Supporting Information

PCCP

Effects of long-short axis skeleton on excited-state properties of ultraviolet hot exciton molecules: luminescence mechanism and molecular design

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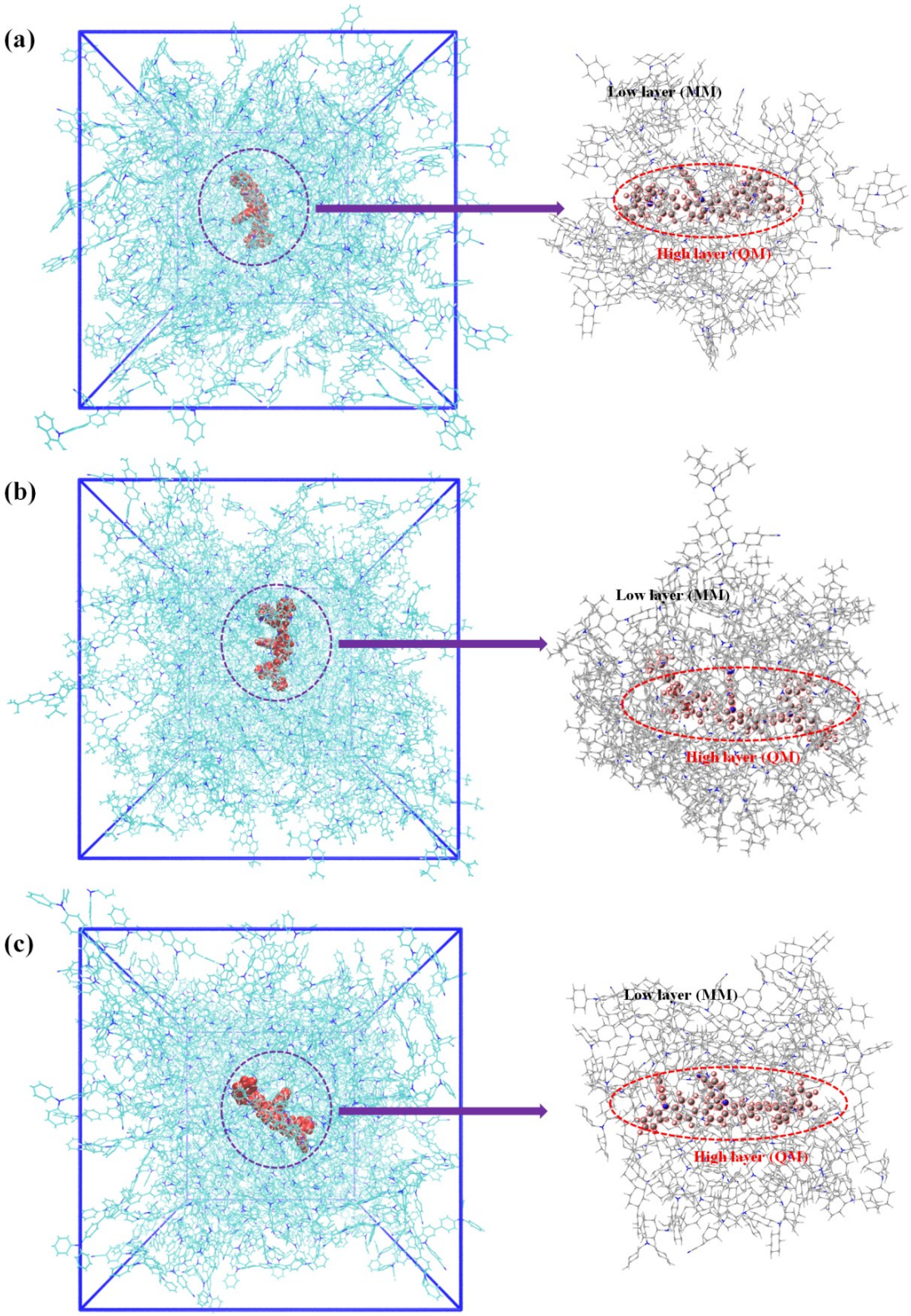
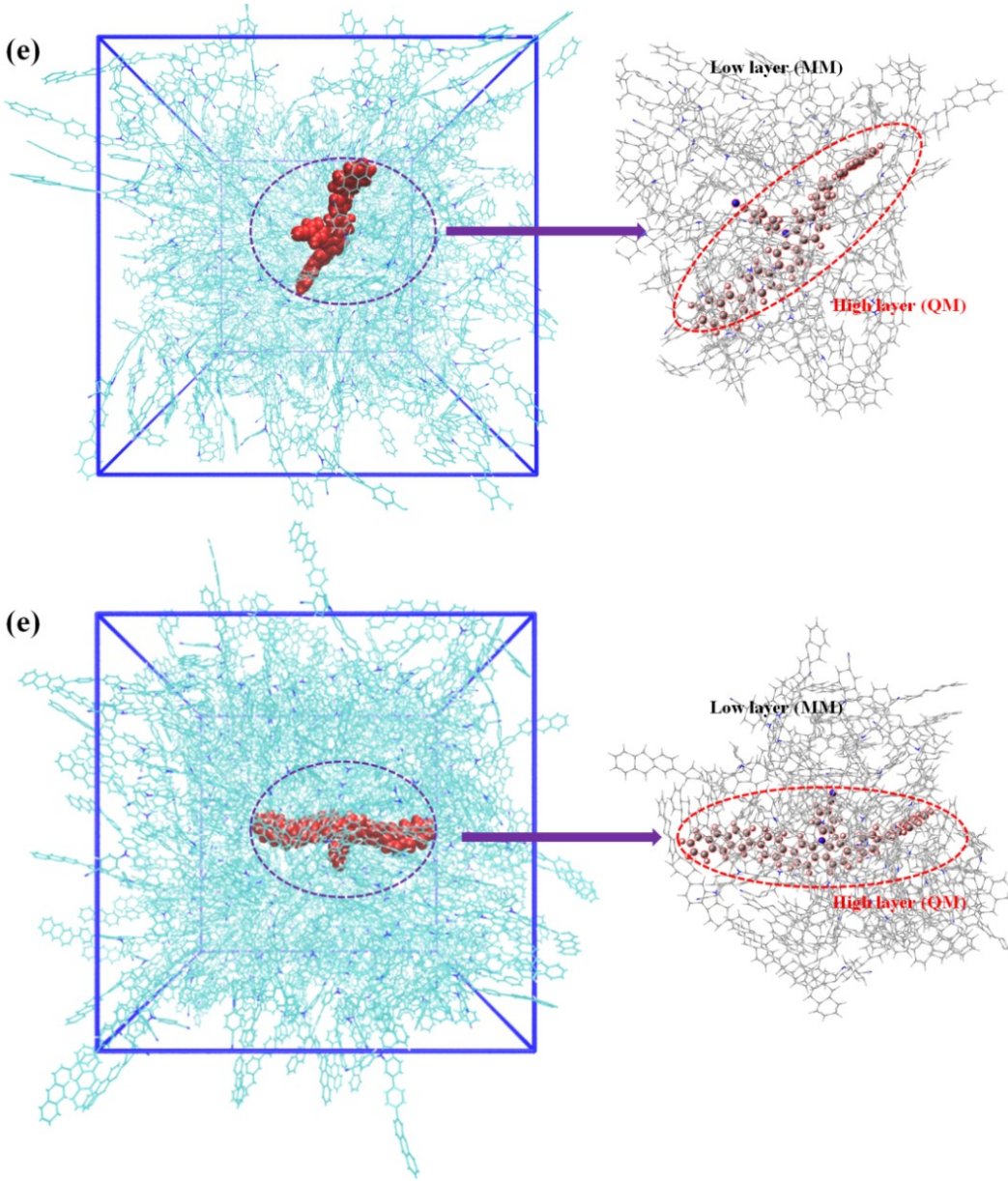
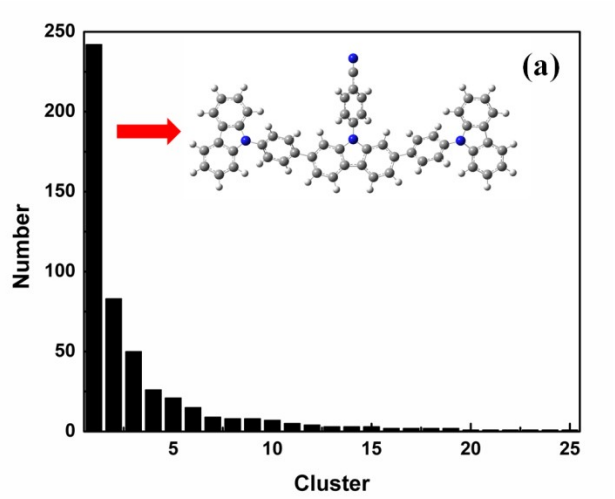
Contents

