

Supplementary Information for

Bayesian Molecular Optimization for Accelerating Reverse Intersystem Crossing

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This PDF file includes:

Figs. S1 to S6

Table S1

Supplementary method and materials

Supplementary synthesis

Supplementary note

1. Supplementary figures

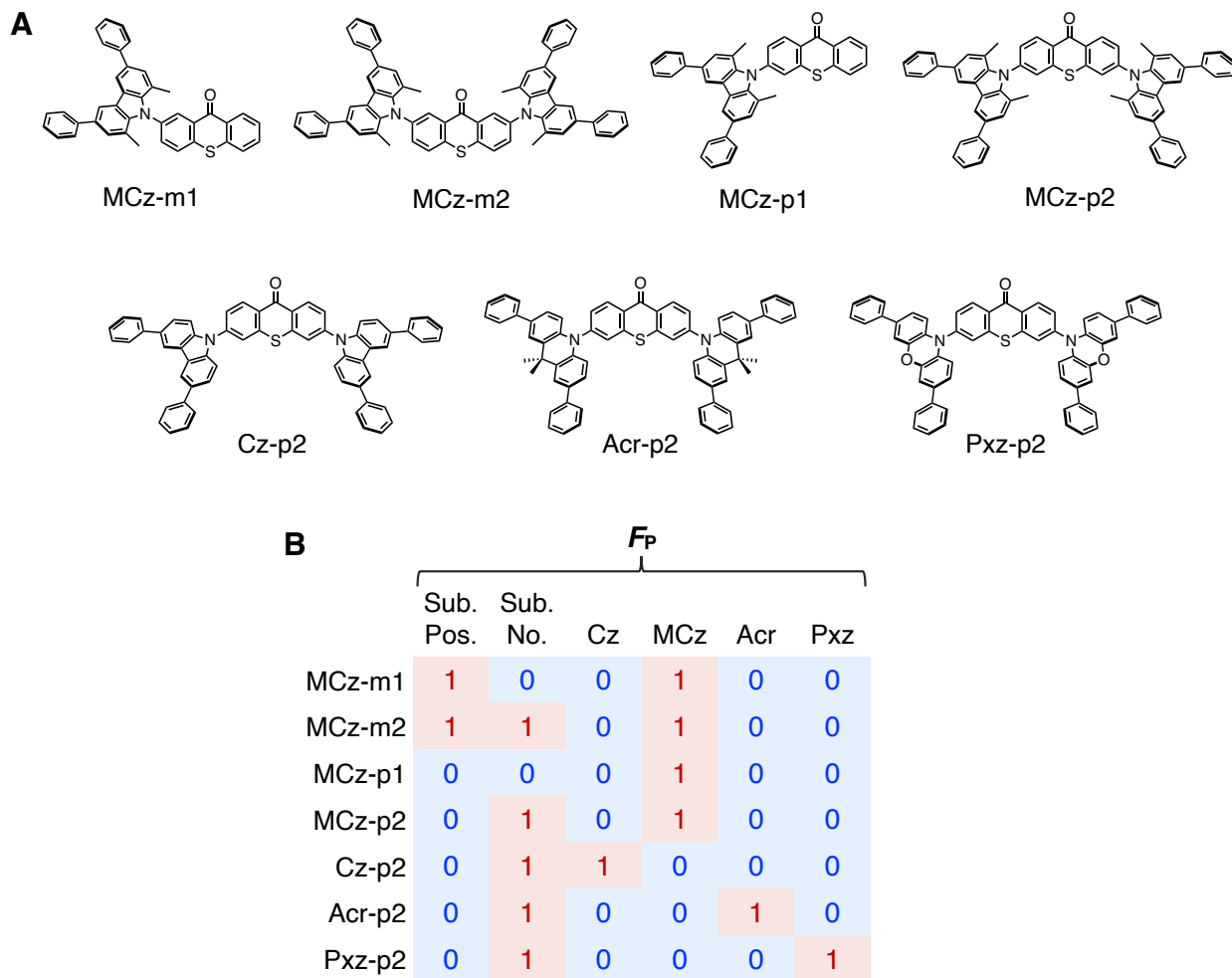


Fig. S1. Seven thioxanthone derivatives. (A) Molecular structures of MCz-m1, MCz-m2, MCz-p1, MCz-p2, Cz-p2, Acr-p2, and Pxz-p2. (B) Relevant F_P in a six-dimensional space.

