Supplementary information

# Computational Design of Efficient Near-Infrared TADF Emitters with Hot-exciton Characteristics

Jesni M Jacob[a], Pralok K. Samanta[b] and Mahesh Kumar Ravva[a]*

[a]*Department of Chemistry, SRM University-AP, Amaravati, India 522240*

[b]*Department of Chemistry, School of Science, GITAM University, Hyderabad, India 502329*

**corresponding author: mahesh.r@srmap.edu.in*

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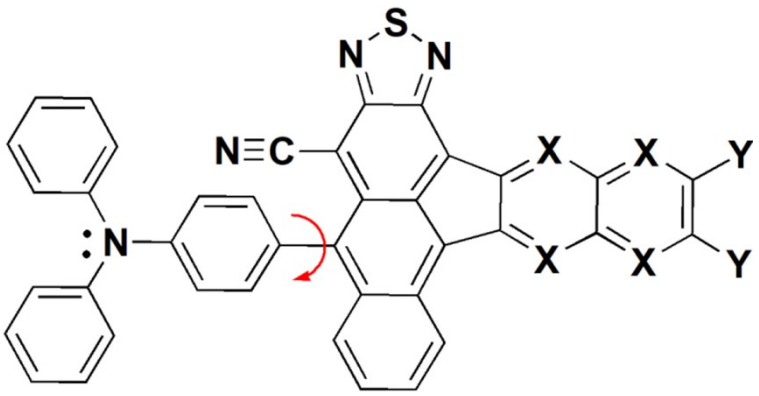
| **Figure S7** | Comparison of new structures based on thiophene, tetrazine and nitrogen substituted D1AZ2BZH at M06-2X/6-31G** level of theory. |

**Table S1.** Calculated dihedral angles between donor and AZ units, HOMO and LUMO energies as obtained from M06-2X/6-31G** level of theory in the gas phase.




| Compounds | Dihedral angle $D-A$Z (in º) | HOMO (eV) | LUMO (eV) | HOMO-LUMO gap (eV) |
|---|---|---|---|---|
| D1AZ2BZH | 85.81 | -6.09 | -2.95 | -3.14 |
| D1AZ2BZF | 85.05 | -6.15 | -3.07 | -3.08 |
| D1AZ2BZCN | 83.36 | -6.32 | -3.42 | -2.90 |
| D1AZ2PZH | 84.18 | -6.25 | -3.28 | -2.97 |
| D1AZ2PZF | 82.22 | -6.32 | -3.41 | -2.91 |
| D1AZ2PZCN | 78.33 | -6.48 | -3.73 | -2.75 |
| D1AZBZPZH | 85.50 | -6.15 | -3.09 | -3.06 |
| D1AZBZPZF | 84.56 | -6.22 | -3.22 | -3.00 |
| D1AZBZPZCN | 82.61 | -6.37 | -3.54 | -2.83 |
| D1AZPZBZH | 84.80 | -6.18 | -3.12 | -3.06 |
| D1AZPZBZHF | 83.70 | -6.24 | -3.24 | -3.00 |
| D1AZPZBZCN | 80.94 | -6.41 | -3.59 | -2.82 |