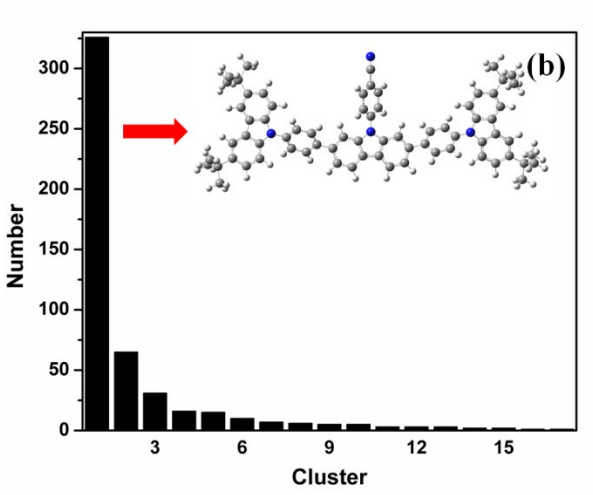
S1: 2Cz-CNCz (a), 2BuCz-CNCz (b), 2TPA-CNCz (c), 2Na-CNCz (d), and 2An-CNCz (e) in solid phase was obtained from all-atom molecular dynamics simulations.

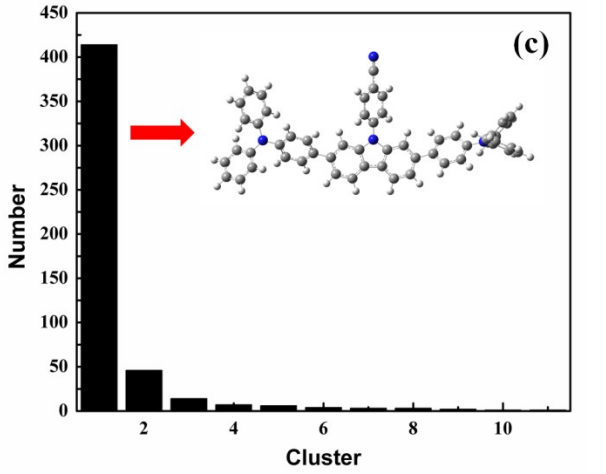


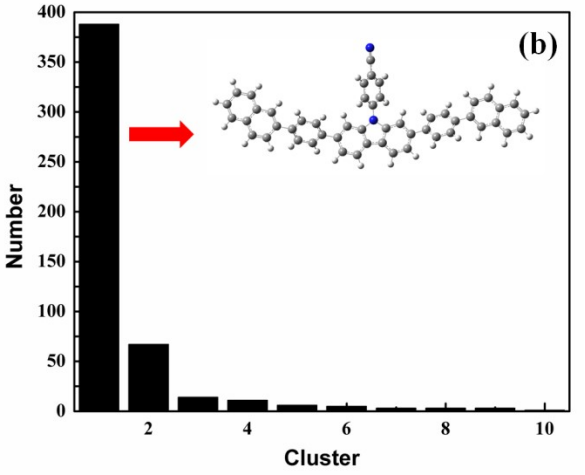

(e)
Low layer (MM)
High layer (QM)
(e)
Low layer (MM)
High layer (QM)

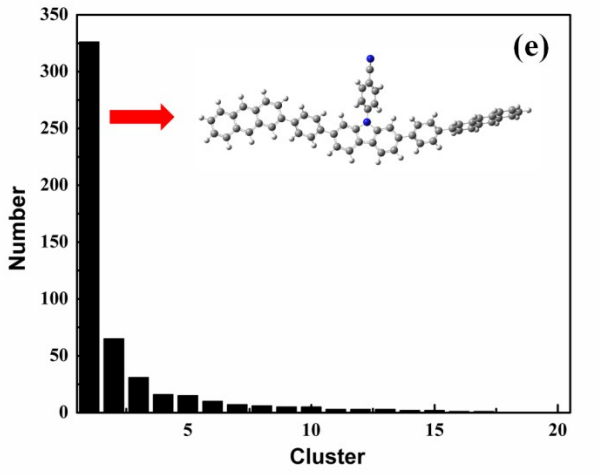
S2: Cluster analysis for the last 10ns of the simulation process for (a) 2Cz-CNCz, (b) 2BuCz-CNCz, (c) 2TPA-CNCz, (d) 2Na-CNCz and (e) 2An-CNCz.