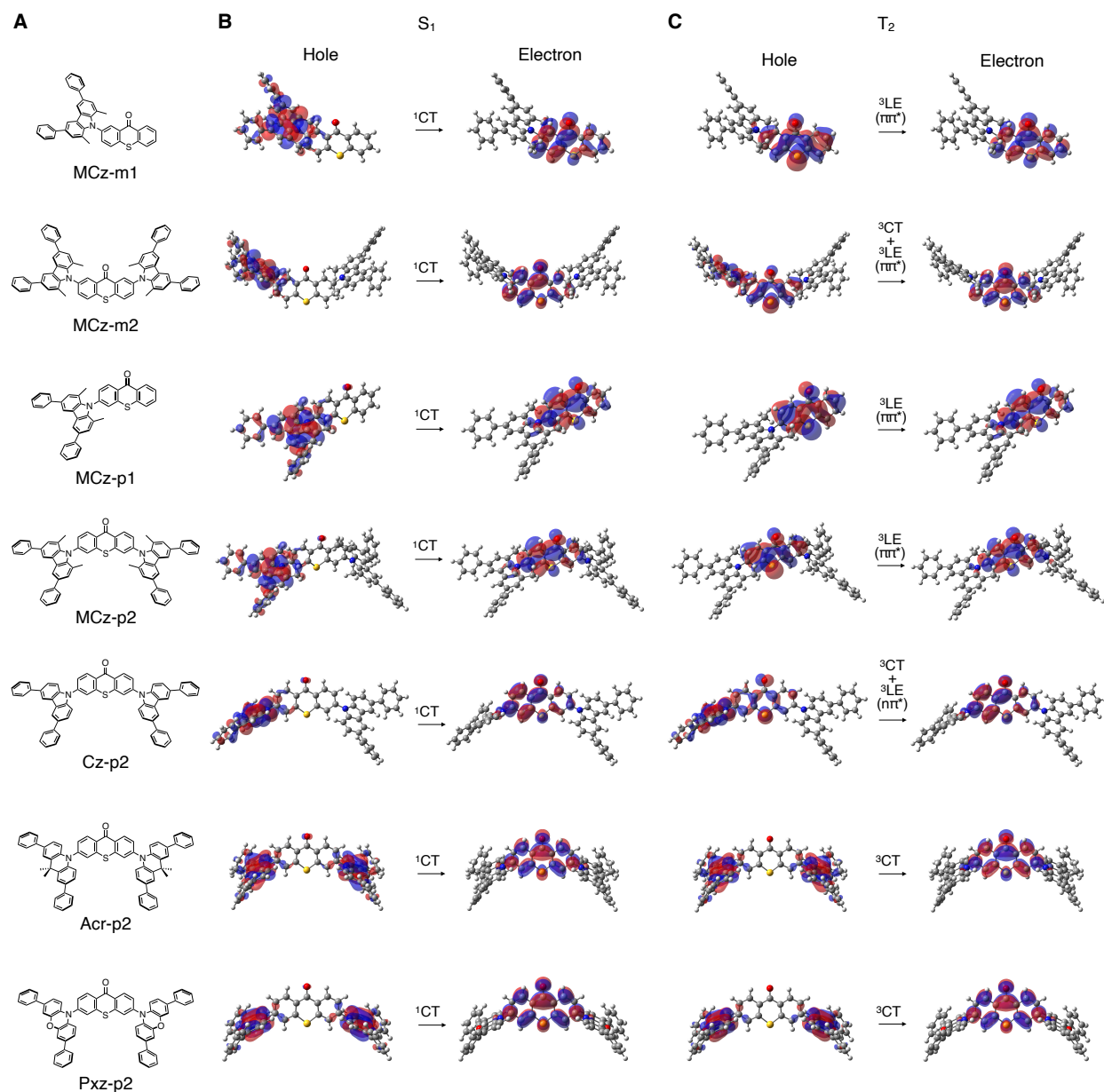


Fig. S2. Electronic configurations at the minimum-energy singlet-triplet crossing seam. (A) Molecular structures of MCz-m1, MCz-m2, MCz-p1, MCz-p2, Cz-p2, Acr-p2, and Pxz-p2. **(B)** Natural transition orbitals (NTOs) for S_1 and T_2 of the seven molecules calculated at the minimum-energy S_1/T_2 crossing seam.

