Are Heptazine-Based Organic Light-Emitting Diode (OLED) Chromophores Thermally Activated Delayed Fluorescence (TADF) or Inverted Singlet-Triplet (IST) Systems?

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Supporting Information

Table S1. Vertical excitation energies (ΔE) and oscillator strengths (f) of the lowest excited states of HAP-3MF, determined with the TDDFT/B3LYP/cc-pVDZ method at the DFT-D3/B3LYP/cc-pVDZ equilibrium geometry of the electronic ground state.

state	ΔE/eV	f
^{3}A'(ππ*)	2.64	-
^{1}A'(ππ*)	2.81	0.0
^{3}E'(ππ*)	2.94	-
^{3}A"(nπ*)	3.45	-
^{1}E'(ππ*)	3.52	0.880
^{3}E"(nπ*)	3.54	-
^{1}A"(nπ*)	3.55	0.0
^{1}E"(nπ*)	3.65	0.0

Table S2. Vertical excitation energies (ΔE) and oscillator strengths (f) of the lowest excited states of HAP-3TPA and truncated HAP-3TPA (HAP-3TPA-t), determined with the TDDFT/B3LYP/cc-pVDZ method at the DFT-D3/B3LYP/cc-pVDZ equilibrium geometry of the electronic ground state.

	HAP-3TPA		HAP-3TPA-t	
state	ΔE/eV	f	ΔE/eV	f
^{3}E(ππ*)	2.15	-	2.22	-
^{3}A$_1$(ππ*)	2.20	-	2.27	-
^{1}E(ππ*)	2.43	1.607	2.52	1.530
^{3}A$_2$(ππ*)	2.65	-	2.65	-
^{1}A$_1$(ππ*)	2.65	0.0	2.74	0.0
^{1}A$_2$(ππ*)	2.81	0.0	2.81	0.0