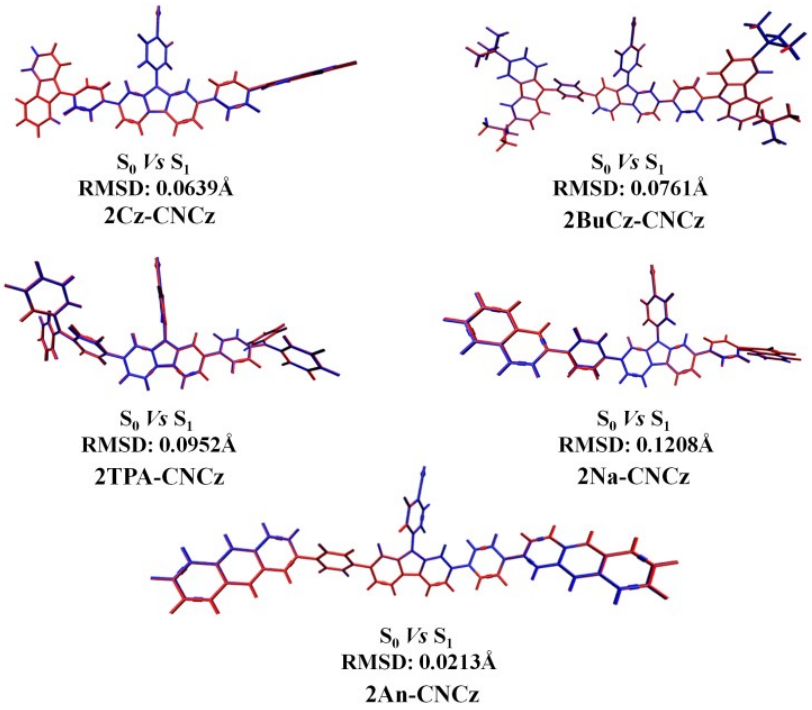




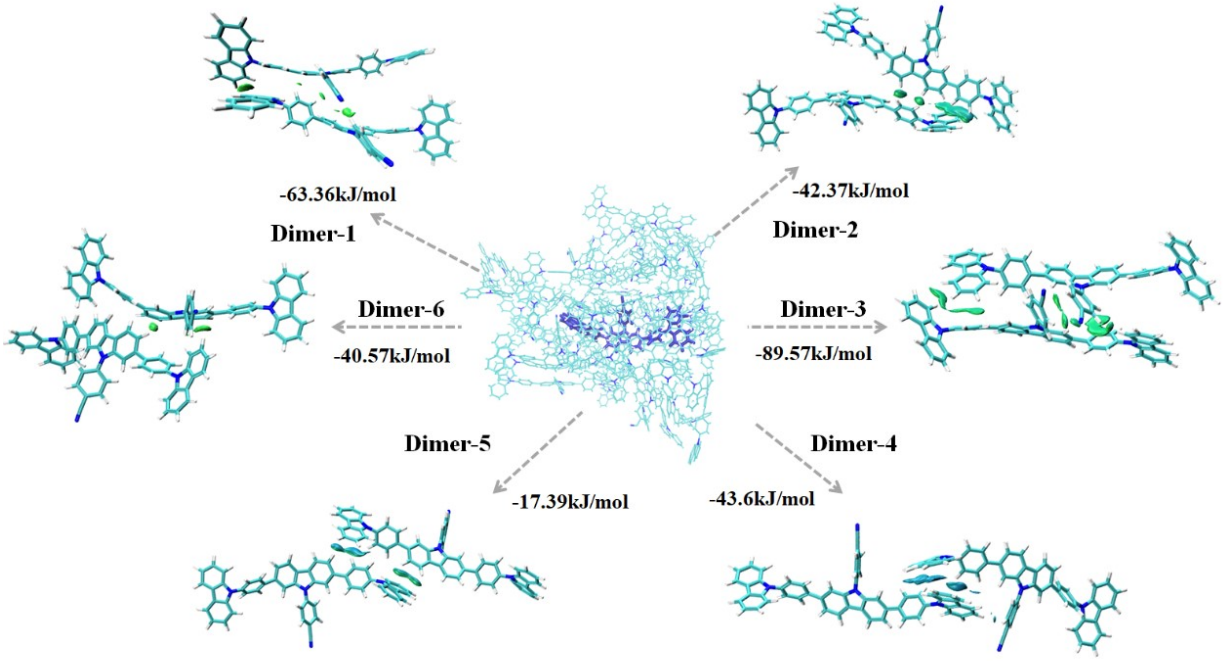




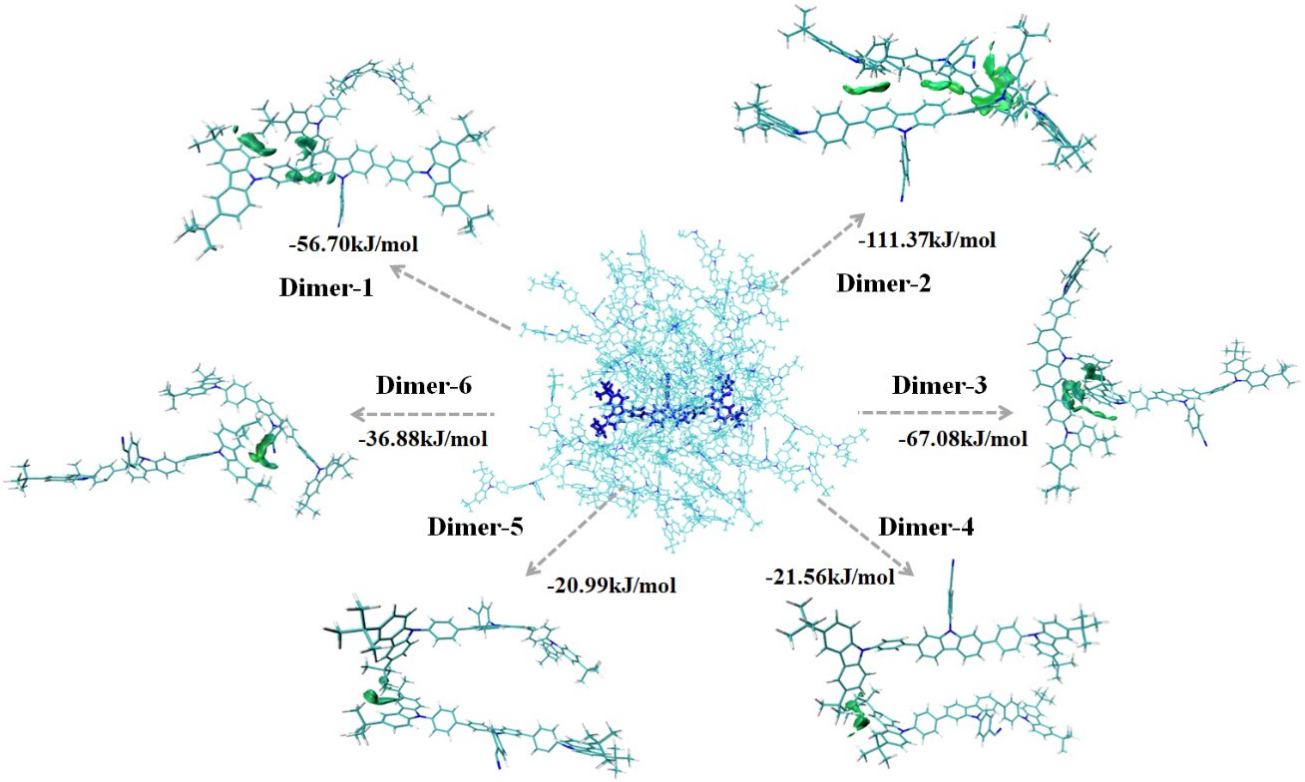
S3: Geometric deviation and RMSD values for 2Cz-CNCz, 2BuCz-CNCz, 2TPA-CNCz, 2Na-CNCz and 2An-CNCz between S_0 and S_1 in solid phase.