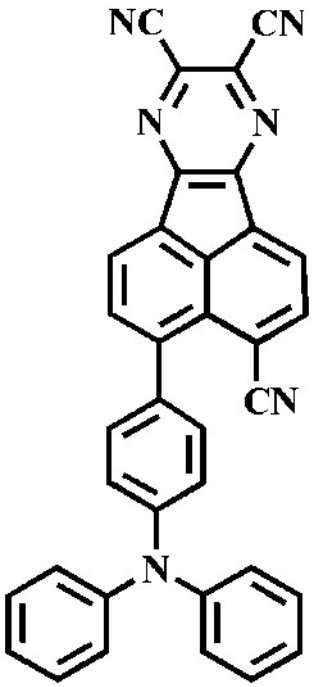



**Figure S1.** Structure of CAT-1.

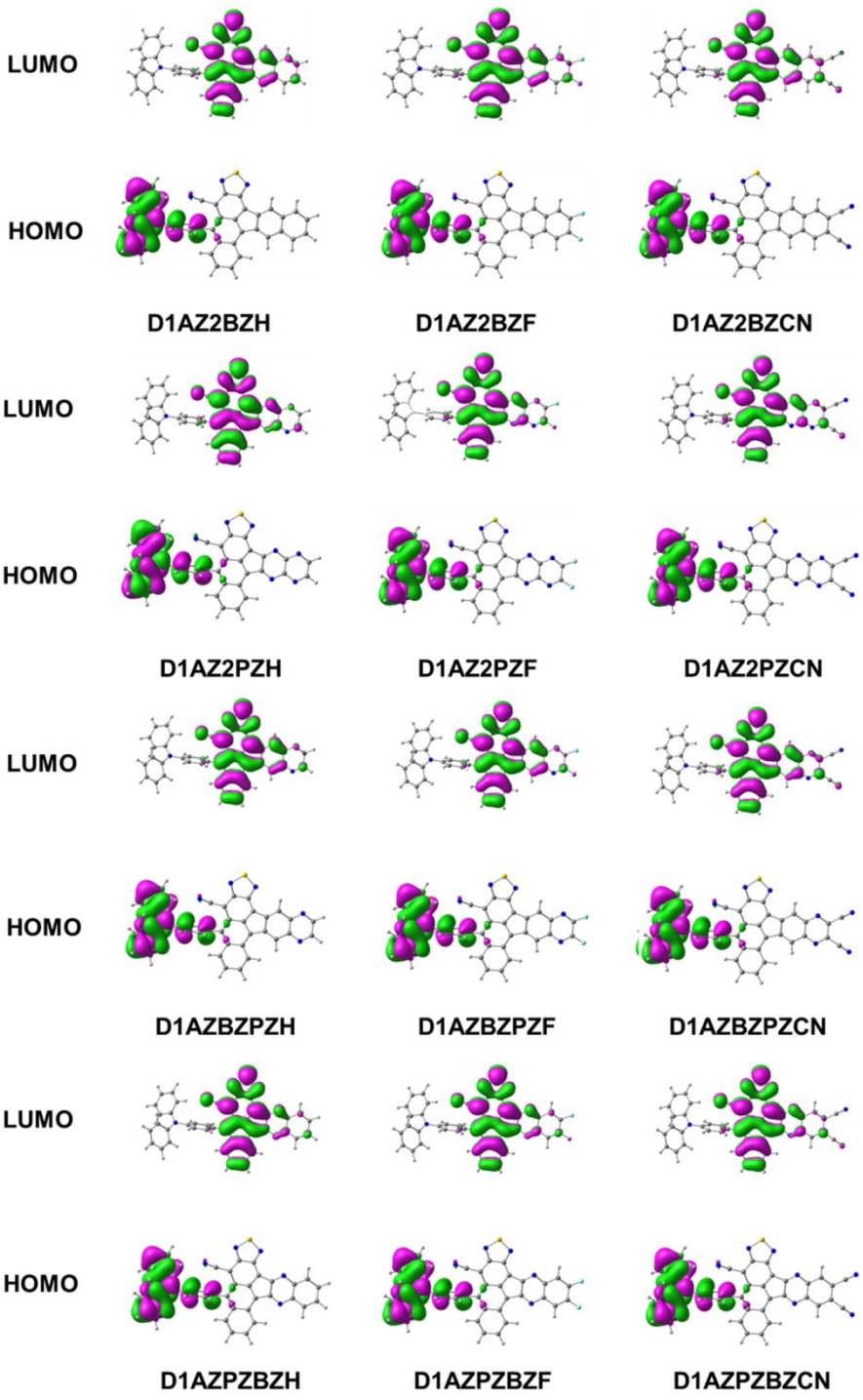



**Figure S2.** HOMO-LUMO wavefunctions for the newly designed molecules using M06-2X/6-31G** level of theory.

**Table S2**. Calculated five lowest singlets, and five lowest triplets state energies as obtained from M06-2X/6-31G** level of theory in the gas phase. All values are in eV.

| | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $S_5$ | $T_1$ | $T_2$ | $T_3$ | $T_4$ | $T_5$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **D1AZ2BZH** | 1.90 | 2.03 | 2.63 | 3.30 | 3.57 | 0.63 | 1.98 | 2.03 | 2.77 | 2.83 |
| **D1AZ2BZF** | 1.91 | 1.98 | 2.62 | 3.38 | 3.56 | 0.64 | 1.95 | 1.99 | 2.76 | 2.93 |
| **D1AZ2BZCN** | 1.77 | 1.94 | 2.77 | 3.43 | 3.49 | 0.66 | 1.77 | 2.03 | 2.72 | 2.88 |
| **D1AZ2PZH** | 1.81 | 2.02 | 2.90 | 3.00 | 3.22 | 0.74 | 1.81 | 2.08 | 2.66 | 2.70 |
| **D1AZ2PZF** | 1.74 | 2.02 | 2.82 | 3.25 | 3.34 | 0.75 | 1.74 | 2.05 | 2.64 | 2.86 |
| **D1AZ2PZCN** | 1.58 | 2.00 | 2.72 | 2.94 | 3.01 | 0.75 | 1.58 | 2.04 | 2.59 | 2.61 |
| **D1AZBZPZH** | 1.92 | 1.97 | 2.74 | 3.50 | 3.60 | 0.66 | 1.94 | 2.02 | 2.74 | 3.00 |
| **D1AZBZPZF** | 1.86 | 1.97 | 2.69 | 3.51 | 3.60 | 0.68 | 1.86 | 2.00 | 2.72 | 3.03 |
| **D1AZBZPZCN** | 1.70 | 1.95 | 2.83 | 3.03 | 3.25 | 0.68 | 1.70 | 2.03 | 2.65 | 2.71 |
| **D1AZPZBZH** | 1.90 | 2.01 | 2.78 | 3.27 | 3.44 | 0.72 | 1.91 | 2.05 | 2.70 | 2.96 |
| **D1AZPZBZF** | 1.84 | 2.01 | 2.76 | 3.38 | 3.40 | 0.73 | 1.84 | 2.04 | 2.68 | 2.92 |
| **D1AZPZBZCN** | 1.66 | 2.00 | 2.91 | 3.14 | 3.32 | 0.74 | 1.66 | 2.07 | 2.65 | 2.80 |

