

Supplementary Information

Origin of Aggregation-Induced Enhanced Emission: Role of Pseudo-Degenerate Electronic States of Excimers Formed in Aggregation Phases

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S1 Dimer Models in Solid Phase

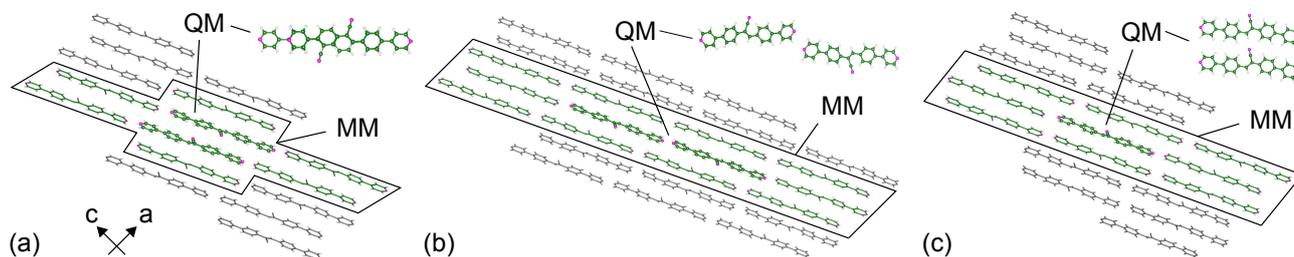


Fig. S1 Dimer Model (a) **1**, (b) **2**, and (c) **3** for the CNPPE solid. In Dimer Model **2**, a dimer aligned in the ca -plane was selected as the QM region and the surrounding 38 molecules were selected as the MM region. In Dimer Model **3**, a dimer aligned in the b -direction was selected as the QM region and the surrounding 29 molecules were selected as the MM region. The QM region was computed at the M06-2X/6-31G(d,p) levels of theory and the MM region was computed using the UFF.

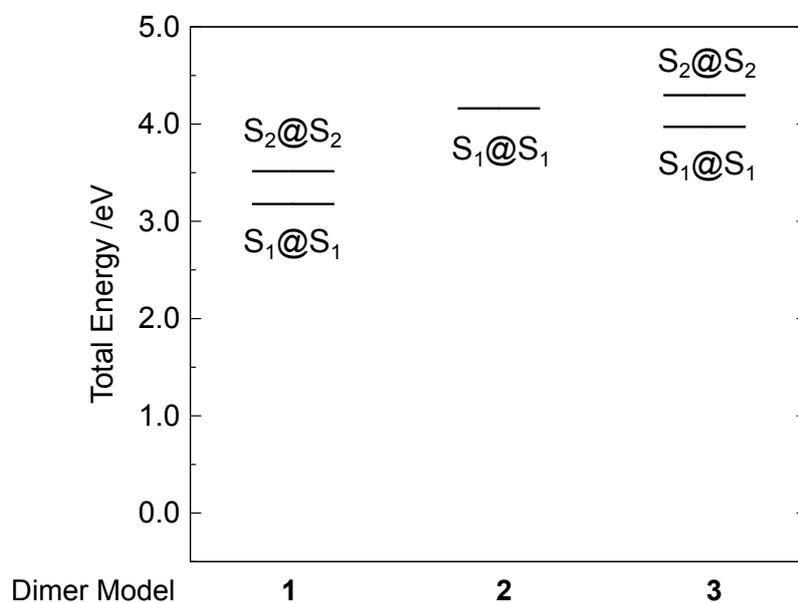


Fig. S2 Total energy of the excited states of Dimer Model **1**, **2**, and **3** in the QM region. The energy reference is the total energy of $S_0@S_0$ of Dimer Model **1**, -2253.41783105 a.u.

S2 Irreducible Representations of Excimers

S2.1 C_i symmetry

Table S1 presents the character table of C_i point group¹. In C_i point group, there are cases where an atom does not exist at the inversion center and where an atom exists at the inversion center. When an atom does not exist at the inversion center, the reducible representation of vibrational modes is decomposed as

$$\Gamma_{\text{vib}} = \frac{3N-6}{2}A_g + \frac{3N-6}{2}A_u, \quad (1)$$

where N denotes the number of atoms. Half of the vibrational modes belongs to A_g and the other half to A_u .

On the other hand, when an atom exists at the inversion center, the number of vibrational modes is

$$\Gamma_{\text{vib}} = \frac{3N-9}{2}A_g + \frac{3N-3}{2}A_u. \quad (2)$$

The numbers of vibrational modes belonging to A_g and A_u are different.

Table S1 Character table of C_i point group.