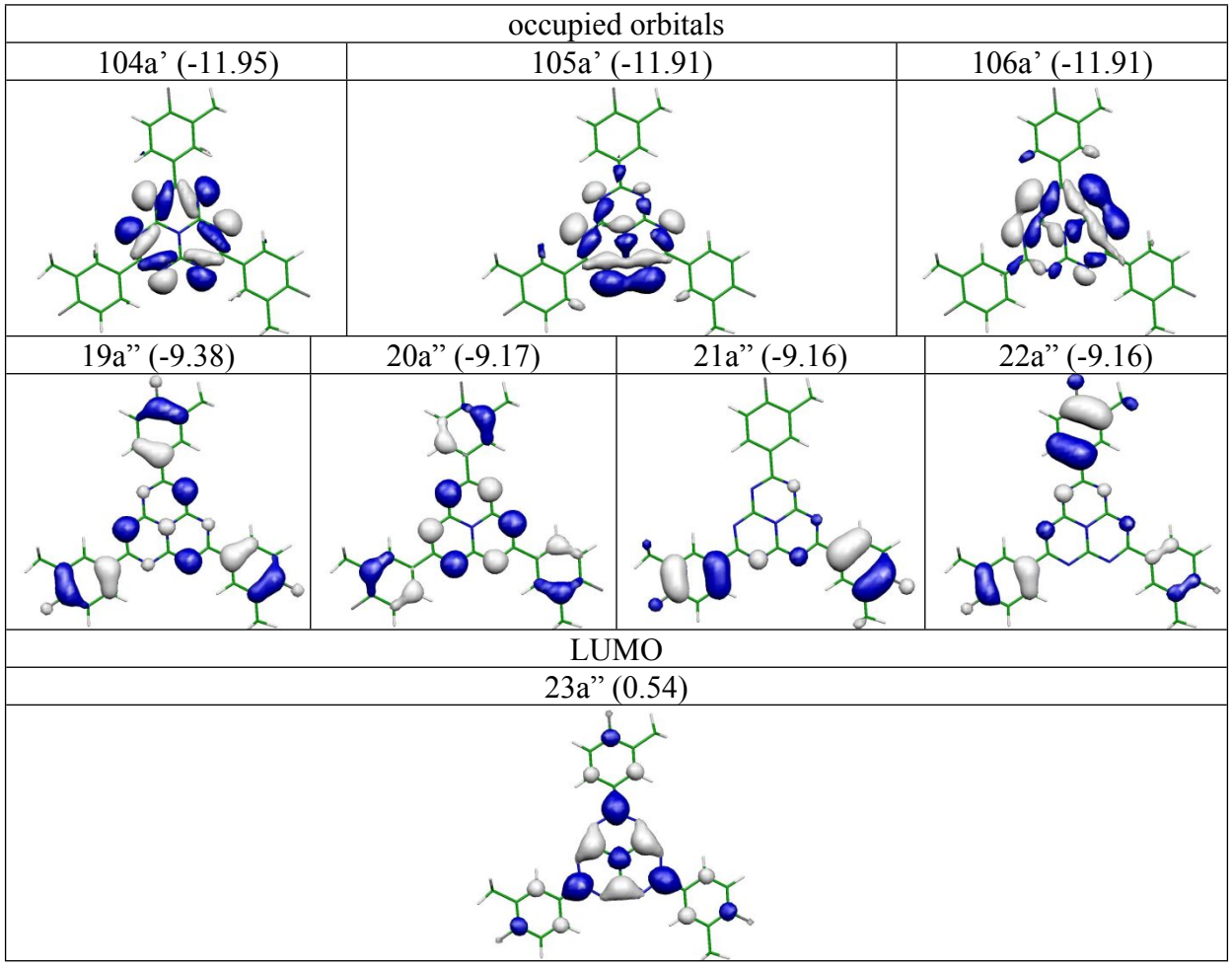


Figure S1. The highest occupied and lowest unoccupied Hartree-Fock orbitals involved in the lowest electronic excitations of HAP-3MF at the ground-state equilibrium geometry. The orbital energies (in eV) are shown in parentheses. Orbitals were plotted with an isosurface value of 0.03.

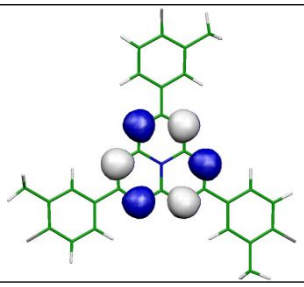
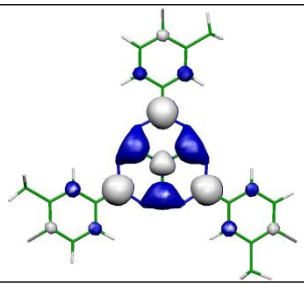
state	occ no.	hole	electron
^{1}A'	0.951		
^{3}A'	0.960		

Figure S2. Occupation numbers and natural transition orbitals involved in the excitation to the ^{1}A' and ^{3}A' excited states of HAP-3MF at the ground-state equilibrium geometry. Orbitals were plotted with an isosurface value of 0.03.

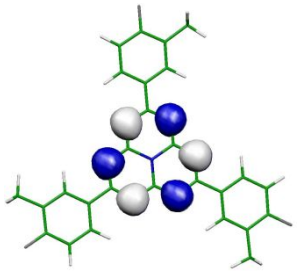
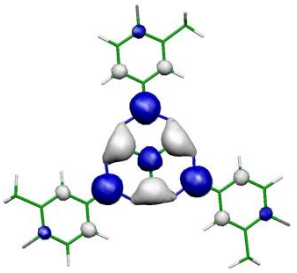
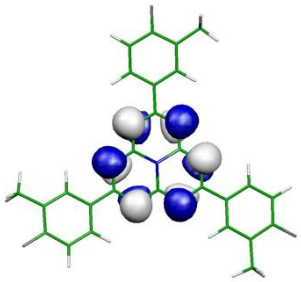
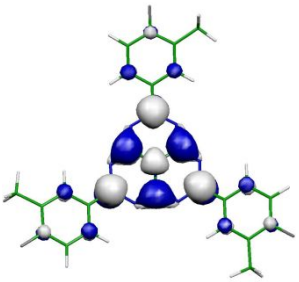
state	E_{ad}/eV	E_{em}/eV	occ. no.	hole	electron
C_{3h} symmetry					
^{1}A'	2.47	2.42	0.951		
^{3}A'	2.72	2.67	0.974		
Δ_{ST}	-0.25	-0.25			
C_3 symmetry					
S_1	2.43	2.06	0.955		
T_1	2.69	2.36	0.957		
Δ_{ST}	-0.26	-0.30			

Figure S3. Adiabatic excitation energies (E_{ad}), vertical emission energies (E_{em}), natural occupation numbers, and natural transition orbitals of the lowest excited states of HAP-3MF, determined with the ADC(2)/cc-pVDZ method with the indicated symmetry constraints. Orbitals were plotted with an isosurface value of 0.03.