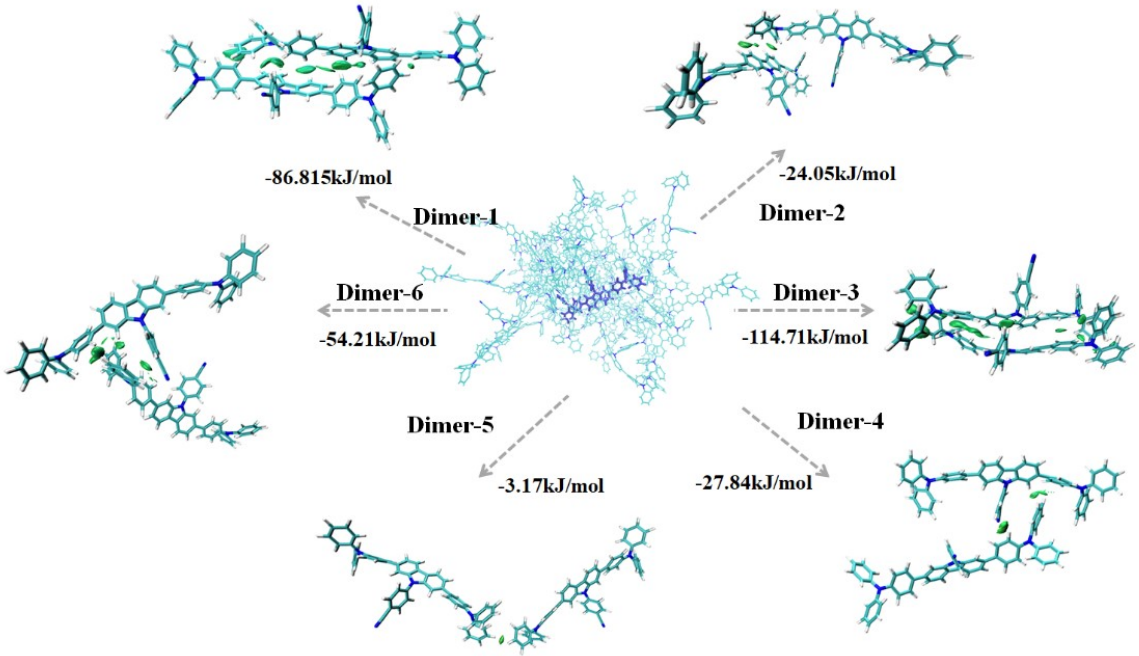
S4: Intermolecular interactions for several dimers described by the IGM method of 2Cz-CNCz, 2BuCz-CNCz, 2TPA-CNCz, 2Na-CNCz and 2An-CNCz.



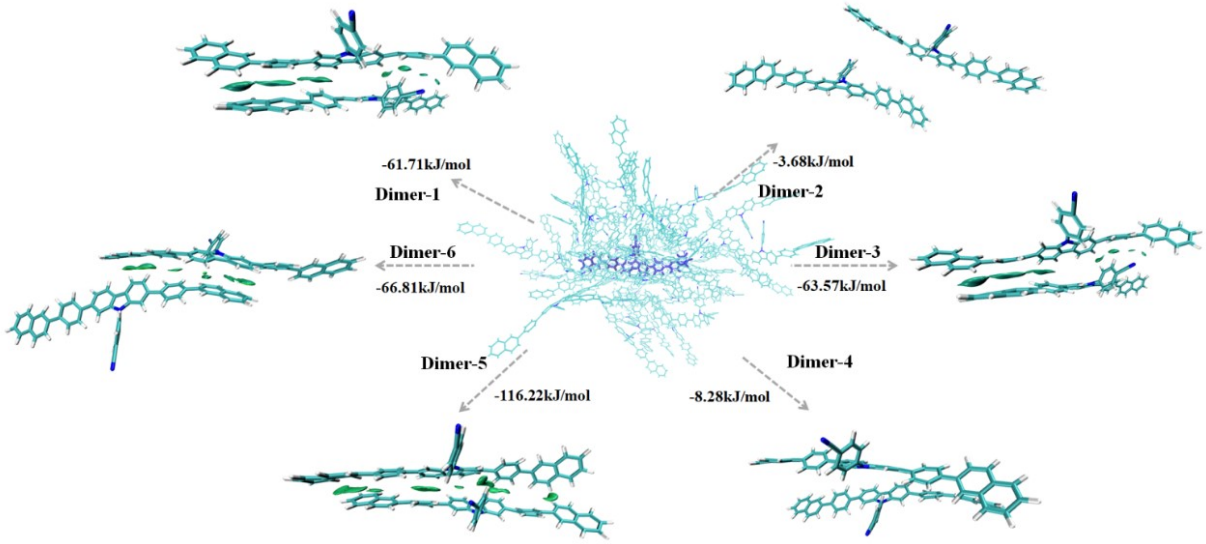
Intermolecular interactions for several dimers described by the IGM method of 2Cz-CNCz.