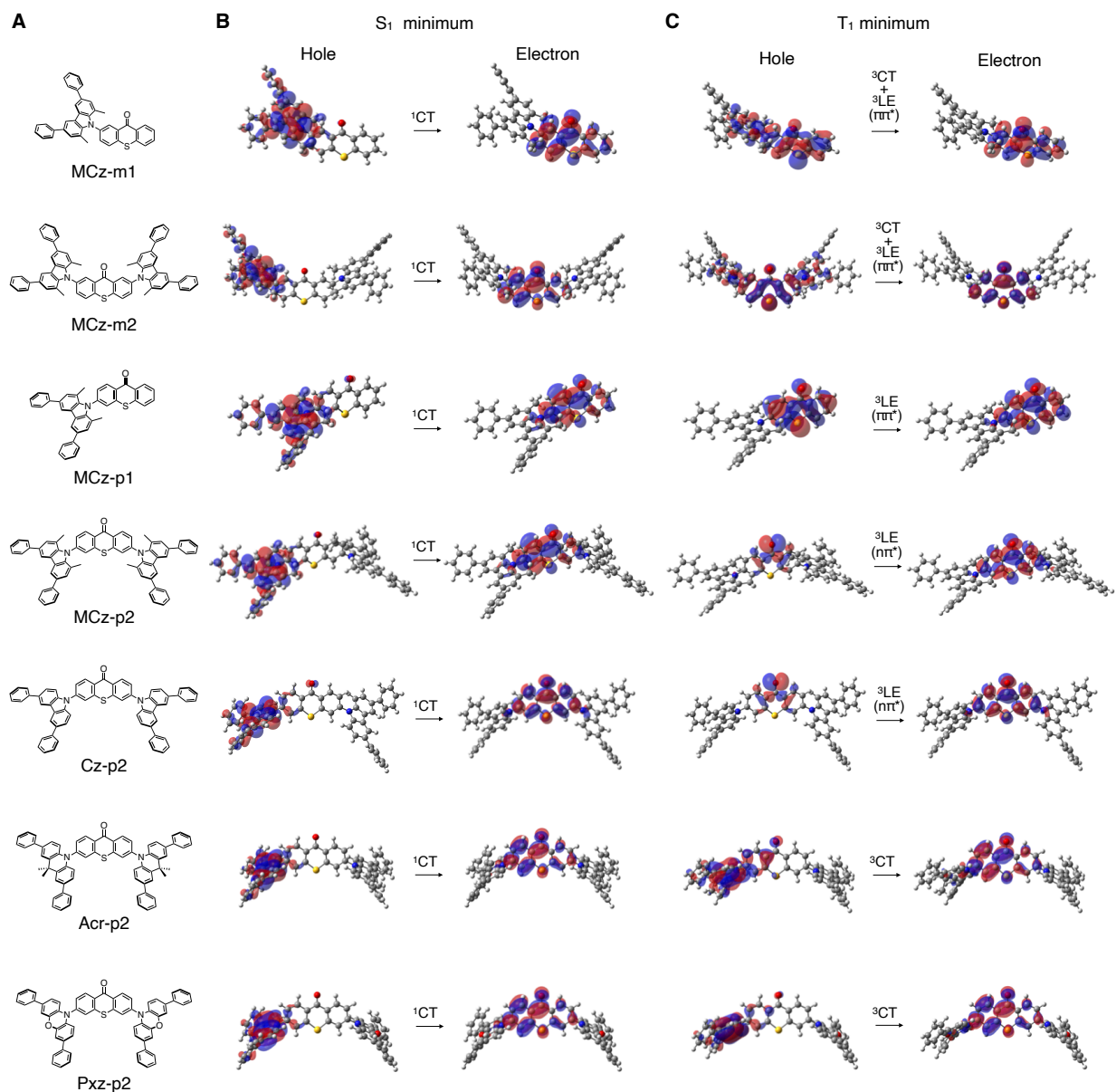


Fig. S3. Electronic configurations at the minimum-energy S_1 and T_1 geometries. (A) Molecular structures of MCz-m1, MCz-m2, MCz-p1, MCz-p2, Cz-p2, Acr-p2, and Pxz-p2. (B) NTOs for S_1 and T_1 of the seven molecules calculated at the minimum-energy S_1 and T_1 geometries.

