Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Excited State Dynamics for Hybridized Local and Charge Transfer State Fluorescent Emitter with Aggregation Induced Emission in Solid Phase: A QM/MM study

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The radiative decay rate is calculated by Einstein spontaneous emission equation as follows

$$k_r = \frac{f \Delta E_{fi}^2}{1.499}.$$

(1)

Where f is oscillator strength and ΔE_{fi} is the vertical emission energy with the unit of wavenumber (cm^{-1}).

The non-radiative decay rate is deduced based on first-order perturbation theory and the Fermi's golden rule (FGR), it can be written

$$K_{nr} = \frac{2\pi}{\hbar^2}\sum_{u,v} P_{iv}\left|H_{fu,iv}\right|^2 \delta\left(E_{iv} - E_{fu}\right) . \qquad (2)$$

The delta function δ is to keep the conservation of energy and H is the interaction between two different Born-Oppenheimer states, it contains two components

$$\hat{H}\Psi_{iv} = \hat{H}^{BO}\Phi_i(r,Q)\Theta_{iv}(Q) + \hat{H}^{SO}\Phi_i(r,Q)\Theta_{iv}(Q). \qquad (3)$$

Here $\hat{H}^{BO}$ is the nonadiabatic coupling and $\hat{H}^{SO}$ denotes the spin-orbit coupling. The non-radiative decay rate constant from S_1 to S_0 can be written as

$$K_{nr} = \frac{2\pi}{\hbar}\sum_{kl} R_{kl} Z_i^{-1} \sum_{vu} e^{-\beta E_{iv}} \langle\Theta_{fu}|\hat{P}_{fk}|\Theta_{iv}\rangle\langle\Theta_{iv}|\hat{P}_{fl}|\Theta_{fu}\rangle \delta\left(E_{iv} - E_{fu}\right) . \qquad (4)$$

Here $R_{kl} = \langle\Phi_f|\hat{P}_{fk}|\Phi_i\rangle\langle\Phi_i|\hat{P}_{fl}|\Phi_f\rangle$ is the nonadiabatic electronic coupling. $\hat{P}_{fk} = -i\hbar\frac{\partial}{\partial Q_{fk}}$ represents the normal momentum operator of the kth normal mode in the final electronic state. Z_i is the partition function. As the $L_{f\delta j,k} = \frac{\partial q_{\delta j}}{\partial Q_{fk}}$ and $q_{\delta j} = \sqrt{M_\delta} R_{\delta j}$, where $R_{\delta j}$ is the Cartesian coordinate of the δth atom along the jth direction, are used, the electronic coupling term at the equilibrium position can be approximately written as

$$\left\langle \Phi_f \middle| \hat{P}_{fk} \middle| \Phi_i \right\rangle = -i\hbar \left\langle \Phi_f \middle| \frac{\partial}{\partial Q_{fk}} \middle| \Phi_i \right\rangle = -i\hbar \frac{\left\langle \Phi_f^0 \middle| \frac{\partial U}{\partial Q_{fk}} \middle| \Phi_i^0 \right\rangle}{E_i^0 - E_f^0} .$$

(5)

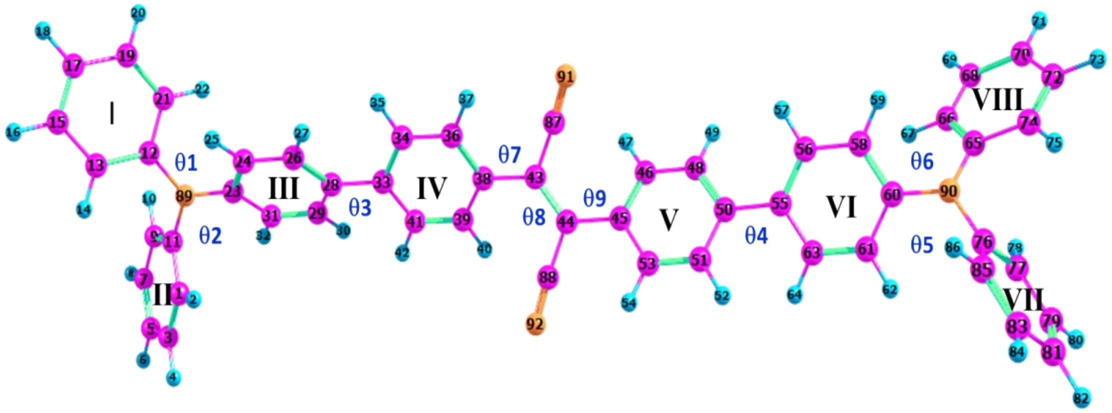
U is the electron-nuclear potential term in the Hamiltonian. $\left\langle \Phi_f^0 \middle| \frac{\partial U}{\partial Q_{fk}} \middle| \Phi_i^0 \right\rangle = -\sum_{\delta} \frac{Z_\delta e^2}{\sqrt{M_\delta}} \sum_{\tau = x,y,z} E_{i \to f, \delta\tau} L_{\delta\tau,k}$, $E_{i \to f, \delta\tau}$ is the transition electric field and it can be calculated by TD-DFT directly. Based on the Franck-Condon principle and applying the Fourier transform of the delta function, the equation can be written as