C_i	E	i	$h=2$
A_g	1	1	R_x, R_y, R_z $x^2, y^2, z^2, xy, yz, zx$
A_u	1	-1	x, y, z

S2.2 C_2 symmetry

Table S2 presents the character table of C_2 point group¹. In C_2 point group, there are cases where no atoms exist on a rotational axis and where atoms exist on a rotational axis. When atoms do not exist on a rotational axis, the reducible representation of vibrational modes is decomposed as

$$\Gamma_{\text{vib}} = \frac{3N-4}{2}A + \frac{3N-8}{2}B. \quad (3)$$

The numbers of vibrational modes belonging to A and B are not the same. When N_a atoms exist on a rotational axis, the number of vibrational modes is

$$\Gamma_{\text{vib}} = \frac{3N-N_a-4}{2}A + \frac{3N+N_a-8}{2}B. \quad (4)$$

The number of vibrational modes belonging to B increases with N_a .

Table S2 Character table of C_2 point group.

C_2	E	C_2		$h=2$
A	1	1	z, R_z	x^2, y^2, z^2, xy
B	1	-1	x, y, R_x, R_y	yz, zx

S2.3 C_s symmetry

Table S3 presents the character table of C_s point group¹. In C_s point group, there are cases where no atoms exist on a mirror plane and where atoms exist on a mirror plane. When atoms do not exist on a mirror plane, the reducible representation of vibrational modes is decomposed as

$$\Gamma_{\text{vib}} = \frac{3N-6}{2}A' + \frac{3N-6}{2}A'' \quad (5)$$

Half of the vibrational modes belongs to A' and the other half to A'' . When N_p atoms exist on a mirror plane, the number of vibrational modes is

$$\Gamma_{\text{vib}} = \frac{3N+N_p-6}{2}A' + \frac{3N-N_p-6}{2}A'' \quad (6)$$

The number of vibrational modes belonging to A' increases with N_p .

Table S3 Character table of C_s point group.

C_s	E	σ_h		$h=2$
A'	1	1	x, y, R_z	x^2, y^2, z^2, xy
A''	1	-1	z, R_x, R_y	yz, zx

S3 Rate Constant of Internal Conversion for Monomer Model and Dimer Model

1

Table S4 Dependence of $k_{n\leftarrow m}^{\text{IC}}(T)$ within a single mode approximation on the linewidth of the Gaussian function σ . $V_{mn,\alpha} = 5 \times 10^{-4}$ a.u., $\omega_\alpha = 1700 \text{ cm}^{-1}$, $E_m - E_n = 3.0 \text{ eV}$, $E_{\text{min}} = -11500 \text{ cm}^{-1}$, and $E_{\text{max}} = 11500 \text{ cm}^{-1}$. $V_{n,\alpha}$ at maximum coupling mode of Monomer model is 8.42×10^{-4} a.u. and of Dimer Model **1** is 5.27×10^{-4} a.u. Ratios of $k_{n\leftarrow m}^{\text{IC}}(T)$ of Monomer Model to Dimer Model **1** are also given.

$\sigma \text{ (cm}^{-1}\text{)}$	$k_{n\leftarrow m}^{\text{IC}} \text{ (s}^{-1}\text{)}$		Ratio
	Monomer Model	Dimer Model 1	
300	1.195×10^{10}	2.998×10^7	388
400	1.335×10^{10}	3.985×10^7	335
500	1.569×10^{10}	5.651×10^7	277
600	1.832×10^{10}	7.552×10^7	242
700	2.092×10^{10}	9.525×10^7	219

S4 Electron Density Differences of Dimer Model 2 and 3

Table S5 Excited states of Dimer Model 2 at the S_0 and S_1 optimized structures.

State	Excitation Energy		f	Major Configuration (CI Coefficient)
	eV	nm		
@ S_0 S_1 (A)	3.8692	320.44	3.2829	HO-1 \rightarrow LU (0.398), HO \rightarrow LU+1 (0.565)
S_2 (A)	3.9294	315.53	0.0977	HO-1 \rightarrow LU (0.565), HO \rightarrow LU+1 (-0.399)
@ S_1 S_1 (A)	3.1122	398.39	1.8360	HO \rightarrow LU (0.700)
S_2 (A)	3.9107	317.04	1.5560	HO-1 \rightarrow LU+1 (0.791)



Fig. S3 Electron density differences of (a) S_1 @ S_1 - S_0 @ S_1 and (b) S_2 @ S_1 - S_0 @ S_1 for Dimer Model 2. Isosurface values are 1.0×10^{-3} a.u.

Table S6 Excited states of Dimer Model 3 at the S_0 and S_2 optimized structures.

