Supporting Information

Singlet reservoir for multi-channel barrierless harvesting of keto triplet excitons for high-efficiency electroluminescence of ESIPT fluorophore

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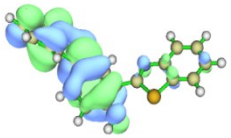
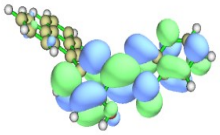
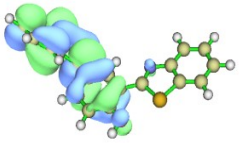
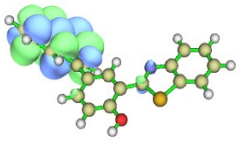
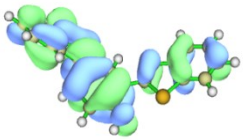
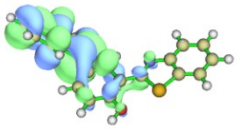
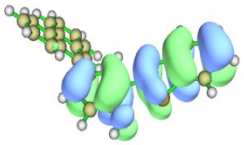
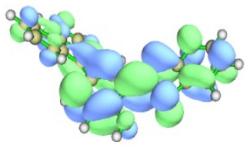
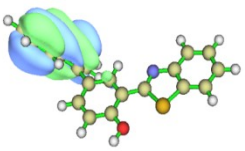
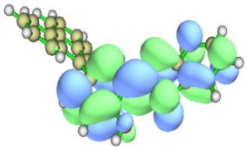
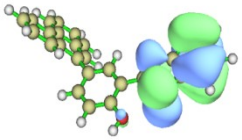
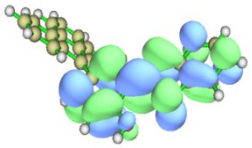
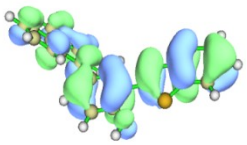
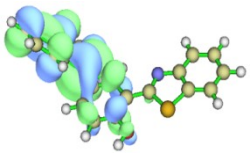
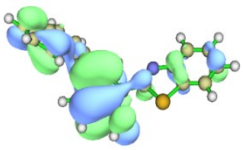
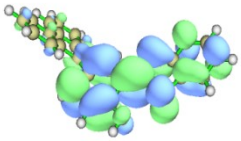
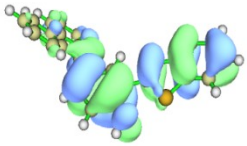
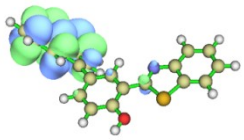
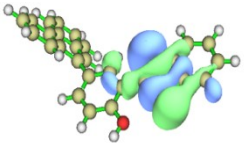
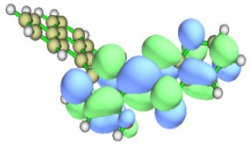
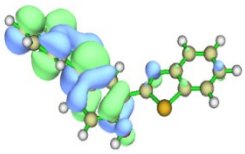
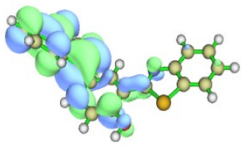
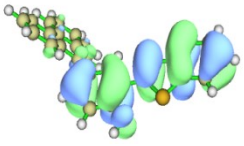
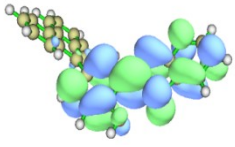
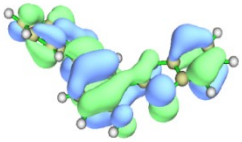
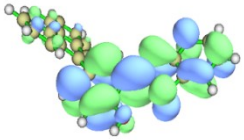
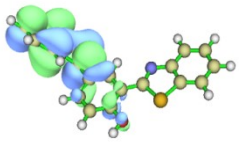
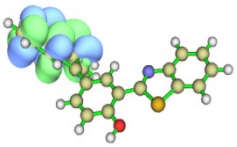
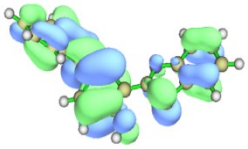
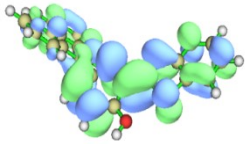
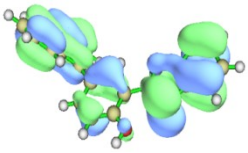
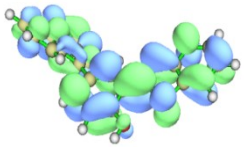
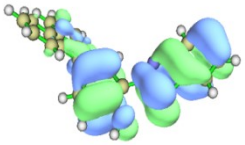
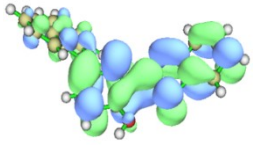
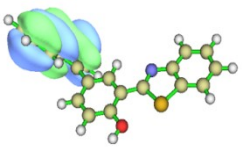
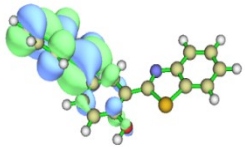
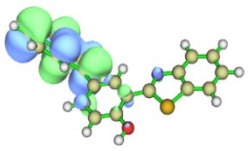
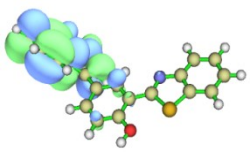
1. Theoretical calculations of energy levels and frontier molecular orbitals