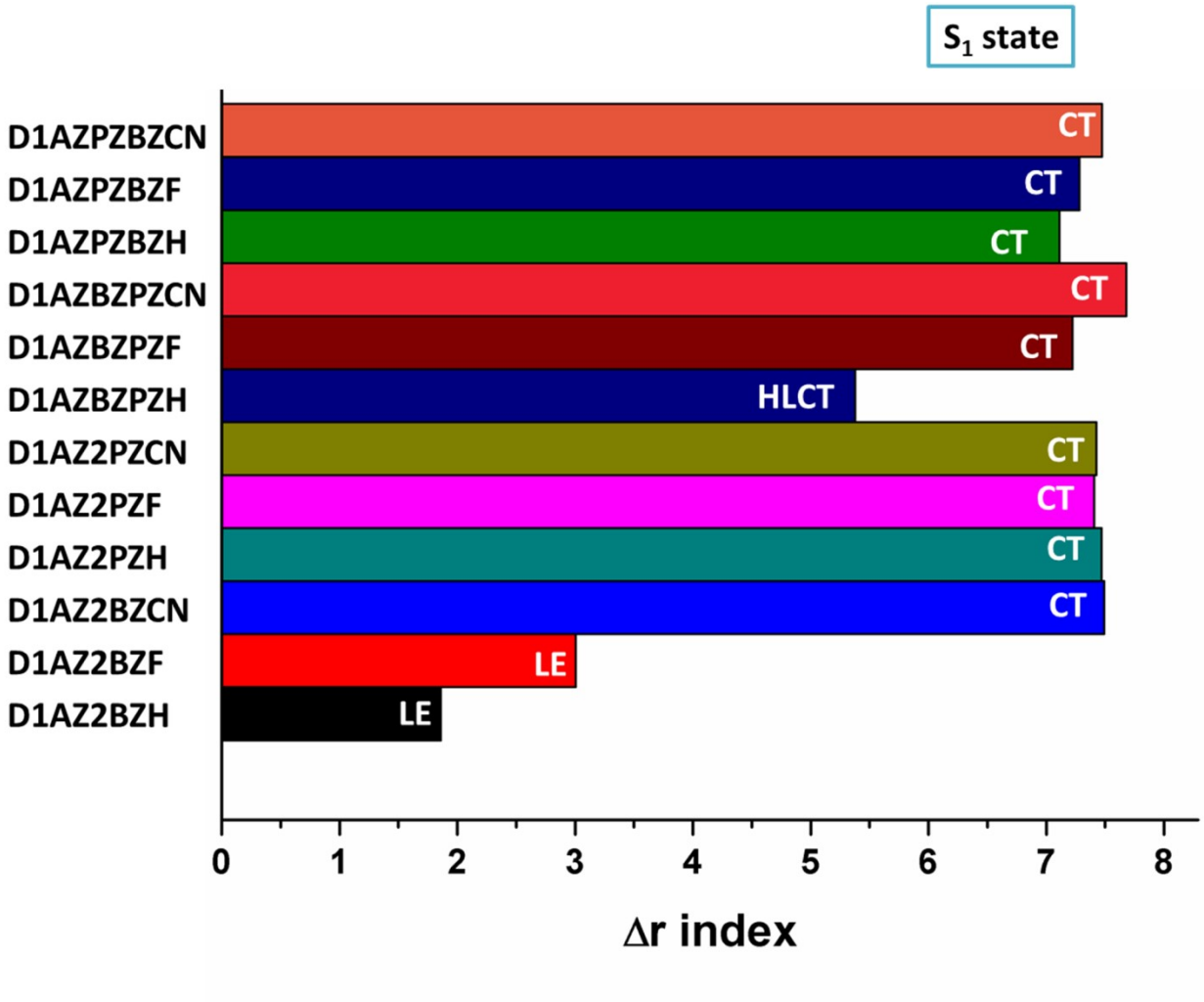
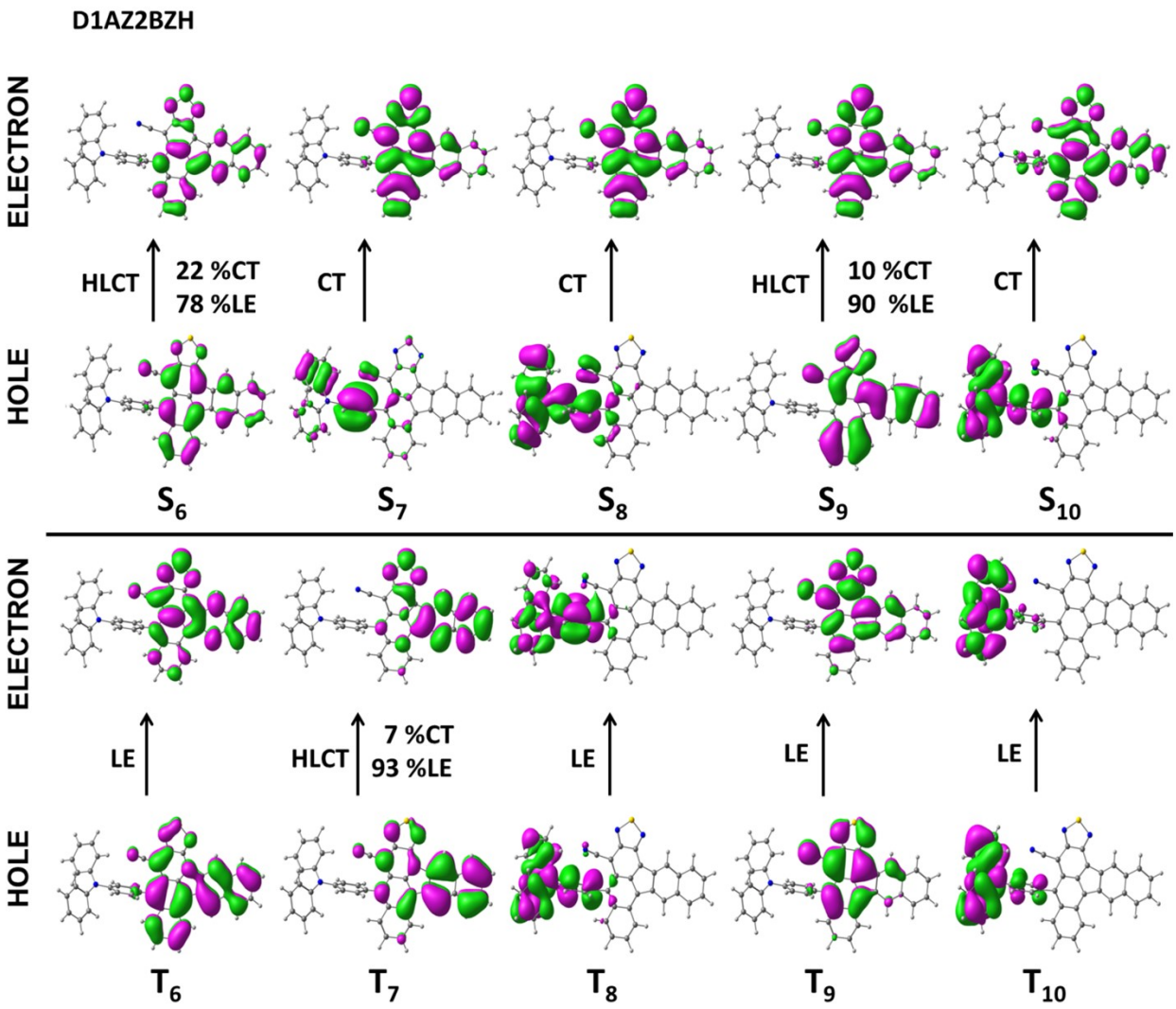
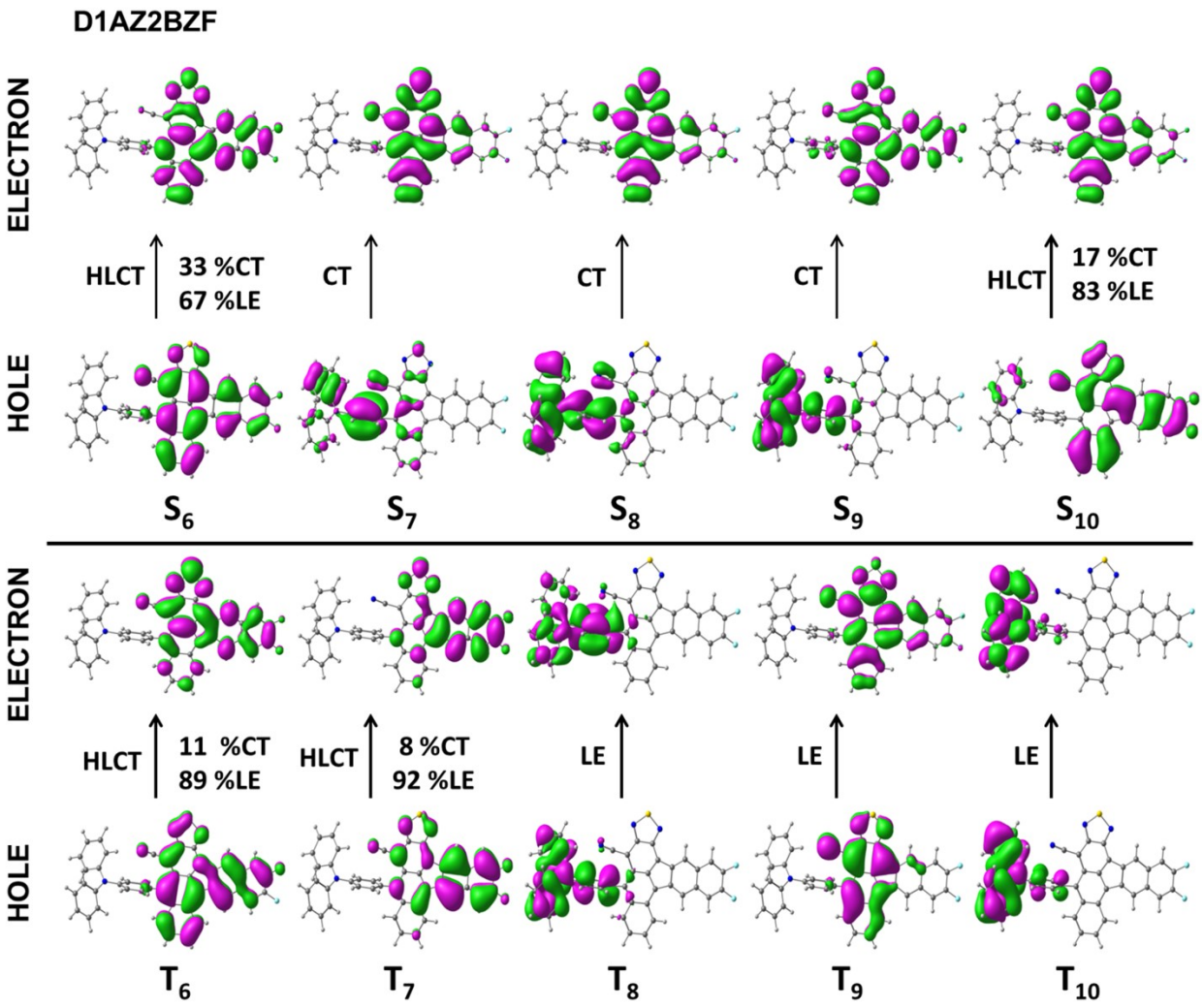



