Supplementary Information

Theoretical Perspective for the Relationship Between Structures and Luminescent Properties of Red Thermally Activated Delayed Fluorescence Molecules

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Calculation details for TBCT and TSCT ratios:

Firstly, the non-relaxation part of charge transfer (CT) can be obtained by analyzing the hole-electron distribution when molecule is excited. CT ratio with this concept can be analyzed by IFCT method, based on the following equation:

$$Q_{R,S} = \Theta_{R,hole}\Theta_{S,ele}$$

Here, $Q_{R,S}$ represents the charge transfer quantity from part R to part S, $\Theta_{R,hole}$ means the excited electron amount occupied by R part, $\Theta_{S,ele}$ is the arrived electron amount occupied by S part. Then pure amount of electron transfer can be calculated by following formula:

$$p_{S \to R} = Q_{S,R} - Q_{R,S}$$

$$\Delta p_R = \sum_{s \neq R} Q_{S,R} - Q_{R,S}$$

Where, $p_{S \to R}$ represents the pure amount of electron transfer of two parts, Δp_R is the charge variation of one part. Based on these functions, the charge transfer ratio can be calculated quantitatively. Among these, the direct CT ratio between D-A can be regarded as through-space CT, the CT ratios of D-π and π-A are regard as through-bond CT.

However, if there is no spatial overlap between holes and electrons in one molecule, the transition is forbidden although with large charge transfer. In other words, this part of charge transfer does not contribute to the absorption or emission. So, what we concerned about is that the CT transition which can contribute to emission and absorption. To solve this

issue, we analyze the transition density by the following function:

$$\rho_{TB} = \rho_{tot} - \rho_{TS}$$

Here, ρ_{tot} means the transition density integral of the whole molecule, and ρ_{TS} represents the transition density integral of the molecule with deleted π bridge, ρ_{TB} is then obtained.

Secondly, following the abovementioned method, we should define the donor part, acceptor part and bridge part. Taking the studied BTDMAc-NAI as example (as shown in Figure S1), the atom number of the donor, acceptor and bridge should be determined initially. Atom numbers of 34, 39, 72-82 are classified as donor, 1-30, 49-61 as acceptor and 31-33, 35-38, 40-48, 62-71 as bridge. Then, we implement the program script provided by Cheng Zhong carried out by Multiwfn in Linux system. After that, we can get the TSCT and TBCT ratios and corresponding results are shown in Figure S2.
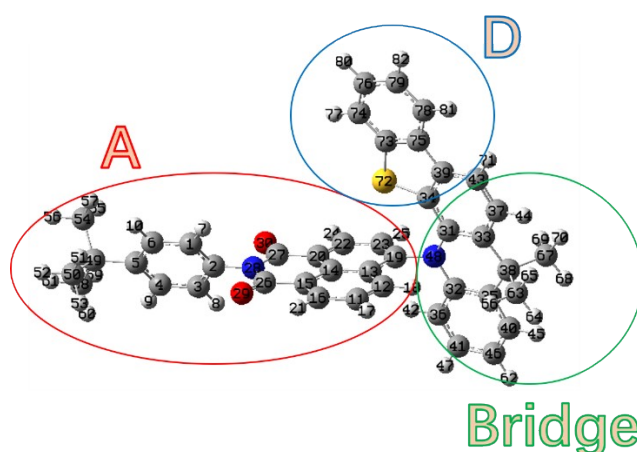

Figure S1. Atom numbers of the donor part, acceptor part and bridge part for studied molecule BTDMAc-NAI.

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TS/TB using transition density:
Through Space CT: 0.17078     68.90%
Through Bond  CT: 0.07706     31.09%
Tot transit dens: 0.24784
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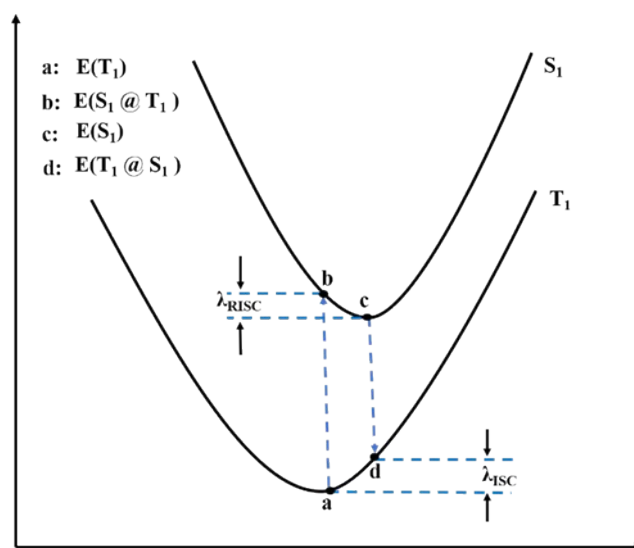Figure S2. Calculation results for BTDMAc-NAI in toluene of S_1 state performed by Multiwfn.

Figure S3. Schematic representation of the adiabatic potential energy surfaces for S_1 and T_1.
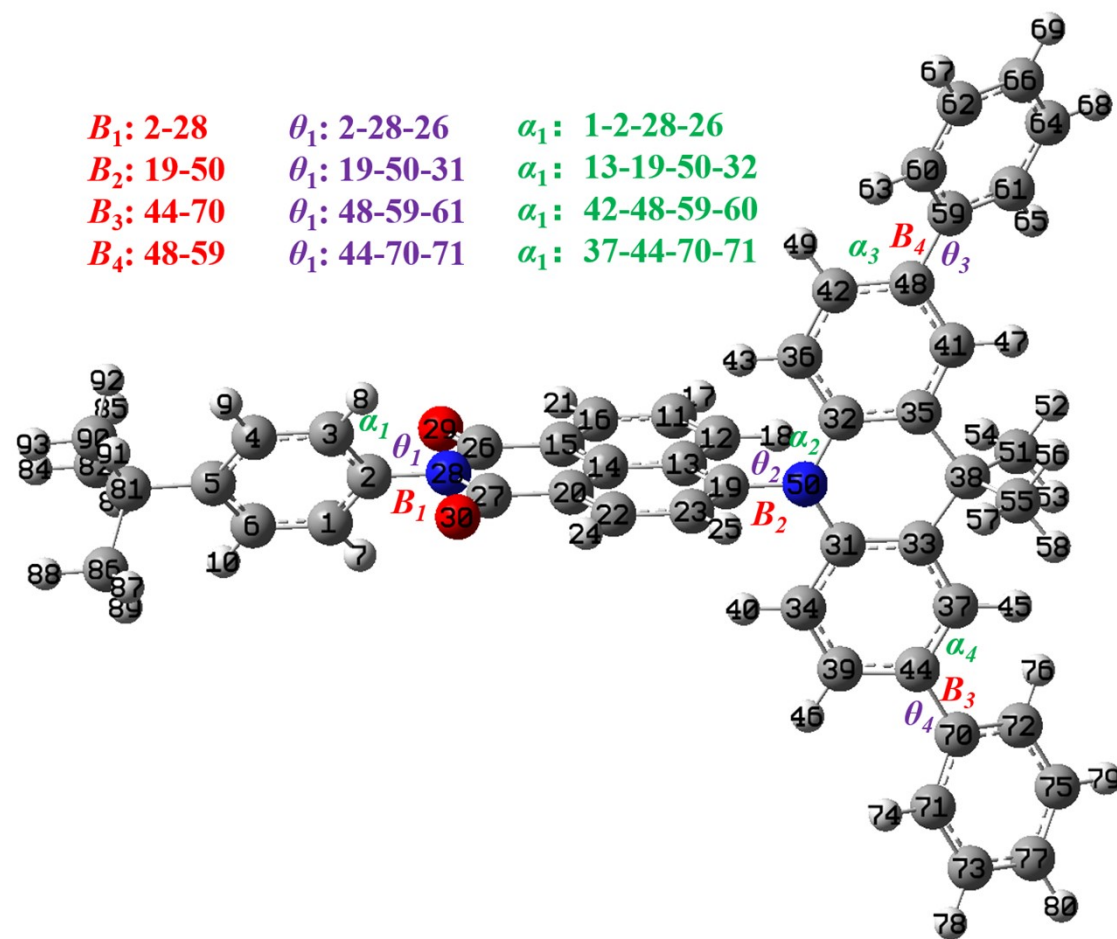
Figure S4. The atomic labels and the interesting bond lengths (B₁, B₂, B₃ and B₄), bond angles (θ₁, θ₂, θ₃ and θ₄) and the dihedral angles (α₁, α₂, α₃ and α₄) of NAI-R2.

