Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information: Breaking the Trade-off Between ΔE_{ST} and Oscillator Strength in Hybrid LR/SR-CT Compounds for Enhanced TADF Performance

Nikhitha R.[1] and Anirban Mondal[1,*]

[1]Department of Chemistry, Indian Institute of Technology Gandhinagar, Gujarat, 382355, India

October 25, 2024

E-mail: amondal@iitgn.ac.in

S1 Internal and External Quantum efficiencies

The Internal Quantum Efficiency (IQE) can be calculated using equation 1:[1]

$$\phi_{\mathrm{IQE}} = \eta_{\mathrm{r}}(S_1)\phi_{\mathrm{PF}} + \eta_{\mathrm{r}}(S_1)\phi_{\mathrm{ISC}}\phi_{\mathrm{RISC}} + \eta_{\mathrm{r}}(T_1)\phi_{\mathrm{RISC}} \tag{1}$$

Here, $\eta_{\mathrm{r}}(S_1) = 0.25$ and $\eta_{\mathrm{r}}(T_1) = 0.75$, which is the splitting of the singlet and triplet excitons according to spin statistics, respectively. ϕ_{PF}, ϕ_{ISC}, and ϕ_{RISC} denote the corresponding efficiencies of prompt fluorescence, inter-system crossing, and reverse inter-system crossing. These values are obtained using the following expressions:[2,3]

$$\phi_{\mathrm{PF}} = 1 - \phi_{\mathrm{ISC}} \tag{2}$$

$$\phi_{\mathrm{ISC}} = \frac{k_{\mathrm{ISC}}}{k_{\mathrm{PF}}} \tag{3}$$

$$\phi_{\mathrm{RISC}} = \frac{\phi_{\mathrm{TADF}}}{\phi_{\mathrm{ISC}}} \tag{4}$$

$$\phi_{\mathrm{TADF}} = \frac{k_{\mathrm{ISC}}\ k_{\mathrm{RISC}}\ \phi_{\mathrm{PF}}}{k_{\mathrm{PF}}k_{\mathrm{TADF}}} \tag{5}$$

where k_{PF}, k_{ISC}, k_{RISC}, and k_{TADF} are the corresponding rates of prompt fluorescence, inter-system crossing, reverse inter-system crossing, and delayed fluorescence in s^{-1}. ϕ_{TADF} is the efficiency of the TADF process.

External Quantum Efficiency (EQE) is evaluated using:[2]

$$\phi_{\mathrm{EQE}} = \phi_{\mathrm{IQE}}\ \eta_{\mathrm{out}} \tag{6}$$

η_{out} is the light outcoupling efficiency having values in the range of 0.2 to 0.3.[2] We have taken a value of 0.25 as the light outcoupling efficiency. The unphysical EQE values obtained for compounds A6 and A11 are attributed to the large k_{ISC} rates that are an order of magnitude higher than the corresponding k_{PF} rates.

Table S1: Calculated spin-orbit coupling ($H_{\text{SO}}^{\text{S}_1\text{T}_1}$ in cm^{-1}), reorganization energy values of ISC (λ_{ISC} in eV) and RISC (λ_{RISC} in eV) for the designed emitters.

Compounds	$H_{\text{SO}}^{\text{S}_1\text{T}_1}$	λ_{ISC}	λ_{RISC}
A1	0.14	0.546	0.198
A2	0.09	0.071	-0.100
A3	0.28	0.304	0.109
A4	0.12	-0.004	0.085
A5	0.06	0.005	0.031
A6	1.47	0.197	-0.011
A7	0.14	0.173	0.061
A8	0.09	0.059	-0.033
A9	0.02	0.001	-0.001
A10	0.11	0.044	-0.024
A11	0.58	0.049	-0.021

Table S2: Computed bary center distance between electron-rich and electron-deficient regions (D_{CT}, Å), their overlap integral ($S_{\pm}$), ground state (μ_{S_0}) and excited state (μ_{S_1}) dipole moments (in Debye) for the designed emitters.