**Figure S3.** Representation of calculated Δr indices for the molecules under study.


D1AZ2BZH
ELECTRON
HOLE
HLCT
22 %CT
78 %LE
CT
CT
HLCT
10 %CT
90 %LE
CT
S6
S7
S8
S9
S10
ELECTRON
HOLE
LE
HLCT
7 %CT
93 %LE
LE
LE
LE
T6
T7
T8
T9
T10


D1AZ2BZF
ELECTRON
HOLE
HLCT
33 %CT
67 %LE
CT
CT
CT
HLCT
17 %CT
83 %LE
S6
S7
S8
S9
S10
ELECTRON
HOLE
HLCT
11 %CT
89 %LE
HLCT
8 %CT
92 %LE
LE
LE
LE
T6
T7
T8
T9
T10

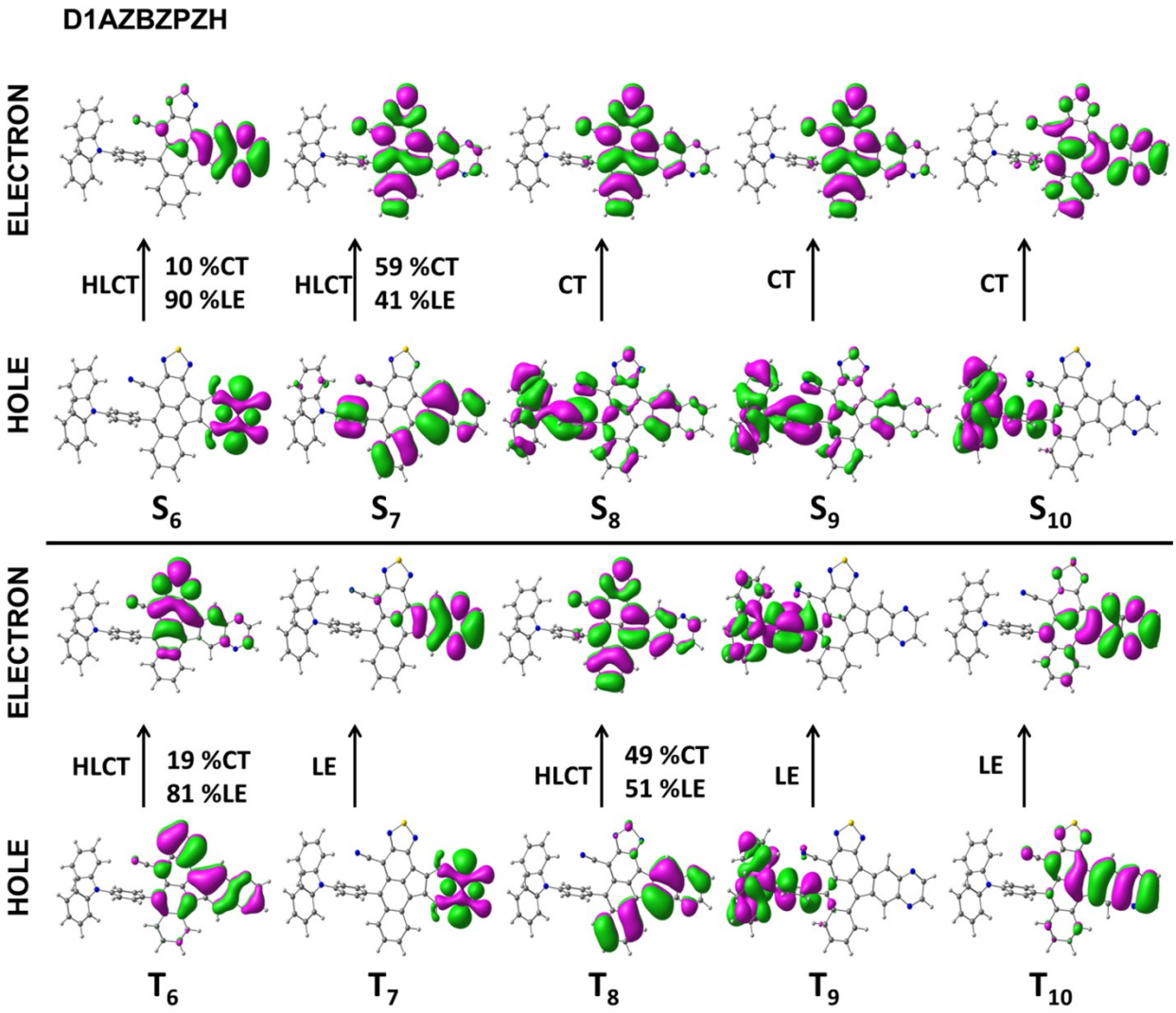



**Figure S4.** Spatial distribution of the hole and electron wavefunctions corresponds to the singlet ($S_6$-$S_{10}$) and triplet ($T_6$-$T_{10}$) excited states of the three potential molecules.