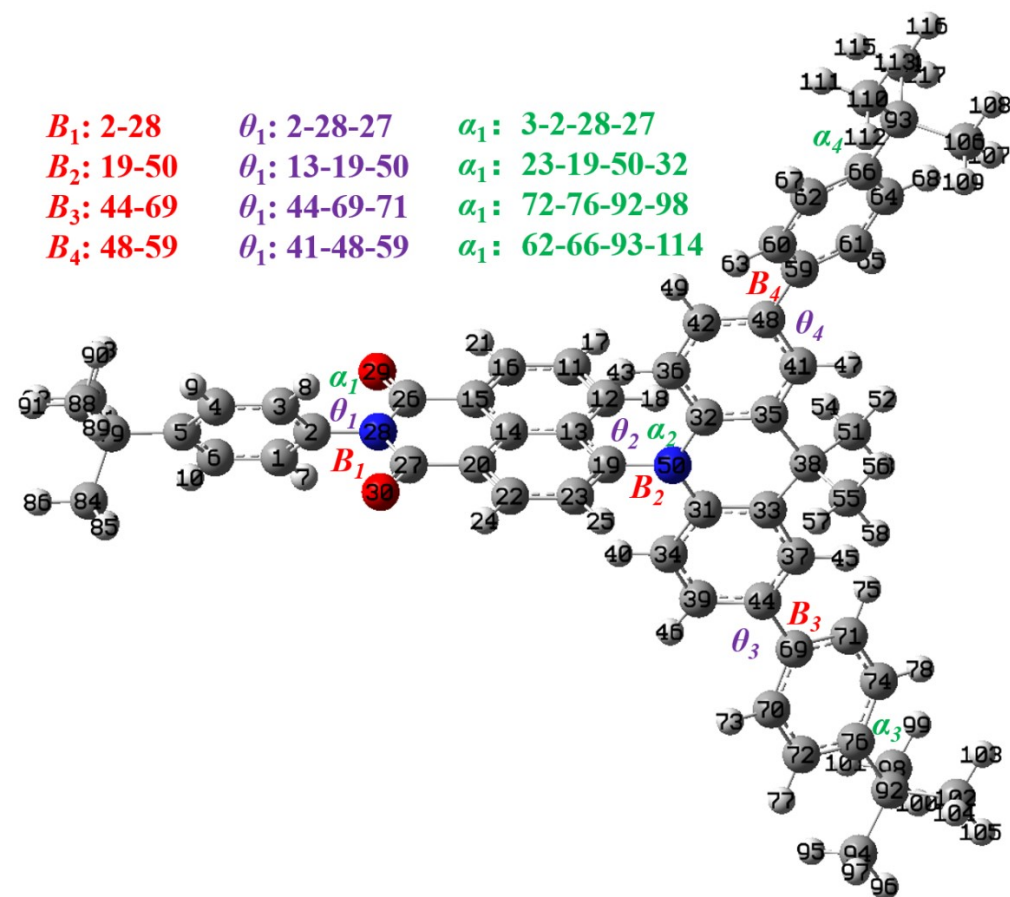**Figure S5.** The atomic labels and the interesting bond lengths (B_1, B_2, B_3 and B_4), bond angles (θ_1, θ_2, θ_3 and θ_4) and the dihedral angles (α_1, α_2, α_3 and α_4) of NAI-R3.

Figure S6. The atomic labels and the interesting bond lengths (B_1, B_2, B_3 and B_4), bond angles (θ_1, θ_2, θ_3 and θ_4) and the dihedral angles (α_1, α_2, α_3 and α_4) of NAI-DPAC.