The B3LYP/6-31G (d, p) method is employed to optimize the geometries for the ground state. Additionally, the excited-state characters and natural transition orbitals (NTOs) are also calculated by this method. The Gaussian09 program package is utilized for all calculations, while ORCA 5.0 is used to calculate the SOC matrix elements.

Table S1. Calculated energy levels and frontier molecular orbitals of enol-form.

Enol-form	Hole		Partical
S_1		98.47%	
S_2		62.59%	
S_3		56.02%	
S_4		67.18%	
S_5		97.53%	

S_6		93.46%	
S_7		76.19%	
S_8		69.52%	
S_9		64.20%	
S_{10}		99.48%	
T_1		63.05%	
T_2		69.02%	

T_3		83.37%	
T_4		58.01%	
T_5		51.67%	
T_6		44.78%	
T_7		37.53%	
T_8		73.08%	
T_9		35.26%	

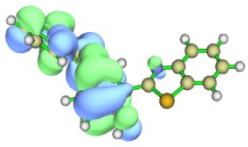
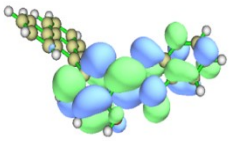
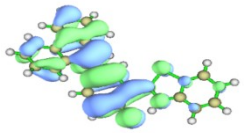
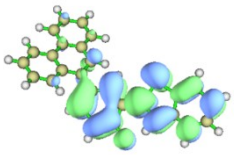
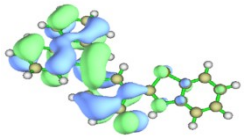
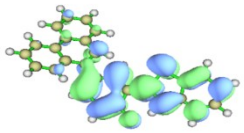
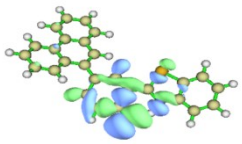
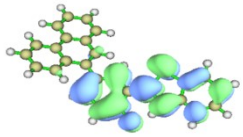
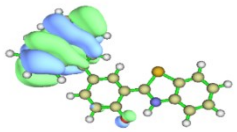
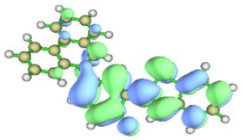
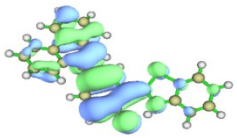
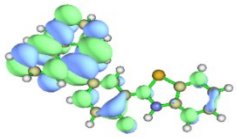
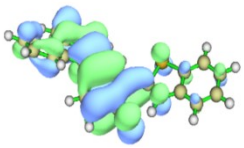
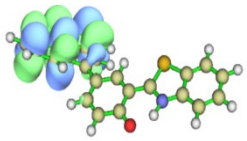
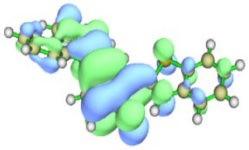
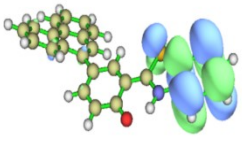
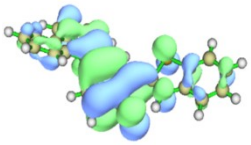
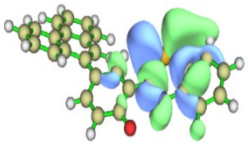
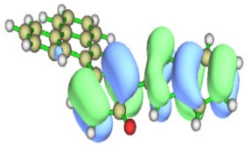
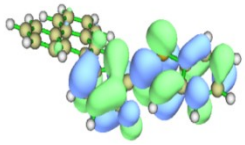
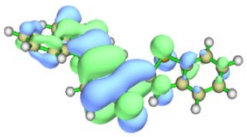
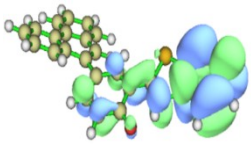
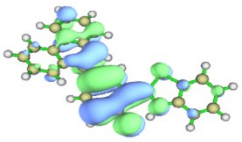
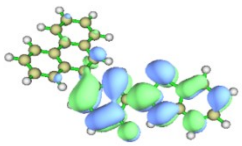
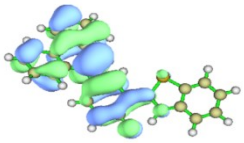
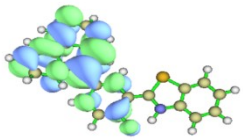
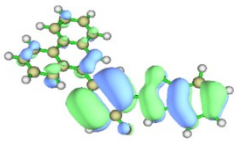
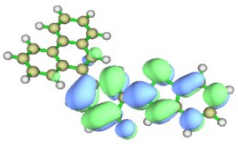
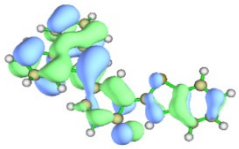
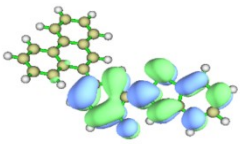
T_{10}		90.36%	

