Supplementary Information for

A QM/MM Study on Through Space Charge Transfer based Thermally Activated Delayed Fluorescence Molecule in Solid State

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Computational 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:

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

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

Where, $p_{S\rightarrow R}$ 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. Take the studied molecule as example (as shown in Figure S1), the atom number of the donor, acceptor and bridge should be determined initially. Atom numbers of 3,5-48 are classified as donor, 1-2,4,59-67 as acceptor and 49-58 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.

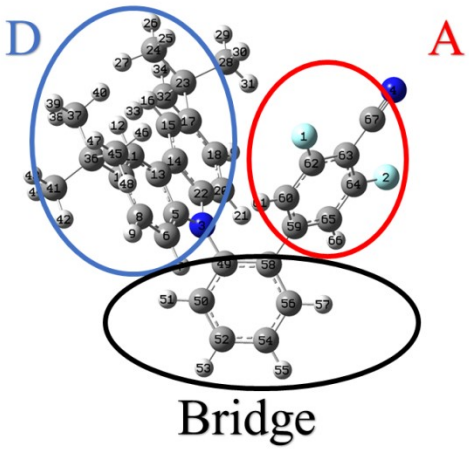

Figure S1. Atom numbers of the donor part, acceptor part and bridge part for studied molecule S-CNDF-S-*t*Cz.

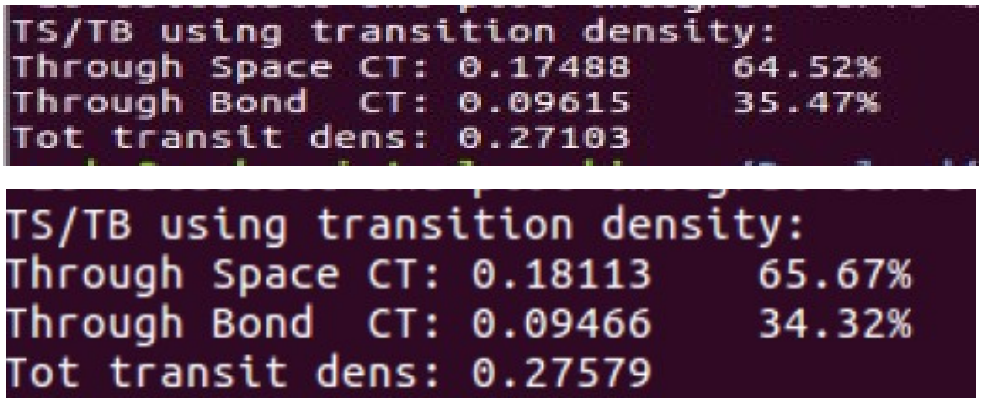

Figure S2. Calculation results for molecule in chloroform and in solid phase of S_1 state performed by Multiwfn.

Table S1. Calculated emission wavelengths with different basis set for molecule in chloroform and solid phase, respectively.

	Emission Wavelength(nm)						
	6-31G*	6-31+G*	6-31++G*	6-31+G**	6-31++G**	6-311G*	Exp
Chloroform	492.13	506.86	506.86	491.87	507.01	498.35	476
Solid	482.25	493.91	493.89	482.41	494.09	488.29	445

Table S2. Calculated absorption wavelengths and oscillator strength for selected states by PBE0 and PBE0-GD3BJ are listed, respectively.

	Excited states	S_1	S_2	S_3	S_4	Exp
Absorption wavelength (nm)	PBE0-GD3BJ	398.80	351.35	301.73	290.43	340
	PBE0	397.16	353.79	301.54	287.04	
Oscillator strength	PBE0-GD3BJ	0.016	0.004	0.068	0.054	----
	PBE0	0.010	0.005	0.071	0.050	

Table S3. Emission wavelength, energy gaps and oscillator strength are calculated by PBE0 and PBE0-GD3BJ, respectively.

	PBE0	PBE0-GD3BJ	Experiment
Emission wavelength (nm)	492	497	476
ΔE_{S1-T1} (eV)	0.29	0.27	----
ΔE_{S1-S0} (eV)	2.81	2.81	----
ΔE_{T1-S0} (eV)	2.52	2.54	----
Oscillator strength	0.017	0.012	----