Figure S7. The atomic labels and the interesting bond lengths (B$_1$, B$_2$, B$_3$, B$_4$, B$_5$ and B$_6$), bond angles (θ_1, θ_2, θ_3 and θ_4) and the dihedral angles (α_1 and α_2) of NAI-DMAC.
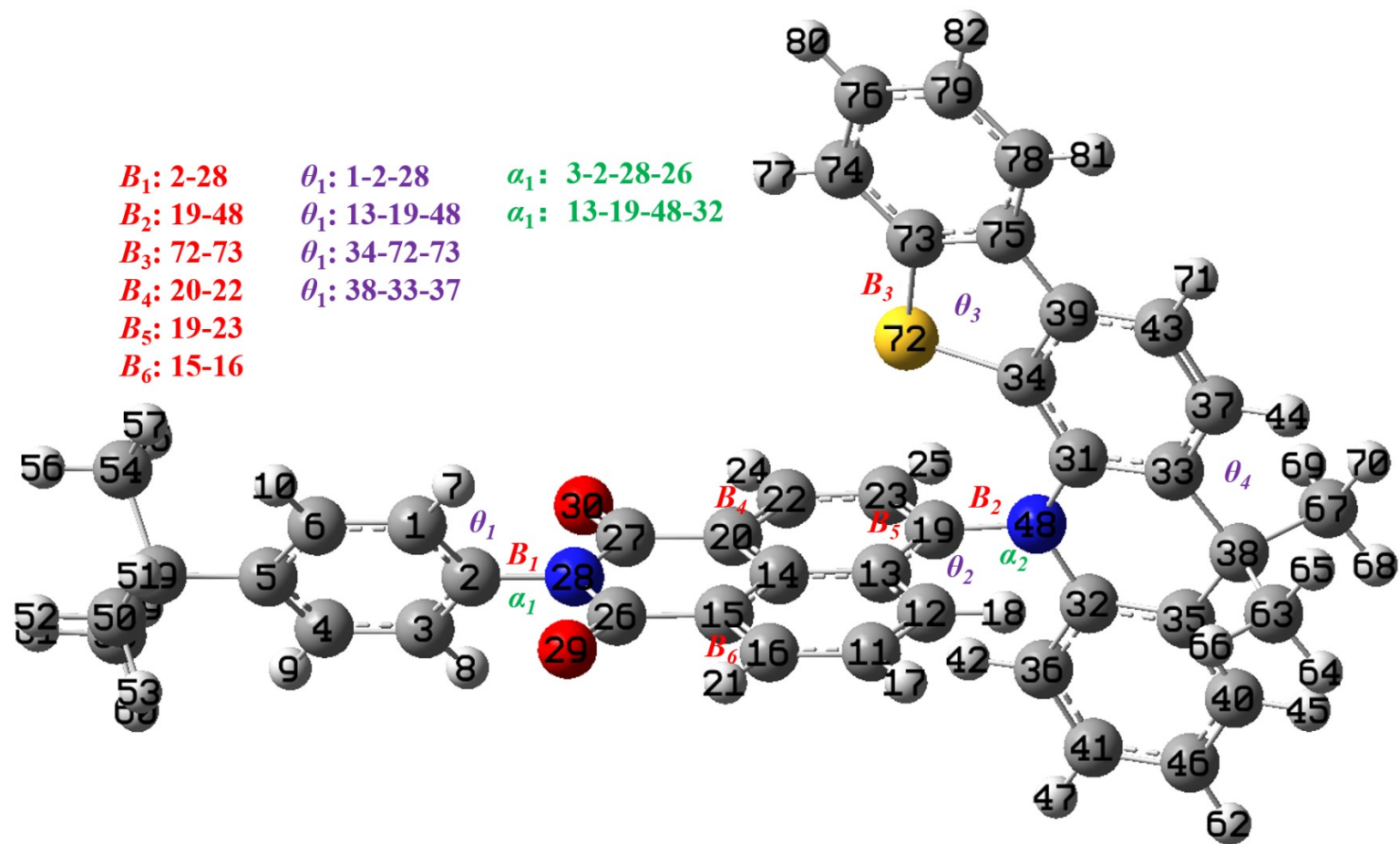
Figure S8. The atomic labels and the interesting bond lengths (B_1, B_2, B_3, B_4, B_5 and B_6), bond angles (θ_1, θ_2, θ_3 and θ_4) and the dihedral angles (α_1 and α_2) of BTDMAc-NAI.
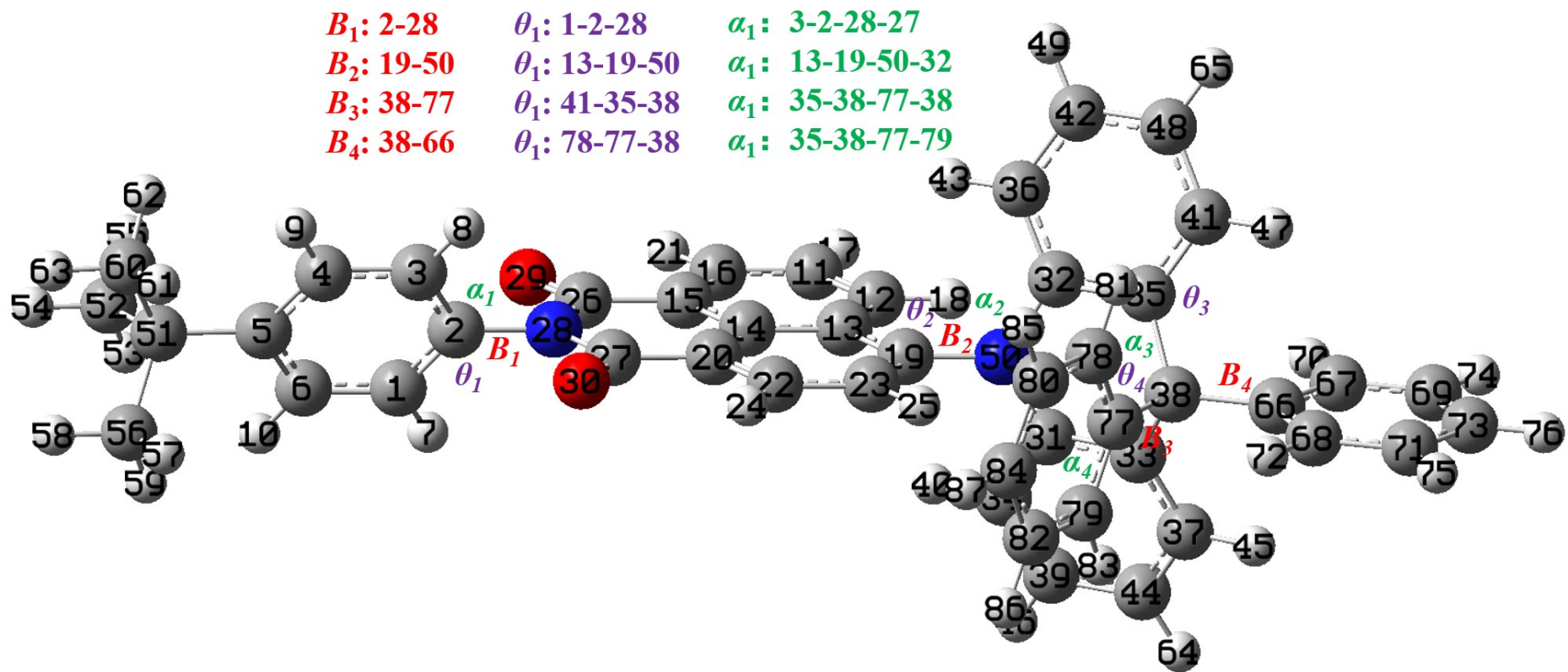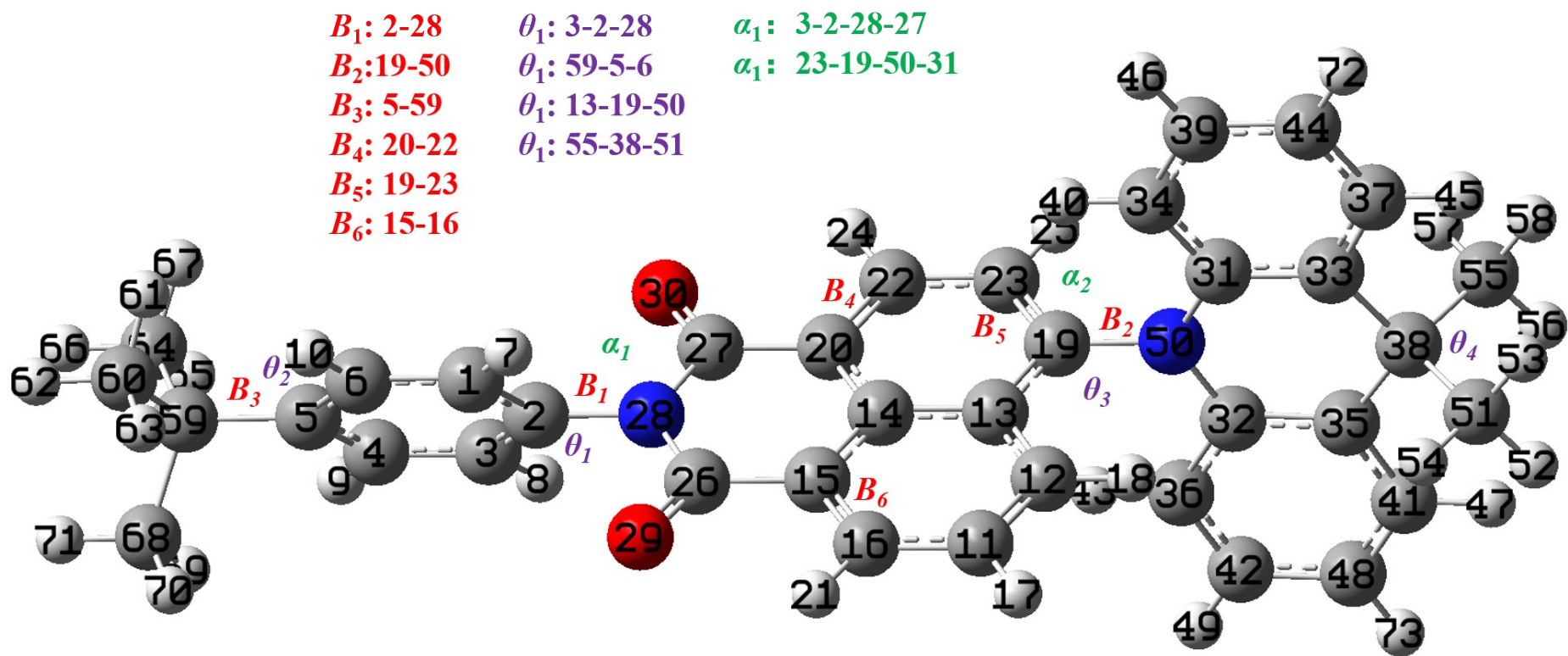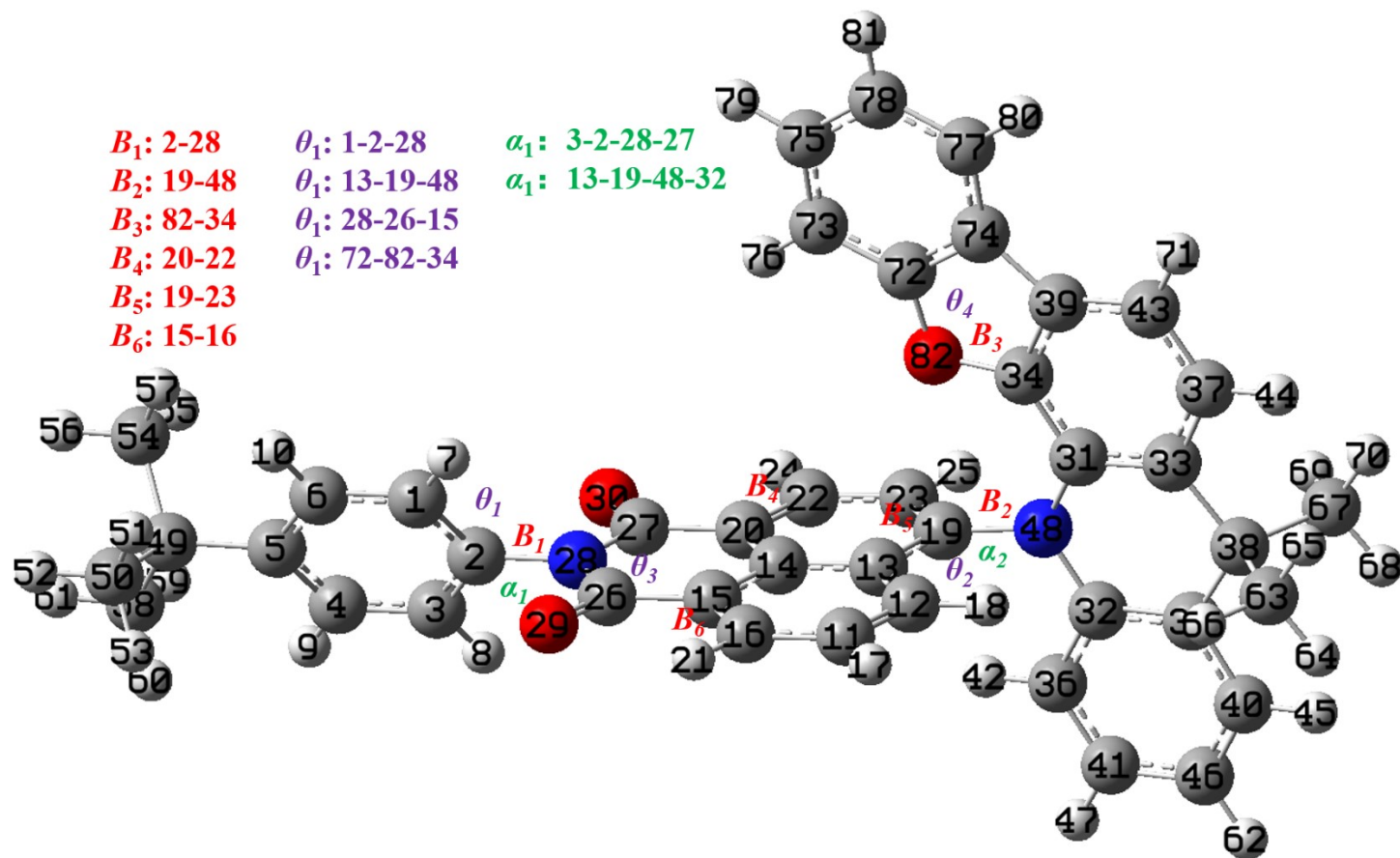