$$K_{nr} = \sum_{kl} \frac{1}{\hbar^2} R_{kl} \int_{-\infty}^{\infty} dt \left[e^{i\omega_{if} t} Z_i^{-1} \rho_{IC}(t,T) \right] . \tag{6}$$

Here $\rho_{IC}(t,T)$ is the thermal vibration correlation function (TVCF). Similarly, the intersystem crossing rate constant between two electronic states with different spin states can be written as

$$K_{ISC} = \frac{1}{\hbar^2} \left\langle \Phi_f \middle| \hat{H}^{SO} \middle| \Phi_i \right\rangle \int_{-\infty}^{\infty} dt \left[e^{i\omega_{if} t} Z_i^{-1} \rho_{ISC}(t,T) \right] . \tag{7}$$

Both the methodology and application of this formalism can be found in Peng's and Shuai's works.[1-3]

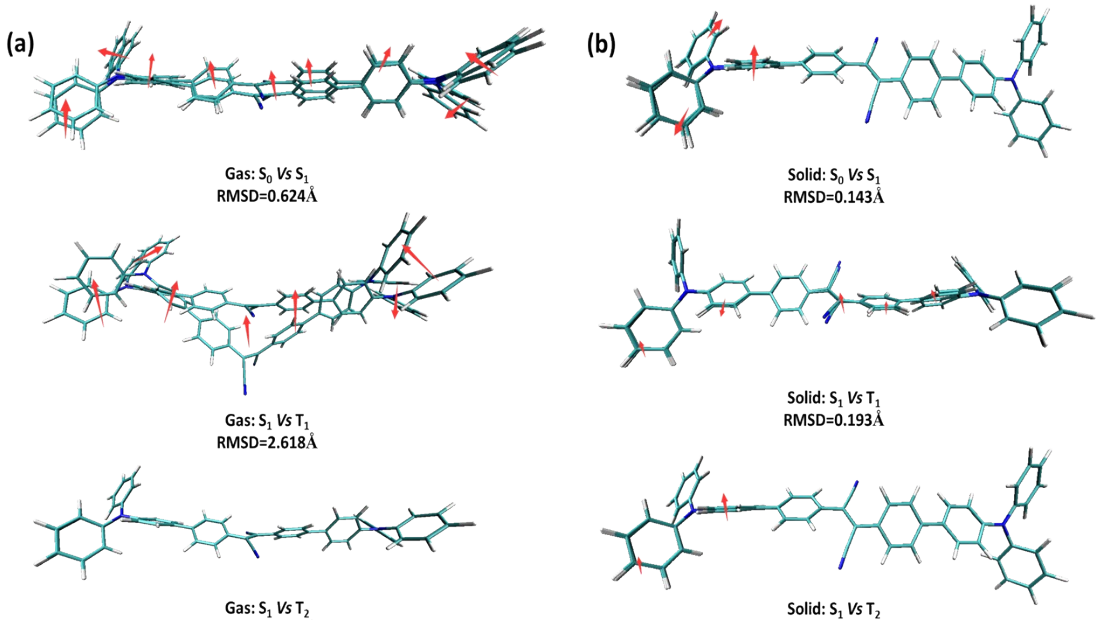


θ1:I&III **θ7: 39-38-43-87** **θ4: V&VI**

θ2:II &III **θ8: 87-43-44-88** **θ5: VI&VII**

θ3: III&IV **θ9: 88-44-45-46** **θ6: VI&VIII**

Figure S1. Atomic labels, the interesting dihedral angles and the index of the phenyl ring of TPATCN.