State	Excitation Energy		f	Major Configuration (CI Coefficient)
	eV	nm		
@ S_0 S_1 (A)	3.7862	327.46	0.1146	HO-1 \rightarrow LU (0.57769), HO \rightarrow LU+1 (-0.37639)
S_2 (A)	3.9346	315.12	2.6588	HO-1 \rightarrow LU (0.38099), HO \rightarrow LU+1 (0.57373)
@ S_2 S_1 (A)	3.3696	367.95	0.0005	HO-1 \rightarrow LU (0.49586), HO \rightarrow LU+1 (-0.48388)
S_2 (A)	3.5310	351.13	2.8119	HO-1 \rightarrow LU (0.48848), HO \rightarrow LU+1 (0.49548)

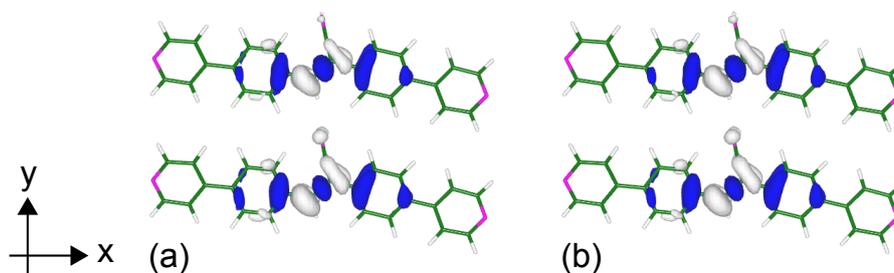


Fig. S4 Electron density differences of (a) S_1 @ S_2 - S_0 @ S_2 and (b) S_2 @ S_2 - S_0 @ S_2 for Dimer Model 3. Isosurface values are 1.0×10^{-3} a.u.