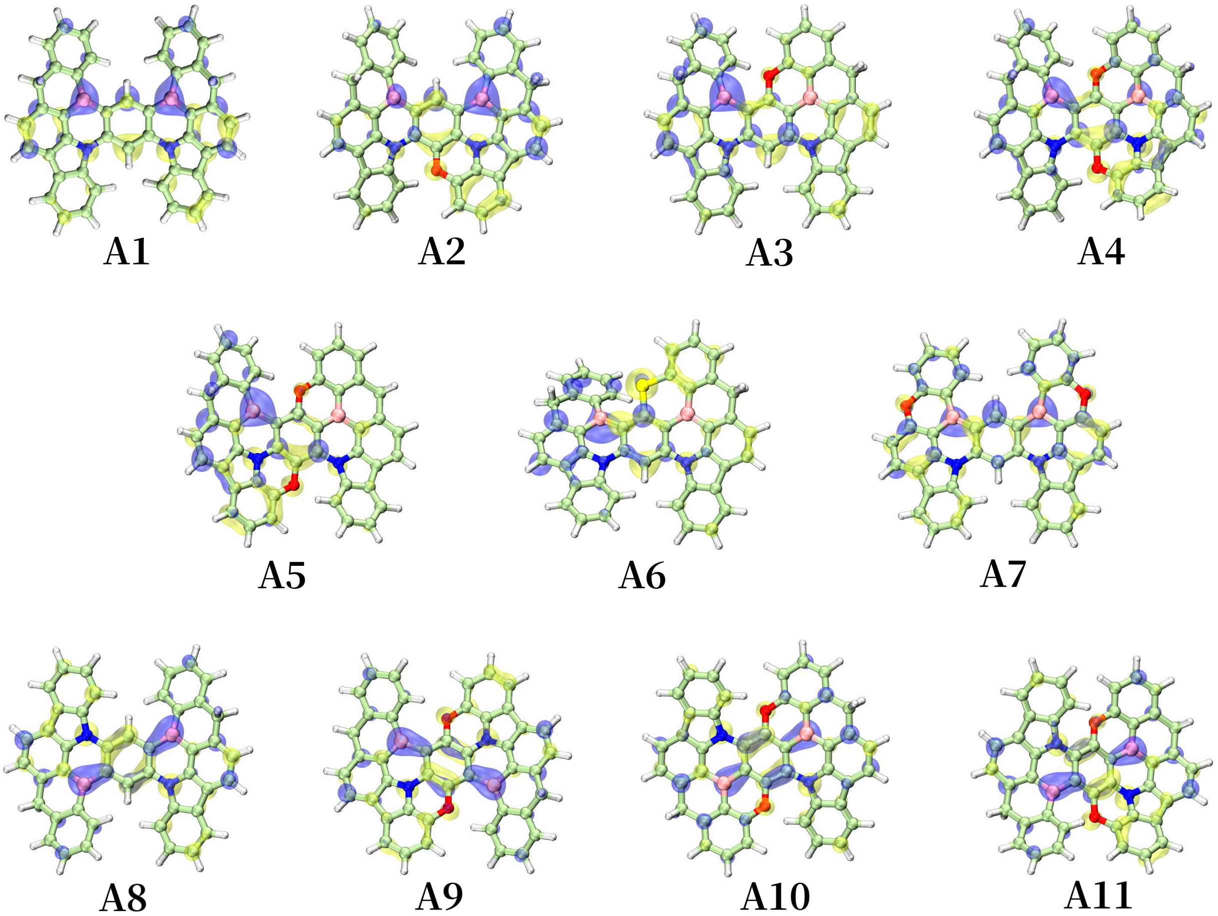
Compounds	D_{CT}	$S_{\pm}$	μ_{S_0}	μ_{S_1}
A1	3.220	0.738	0.7485	0.5868
A2	3.457	0.654	1.3498	1.1428
A3	3.556	0.760	0.9505	0.6482
A4	3.369	0.705	2.3172	2.5366
A5	3.975	0.643	0.8589	0.8470
A6	4.266	0.622	1.0276	0.6596
A7	4.175	0.700	0.6853	0.6577
A8	0.005	0.943	0.0002	0.0002
A9	0.004	0.845	0.0005	0.0004
A10	0.001	0.986	0.0002	0.0002
A11	1.951	0.859	2.1637	2.3937

Table S3: Computed IFCT values for the designed emitters.