Gas: S_0 *Vs* S_1 RMSD=0.624Å

Solid: S_0 *Vs* S_1 RMSD=0.143Å

Gas: S_1 *Vs* T_1 RMSD=2.618Å

Solid: S_1 *Vs* T_1 RMSD=0.193Å

Gas: S_1 *Vs* T_2 RMSD=0.042Å

Solid: S_1 *Vs* T_2 RMSD=0.064Å

Figure S2. Visible geometry changes between selected two states in gas (a) and solid phase (b) respectively.

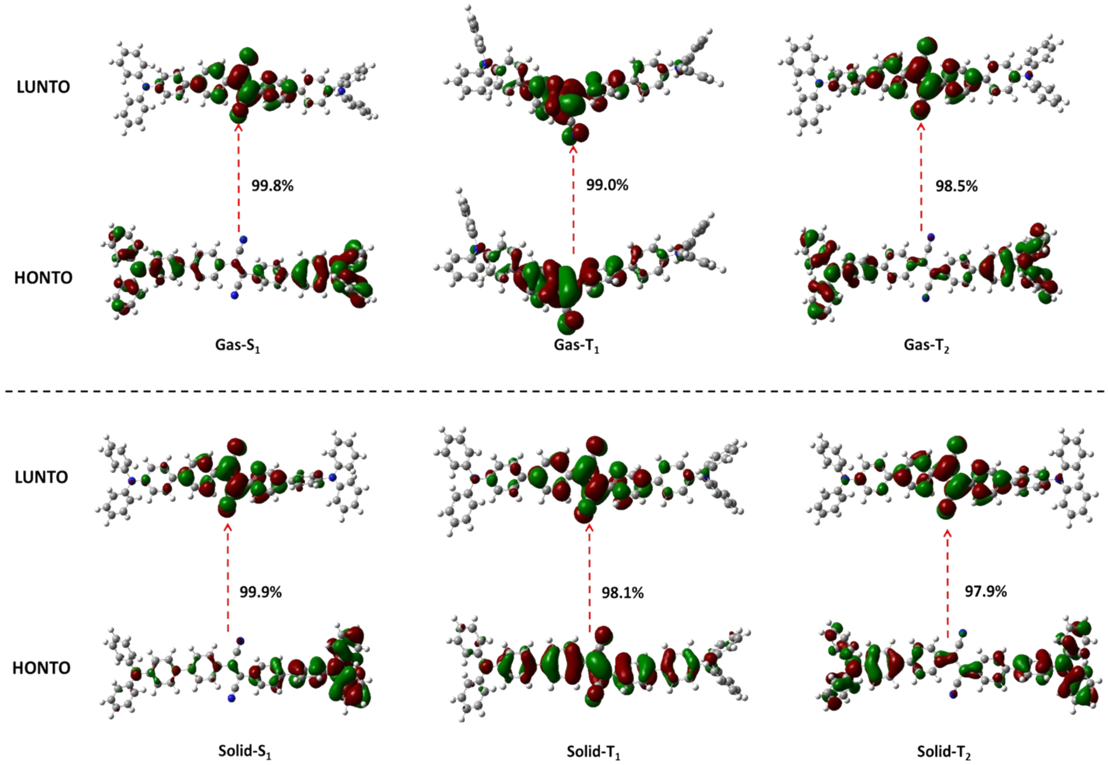


Figure S3. Transition characteristics for S_1, T_1 and T_2 sates of TPATCN in gas (up) and solid phase (down) respectively.