Table S2. Calculated energy levels and frontier molecular orbitals of keto-form.

Keto-form	Hole		Partical
S_1		100.00%	
S_2		81.99%	
S_3		97.70%	
S_4		87.80%	
S_5		75.30%	
S_6		83.75%	
S_7		98.41%	

S_8		99.95%	
S_9		79.32%	
S_{10}		82.25%	
T_1		100.00%	
T_2		84.39%	
T_3		86.54%	
T_4		92.37%	

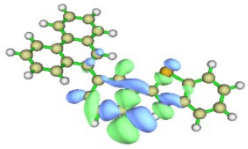
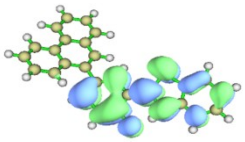
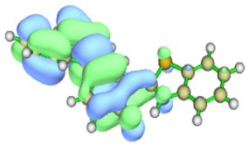
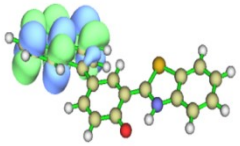
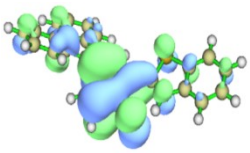
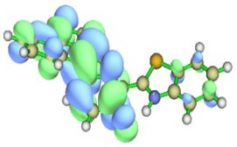
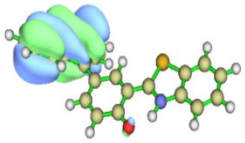
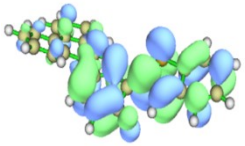
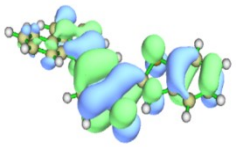
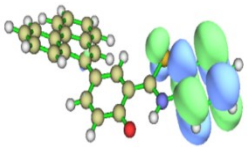
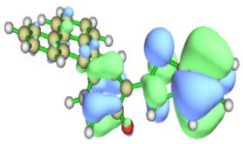
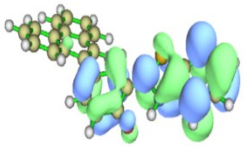
T_5		99.53%	
T_6		81.20%	
T_7		47.00%	
T_8		85.77%	
T_9		95.38%	
T_{10}		56.35%	

Table S3. Calculated excitation energies, oscillator strengths and transition contributions of enol-form of the singlet and triplet excited states.