S5 Potential Derivatives of Monomer Model and Dimer Model 1

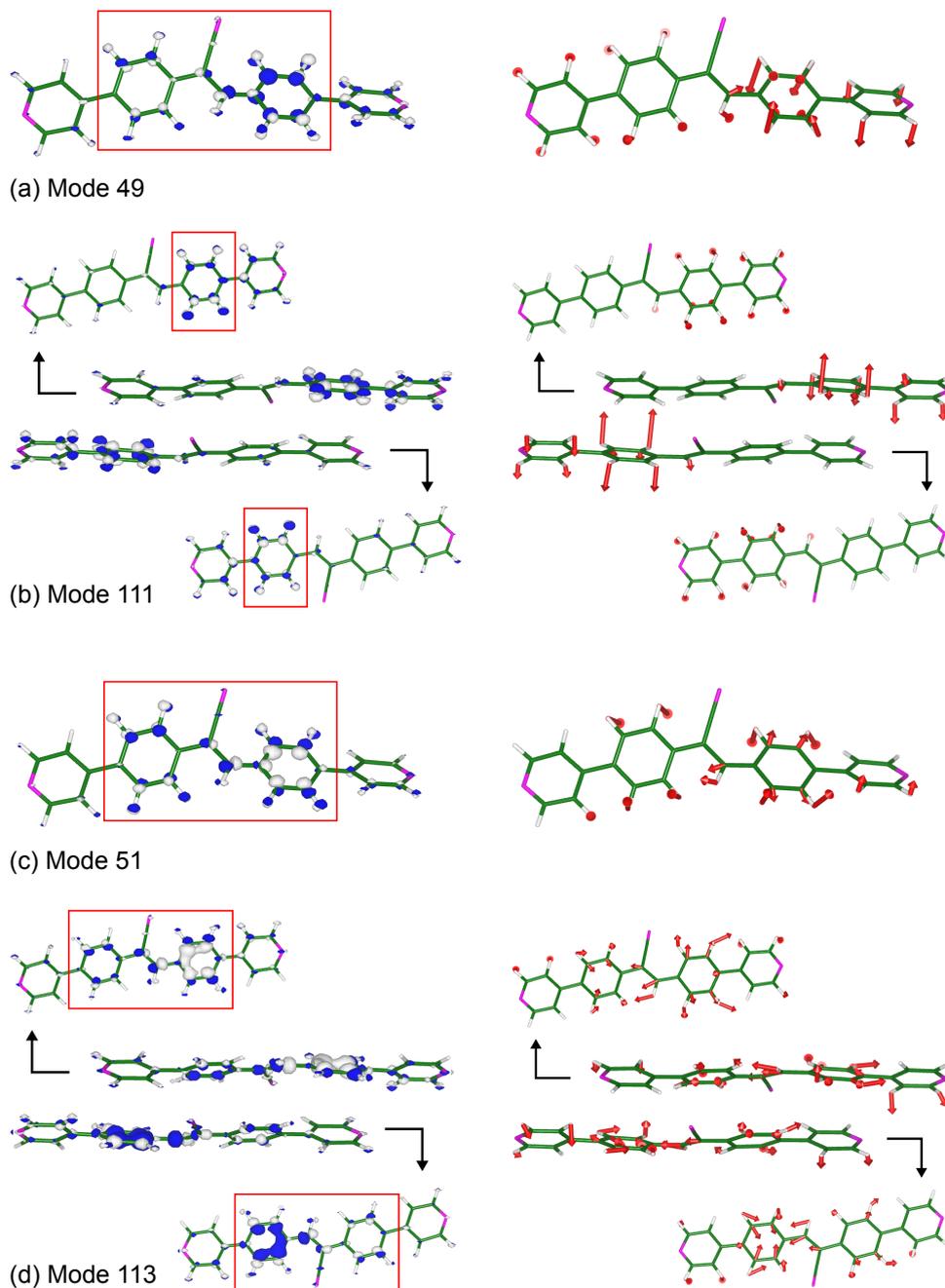


Fig. S5 Potential derivatives of (a) mode 49 for Monomer Model and (b) mode 111 for Dimer Model **1** of which the off-diagonal VCC is reduced by the packing effect. Potential derivatives of (c) mode 51 for Monomer Model and (d) mode 113 for Dimer Model **1** of which the off-diagonal VCC is not reduced by the packing effect. Isosurface value for Monomer Model is 1×10^{-2} a.u. and for Dimer Model **1** is $1/\sqrt{2} \times 10^{-2}$ a.u.