**Table S3**. Calculated Δr indices of the newly designed molecules for the $S_n$ and $T_m$ states in Å units.

| | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S9 | S10 | T1 | T2 | T3 | T4 | T5 | T6 | T7 | T8 | T9 | T10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **D1AZ2BZH** | 1.86 | 7.36 | 2.60 | 3.67 | 2.73 | 1.75 | 6.05 | 8.06 | 2.43 | 9.15 | 1.43 | 2.98 | 7.32 | 2.48 | 3.41 | 1.72 | 2.28 | 1.64 | 1.88 | 1.36 |
| | **LE** | **CT** | **HLCT** | **HLCT** | **HLCT** | **LE** | **CT** | **CT** | **HLCT** | **CT** | **LE** | **HLCT** | **CT** | **HLCT** | **HLCT** | **LE** | **HLCT** | **LE** | **LE** | **LE** |
| **D1AZ2BZF** | 3.01 | 6.15 | 2.83 | 3.39 | 2.64 | 2.49 | 5.44 | 7.57 | 8.50 | 3.13 | 1.43 | 6.33 | 4.12 | 2.11 | 3.15 | 2.02 | 2.09 | 1.64 | 1.92 | 1.46 |
| | **HLCT** | **CT** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **CT** | **CT** | **CT** | **HLCT** | **LE** | **CT** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **LE** | **LE** | **LE** |
| **D1AZ2BZCN** | 7.49 | 1.67 | 2.22 | 3.54 | 3.72 | 4.85 | 7.47 | 4.26 | 9.92 | 5.77 | 1.39 | 7.70 | 2.43 | 1.70 | 2.65 | 3.05 | 2.54 | 2.22 | 2.96 | 6.47 |
| | **CT** | **LE** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **CT** | **HLCT** | **CT** | **CT** | **LE** | **CT** | **HLCT** | **LE** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **CT** |
| **D1AZ2PZH** | 7.47 | 1.73 | 1.98 | 2.95 | 3.23 | 3.59 | 10.36 | 4.09 | 4.61 | 7.00 | 1.61 | 7.45 | 2.34 | 2.10 | 1.87 | 3.02 | 4.32 | 2.93 | 3.21 | 8.20 |
| | **CT** | **LE** | **LE** | **HLCT** | **HLCT** | **HLCT** | **CT** | **HLCT** | **HLCT** | **CT** | **LE** | **CT** | **HLCT** | **HLCT** | **LE** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **CT** |
| **D1AZ2PZF** | 7.41 | 1.72 | 2.26 | 4.26 | 3.23 | 9.79 | 5.14 | 1.22 | 3.47 | 7.42 | 1.61 | 7.39 | 2.51 | 1.85 | 3.11 | 1.33 | 2.74 | 2.40 | 3.19 | 8.69 |
| | **CT** | **LE** | **HLCT** | **HLCT** | **HLCT** | **CT** | **HLCT** | **LE** | **HLCT** | **CT** | **LE** | **CT** | **HLCT** | **LE** | **HLCT** | **LE** | **HLCT** | **HLCT** | **HLCT** | **CT** |
| **D1AZ2PZCN** | 7.43 | 1.69 | 6.06 | 9.07 | 0.83 | 2.67 | 6.57 | 3.54 | 7.39 | 1.94 | 1.68 | 7.26 | 2.96 | 3.98 | 1.62 | 0.63 | 10.72 | 2.22 | 2.95 | 3.74 |
| | **CT** | **LE** | **CT** | **CT** | **LE** | **HLCT** | **CT** | **HLCT** | **CT** | **LE** | **LE** | **CT** | **HLCT** | **HLCT** | **LE** | **LE** | **CT** | **HLCT** | **HLCT** | **HLCT** |
| **D1AZBZPZH** | 5.38 | 3.74 | 2.21 | 2.93 | 3.11 | 3.24 | 3.97 | 5.82 | 6.27 | 10.52 | 1.42 | 7.48 | 2.63 | 1.83 | 3.15 | 2.29 | 3.29 | 2.41 | 1.66 | 1.72 |
| | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **CT** | **CT** | **CT** | **LE** | **CT** | **HLCT** | **LE** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **LE** | **LE** |
| **D1AZBZPZF** | 7.22 | 1.90 | 2.36 | 3.08 | 4.95 | 5.24 | 7.42 | 2.32 | 10.57 | 7.81 | 1.43 | 7.60 | 2.62 | 2.28 | 3.17 | 2.58 | 2.01 | 1.78 | 1.75 | 3.33 |

| | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **CT** | **LE** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **CT** | **HLCT** | **CT** | **CT** | **LE** | **CT** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **LE** | **LE** | **HLCT** |
| **D1AZBZPZCN** | 7.68 | 1.49 | 2.25 | 4.90 | 11.59 | 6.00 | 3.71 | 6.86 | 3.10 | 7.46 | 1.39 | 7.68 | 2.50 | 3.43 | 2.31 | 2.73 | 1.34 | 12.20 | 2.47 | 3.10 |
| | **CT** | **LE** | **HLCT** | **HLCT** | **CT** | **CT** | **HLCT** | **CT** | **HLCT** | **CT** | **LE** | **CT** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **LE** | **CT** | **HLCT** | **HLCT** |
| **D1AZPZBZH** | 7.11 | 2.08 | 2.85 | 3.42 | 2.59 | 3.63 | 4.61 | 1.04 | 6.31 | 6.62 | 1.60 | 7.52 | 2.72 | 2.34 | 2.46 | 2.34 | 2.39 | 2.19 | 3.81 | 0.99 |
| | **CT** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **LE** | **CT** | **CT** | **LE** | **CT** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **LE** |
| **D1AZPZBZF** | 7.28 | 1.88 | 3.15 | 3.42 | 2.91 | 3.84 | 6.20 | 6.01 | 0.94 | 8.35 | 1.61 | 7.48 | 2.97 | 1.89 | 2.68 | 2.03 | 2.59 | 1.02 | 2.39 | 2.17 |
| | **CT** | **LE** | **HLCT** | **HLCT** | **HLCT** | **HLCT** | **CT** | **CT** | **LE** | **CT** | **LE** | **CT** | **HLCT** | **LE** | **HLCT** | **HLCT** | **HLCT** | **LE** | **HLCT** | **HLCT** |
| **D1AZPZBZCN** | 7.48 | 1.66 | 2.63 | 4.50 | 9.32 | 2.65 | 6.34 | 5.25 | 5.41 | 1.26 | 1.57 | 7.46 | 2.74 | 2.65 | 3.21 | 1.10 | 2.24 | 9.92 | 1.53 | 2.75 |
| | **CT** | **LE** | **HLCT** | **HLCT** | **CT** | **HLCT** | **CT** | **HLCT** | **HLCT** | **LE** | **LE** | **CT** | **HLCT** | **HLCT** | **HLCT** | **LE** | **HLCT** | **CT** | **LE** | **HLCT** |