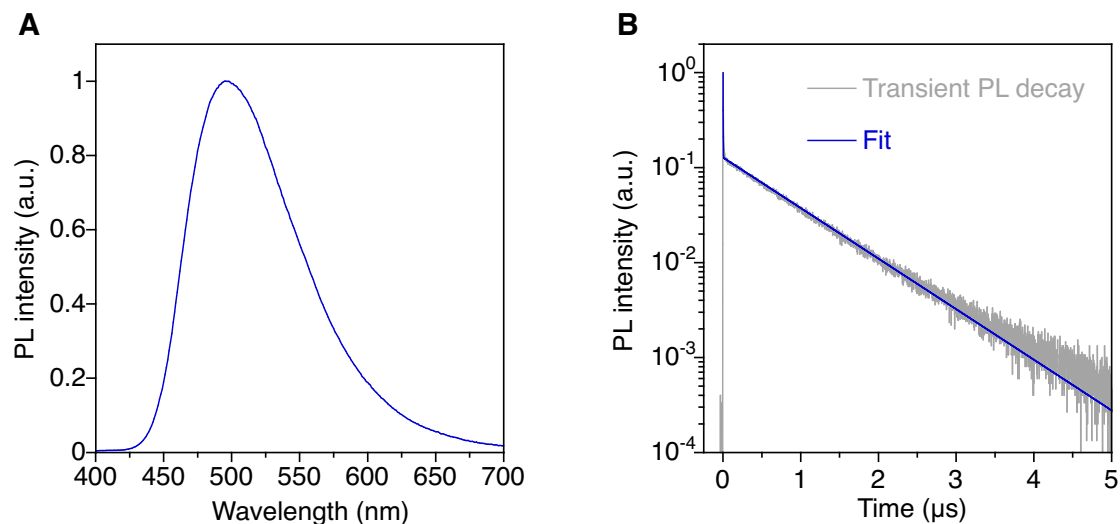


Fig. S4. PL of mCBP. (A) Steady-state PL spectra of a 12wt% MCz-p2:mCBP film. (B) Transient PL decays of a MCz-p2:mCBP film measured with picosecond pulsed excitation at 375 nm. The blue line in (B) shows the fit of the transient PL decay to Eq. (2) in ‘Methods’ in the main text.

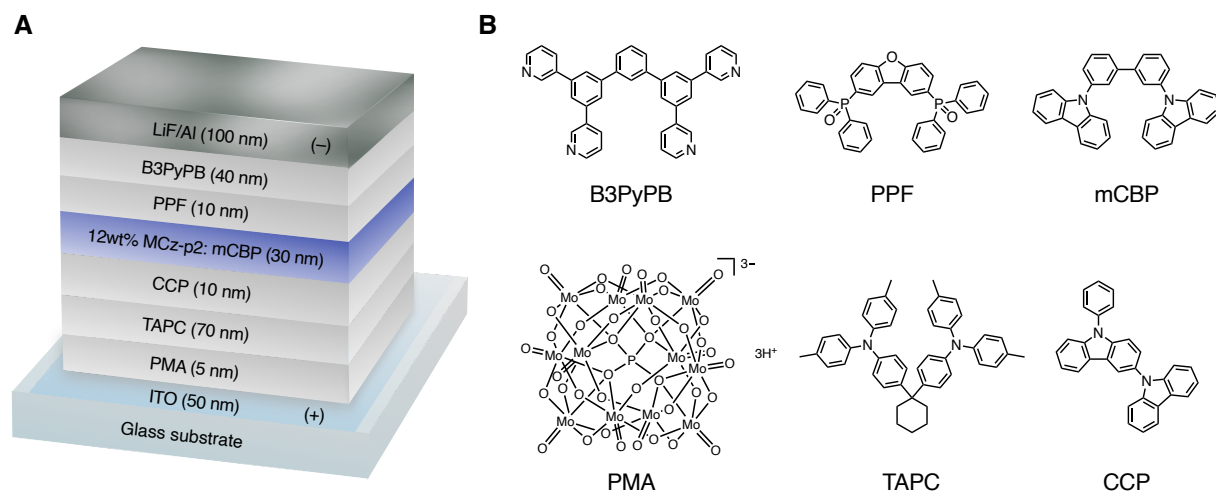


Fig. S5. OLED structure and molecular structures. (A) Device structure of the fabricated OLEDs. (B) Molecular structures of relevant materials.

Table S1. Experimental emission properties of a 12wt%-MCz-p2:mCBP fim

λ_{PL} (nm) ^a	Φ_{PL} (%) ^b	τ_{PF} (ns) ^c	τ_{DF} (ns) ^d	k_{r} (s ⁻¹) ^e	k_{nr} (s ⁻¹) ^f	k_{ISC} (s ⁻¹) ^g	k_{RISC} (s ⁻¹) ^h	ΔE_{ST} ⁱ (eV)
495	78	1.4	816	7.4×10^6	2.1×10^6	6.1×10^8	9.2×10^7	0.021

^aPhotoluminescence (PL) peak wavelength. ^bPL quantum yield. ^cTime constant of prompt fluorescence.

