Electronic Supplementary Information

A Light-Emitting Mechanism for

Organic Light-Emitting Diodes: Molecular Design for

Inverted Singlet-Triplet Structure and

Symmetry-Controlled Thermally Activated Delayed Fluorescence

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S1 Selection Rules

S1.1 Selection rules for transition dipole moment, spin-orbit coupling, and vibronic coupling

The *N*th excited electronic state $|N, \Gamma, \gamma; S, M\rangle$ is labeled by the quantum number of the spin angular momentum, *S*, the quantum number of the *z* component of the spin angular momentum, *M*, the irreducible representation (irrep) Γ , and γ ($\gamma = 1, ..., \dim(\Gamma)$), which distinguishes the irrep of a degenerate Γ .

The transition dipole moment (TDM) is given by

$$\boldsymbol{\mu}_{N_1\Gamma_1S_1 \to N_2\Gamma_2S_2} = \langle N_2, \Gamma_2, \gamma_2; S_2, M_2 | \hat{\boldsymbol{\mu}} | N_1, \Gamma_1, \gamma_1; S_1, M_1 \rangle,$$
(1)

where $\hat{\mu}$ is the electric dipole moment operator and the initial and final states are denoted by subscripts 1 and 2, respectively. The electric dipole moment operator is written as

$$\boldsymbol{\mu} = \sum_{i} -e\mathbf{r}_{i},\tag{2}$$

where \mathbf{r}_i indicates the position vector for electron *i*. In the case of $S_1 = S_2$, forbidden/allowed of a transition depends on the combination of Γ_1 and Γ_2 . Otherwise, it is forbidden.

We consider the one-electron term of the spin-orbit coupling as the origin of the intersystem crossing.¹ The one-electron term of the spin-orbit integral is given by the matrix element of the one-electron part of the spin-orbit coupling operator:

$$\zeta_{N_1\Gamma_1S_1 \to N_2\Gamma_2S_2} = \langle N_2, \Gamma_2, \gamma_2; S_2, M_2 | \hat{H}_{\rm SO} | N_1, \Gamma_1, \gamma_1; S_1, M_1 \rangle.$$
(3)

The spin-orbit coupling operator 1-3 is written as

$$\hat{H}_{\rm SO} = \sum_{i} \sum_{A} \frac{\alpha^2 Z_A}{2r_{iA}^3} \hat{\boldsymbol{l}}_{i,A} \cdot \hat{\boldsymbol{s}}_i, \tag{4}$$

where r_{iA} indicates the distance between atom A and electron *i*, $\hat{\mathbf{s}}_i$ and $\hat{\mathbf{l}}_{i,A}$ denote the spin and orbital angular moment operators, respectively, Z_A indicates the atomic charge, and α is the fine-structure constant. Here, we replace Z_A by the effective nuclear charge $Z_{A,eff}^3$ to incorporate the two-electron term of the spin-orbit coupling. Accordingly,

$$\zeta_{N_1\Gamma_1S_1\to N_2\Gamma_2S_2} = \frac{\alpha^2}{2} \sum_i \sum_A \langle N_2, \Gamma_2, \gamma_2 | \frac{Z_{A,\text{eff}}}{r_{iA}^3} \hat{\boldsymbol{l}}_{i,A} | N_1, \Gamma_1, \gamma_1 \rangle \cdot \langle S_2, M_2 | \hat{\boldsymbol{s}}_i | S_1, M_1 \rangle.$$
(5)

An intersystem crossing is forbidden if the matrix element of the orbital angular momentum is equal to zero. Because the one-electron operators of the electric dipole moment $\boldsymbol{\mu} = -e\hat{\mathbf{r}}$ and orbital angular momentum \hat{l} are tensor operators, we can derive their selection rules based on their irreps: If a tensor operator belongs to Γ_3 irrep and the inclusion relation⁴

$$\Gamma_2 \in \Gamma_3 \times \Gamma_1 \tag{6}$$

holds, the transition between Γ_1 and Γ_2 states is allowed; otherwise, the transition is forbidden. For the electric dipole and spin-orbit interactions, we will discuss the allowed or forbidden pairs of irreps for some point groups later.