Compounds	CT (%)	LE (%)
A1	35.311	64.689
A2	45.964	54.036
A3	37.904	62.096
A4	38.085	61.915
A5	40.362	59.638
A6	30.323	69.677
A7	25.554	74.446
A8	0.047	99.953
A9	0.013	99.987
A10	2.896	97.104
A11	24.030	75.970

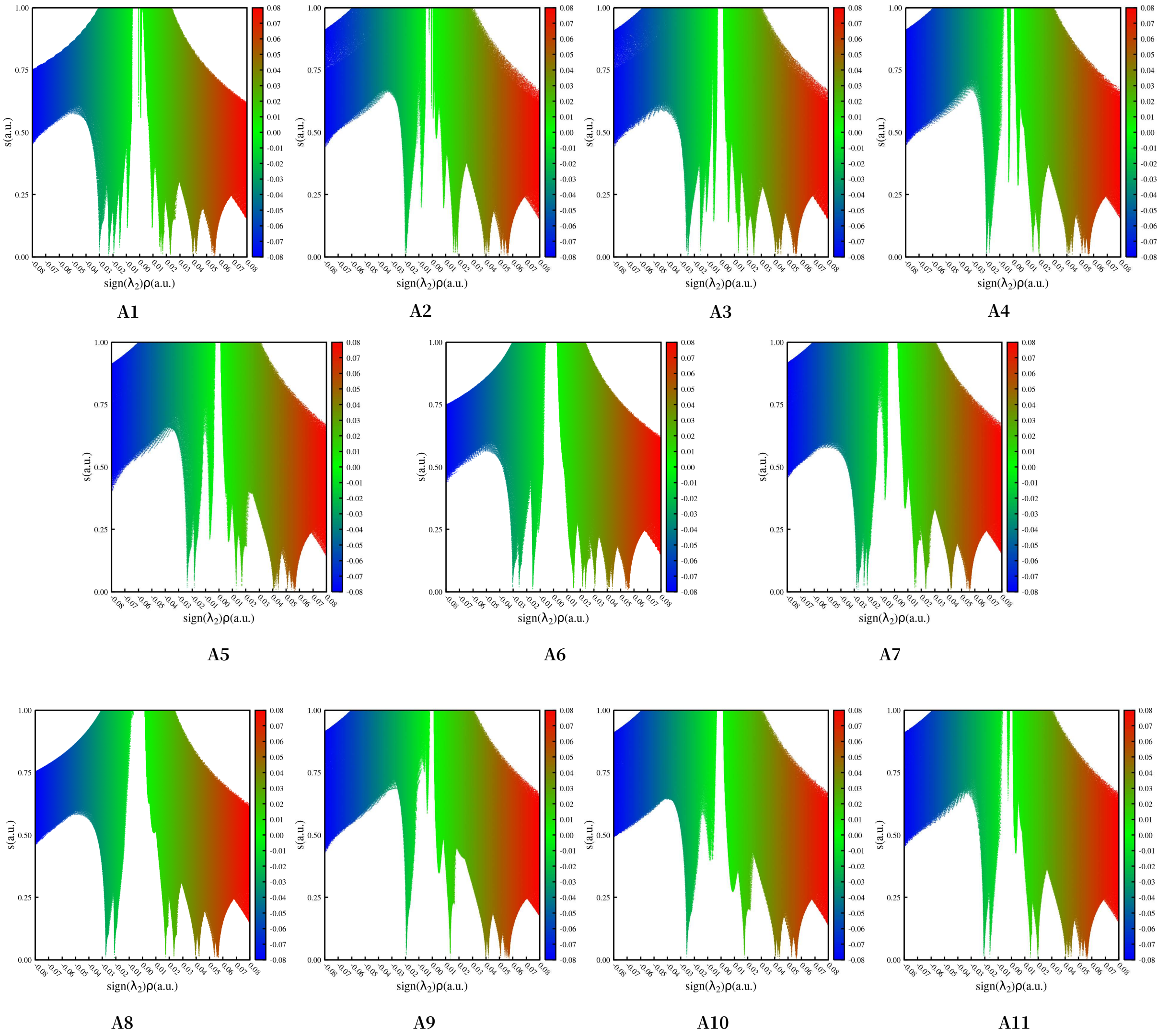
Table S4: Computed EQE (%) for the designed emitters.