Figure S9. The atomic labels and the interesting bond lengths (B₁, B₂, B₃, B₄, B₅ and B₆), bond angles (θ₁, θ₂, θ₃ and θ₄) and the dihedral angles (α₁ and α₂) of BFDMAc-NAI.
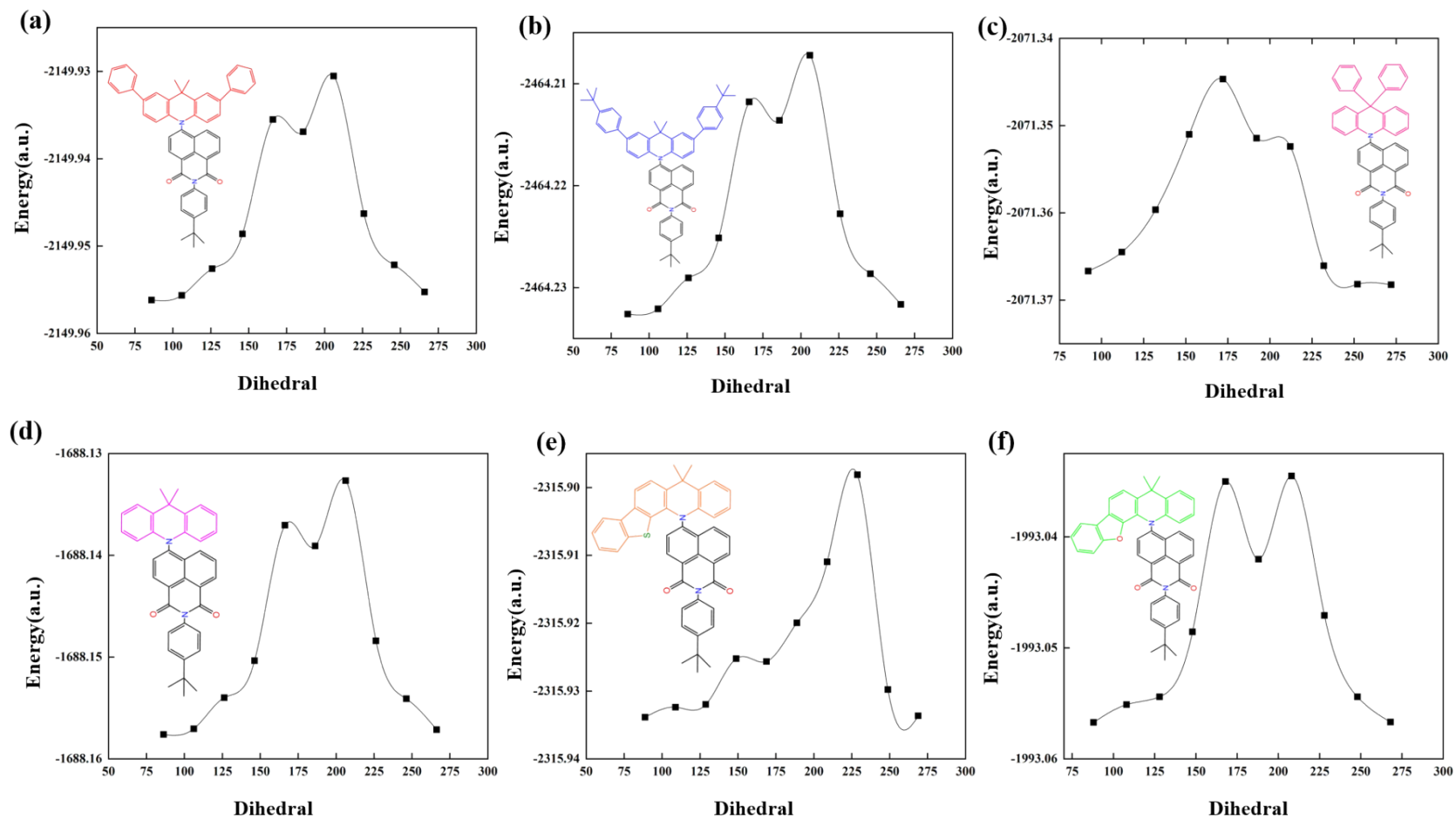
Figure S10. Potential energy curves of ground states for six molecules.
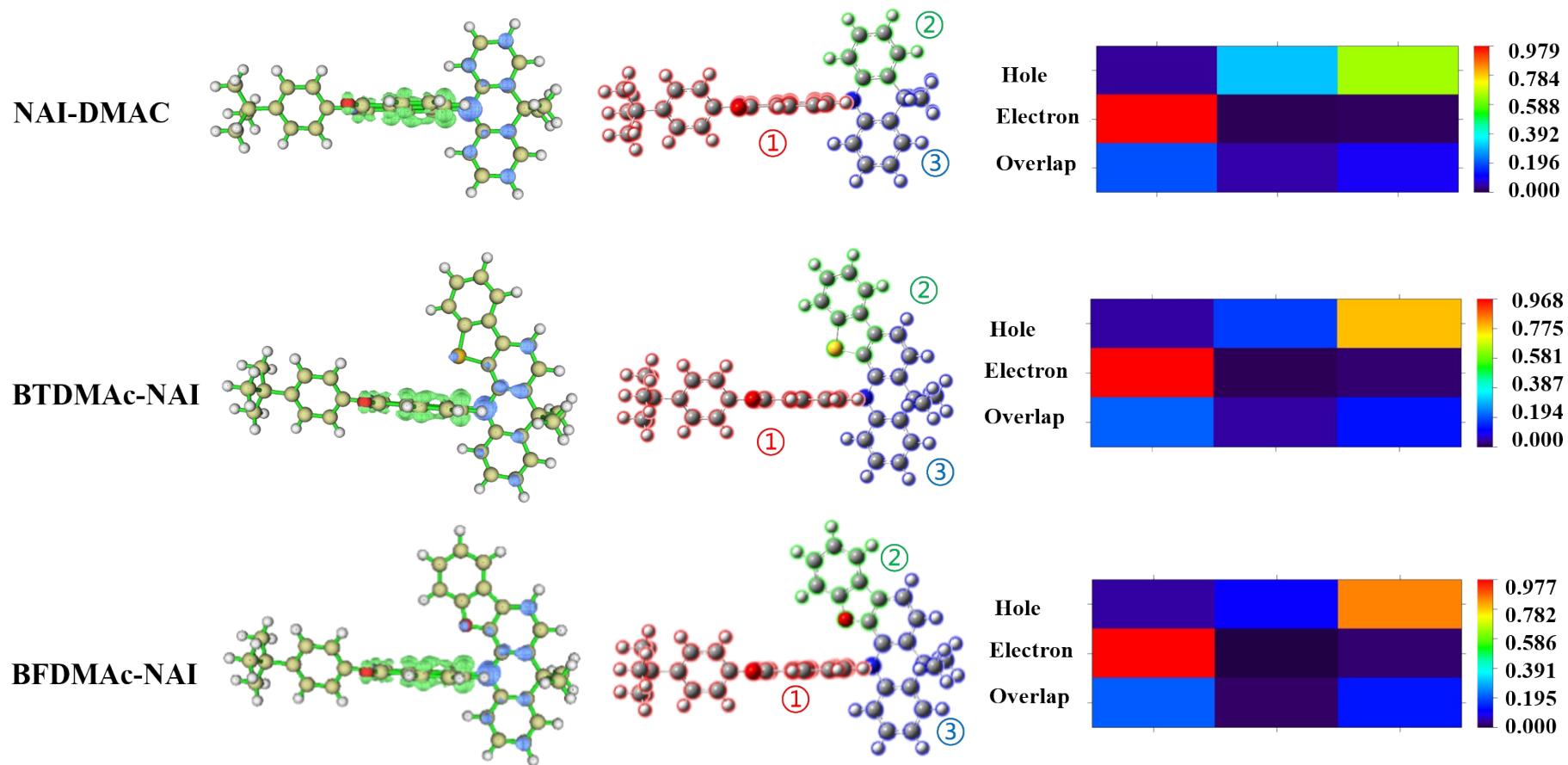
Figure S11. Distributions of holes and electrons and heat maps of S_1 state for NAI-DMAC, BTDMAc-NAI and BFDMAc-NAI in toluene.
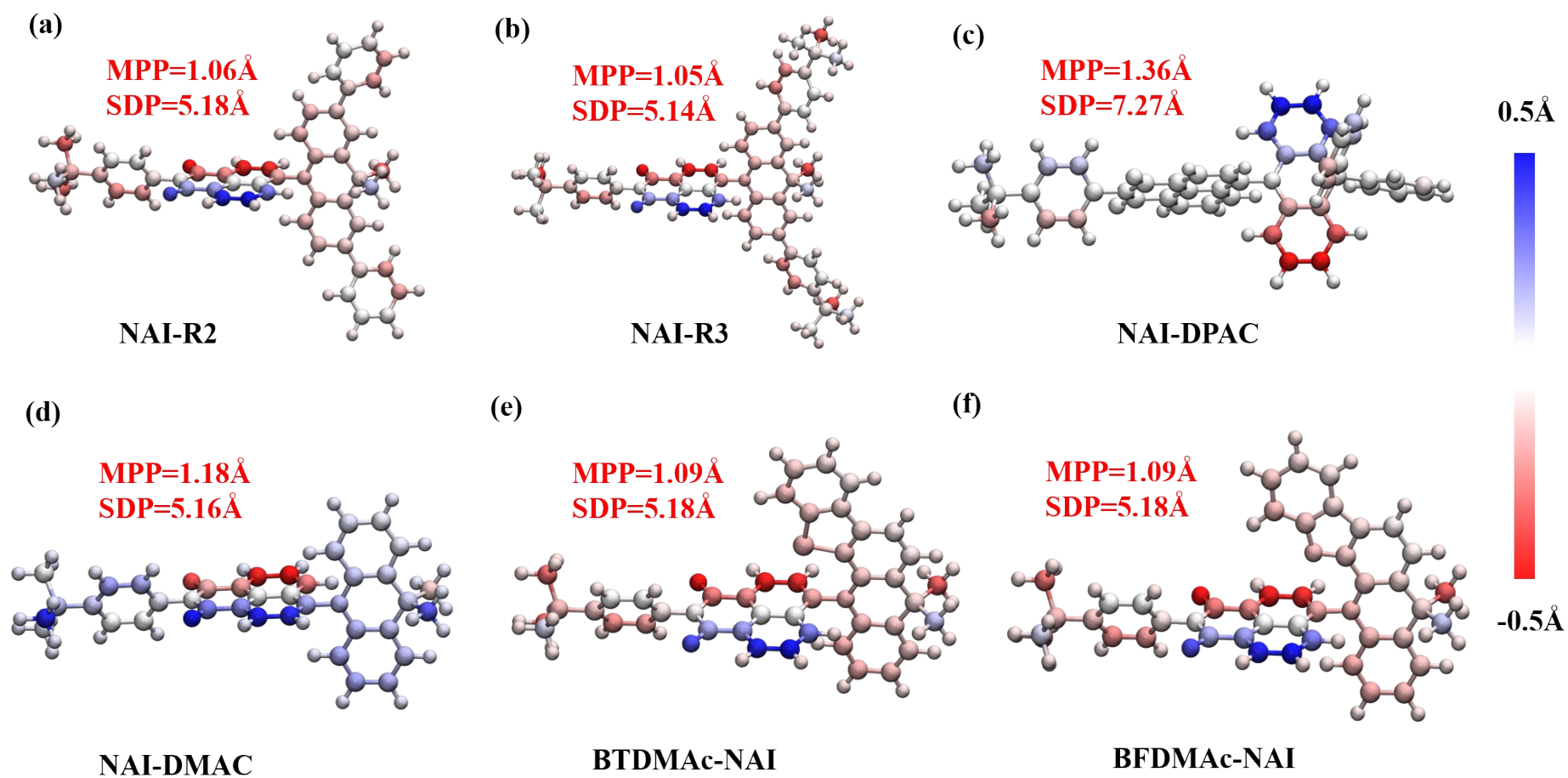
Figure S12. The planarity analysis of the six molecules based on S1 state.