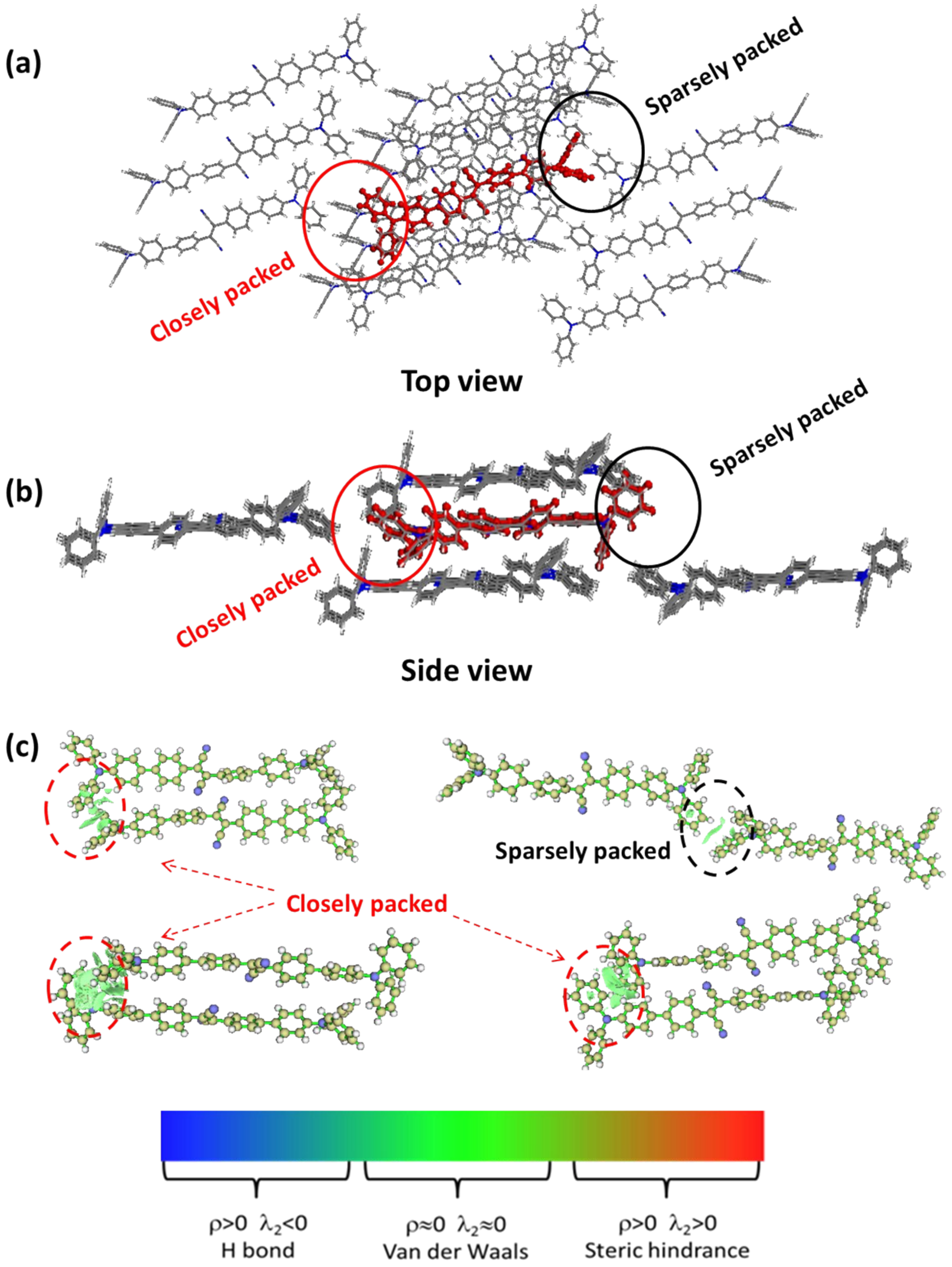


Figure S4. Molecular packing from top view (a) and side view (b). Visualization of the intermolecular interaction by RDG function (c).