S6 Potential Energy Surface of Monomer Model

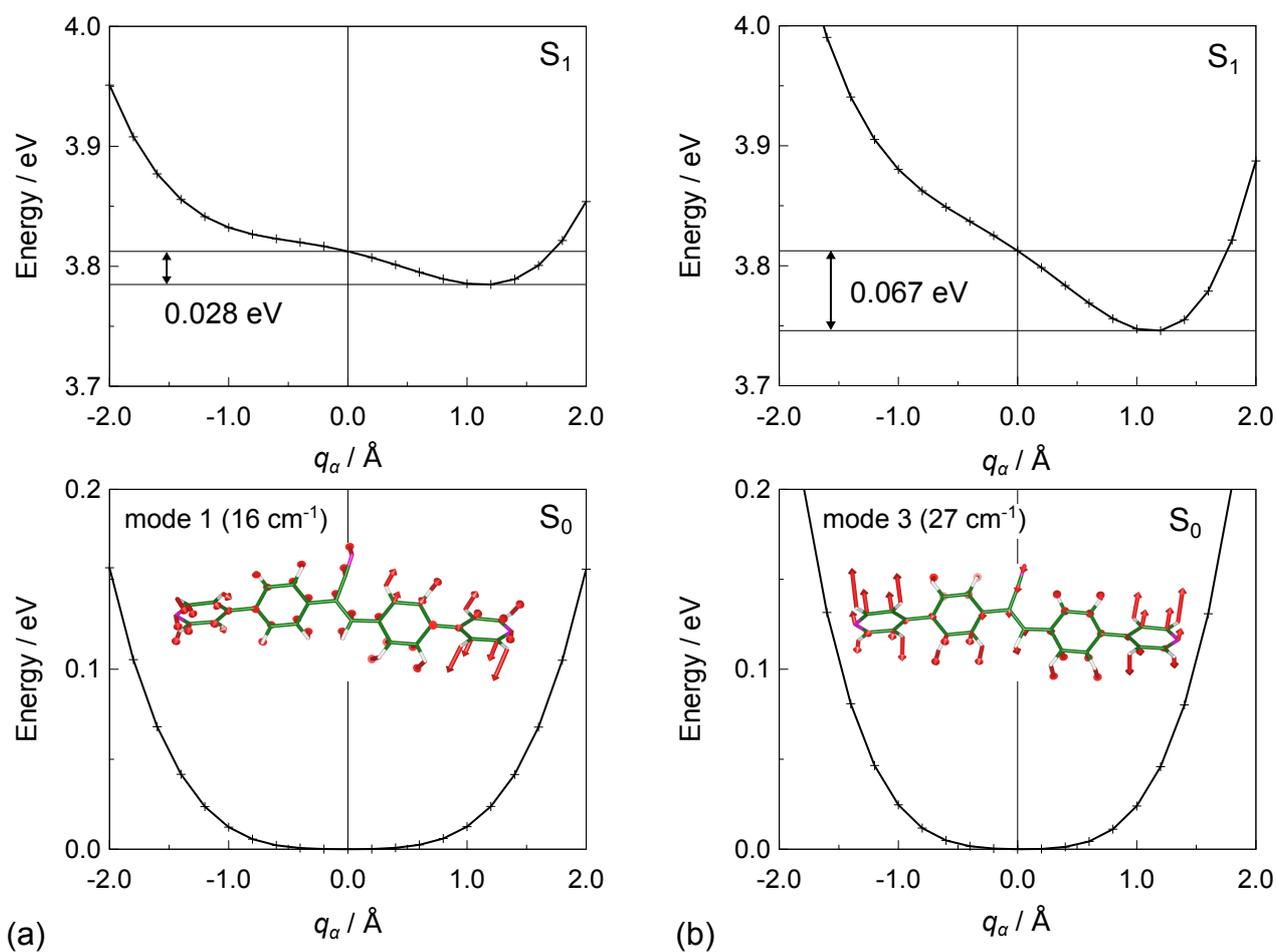


Fig. S6 Potential energy surfaces of S_0 and S_1 of Monomer Model along with (a) mode 1 and (b) mode 3. q_α denotes the Cartesian displacement from the S_0 optimized structure. The potential energy surfaces along with these modes were not approximated to harmonic potentials. The reorganization energies of modes 1 and 3 including the anharmonicity effect were calculated to be 0.028 and 0.067 eV, respectively.

S7 Decamer Model in Solid Phase

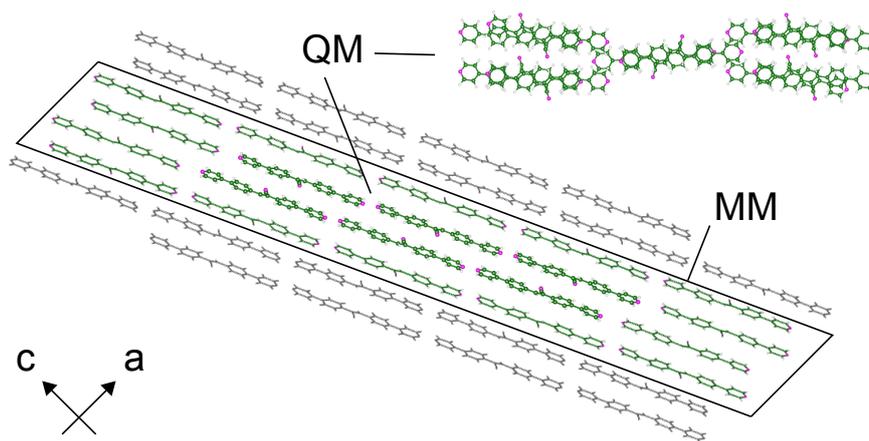


Fig. S7 Decamer Model for the CNPPE solid. Centered decamer is selected as the QM region (M06-2X/3-21G) and the surrounding 60 molecules are selected as the MM region (UFF).

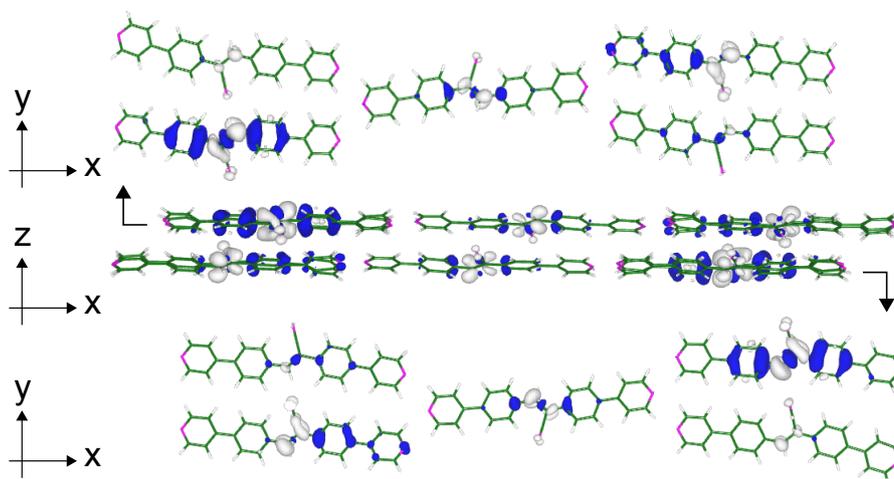


Fig. S8 Electron density difference of $S_8@S_0-S_0@S_0$ for Decamer Model. Isosurface value is 3.0×10^{-4} a.u.

Table S7 Excited states of Decamer Model at the S_0 optimized structure.