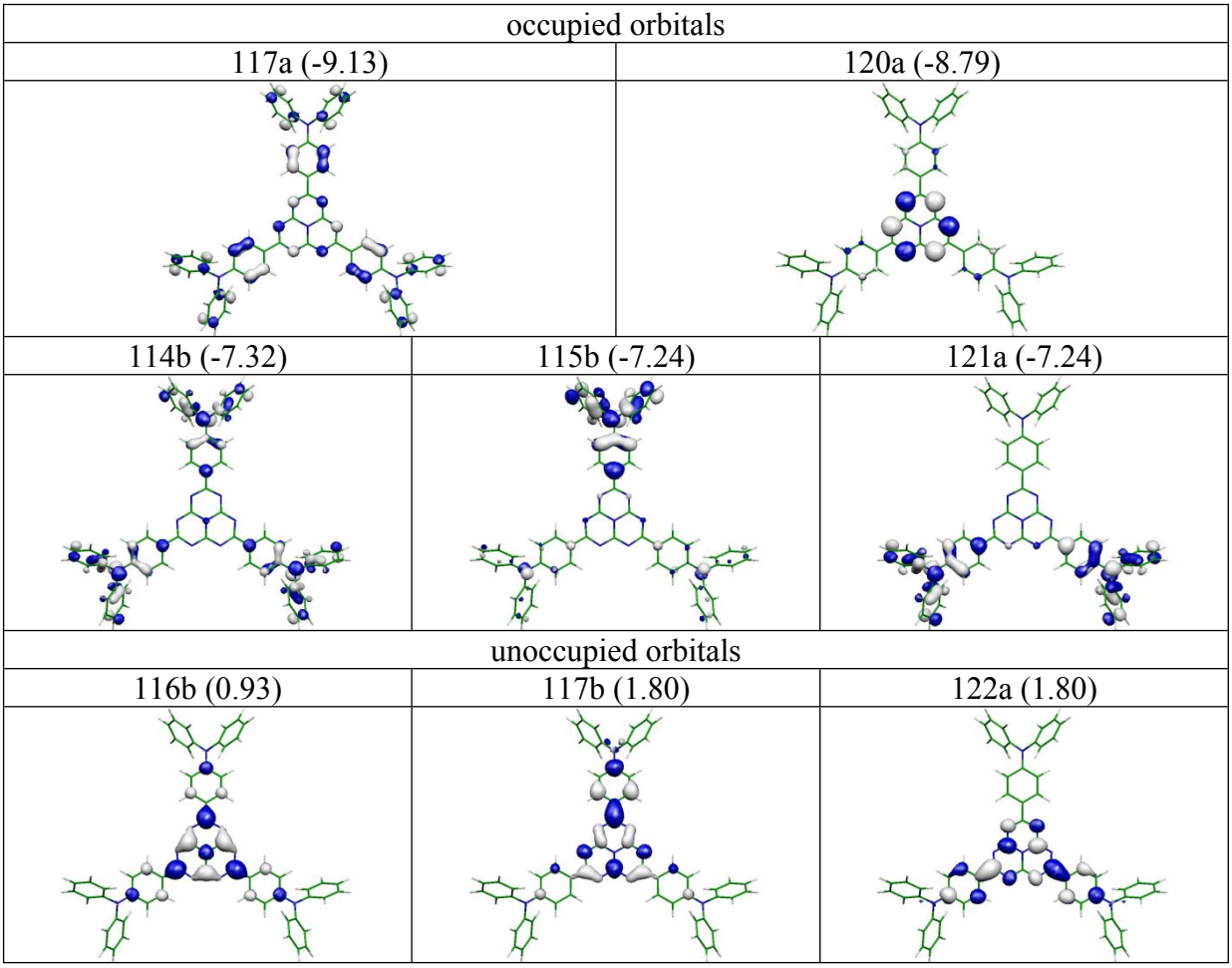


Figure S4. The highest occupied and lowest unoccupied Hartree-Fock orbitals involved in the lowest electronic excitations of HAP-3TPA-t at the ground-state equilibrium geometry. The orbital energies (in eV) are shown in parentheses. Orbitals were plotted with an isosurface value of 0.03.