Enol-form	Excitation energy (eV)	Oscillator strength	Main transitions
S_1	3.5999	0.0975	H → L (93.9%)
S_2	3.9241	0.0028	H → L+2 (55.8%), H-2 → L+1 (33.4%)
S_3	3.9800	0.4328	H → L+1 (53.3%), H-1 → L (37.3%)
S_4	4.1063	0.3334	H-1 → L (53.1%), H → L+1 (30.9%)
S_5	4.1445	0.0314	H-2 → L (96.2%)
S_6	4.1592	0.0330	H-3 → L (88.1%)
S_7	4.3280	0.0138	H-1 → L+1 (72.8%), H-4 → L (15.7%), H-2 → L+2 (5.9%)
S_8	4.5003	0.0694	H-4 → L (67.0%), H-1 → L+1 (14.5%)
S_9	4.5261	0.0532	H → L+2 (35.4%), H-2 → L+1 (32.1%), H-1 → L+2 (23.0%)
S_{10}	4.7035	0.0004	H-6 → L (97.2%)
T_1	2.6411	0.0000	H → L+1 (47.0%), H → L (12.7%), H-1 → L (11.0%), H-2 → L+2 (10.4%), H-1 → L+1 (9.1%)
T_2	2.7339	0.0000	H-1 → L (43.4%), H → L (20.4%), H → L+1 (16.4%), H-2 → L+2 (5.4%)
T_3	3.3516	0.0000	H → L (39.4%), H-3 → L (14.1%), H-1 → L (12.4%), H-4 → L (12.0%)
T_4	3.4603	0.0000	H → L+2 (43.9%), H-2 → L+1 (16.4%), H-3 → L (12.3%), H-1 → L+2 (7.8%)
T_5	3.4946	0.0000	H-2 → L+2 (29.4%), H-3 → L (13.8%), H → L+1 (9.7%), H → L (9.5%), H-4 → L (7.2%)
T_6	3.5252	0.0000	H-2 → L+2 (34.0%), H-3 → L (31.9%), H → L+1 (9.2%)

T_7	3.7900	0.0000	H → L+3 (14.5%), H-3 → L (14.3%), H-7 → L (12.0%), H-4 → L+1 (8.6%), H-4 → L+3 (6.7%)
T_8	3.8045	0.0000	H-2 → L+1 (66.6%), H → L+2 (20.2%)
T_9	3.9143	0.0000	H-5 → L+1 (19.1%), H → L+3 (9.8%), H-1 → L+5 (9.1%), H → L+6 (7.3%), H-3 → L+4 (7.3%), H-7 → L (6.9%), H → L+2 (5.3%)
T_{10}	3.9949	0.0000	H-4 → L (49.9%), H-1 → L (18.9%), H → L (11.5%), H+2 → L (5.6%)

Table S4. Calculated excitation energies, oscillator strengths and transition contributions of keto-form of the singlet and triplet excited states.

Keto-form	Excitation energy (eV)	Oscillator strength	Main transitions
S_1	2.2807	0.2463	H → L (100.0%)
S_2	3.1423	0.0839	H-1 → L (77.7%), H → L+1 (17.8%)
S_3	3.2354	0.0092	H-3 → L (92.2%)
S_4	3.3499	0.0085	H-2 → L (81.4%), H → L+3 (8.5%)
S_5	3.4117	0.2763	H → L+1 (72.5%), H-1 → L (15.6%)
S_6	3.5106	0.0333	H → L+3 (81.6%), H-2 → L (9.1%)
S_7	3.5227	0.0195	H → L+2 (96.1%)
S_8	3.7115	0.0001	H → L+4 (98.2%)
S_9	3.9005	0.3234	H-4 → L (77.3%), H → L+5 (16.3%)
S_{10}	4.0521	0.1596	H → L+5 (81.1%), H-4 → L (14.7%)
T_1	1.4253	0.0000	H → L (94.0%)
T_2	2.2862	0.0000	H → L+1 (71.8%), H-1 → L+1 (10.2%), H-1 → L (7.5%)
T_3	2.8982	0.0000	H-4 → L (75.4%), H-1 → L (5.3%)
T_4	2.9936	0.0000	H-1 → L (71.9%), H-4 → L (6.6%), H → L+1 (6.4%)
T_5	3.0537	0.0000	H-3 → L (91.2%)
T_6	3.1556	0.0000	H → L+3 (65.7%), H-2 → L (8.2%), H-2 → L+3 (7.5%), H-1 → L+3 (5.9%), H-2 → L+1 (5.5%)
T_7	3.2333	0.0000	H-1 → L+1 (28.6%), H-2 → L+3 (23.9%), H → L+1 (11.3%), H → L+7 (5.5%), H → L+6 (5.3%)
T_8	3.3207	0.0000	H-2 → L (76.7%), H → L+3 (11.9%)
T_9	3.3929	0.0000	H → L+2 (86.5%)

T_{10}	3.5400	0.0000	H-6 → L (33.8%), H-6 → L+2 (10.5%), H → L+5 (8.6%), H-2 → L+3 (7.2%), H-4 → L+5 (6.2%)

Table S5. Fluorescence decay lifetimes of HBT-PA before and after deoxygenation (excited at 379 nm).

