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## **Supplementary Information**

Efficient tuning of the conversion from ISC to high-level RISC via adjusting the triplet energies of charge-transporting layers in rubrene-doped OLEDs

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Abbreviation	HOMO [eV]	LUMO [eV]	Ref.
<i>m</i> -MTDATA	-5.1	-2.0	[1]
TCTA	-5.2	-1.7	[2]
NPB	-5.4	-2.4	[3]
CBP	-6.0	-2.3	[4]
Rubrene	-5.4	-3.2	[5]
Alq <sub>3</sub>	-5.6	-3.0	[6]
BCP	-6.4	-2.9	[7]
PO-T2T	-7.5	-3.5	[8]

 Table S1. Energy levels of the materials used in the main article.



Figure S1 Photoluminescence spectrum of CBP film and absorption spectrum of rubrene film at room temperature.



**Figure S2** (a) Schematic diagrams of the ISC process from singlet ( $PP_1$ ) to triplet polaron pairs ( $PP_3$ ) states in absence and presence of an external magnetic field and ISC-determined MEL fingerprint curve. (b) Schematic diagrams of the RISC process from triplet ( $CT_3$ ) to singlet charge-transfer ( $CT_1$ ) states without and with magnetic field and RISC-induced MEL fingerprint curve.



Figure S3 (a) The current dependence of MEL responses in reference device at 300 K. (b) Temperature-dependent MEL responses of reference device at a fixed bias current of 50  $\mu$ A.



Figure S4 Schematic diagram of microscopic mechanisms in Device 2 and its energy level structure.



Figure S5 (a) Temperature-dependent normalized EL spectra for Device 4 at a bias current of 100  $\mu$ A. (b) Current-dependent EL spectra for Device 4 at 300 K.



Figure S6 (a) Energy level alignment of Device 4. (b) Schematic diagram of microscopic mechanisms in Device 4.



Figure S7 Temperature-dependent MEL responses of (a) Device 6, (b) Device 7, and (c) Device 8.

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