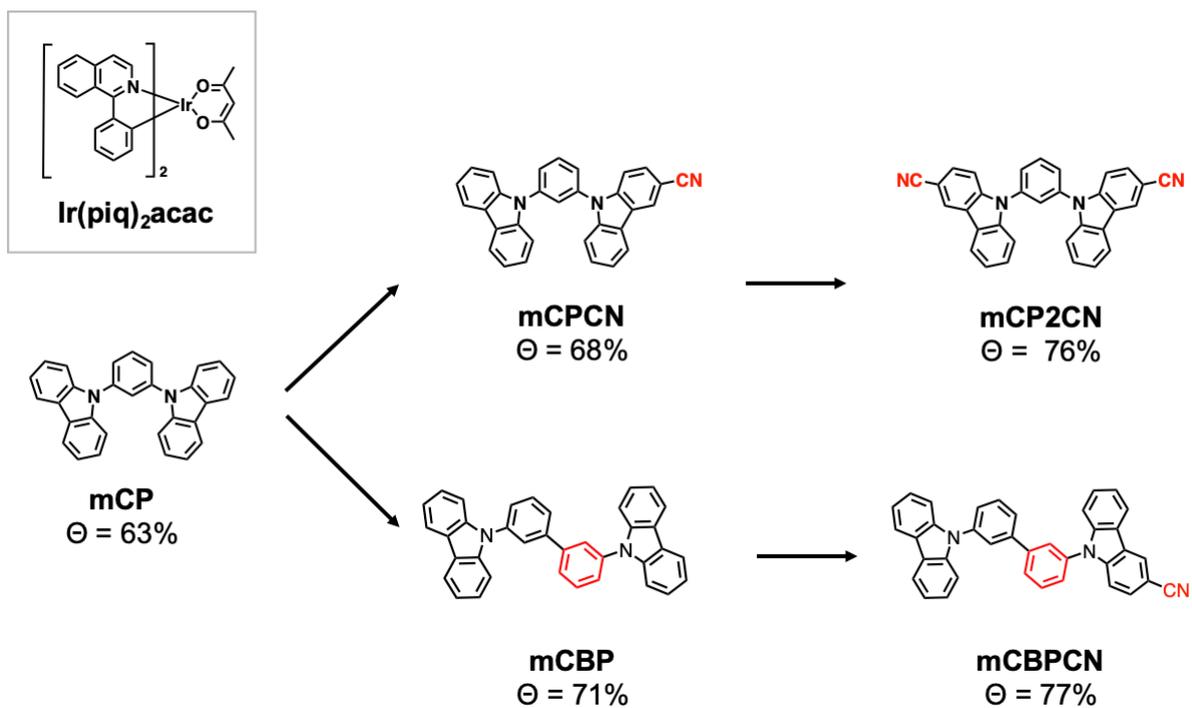


Figure S21. Chemical structures of $\text{Ir}(\text{piq})_2\text{acac}$ and host molecules with horizontal orientation ratios (Θ).

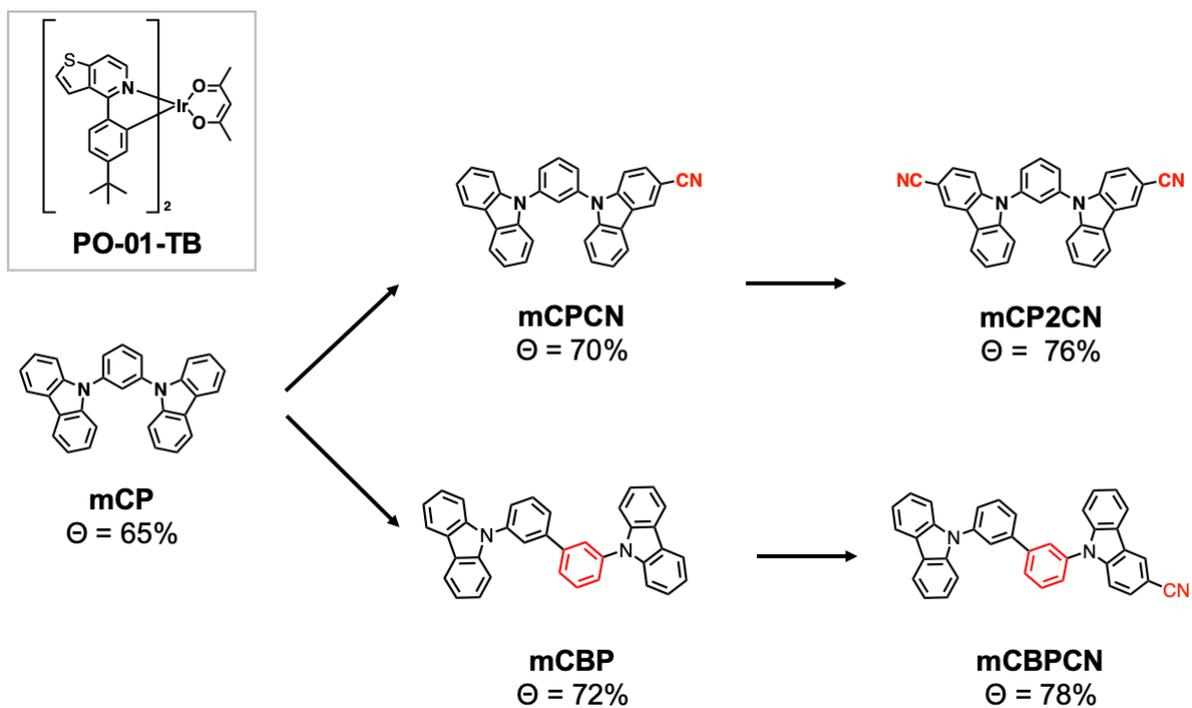


Figure S22. Chemical structures of **PO-01-TB** and host molecules with horizontal orientation ratios (Θ).

Table S1. Summary of the squared correlation coefficient (R^2) values in the relationship between the emitter orientation ratio (Θ) and i) Dipole moment, ii) T_g value, iii) Molecular weight, v) Orientation order parameter (S) of the host materials shown in **Figure 2, S8, S10 and S12.**

	PO-01-TB	Ir(ppy)₂acac	Ir(pq)₂acac	Ir(piq)₂acac	Average
T_g	0.86	0.42	0.69	0.86	0.71
Dipole moment	0.49	0.12	0.50	0.45	0.39
Molecular weight	0.74	0.77	0.77	0.72	0.75
Orientation order parameter (S)	0.76	0.76	0.46	0.83	0.71