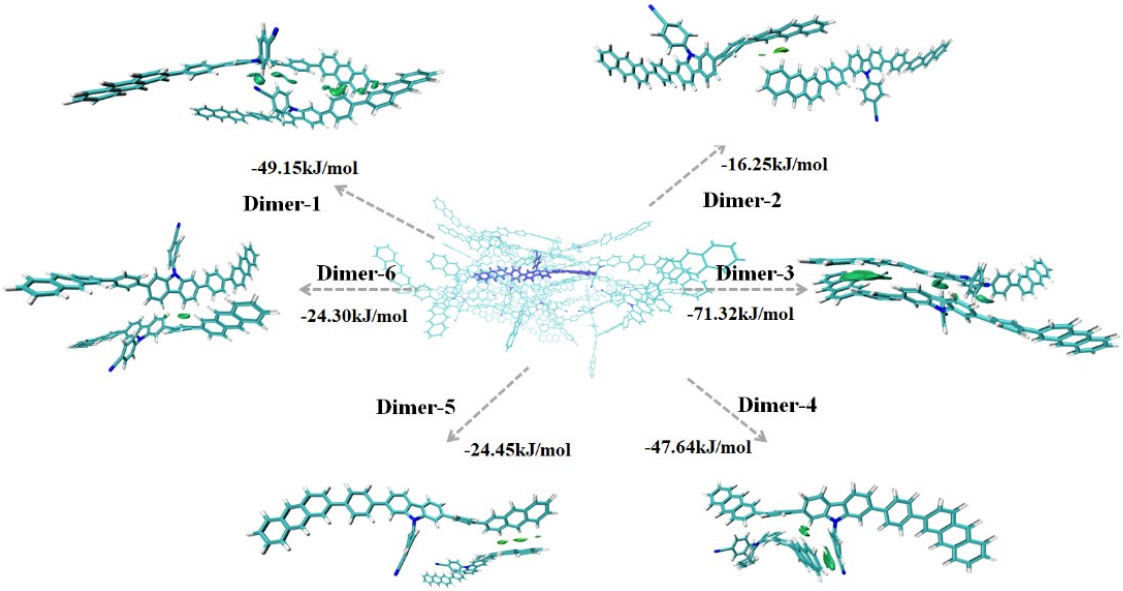
Intermolecular interactions for several dimers described by the IGM method of 2BuCz-CNCz.



Intermolecular interactions for several dimers described by the IGM method of 2TPA-CNCz.



Intermolecular interactions for several dimers described by the IGM method of 2Na-CNCz.



Intermolecular interactions for several dimers described by the IGM method of 2An-CNCz.

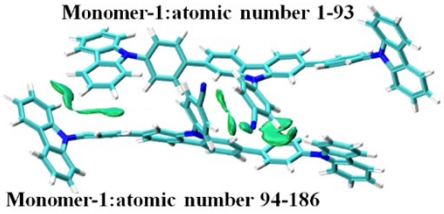
S5: Intermolecular Interaction Energy Including Electronic, Repulsion, and Dispersion Interactions in several dimers extracted from the film structure

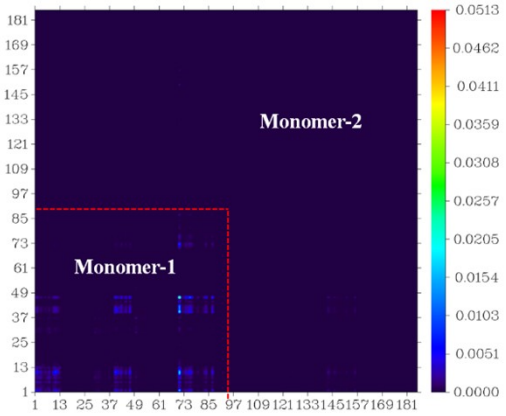
2Cz-CNCz	Electrostatic	Repulsion	Dispersion	Total
Dimer-1	-7.75	21.12	-76.73	-63.36
Dimer-2	-5.23	47.32	-84.46	-42.37
Dimer-3	-6.67	55.89	-138.79	-89.57
Dimer-4	1.55	49.72	-94.87	-43.6
Dimer-5	-6.17	40.64	-51.86	-17.39
Dimer-6	-1.06	11.44	-39.27	-28.9
2BuCz-CNCz	Electrostatic	Repulsion	Dispersion	Total
Dimer-1	0.51	49.57	-106.78	-56.7
Dimer-2	-2.27	53.64	-162.74	-111.37
Dimer-3	-0.82	33.3	-99.56	-67.08
Dimer-4	0.31	11.95	-33.82	-21.56
Dimer-5	1.13	15.6	-37.71	-20.99
Dimer-6	-11.26	13.41	-36.21	-34.06
2TPA-CNCz	Electrostatic	Repulsion	Dispersion	Total
Dimer-1	-3.08	49.87	-133.6	-86.81
Dimer-2	-1.5	19.1	-41.65	-24.05
Dimer-3	-3.66	88.42	-199.47	-114.71
Dimer-4	8.23	15.88	-51.96	-27.84
Dimer-5	0.51	3.95	-7.64	-3.17
Dimer-6	2.38	37.1	-93.68	-54.21
2Na-CNCz	Electrostatic	Repulsion	Dispersion	Total
Dimer-1	-2.37	64.49	-123.83	-61.71
Dimer-2	-0.62	0.01	-3.07	-3.68
Dimer-3	-2.37	64.49	-123.83	61.71
Dimer-4	-1.51	0.08	-6.85	-8.28
Dimer-5	-4.72	88.77	-200.27	-116.22
Dimer-6	6.82	56.3	-130.02	66.81
2An-CNCz	Electrostatic	Repulsion	Dispersion	Total
Dimer-1	-3.2	15.11	-36.21	-24.3
Dimer-2	-0.85	8.92	-24.32	-16.25
Dimer-3	5.88	97.93	-175.13	-71.32
Dimer-4	-7.27	34.97	-75.34	-47.64
Dimer-5	-2.9	18.51	-40.06	-24.45
Dimer-6	-12.31	55.79	-92.63	-49.15

S6: The transition properties of dimers which with the strongest interaction energy.