State	Excitation Energy		f	Major Configuration (CI Coefficient)
	eV	nm		
$S_1 (A_u)$	3.7447	331.09	0.0052	HO-4 \rightarrow LU (0.2715), HO-4 \rightarrow LU+5 (-0.2389) HO-3 \rightarrow LU+1 (-0.2715), HO-3 \rightarrow LU+4 (-0.2389)
$S_2 (A_g)$	3.7447	331.09	0.0000	HO-4 \rightarrow LU+1 (0.2717), HO-4 \rightarrow LU+4 (0.2392) HO-3 \rightarrow LU (-0.2717), HO-3 \rightarrow LU+5 (0.2392)
$S_3 (A_g)$	3.7775	328.21	0.0000	HO-4 \rightarrow LU+1 (0.2197), HO-3 \rightarrow LU (-0.2199) HO-2 \rightarrow LU+3 (0.2583), HO-1 \rightarrow LU+2 (0.2583)
$S_4 (A_u)$	3.7775	328.21	0.0618	HO-4 \rightarrow LU (-0.2204), HO-3 \rightarrow LU+1 (0.2204) HO-2 \rightarrow LU+2 (0.2580), HO-1 \rightarrow LU+3 (0.2580)
$S_5 (A_u)$	3.8860	319.06	0.7377	HO-4 \rightarrow LU+2 (-0.2070), HO-4 \rightarrow LU+5 (0.2771) HO-3 \rightarrow LU+3 (-0.2070), HO-3 \rightarrow LU+4 (0.2771) HO-2 \rightarrow LU+6 (-0.2052), HO-1 \rightarrow LU+7 (0.2052)
$S_6 (A_g)$	3.8871	318.96	0.0000	HO-4 \rightarrow LU+3 (-0.2030), HO-4 \rightarrow LU+4 (0.2690) HO-3 \rightarrow LU+2 (-0.2030), HO-3 \rightarrow LU+5 (0.2690) HO-2 \rightarrow LU+7 (0.2208), HO-1 \rightarrow LU+6 (-0.2208)
$S_7 (A_g)$	3.9259	315.81	0.0000	HO-5 \rightarrow LU+9 (-0.2354), HO \rightarrow LU+8 (0.6484)
$S_8 (A_u)$	3.9942	310.41	9.0385	HO-2 \rightarrow LU+6 (-0.3474), HO-1 \rightarrow LU+7 (0.3474) HO \rightarrow LU+9 (-0.2498)
$S_9 (A_g)$	4.0290	307.73	0.0000	HO-2 \rightarrow LU+7 (-0.3649), HO-1 \rightarrow LU+6 (0.3649)
$S_{10} (A_u)$	4.1224	300.76	1.1521	HO \rightarrow LU+9 (-0.5282)

S8 Dimer Model 1 Calculated by ω B97X-D Functional

Table S8 Excited states of Dimer Model 1 at the S_0 and S_2 optimized structures calculated by ω B97X-D/6-31G(d,p) level of theory. f denotes the oscillator strength.

State	Excitation Energy			Major Configuration (CI coefficient)
	eV	nm	f	
@ S_0 $S_1(A_g)$	3.8193	324.63	0.0000	HO-1 \rightarrow LU+1 (-0.379) HO \rightarrow LU (0.564)
$S_2(A_u)$	3.9453	314.26	2.3698	HO-1 \rightarrow LU (-0.406) HO \rightarrow LU+1 (0.542)
@ S_2 $S_1(A_g)$	3.3319	372.12	0.0000	HO-1 \rightarrow LU+1 (0.347) HO \rightarrow LU (0.592)
$S_2(A_u)$	3.4697	357.33	2.3091	HO-1 \rightarrow LU (0.379) HO \rightarrow LU+1 (0.570)