Compounds	EQE
A1	26.65
A2	24.15
A3	26.65
A4	23.06
A5	24.56
A6	—
A7	24.81
A8	23.92
A9	24.87
A10	23.87
A11	—



A1 A2 A3 A4 A5 A6 A7 A8 A9 A10 A11

Figure S1: Frontier molecular orbital (HOMO in yellow and LUMO in blue) plot of the designed hybrid TADF emitters in the present study.



A1 A2 A3 A4

A5 A6 A7

A8 A9 A10 A11

Figure S2: Reduced density gradient (RDG) plots for the designed emitters.

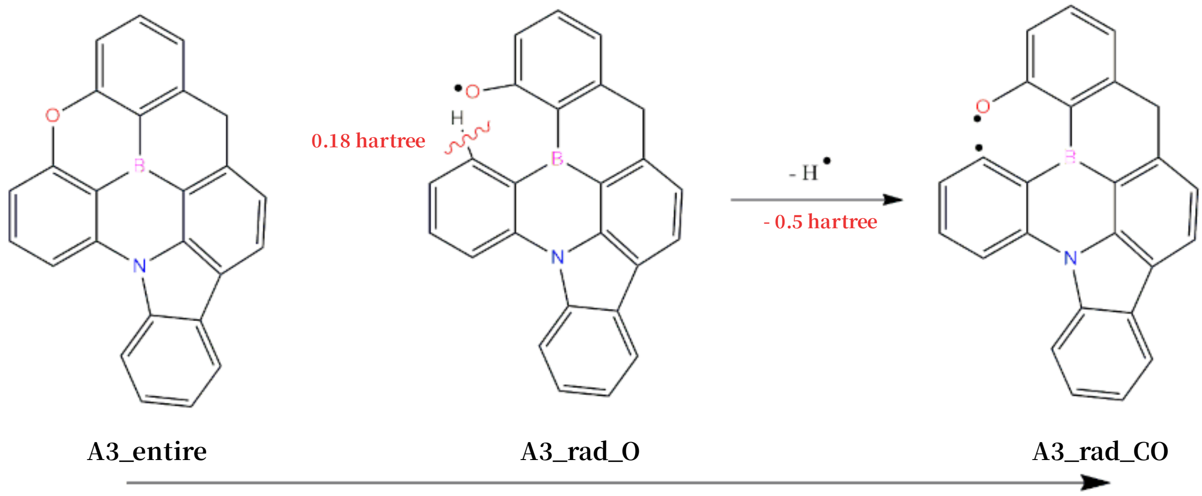


Figure S3: Schematic representation of the bond dissociation energy (BDE) calculation for the C-O bond in Compound A3. The intact molecule (A3_entire) is fragmented into a radical (A3_rad_O) by cleaving the C-O bond. The geometries of both the entire molecule and the radical fragment were optimized at the B3LYP/6-31G(d,p) level with D3BJ dispersion correction. The BDE is determined by subtracting the energy of the radical fragment from that of the intact molecule.

S2 References

[S1] Endo, A.; Sato, K.; Yoshimura, K.; Kai, T.; Kawada, A.; Miyazaki, H.; Adachi, C. Efficient up-conversion of triplet excitons into a singlet state and its application for organic light emitting diodes. *Appl. Phys. Lett.* **2011**, *98*, 083302.

[S2] Lee, S. Y.; Yasuda, T.; Komiyama, H.; Lee, J.; Adachi, C. Thermally Activated Delayed Fluorescence Polymers for Efficient Solution-Processed Organic Light-Emitting Diodes. *Adv. Mater.* **2016**, *28*, 4019–4024.

[S3] Shakeel, U.; Singh, J. Study of processes of reverse intersystem crossing (RISC) and thermally activated delayed fluorescence (TADF) in organic light emitting diodes (OLEDs). *Org. Electron.* **2018**, *59*, 121–124.