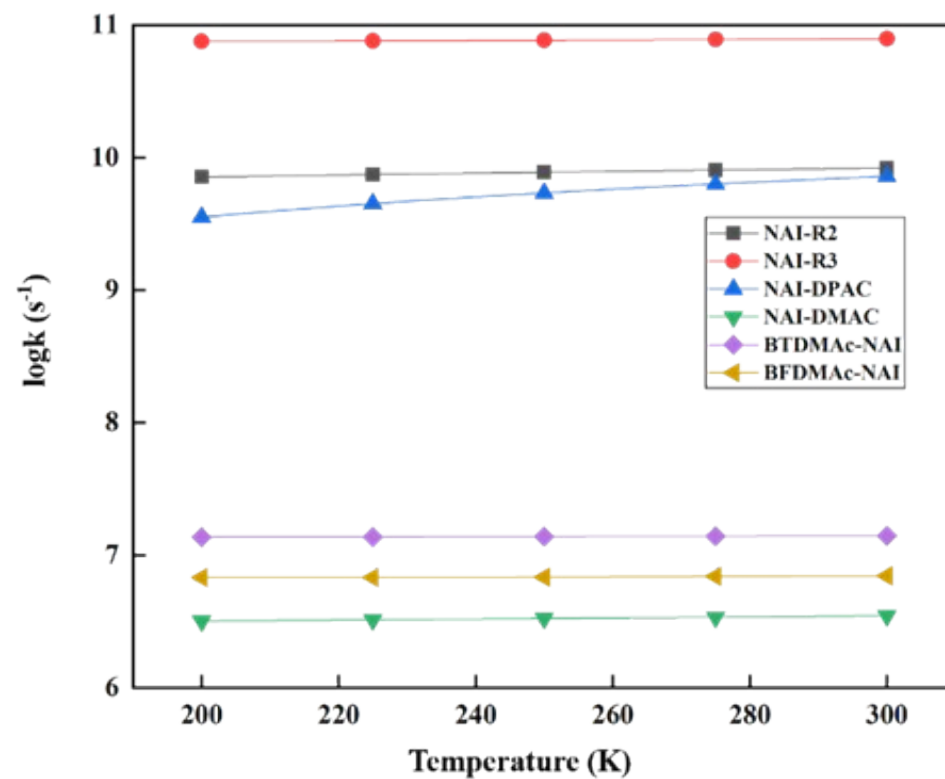
Figure S13. Variations of the knr with temperatures for NAI-R2，NAI-R3，NAI-DPAC，NAI-DMAC，BTDMAc-NAI and BFDMAc-NAI in toluene.
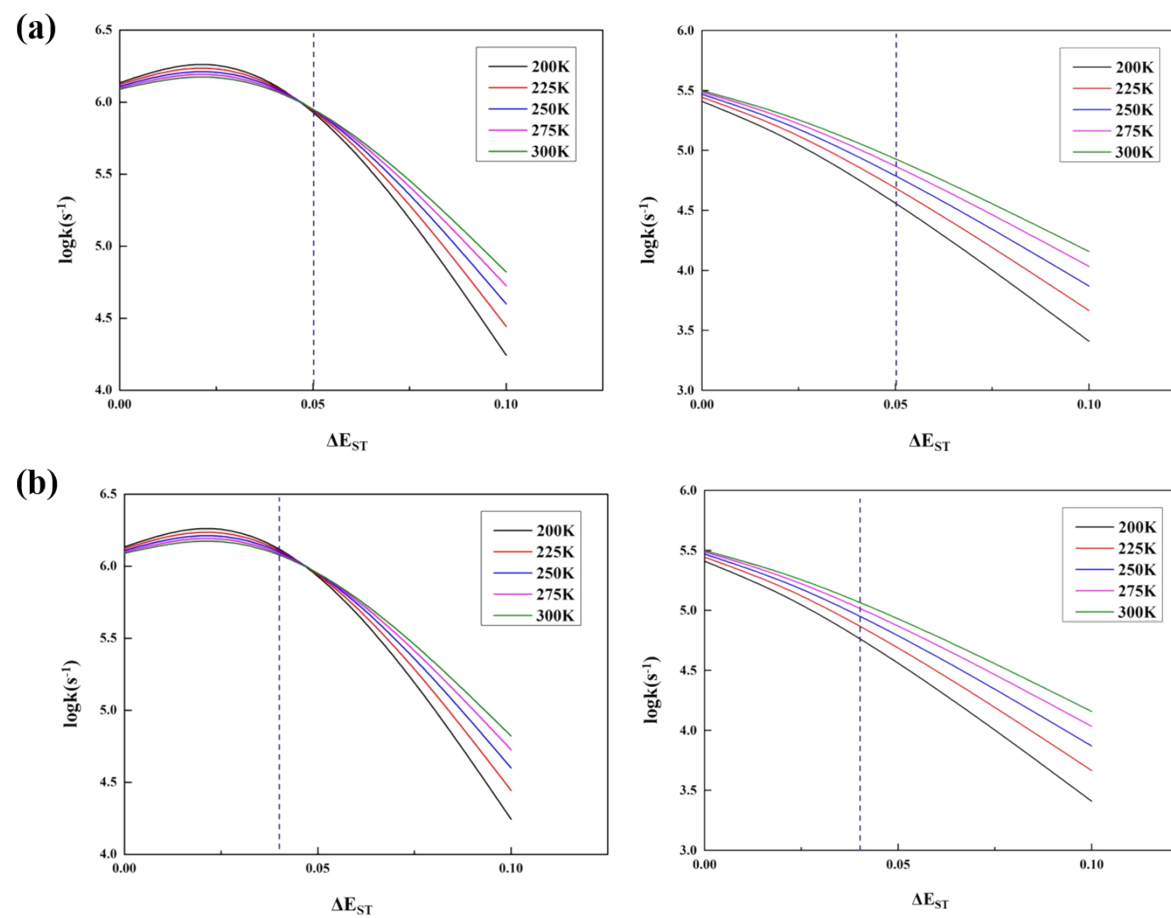
Figure S14. ISC rate constants and RISC rate constants as a function of the energy gap for NAI-R2 (a) and NAI-R3 (b) of different temperature in toluene.
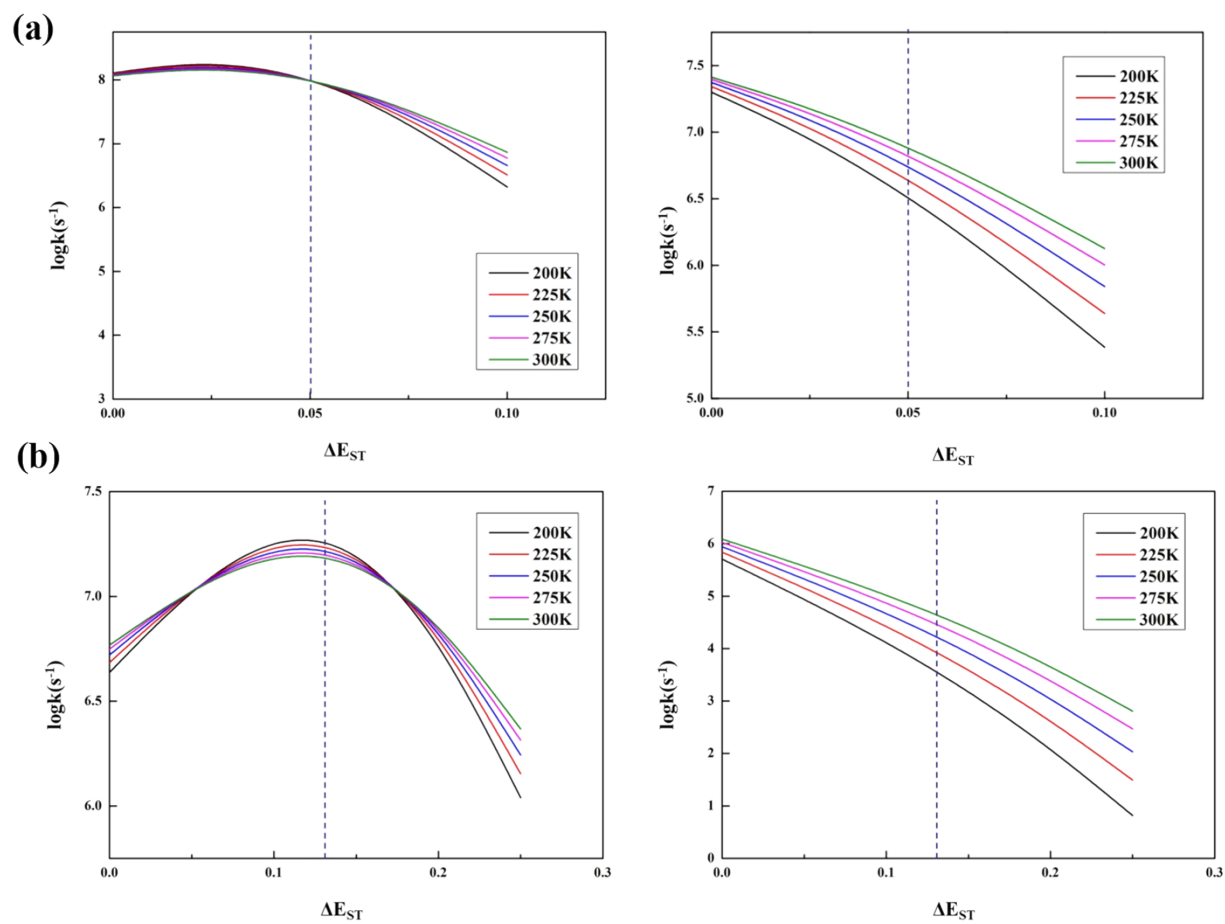
Figure S15. ISC rate constants and RISC rate constants as a function of the energy gap for NAI-DPAC (a) and NAI-DMAC (b) of different temperature in toluene.