In addition to the electric dipole and spin-orbit couplings we discuss the selection rule for the vibronic coupling. The vibronic coupling constant (VCC) is defined by

$$V_{N_{1}\Gamma_{1}\gamma_{1}N_{2}\Gamma_{2}\gamma_{2},N_{3}\Gamma_{3}\gamma_{3}} = \left\langle N_{2},\Gamma_{2},\gamma_{2} \left| \left(\frac{\partial \hat{H}}{\partial Q_{N_{3}\Gamma_{3}\gamma_{3}}} \right)_{\mathbf{R}_{0}} \right| N_{1},\Gamma_{1},\gamma_{1} \right\rangle,$$
(7)

where \hat{H} denotes the molecular Hamiltonian, $Q_{N_3\Gamma_3\gamma_3}$ denotes the normal coordinate for normal mode $N_3\Gamma_3\gamma_3$, and \mathbf{R}_0 denotes the equilibrium nuclear configuration for the reference state⁵. When we consider the transition $N_1\Gamma_1\gamma_1 \rightarrow N_2, \Gamma_2, \gamma_2$ the $N_1\Gamma_1\gamma_1$ state at \mathbf{R}_0 should be taken as the reference state. The diagonal VCC with $N_1 = N_2$, $\Gamma_1 = \Gamma_2$, and $\gamma_1 = \gamma_2$ gives rise to vibrational relaxation. The off-diagonal VCC with $N_1 \neq N_2, \Gamma_1 \neq \Gamma_2$, or $\gamma_1 \neq \gamma_2$ is a factor of the rate of internal conversion.

S1.2 *D*_{2*h*}

	Table 51. Character table for D_{2h} .										
	Ε	C_{2z}	C_{2y}	C_{2x}	Ι	σ_z	σ_y	σ_x	Base		
A_g	1	1	1	1	1	1	1	1	x^2, y^2, z^2		
B_{1g}	1	1	-1	-1	1	1	-1	-1	xy	L_z	
B_{2g}	1	-1	1	-1	1	-1	1	-1	XZ	L_y	
B_{3g}	1	-1	-1	1	1	-1	-1	1	yz.	L_x	
A_u	1	1	1	1	-1	-1	-1	-1	xyz.		
B_{1u}	1	1	-1	-1	-1	-1	1	1	Z.	p_z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	у	p_y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	p_x	

Table S1: Character table for D_{2h} .⁶

S1.3 *D*_{3*h*}

Character table for D_{3h} is shown in Table S2⁶. The *x*-, *y*-, and *z*- components of the electric dipole moment operator $\hat{\mu}$ belong to *E'*, and *E'*, and *A''*, respectively. The orbital angular momentum operator components, \hat{l}_x , \hat{l}_y , and \hat{l}_z , belong to *E''*, and *E''*, and *A'*, respectively. The selection rules can be obtained from Table S2. In the case of the selection rule for *x*- and *y*- components of electric dipole transition which transform as the *E'* irreducible representation (irrep), the direct product of the irreps for the operator and each electronic state is decomposed as follows:

$$E' \times A'_1 = E', \quad E' \times A'_2 = E', \quad E' \times A''_1 = E'', \quad E' \times A''_2 = E'',$$
$$E' \times E' = A'_1 + A'_2 + E', \quad E' \times E'' = A''_1 + A''_2 + E''.$$
(8)

Therefore, the pair of irreps for electronic states (A'_1, E') , (A'_2, E') , (A''_1, E'') , (A''_2, E'') , (E', E'), (E'', E'') are allowed for the electric dipole transition in the *x*- or *y*- direction. The selection rule in the electric dipole transition is summarised in Table S3. One sees that the ratio of forbidden irrep pairs are 20 of 36. The forbidden ratio for D_{3h} is lower than that for D_{2h} (Table 6) although the order for D_{3h} is higher than that for D_{2h} . This indicates the importance of the inversion symmetry since D_{3h} does not contain the inversion while D_{2h} does.

The selection rule for the orbital angular momentum is summarised in Table S4. The forbidden ratio of \hat{l} is the same as that of \mathbf{r} . The D_{3h} symmetry gives small forbidden ratio, also originating from the lack of inversion symmetry.