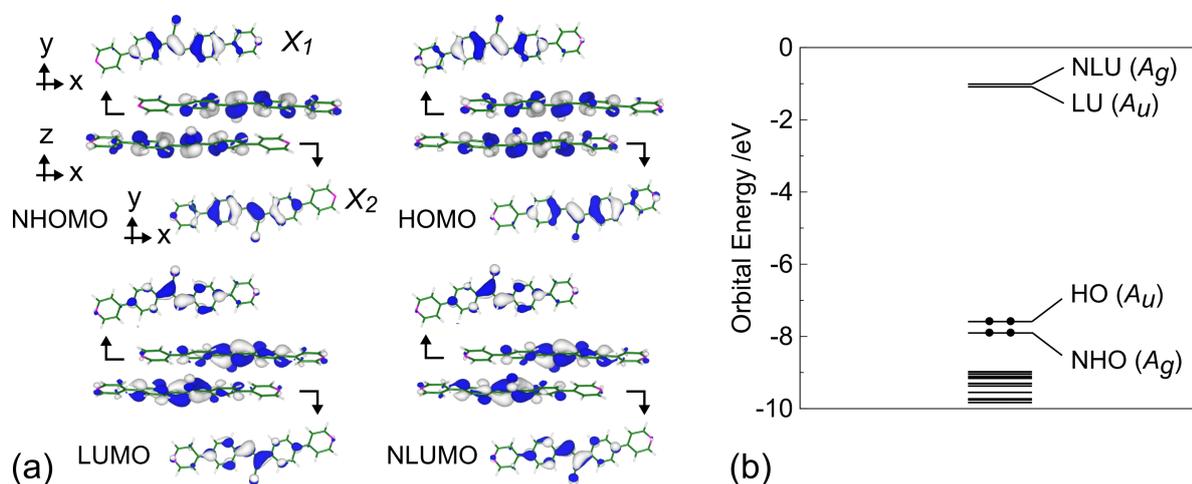


Fig. S9 (a) Frontier orbitals and (b) orbital levels of Dimer Model 1 at the S_2 optimized structure calculated by ω B97X-D/6-31G(d,p) level of theory. X_1 and X_2 are the constituent molecules of Dimer Model 1. Isosurface values of the frontier orbitals are 3.0×10^{-2} a.u.

S9 Hubbard Model of a Pseudo-Degenerate Electronic System

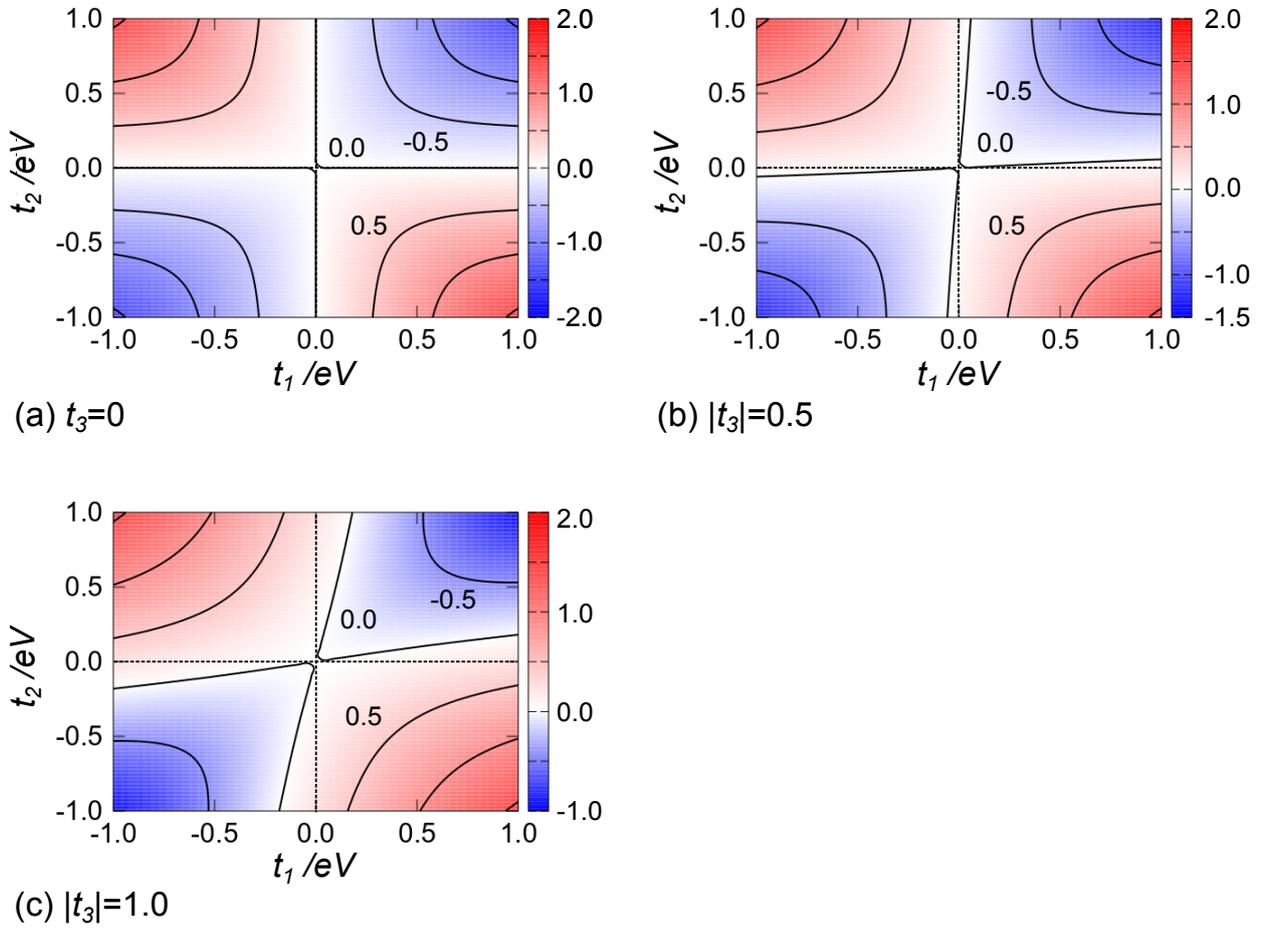


Fig. S10 Energy difference between first and second excited states, $E_1^s - E_1^a$, calculated by numerically diagonalizing the Hubbard Hamiltonian. ε , U_1 , and U_2 were set to 3.0, 1.0, and 1.0, respectively.