**Table S4.** Charge transfer ratio among fragments of potential hot-exciton NIR-TADF emitters.

| D1AZ2BZH | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $S_1$ | 1 | 2 | 3 | $S_2$ | 1 | 2 | 3 | $S_3$ | 1 | 2 | 3 | $S_4$ | 1 | 2 | 3 | $S_5$ | 1 | 2 | 3 |
| 1 | 0.000 | 0.032 | 0.003 | 1 | 0.000 | 0.850 | 0.104 | 1 | 0.000 | 0.004 | -0.001 | 1 | 0.000 | 0.006 | -0.002 | 1 | 0.000 | 0.032 | 0.005 |
| 2 | | 0.000 | -0.135 | 2 | | 0.000 | -0.003 | 2 | | 0.000 | -0.457 | 2 | | 0.000 | -0.624 | 2 | | 0.000 | 0.056 |
| 3 | | | 0.000 | 3 | | | 0.000 | 3 | | | 0.000 | 3 | | | 0.000 | 3 | | | 0.000 |
| | | | | | | | | | | | | | | | | | | | |
| $S_6$ | 1 | 2 | 3 | $S_7$ | 1 | 2 | 3 | $S_8$ | 1 | 2 | 3 | $S_9$ | 1 | 2 | 3 | $S_{10}$ | 1 | 2 | 3 |
| 1 | 0.000 | 0.033 | 0.024 | 1 | 0.000 | 0.819 | 0.101 | 1 | 0.000 | 0.812 | 0.115 | 1 | 0.000 | 0.004 | 0.001 | 1 | 0.000 | 0.587 | 0.388 |
| 2 | | 0.000 | 0.160 | 2 | | 0.000 | -0.001 | 2 | | 0.000 | 0.005 | 2 | | 0.000 | -0.097 | 2 | | 0.000 | 0.005 |
| 3 | | | 0.000 | 3 | | | 0.000 | 3 | | | 0.000 | 3 | | | 0.000 | 3 | | | 0.000 |
| | | | | | | | | | | | | | | | | | | | |
| $T_1$ | 1 | 2 | 3 | $T_2$ | 1 | 2 | 3 | $T_3$ | 1 | 2 | 3 | $T_4$ | 1 | 2 | 3 | $T_5$ | 1 | 2 | 3 |
| 1 | 0.000 | 0.013 | 0.002 | 1 | 0.000 | 0.096 | 0.018 | 1 | 0.000 | 0.003 | 0.039 | 1 | 0.000 | 0.013 | 0.002 | 1 | 0.000 | 0.005 | -0.002 |
| 2 | | 0.000 | -0.001 | 2 | | 0.000 | -0.164 | 2 | | 0.000 | 0.005 | 2 | | 0.000 | 0.080 | 2 | | 0.000 | -0.625 |
| 3 | | | 0.000 | 3 | | | 0.000 | 3 | | | 0.000 | 3 | | | 0.000 | 3 | | | 0.000 |
| | | | | | | | | | | | | | | | | | | | |
| $T_6$ | 1 | 2 | 3 | $T_7$ | 1 | 2 | 3 | $T_8$ | 1 | 2 | 3 | $T_9$ | 1 | 2 | 3 | $T_{10}$ | 1 | 2 | 3 |
| 1 | 0.000 | 0.011 | 0.005 | 1 | 0.000 | 0.001 | 0.001 | 1 | 0.000 | 0.031 | 0.000 | 1 | 0.000 | 0.018 | 0.005 | 1 | 0.000 | -0.012 | 0.001 |
| 2 | | 0.000 | -0.088 | 2 | | 0.000 | -0.064 | 2 | | 0.000 | 0.000 | 2 | | 0.000 | 0.038 | 2 | | 0.000 | 0.000 |
| 3 | | | 0.000 | 3 | | | 0.000 | 3 | | | 0.000 | 3 | | | 0.000 | 3 | | | 0.000 |

| D1AZ2BZF | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $S_1$ | 1 | 2 | 3 | $S_2$ | 1 | 2 | 3 | $S_3$ | 1 | 2 | 3 | $S_4$ | 1 | 2 | 3 | $S_5$ | 1 | 2 | 3 |
| 1 | 0.000 | 0.170 | 0.020 | 1 | 0.000 | 0.712 | 0.085 | 1 | 0.000 | 0.004 | -0.001 | 1 | 0.000 | 0.022 | 0.001 | 1 | 0.000 | 0.049 | 0.008 |
| 2 | | 0.000 | -0.096 | 2 | | 0.000 | -0.022 | 2 | | 0.000 | -0.488 | 2 | | 0.000 | -0.607 | 2 | | 0.000 | 0.067 |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 |
| | | | | | | | | | | | | | | | | | | | |
| **$S_6$** | **1** | **2** | **3** | **$S_7$** | **1** | **2** | **3** | **$S_8$** | **1** | **2** | **3** | **$S_9$** | **1** | **2** | **3** | **$S_{10}$** | **1** | **2** | **3** |
| **1** | 0.000 | 0.086 | 0.069 | **1** | 0.000 | 0.705 | 0.104 | **1** | 0.000 | 0.807 | 0.113 | **1** | 0.000 | 0.496 | 0.351 | **1** | 0.000 | 0.085 | 0.036 |
| **2** | | 0.000 | 0.175 | **2** | | 0.000 | -0.011 | **2** | | 0.000 | 0.004 | **2** | | 0.000 | 0.016 | **2** | | 0.000 | -0.044 |
| **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 |
| | | | | | | | | | | | | | | | | | | | |
| **$T_1$** | **1** | **2** | **3** | **$T_2$** | **1** | **2** | **3** | **$T_3$** | **1** | **2** | **3** | **$T_4$** | **1** | **2** | **3** | **$T_5$** | **1** | **2** | **3** |
| **1** | 0.000 | 0.014 | 0.002 | **1** | 0.000 | 0.622 | 0.088 | **1** | 0.000 | 0.257 | 0.046 | **1** | 0.000 | 0.007 | 0.002 | **1** | 0.000 | 0.025 | 0.002 |
| **2** | | 0.000 | 0.0004 | **2** | | 0.000 | -0.107 | **2** | | 0.000 | -0.133 | **2** | | 0.000 | 0.098 | **2** | | 0.000 | -0.598 |
| **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 |
| | | | | | | | | | | | | | | | | | | | |
| **$T_6$** | **1** | **2** | **3** | **$T_7$** | **1** | **2** | **3** | **$T_8$** | **1** | **2** | **3** | **$T_9$** | **1** | **2** | **3** | **$T_{10}$** | **1** | **2** | **3** |
| **1** | 0.000 | 0.010 | 0.005 | **1** | 0.000 | 0.007 | 0.006 | **1** | 0.000 | 0.031 | -0.0002 | **1** | 0.000 | 0.028 | 0.009 | **1** | 0.000 | -0.001 | 0.006 |
| **2** | | 0.000 | -0.090 | **2** | | 0.000 | -0.069 | **2** | | 0.000 | -0.0001 | **2** | | 0.000 | 0.008 | **2** | | 0.000 | 0.0001 |
| **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 |