Table S1. Geometry parameters of S_0, S_1 and T_1 states for NAI-R3 as well as their differences (Δ). (Bond length: Å. Bond angle: º. Dihedral angle: º.)

	Geometry	Atomic number	S_0	S_1	T_1	$\Delta|S_0 - S_1|$	$\Delta|S_1 - T_1|$
Bond length	B_1	2-28	1.439	1.435	1.437	0.004	0.002
	B_2	19-50	1.426	1.437	1.410	0.011	0.027
	B_3	44-69	1.488	1.480	1.486	0.008	0.006
	B_4	48-59	1.488	1.480	1.487	0.008	0.006
Bond angle	θ_1	2-28-27	117.5	117.2	117.7	0.3	0.5
	θ_2	13-19-50	119.0	118.0	121.4	1.1	3.4
	θ_3	44-69-71	121.3	121.3	120.9	0.04	0.4
	θ_4	41-48-59	121.3	121.0	121.2	0.3	0.2
Dihedral angle	α_1	3-2-28-27	62.6	59.6	60.9	3.1	0.7
	α_2	23-19-50-32	101.8	88.7	68.4	13.1	20.3
	α_3	72-76-92-98	119.8	59.1	119.7	60.0	59.7
	α_4	62-66-93-114	71.9	125.6	71.7	53.7	53.9