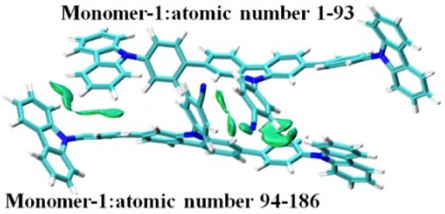
We have performed excited state calculations for the dimer with larger interactions. The atomic labeling of the molecules has been illustrated in the figure below (left), and the transition density matrix is plotted on the right side of the figure, with the bright spots in the figure indicating the inter-atomic transitions. The calculations reveal that all the dimer transitions in the figure occur on a single molecule.

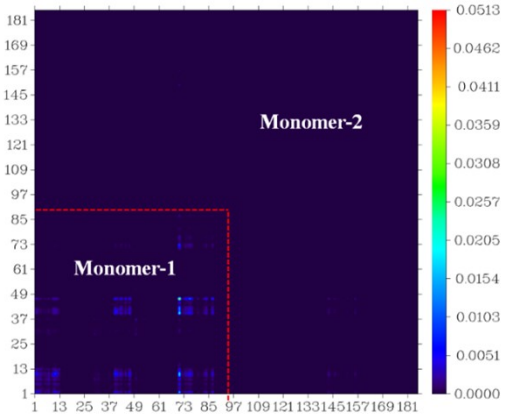
(a)


Monomer-1:atomic number 1-93
Monomer-1:atomic number 94-186

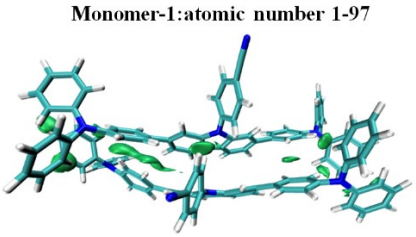

Monomer-2
Monomer-1
181 169 157 145 133 121 109 97 85 73 61 49 37 25 13 1
1 13 25 37 49 61 73 85 97 109 121 133 145 157 169 181
0.0513 0.0462 0.0411 0.0359 0.0308 0.0257 0.0205 0.0154 0.0103 0.0051 0.0000

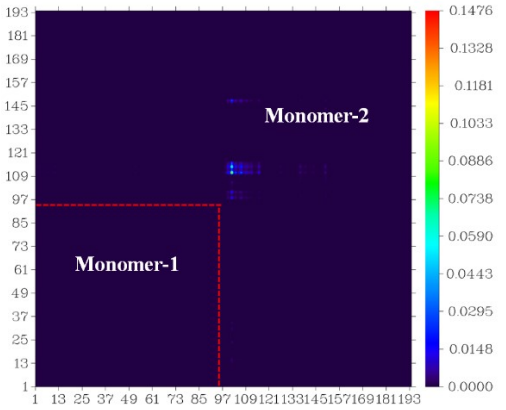
(a)


Monomer-1:atomic number 1-93
Monomer-1:atomic number 94-186

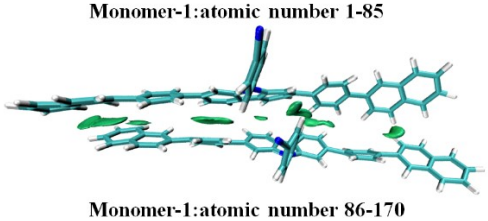

Monomer-2
Monomer-1
181 169 157 145 133 121 109 97 85 73 61 49 37 25 13 1
1 13 25 37 49 61 73 85 97 109 121 133 145 157 169 181
0.0513 0.0462 0.0411 0.0359 0.0308 0.0257 0.0205 0.0154 0.0103 0.0051 0.0000

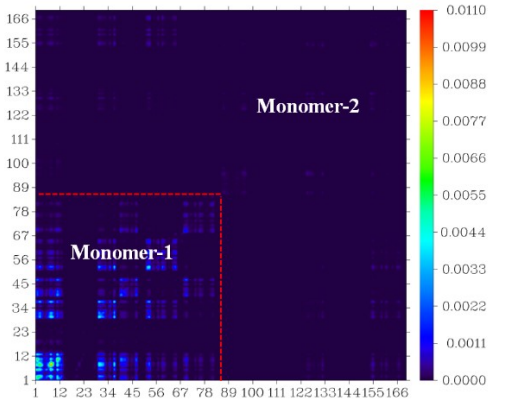
(c)