| **D1AZBZPZH** | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$S_1$** | **1** | **2** | **3** | **$S_2$** | **1** | **2** | **3** | **$S_3$** | **1** | **2** | **3** | **$S_4$** | **1** | **2** | **3** | **$S_5$** | **1** | **2** | **3** |
| **1** | 0.000 | 0.511 | 0.060 | **1** | 0.000 | 0.367 | 0.043 | **1** | 0.000 | 0.005 | -0.001 | **1** | 0.000 | 0.002 | 0.005 | **1** | 0.000 | 0.071 | 0.035 |
| **2** | | 0.000 | -0.026 | **2** | | 0.000 | -0.036 | **2** | | 0.000 | -0.400 | **2** | | 0.000 | 0.319 | **2** | | 0.000 | 0.207 |
| **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 |
| | | | | | | | | | | | | | | | | | | | |
| **$S_6$** | **1** | **2** | **3** | **$S_7$** | **1** | **2** | **3** | **$S_8$** | **1** | **2** | **3** | **$S_9$** | **1** | **2** | **3** | **$S_{10}$** | **1** | **2** | **3** |
| **1** | 0.000 | -0.00003 | -0.013 | **1** | 0.000 | 0.177 | 0.035 | **1** | 0.000 | 0.658 | 0.123 | **1** | 0.000 | 0.675 | 0.122 | **1** | 0.000 | 0.464 | 0.510 |
| **2** | | 0.000 | -0.081 | **2** | | 0.000 | -0.374 | **2** | | 0.000 | -0.070 | **2** | | 0.000 | -0.055 | **2** | | 0.000 | 0.009 |
| **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 |
| | | | | | | | | | | | | | | | | | | | |

| $T_1$ | 1 | 2 | 3 | $T_2$ | 1 | 2 | 3 | $T_3$ | 1 | 2 | 3 | $T_4$ | 1 | 2 | 3 | $T_5$ | 1 | 2 | 3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 0.000 | 0.008 | 0.001 | **1** | 0.000 | 0.845 | 0.100 | **1** | 0.000 | 0.041 | 0.007 | **1** | 0.000 | 0.004 | 0.001 | **1** | 0.000 | 0.004 | 0.009 |
| **2** | | 0.000 | -0.036 | **2** | | 0.000 | -0.012 | **2** | | 0.000 | -0.143 | **2** | | 0.000 | 0.113 | **2** | | 0.000 | 0.224 |
| **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 |
| | | | | | | | | | | | | | | | | | | | |
| $T_6$ | 1 | 2 | 3 | $T_7$ | 1 | 2 | 3 | $T_8$ | 1 | 2 | 3 | $T_9$ | 1 | 2 | 3 | $T_{10}$ | 1 | 2 | 3 |
| **1** | 0.000 | 0.006 | 0.001 | **1** | 0.000 | -0.0001 | -0.018 | **1** | 0.000 | 0.010 | -0.006 | **1** | 0.000 | 0.032 | 0.001 | **1** | 0.000 | 0.002 | 0.004 |
| **2** | | 0.000 | -0.180 | **2** | | 0.000 | -0.035 | **2** | | 0.000 | -0.469 | **2** | | 0.000 | 0.00002 | **2** | | 0.000 | 0.088 |
| **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 | **3** | | | 0.000 |

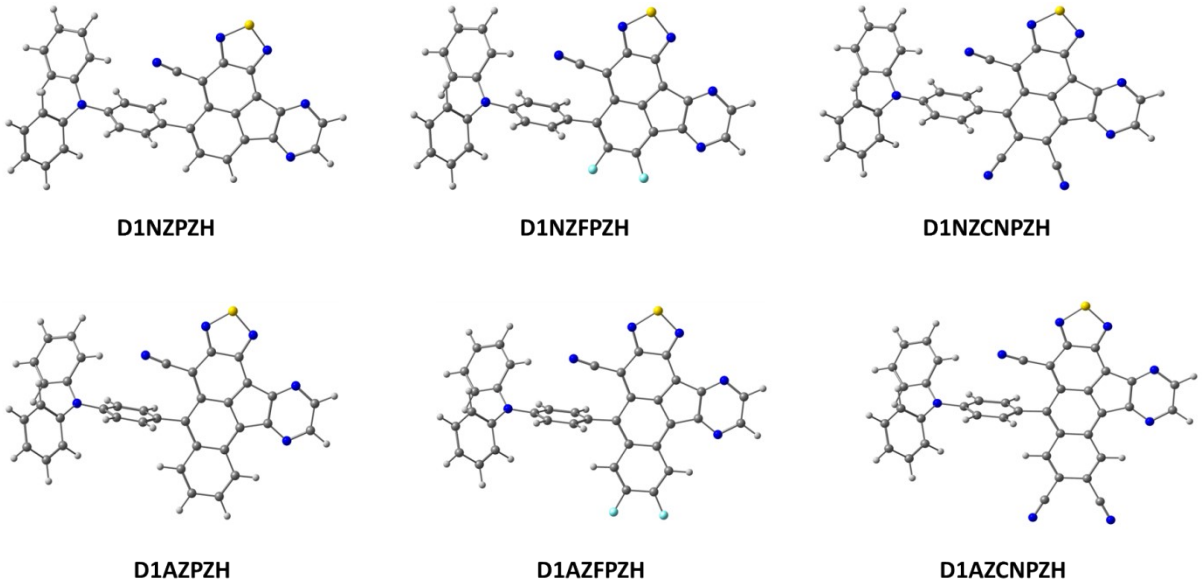



**Figure S5.** Optimized geometries of NZ and AZ based newly designed molecules (D1NZPZH, D1NZFPZH, D1NZCNPZH, D1AZPZH, D1AZFPZH, and D1AZCNPZH) as determined at the M06-2X/6-31G** level of theory.