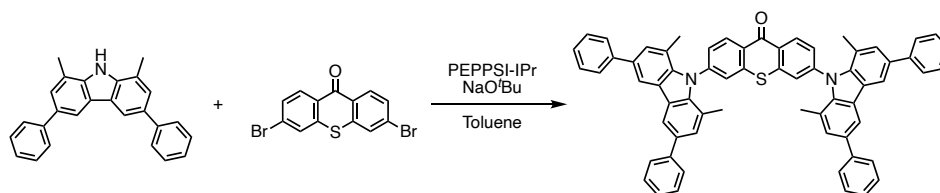
^dTime constant of delayed fluorescence. ^eRate constant of radiative decay of the S₁ state to the S₀ state. ^fRate constant of non-radiative decay of the S₁ state to the S₀ state. ^gRate constant of intersystem crossing (ISC) of the S₁ state to the T₁ state. ^hRate constant of reverse intersystem crossing (RISC) of the T₁ state to the S₁ state. ⁱEnergy gap between the S₁ and T₁ states, estimated from the $k_{\text{RISC}}/k_{\text{ISC}}$ ratio, assuming the equilibrium between the S₁ state and the three T₁ sublevels.

2. Supplementary method and materials

¹H and ¹³C NMR spectra were recorded on a Bruker Avance III HD. The chemical shifts (δ in ppm) were determined using tetramethylsilane as an internal reference. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker Autoflex III in the reflector mode using dithranol as a matrix. Commercially available reagents and solvents were used as received unless otherwise noted. 2,4,5,6-Tetra(carbazol-9-yl)isophthalonitrile (4CzIPN) was purchased from Luminescence Technology Corporation. Phosphomolybdic acid (PMA) and 1,1-bis(4-di-*p*-tolylaminophenyl)cyclohexane (TAPC) were purchased from Tokyo Chemical Industry. LiF and Al were purchased from Furuuchi Chemical. 9-Phenyl-3,9'-bicarbazole (CCP), 3,3'-bis(carbazol-9-yl)biphenyl (mCBP), 2,8-bis(diphenylphosphoryl)dibenzo[*b,d*]furan (PPF), and 1,3-bis[3,5-di(pyridine-3-yl)phenyl]benzene (B3PyPB) were prepared according to procedures described in the literature.

3. Supplementary synthesis

Scheme S1. Synthesis of MCz-p2. Palladium-catalyzed Buchwald–Hartwig amination of 3,6-dibromothioxanthone with 1,8-dimethyl-3,6-diphenyl-9*H*-carbazole.



A mixture of 1,8-dimethyl-3,6-diphenyl-9*H*-carbazole (0.35 g, 1.0 mmol), 3,6-dibromothioxanthone (0.17 g, 0.46 mmol), PEPPSI-IPr (0.04 g, 0.05 mmol), and Sodium *t*-butoxide (0.15 g, 1.6 mmol) in dry toluene (15 mL) was refluxed for 36 hours. After cooling to room temperature, the reaction mixture was poured into water and extracted with CHCl₃. The combined organic layers were concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography (eluent: CHCl₃/*n*-hexane = 1:2, v/v) to afford MCz-p2 as a yellow solid (0.30 g, 72%). ¹H NMR (600 MHz, CDCl₃): δ 8.84 (d, *J* = 8.4 Hz, 2H), 8.27 (s, 4H), 7.81 (s, 2H), 7.78 (d, *J* = 9.0 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 8H), 7.48 (t, *J* = 7.7 Hz, 8H), 7.41 (s, 4H), 7.35 (t, *J* = 7.4 Hz, 4H), 2.06 (s, 12H). ¹³C NMR (150 MHz, CDCl₃): δ 178.88, 146.24, 141.53, 140.64, 137.16, 134.16, 130.47, 129.94, 129.86, 128.93, 128.78, 128.33, 127.26, 126.73, 125.21, 121.70, 116.66, 20.07. MS (MALDI-TOF): *m/z* 902.33355 [M]⁺; calcd. for C₆₅H₄₆N₂OS 902.33308, error = 2.68 ppm.

4. Supplementary note

The virtual search space of 1.4 thousand molecules is listed below. All molecules share a common thioxanthone acceptor unit incorporate diverse donor units.