Table S2. Geometry parameters of S_0, S_1 and T_1 states for NAI-DPAC as well as their differences (Δ). (Bond length: Å. Bond angle: º. Dihedral angle: º.)

	Geometry	Atomic number	S_0	S_1	T_1	$\Delta|S_0 - S_1|$	$\Delta|S_1 - T_1|$
Bond length	B_1	2-28	1.439	1.435	1.438	0.004	0.003
	B_2	19-50	1.424	1.436	1.413	0.012	0.023
	B_3	38-77	1.562	1.567	1.562	0.005	0.004
	B_4	38-66	1.537	1.543	1.538	0.006	0.006
Bond angle	θ_1	1-2-28	119.8	120.3	119.9	0.4	0.4
	θ_2	13-19-50	120.2	118.7	122.0	1.4	3.2
	θ_3	41-35-38	124.6	122.4	124.9	2.2	2.5
	θ_4	78-77-38	120.7	118.8	119.5	1.9	0.7
Dihedral angle	α_1	3-2-28-27	63.1	59.8	60.1	3.3	0.3
	α_2	13-19-50-32	92.1	86.0	110.5	6.1	24.5
	α_3	35-38-77-78	148.4	129.0	142.4	19.4	13.4
	α_4	35-38-77-79	113.6	117.4	134.3	3.8	16.9