**Table S5.** Calculated excited state energies, absorption wavelengths and HOMO and LUMO gap of some inspirational molecules towards D-A1-A2 type molecules as obtained from M06-2X/6-31G** level of theory in the gas phase.

| | $S_1$ (eV) | $S_2$ (eV) | $S_3$ (eV) | $S_4$ (eV) | $S_5$ (eV) | $T_1$ (eV) | $T_2$ (eV) | $T_3$ (eV) | $T_4$ (eV) | $T_5$ (eV) | $S_1$-$T_1$ (eV) | $T_2$-$T_1$ (eV) | Absorption λ (nm) | HLG (eV) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **D1NZPZH** | 2.08 | 2.85 | 3.03 | 3.48 | 3.83 | 1.42 | 2.05 | 2.53 | 2.90 | 3.29 | 0.66 | 0.64 | 597 | 3.23 |
| **D1NZFPZH** | 2.06 | 2.92 | 3.15 | 3.53 | 3.82 | 1.53 | 2.05 | 2.61 | 2.80 | 3.30 | 0.53 | 0.52 | 602 | 3.20 |
| **D1NZCNPZH** | 1.63 | 2.73 | 2.98 | 3.25 | 3.40 | 1.33 | 1.63 | 2.44 | 2.84 | 3.16 | 0.30 | 0.30 | 761 | 2.78 |
| **D1AZPZH** | 1.86 | 2.02 | 2.66 | 3.25 | 3.50 | 0.76 | 1.85 | 1.93 | 2.64 | 3.09 | 1.10 | 1.10 | 667 | 3.03 |
| **D1AZFPZH** | 1.81 | 2.11 | 2.67 | 3.28 | 3.48 | 0.82 | 1.81 | 1.97 | 2.60 | 3.13 | 0.99 | 0.99 | 684 | 2.98 |
| **D1AZCNPZH** | 1.51 | 2.16 | 2.56 | 3.16 | 3.32 | 0.78 | 1.50 | 1.91 | 2.69 | 3.03 | 0.73 | 0.72 | 820 | 2.68 |

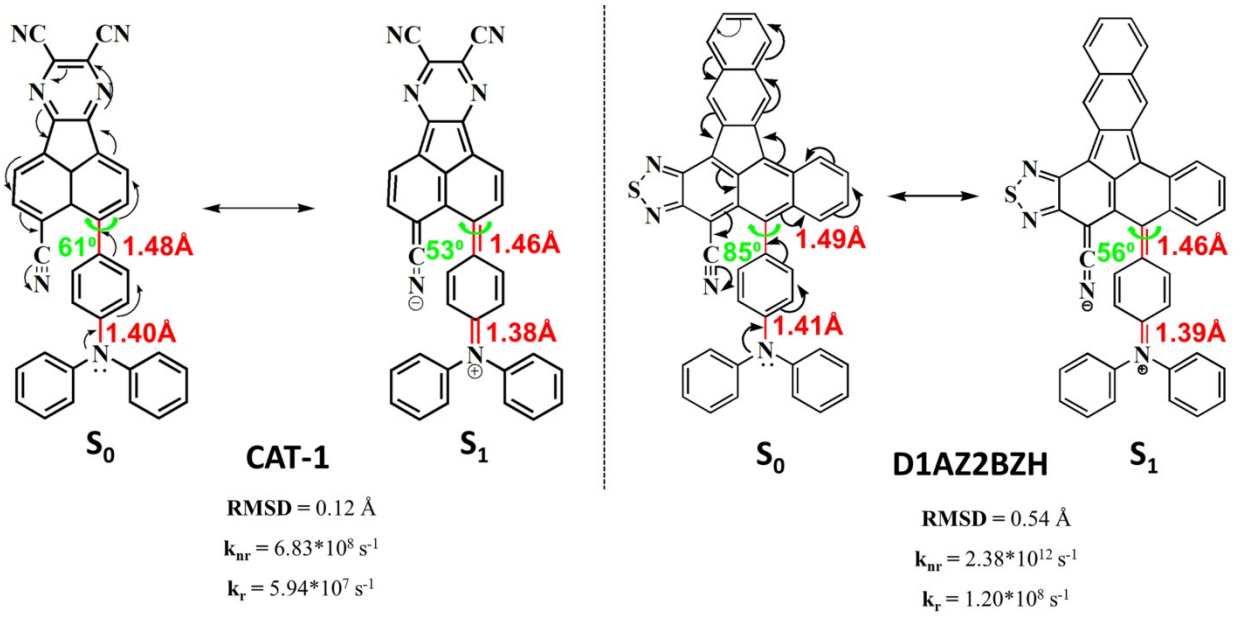



**Figure S6**. Comparison of geometrical parameters, RMSD, $k_{nr}$ and $k_r$ of CAT-1 and D1AZ2BZH at M06-2X/6-31G** level of theory.

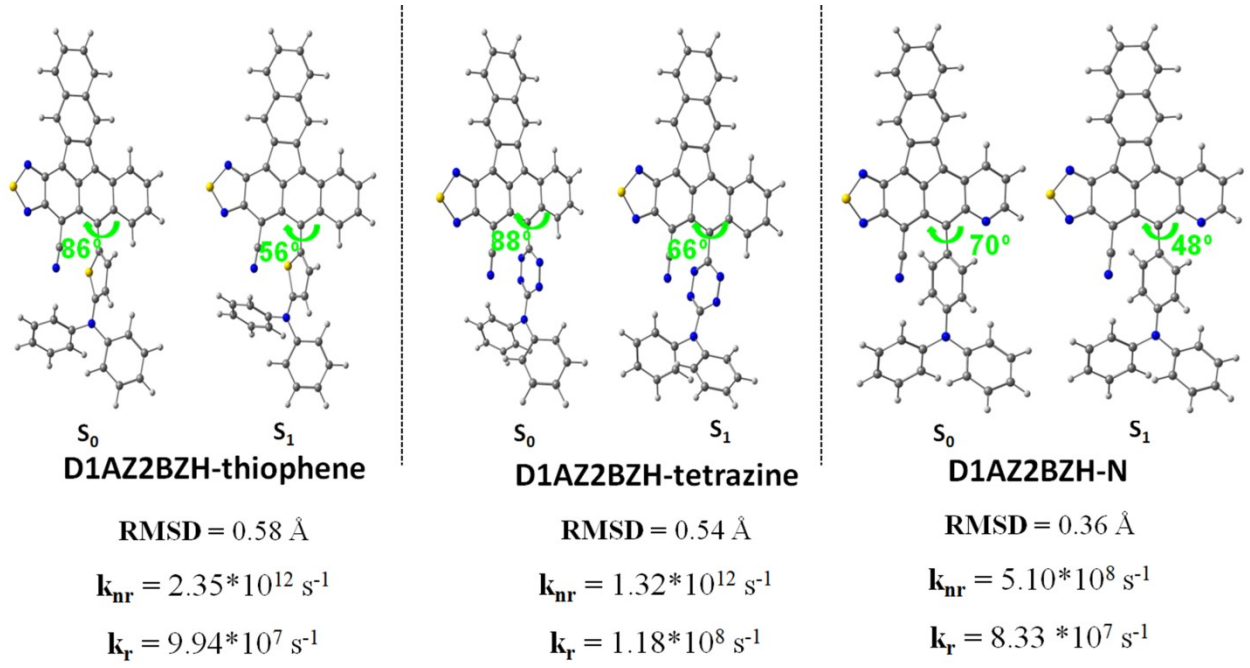



**Figure S7.** Comparison of new structures based on thiophene and tetrazine substituted D1AZ2BZH at M06-2X/6-31G** level of theory.