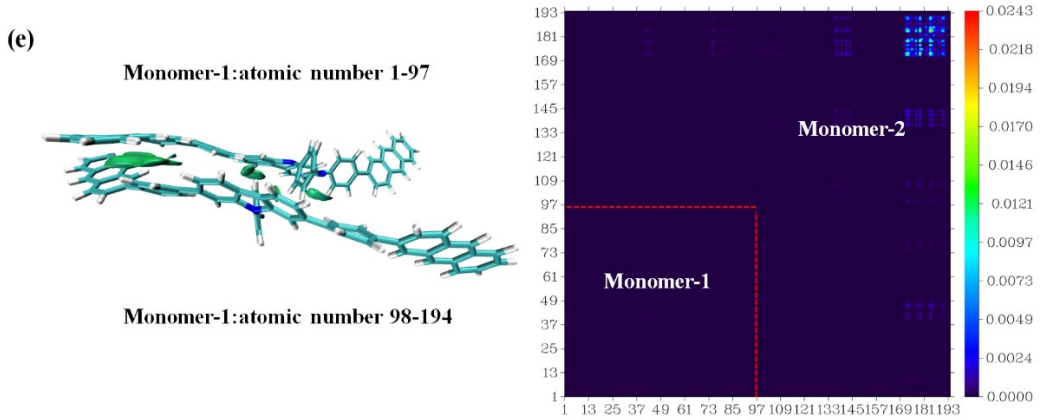

Monomer-1:atomic number 1-97
Monomer-1:atomic number 98-194


Monomer-2
Monomer-1
193 181 169 157 145 133 121 109 97 85 73 61 49 37 25 13 1
1 13 25 37 49 61 73 85 97 109 121 133 145 157 169 181 193
0.1476 0.1328 0.1181 0.1033 0.0886 0.0738 0.0590 0.0443 0.0295 0.0148 0.0000

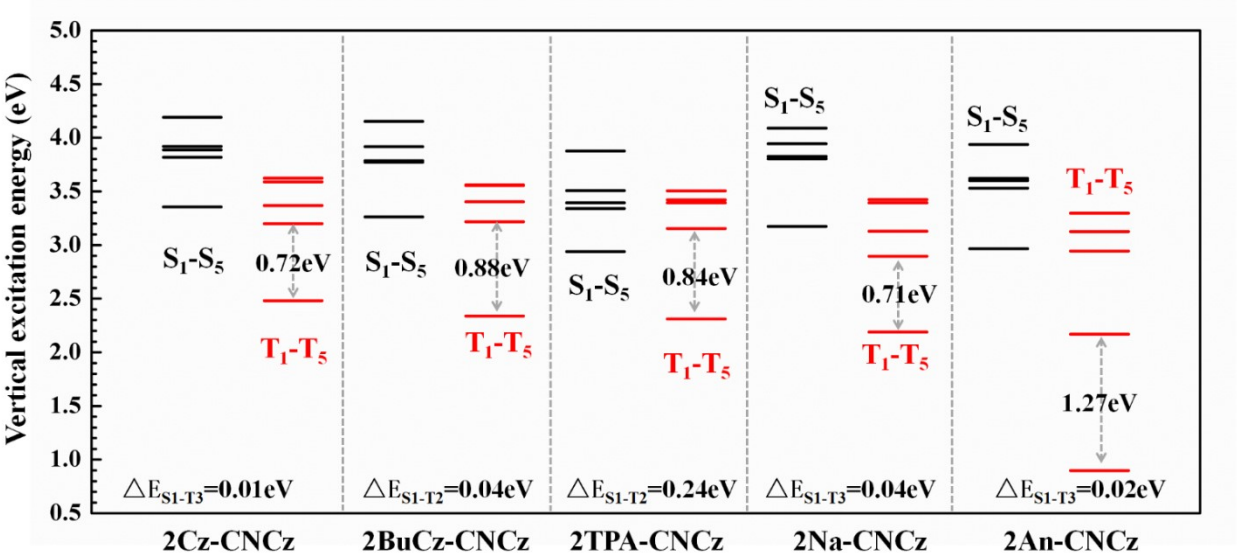
(d)


Monomer-1:atomic number 1-85
Monomer-1:atomic number 86-170


Monomer-2
Monomer-1
166 155 144 133 122 111 100 89 78 67 56 45 34 23 12 1
1 12 23 34 45 56 67 78 89 100 111 122 133 144 155 166
0.0110 0.0099 0.0088 0.0077 0.0066 0.0055 0.0044 0.0033 0.0022 0.0011 0.0000



S7: Adiabatic vertical excitation energies of the first five singlet and triplet states of the 2Cz-CNCz, 2BuCz-CNCz, 2TPA-CNCz, 2Na-CNCz and 2An-CNCz molecule in solid phase.



S8: Oscillator strength of S_1 state, spin-orbit coupling constants (cm^{-1}) between S_1 and T_2 or T_3, radiative and nonradiative rates (s^{-1}) from S_1 to S_0 as well as the ISC and RISC Rates (s^{-1}) between S_1 and T_2 or T_3 in solid phase.

	f (S_1)	k_r	k_{nr}	k_{ISC}	k_{RISC}
2Cz-CNCz	2.4542	2.11×10^{8}	9.99×10^{10}	3.13×10^{7}	9.31×10^{6}
2BuCz-CNCz	2.4054	1.06×10^{8}	8.59×10^{9}	1.05×10^{7}	9.21×10^{6}
2TPA-CNCz	2.1634	8.72×10^{7}	6.92×10^{11}	3.76×10^{7}	2.65×10^{6}
2Na-CNCz	2.5162	1.69×10^{8}	9.99×10^{9}	3.99×10^{7}	1.16×10^{8}
2An-CNCz	0.1818	8.99×10^{7}	8.81×10^{9}	8.97×10^{7}	9.91×10^{7}

S9: The reorganization energy versus the normal mode frequencies in the solvents and aggregation states.