Table S3. Geometry parameters of S_0, S_1 and T_1 states for NAI-DMAC as well as their differences (Δ). (Bond length: Å. Bond angle: º. Dihedral angle: º.)

	Geometry	Atomic number	S_0	S_1	T_1	$\Delta\|S_0 - S_1\|$	$\Delta\|S_1 - T_1\|$
	B_1	2-28	1.439	1.435	1.438	0.004	0.002
	B_2	19-50	1.426	1.436	1.409	0.010	0.026
Bond length	B_3	5-59	1.539	1.540	1.539	0.0003	0.0002
	B_4	20-22	1.384	1.420	1.448	0.036	0.272
	B_5	19-23	1.382	1.413	1.455	0.031	0.042
	B_6	15-16	1.384	1.413	1.434	0.029	0.021
	θ_1	3-2-28	119.9	120.2	120.1	0.3	0.2
Bond angle	θ_2	13-19-50	119.2	118.0	121.4	1.2	3.4
	θ_3	59-5-6	123.0	123.0	123.0	0.1	0.05
	θ_4	55-38-51	109.3	109.5	109.4	0.2	0.1
Dihedral angle	α_1	3-2-28-27	63.1	60.8	61.4	2.3	0.7
	α_2	23-19-50-31	94.2	91.2	112.8	3.0	21.6

Table S4. Geometry parameters of S_0, S_1 and T_1 states for BTDMAc-NAI as well as their differences (Δ). (Bond length: Å. Bond angle: º. Dihedral angle: º.)

	Geometry	Atomic number	S_0	S_1	T_1	$\Delta\|S_0 - S_1\|$	$\Delta\|S_1 - T_1\|$
Bond length	B_1	2-28	1.439	1.436	1.438	0.003	0.002
	B_2	19-48	1.428	1.431	1.411	0.003	0.020
	B_3	72-73	1.774	1.773	1.775	0.002	0.003
	B_4	20-22	1.384	1.384	1.384	0	0
	B_5	19-23	1.383	1.416	1.456	0.033	0.04
	B_6	15-16	1.384	1.412	1.437	0.028	0.025
Bond angle	θ_1	1-2-28	119.9	120.2	120.0	0.3	0.1
	θ_2	13-19-48	119.0	117.9	120.3	1.1	2.4
	θ_3	34-72-73	91.3	91.4	91.3	0.2	0.2
	θ_4	38-33-37	117.4	118.2	117.7	0.8	0.5
Dihedral angle	α_1	1-2-28-26	62.5	59.9	60.5	2.5	0.6
	α_2	13-19-48-32	88.8	88.2	108.9	0.7	20.7

Table S5. Geometry parameters of S_0, S_1 and T_1 states for BFDMAc-NAI as well as their differences (Δ). (Bond length: Å. Bond angle: º. Dihedral angle: º.)

	Geometry	Atomic number	S_0	S_1	T_1	$\Delta|S_0 - S_1|$	$\Delta|S_1 - T_1|$
	B_1	2-28	1.439	1.435	1.438	0.004	0.003
	B_2	19-48	1.429	1.434	1.411	0.005	0.024
Bond length	B_3	82-34	1.368	1.344	1.363	0.024	0.019
	B_4	20-22	1.384	1.421	1.450	0.037	0.029
	B_5	19-23	1.380	1.410	1.454	0.030	0.044
	B_6	15-16	1.385	1.141	1.436	0.244	0.295
	θ_1	1-2-28	119.8	120.3	120.0	0.5	0.2
Bond angle	θ_2	13-19-48	118.8	117.7	120.3	1.2	2.6
	θ_3	28-26-15	116.8	116.4	117.0	0.4	0.6
	θ_4	72-82-34	107.1	107.7	107.1	0.6	0.6
Dihedral angle	α_1	3-2-28-27	62.2	59.4	59.9	2.7	0.5
	α_2	13-19-48-32	88.0	91.7	114.1	3.8	22.3

Table S6. Calculated radiative and non-radiative rates (s^{-1}) from S_1 to S_0, the SOC constants (cm^{-1}), the ISC and RISC rates (s^{-1}) as well as the energy gap ΔE_{st} (eV) between S_1 and T_1.

	ΔE_{st}	SOC	K_r	K_{nr}	ISC	RISC
NAI-R2	0.05	0.024	3.7×10^4	8.3×10^9	7.4×10^5	3.5×10^4
NAI-R3	0.04	0.029	1.1×10^5	7.9×10^{10}	1.2×10^6	1.2×10^5
NAI-DPAC	0.21	0.532	0.3×10^5	7.2×10^9	1.7×10^8	3.7×10^4
NAI-DMAC	0.09	0.023	2.0×10^4	3.5×10^6	4.9×10^5	4.9×10^3
BTDMAc-NAI	0.06	0.281	1.6×10^5	1.4×10^7	7.0×10^7	5.7×10^6
BFDMAc-NAI	0.13	0.143	1.7×10^5	7.0×10^6	1.5×10^7	4.5×10^4