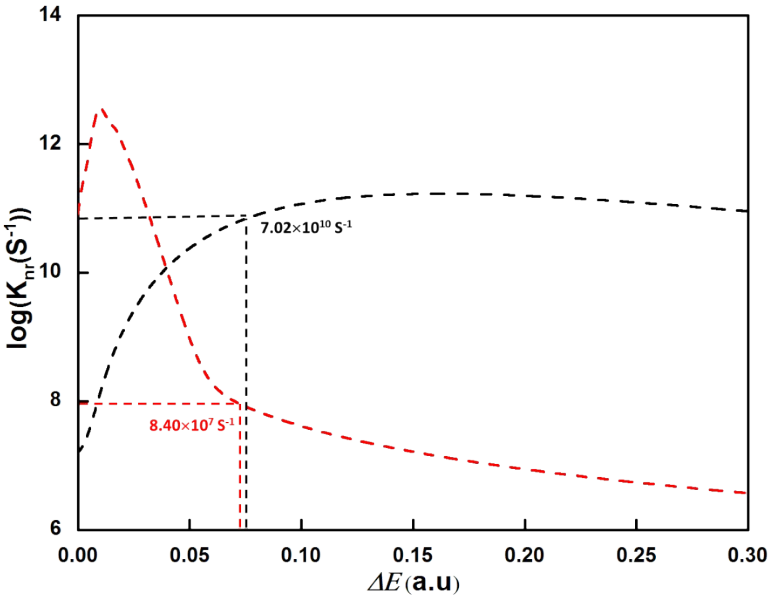


Figure S5. Non-radiative decay rate k_{nr} from S_1 to S_0 versus the adiabatic energy gap ΔE in gas (black) and solid phase (red) respectively.

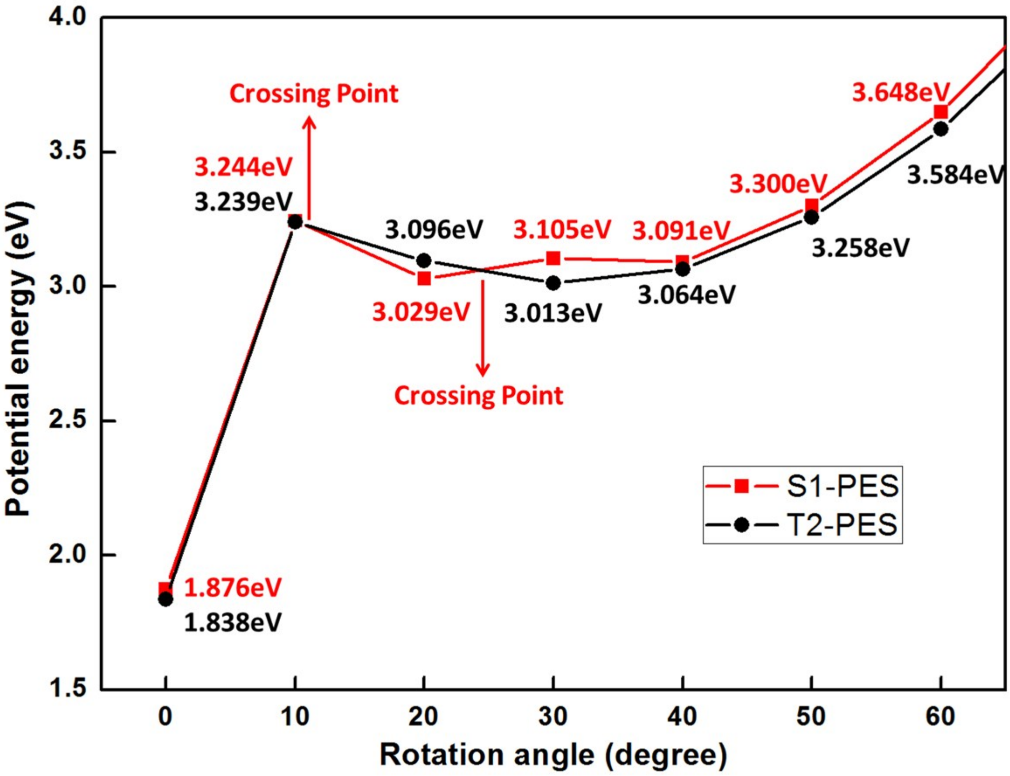


Figure S6. Potential energy surfaces of S_1 and T_2. The crossing point is marked.

Reference

1. Z. Shuai, D. Wang, Q. Peng and H. Geng, *Acc. Chem. Res*, 2014, **47**, 3301-3309.
2. Z. Shuai and Q. Peng, *Phys. Rep*, 2014, **537**, 123-156.
3. Q. Peng, Y. L. Niu, Q. H. Shi, X. Gao and Z. G. Shuai, *J. Chem. Theory. Comput*, 2013, **9**, 1132-1143.