In this section, we describe the electron density differences and overlap densities in the pseudo-degenerate electronic system using the Hubbard model. The electron density in the ground state is defined by ρ_0 . The orbital overlap densities are defined by

$$p_1 = |\phi_{\text{HO}}(X_1)|^2, \quad p_2 = |\phi_{\text{HO}}(X_2)|^2, \quad q_1 = |\phi_{\text{LU}}(X_1)|^2, \quad q_2 = |\phi_{\text{LU}}(X_2)|^2, \quad (7)$$

$$r_1 = \phi_{\text{HO}}(X_1)\phi_{\text{LU}}(X_1), \quad r_2 = \phi_{\text{HO}}(X_2)\phi_{\text{LU}}(X_2), \quad (8)$$

$$s_1 = \phi_{\text{HO}}(X_1)\phi_{\text{HO}}(X_2), \quad s_2 = \phi_{\text{LU}}(X_1)\phi_{\text{LU}}(X_2), \quad s_3 = \phi_{\text{HO}}(X_1)\phi_{\text{LU}}(X_2) = \phi_{\text{LU}}(X_1)\phi_{\text{HO}}(X_2), \quad (9)$$

where $\phi_{\text{HO/LU}}(X_1/X_2)$ represent the HOMO/LUMO of X_1/X_2 . The overlaps between X_1 and X_2 separated from each other, namely s_1 , s_2 and s_3 , are supposed to be 0. Table S9 and S10 respectively present the electron density differences and overlap densities in the pseudo-degenerate electronic system.

Table S9 Electron density differences in the pseudo-degenerate system. $\alpha = \frac{1}{2}((\rho_0 - p_1 + q_1) + (\rho_0 - p_2 + q_2))$. For Dimer Model **1** of the CNPPE solid, S_1 corresponds to $|\Psi_1^s\rangle$, and S_2 $|\Psi_1^a\rangle$. Therefore, the electron density difference between S_1 and S_2 is given by 0.

	Ψ_0	Ψ_1^s	Ψ_2^s	Ψ_1^a	Ψ_2^a
Ψ_0	0	$\rho_0 - \alpha$	$\rho_0 - \alpha$	$\rho_0 - \alpha$	$\rho_0 - \alpha$
Ψ_1^s		0	0	0	0
Ψ_2^s			0	0	0
Ψ_1^a				0	0
Ψ_2^a					0

Table S10 Overlap densities in the pseudo-degenerate system. $\alpha = \frac{1}{2}((\rho_0 - p_1 + q_1) + (\rho_0 - p_2 + q_2))$, $\beta_1 = \frac{1}{2}(q_1 - p_1 - q_2 + p_2) \approx 0$, $\beta_2 = \frac{1}{2}(q_2 - p_1 - q_1 + p_2)$, $\gamma_1 = \frac{1}{\sqrt{2}}(r_1 + r_2)$, $\gamma_2 = \frac{1}{\sqrt{2}}(r_1 - r_2)$. For Dimer Model **1** of the CNPPE solid, S_1 corresponds to $|\Psi_1^s\rangle$, and S_2 $|\Psi_1^a\rangle$. Therefore, the overlap density between S_1 and S_2 is given by $\beta_1 \approx 0$.

	Ψ_0	Ψ_1^s	Ψ_2^s	Ψ_1^a	Ψ_2^a
Ψ_0	ρ_0	γ_1	$\frac{t_1+t_2}{U_2}\gamma_1 - \frac{t_3}{\varepsilon-U_1+2U_2}\alpha$	γ_2	$\frac{t_2-t_1}{U_2}\gamma_2 - \frac{t_3}{\varepsilon-U_1+2U_2}\beta_2$
Ψ_1^s		α	0	$\beta_1(\approx 0)$	$\frac{t_2-t_1}{U_2}\beta_1 - \frac{t_1+t_2}{U_2}\beta_2$
Ψ_2^s			α	$\frac{t_1+t_2}{U_2}\beta_1 - \frac{t_2-t_1}{U_2}\beta_2$	β_2
Ψ_1^a				α	0
Ψ_2^a					α

References

- 1 Atkins, P.; Overton, T.; Rourke, J.; Weller, J.; Armstrong, F. Shriver and Atkins' Inorganic Chemistry, 5th ed.; Oxford University Press, USA, 2010.