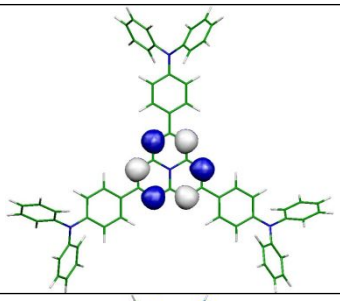
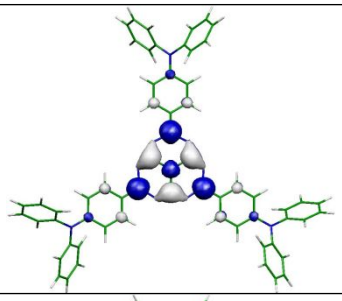
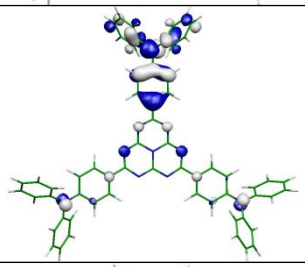
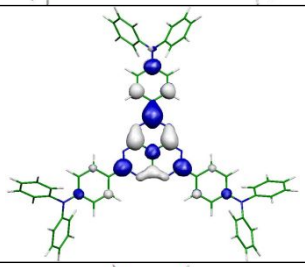
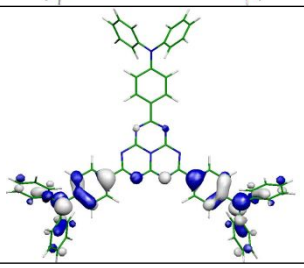
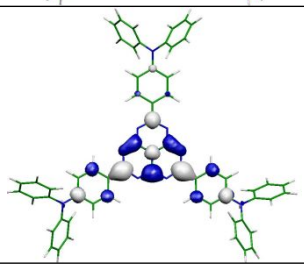
state	occ no.	hole	electron
$^1A_1$	0.949		
$^3A_1$	0.957		
^1E_x	0.831		
^3E_x	0.770		
^1E_y	0.827		
^3E_y	0.759		

Figure S5. Occupation numbers and natural transition orbitals involved in the excitation to the lowest excited electronic states of HAP-3TPA-t at the ground-state equilibrium geometry. Orbitals were plotted with an isosurface value of 0.03.

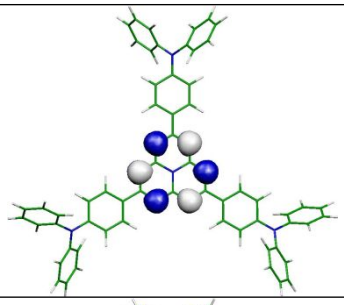
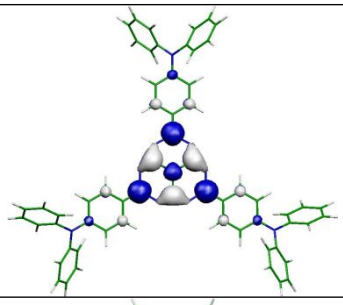
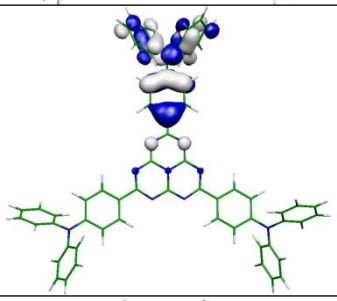
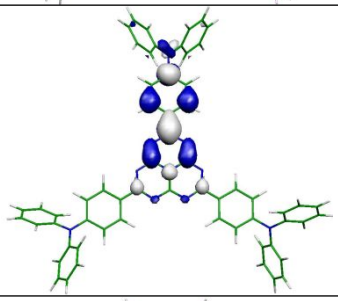
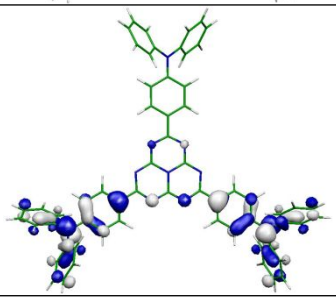
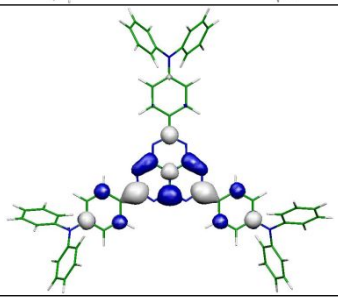
state	E_{ad}/eV	E_{em}/eV	occ. no.	hole	electron
^1B	2.50	2.42	0.950		
^3E_x	2.49	2.36	0.947		
^3E_y	2.55	2.48	0.768		

Figure S6. Adiabatic excitation energies (E_{ad}) vertical emission energies (E_{em}), natural occupation numbers, and natural transition orbitals of the lowest excited states of HAP-3TPA-t determined with the ADC(2)/def-SV(P) method at the equilibrium geometry of a given excited state. Orbitals were plotted with an isosurface value of 0.03.