Solvent	atmosphere	τ_1 (ns)	τ_2 (ns)	$\langle\tau\rangle^{a)}$ (ns)	χ^2
THF	O_2	0.38 (72.20%)	3.81 (27.80%)	1.33	1.39
	N_2	0.39 (67.83%)	3.97 (32.17%)	1.54	1.34
TOL	O_2	0.77 (89.90%)	3.52 (10.10%)	1.05	1.36
	N_2	0.78 (88.74%)	4.59 (11.26%)	1.21	1.36

a) The average lifetime.

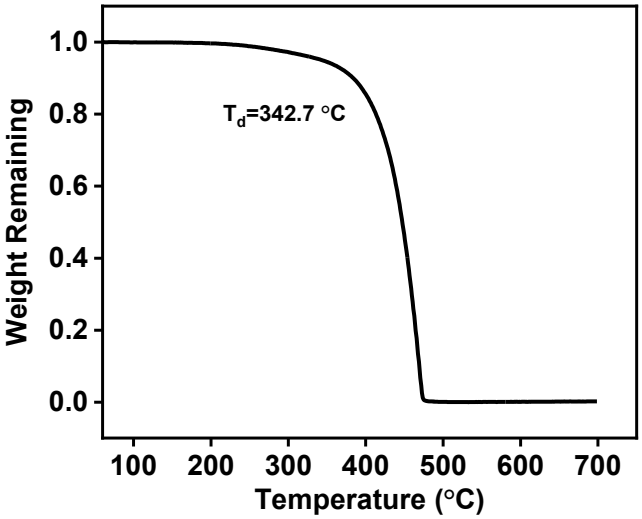


Figure S1. TGA curve of HBT-PA.

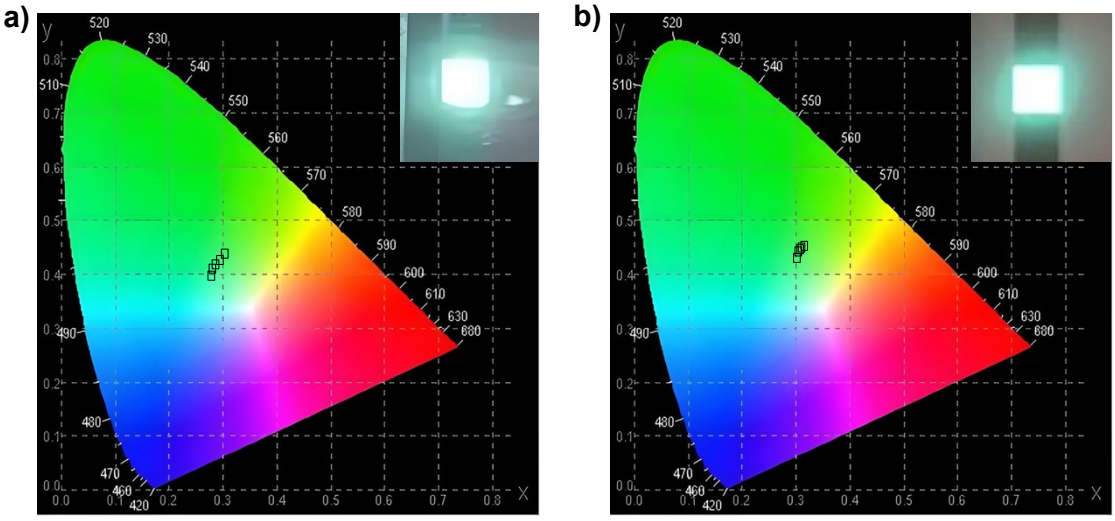


Figure S2. CIE diagrams of a) Device C and b) Device D at different operating voltages (inset: luminescence photos).