	Table S2: Character table for D_{3h}°											
	E	$2IC_6$	2 <i>C</i> ₃	σ_h	$3C_{2y}$	$3\sigma_x$	Ba	se				
A'_1	1	1	1	1	1	1	$y^3 - 3x^2y$					
A_2'	1	1	1	1	-1	-1	$x^3 - 3xy^2$	l_z				
A_1''	1	-1	1	-1	1	-1						
A_2''	1	-1	1	-1	-1	1	Z	p_z				
E''	2	1	-1	-2	0	0	$\{zx, zy\}$	$\{l_x, l_y\}$				
E'	2	-1	-1	2	0	0	$\{x, y\}$	$\{p_x, p_y\}$				

	A'_1	A_2'	A_1''	A_2''	E'	E''
A'_1	×	×	×	Z.	$\{x, y\}$	×
A_2'		×	Z.	×	$\{x,y\}$	×
A_1''			×	×	×	$\{x, y\}$
A_2''				×	×	$\{x, y\}$
E'					$\{x,y\}$	Z,
E''						$\{x, y\}$

Table S3: Selection rule for the electric dipole moment operator in the D_{3h} symmetry.

Table S4: Selection rule for the orbital angular momentum operator in the D_{3h} symmetry.

	A'_1	A_2'	A_1''	A_2''	E'	E''
A'_1	×	l_z	×	×	×	$\{l_x, l_y\}$
A_2'		×	l_z	×	×	$\{l_x, l_y\}$
A_1''			×	×	$\{l_x, l_y\}$	×
A_2''				\times	$\{l_x, l_y\}$	×
E'					l_z	$\{l_x, l_y\}$
E''						l_z

S1.4 *D*_{4*h*}

Character table for D_{4h} is listed in Table S5⁶. The *x*, *y*, and *z* components of the electric dipole moment operator $\hat{\mu}$ belong to E_u , and E_u , and B_{1u} , respectively. On the other hand, the orbital angular momentum operator components, \hat{l}_x , \hat{l}_y , and \hat{l}_z belong to E_g , and E_g , and A_{2g} , respectively. The selection rules can be obtained from Table S5. In the case of the selection rule for *x*- and *y*- components of electric dipole transition which transform as the E_u irreps, the direct product of the irreps for the operator and each electronic state is decomposed as follows:

$$E_{u} \times A_{1g} = E_{u}, \quad E_{u} \times A_{2g} = E_{u}, \quad E_{u} \times B_{1g} = E_{u}, \quad E_{u} \times B_{2g} = E_{u},$$

$$E_{u} \times E_{g} = A_{1u} + A_{2u} + B_{1u} + B_{2u}$$

$$E_{u} \times A_{1u} = E_{g}, \quad E_{u} \times A_{2u} = E_{g}, \quad E_{u} \times B_{1u} = E_{g}, \quad E_{u} \times B_{2u} = E_{g},$$

$$E_{u} \times E_{u} = A_{1g} + A_{2g} + B_{1g} + B_{2g}.$$
(9)

Hence, the electric dipole transition in the *x*-or *y*- direction is allowed when the pair of irreps for electronic states (Γ_1, Γ_2) is (A_{1g}, E_u) , (A_{2g}, E_u) , (B_{1g}, E_u) , (B_{2g}, E_u) , (A_{1u}, E_g) , (A_{2u}, E_g) , (B_{1u}, E_g) , or (B_{2u}, E_g) . Thus, we can obtain the selection rule for the electric dipole transition in the *x*-and *y*- direction. Table S6 is the summary of the selection rule for the electric dipole transition. Because of the Laporte rule, the ratio of the forbidden pairs are over 50%; the forbidden pairs are 74 of 100.

The selection rule for the orbital angular momentum is summarised in Table S7. The selection rule of \hat{l} is almost the same as that of $\hat{\mathbf{r}}$ except for the difference of gerade and ungerade. Therefore, the same ratio of forbidden irrep pairs is obtained.

	Table 55. Character table 101 D_{4h}											
	Ε	$2C_4$	C_4^2	$2C'_2$	$2C_{2}''$	Ι	$2IC_4$	σ_h	$2\sigma_v$	$2\sigma_d$	Base	e
A_{1g}	1	1	1	1	1	1	1	1	1	1	$z^2, x^2 + y^2$	
A_{2g}	1	1	1	-1	1	1	1	1	-1	-1	$xy(x^2 - y^2)$	l_z
B_{1g}	1	-1	1	1	1	-1	-1	1	1	-1	$x^2 - y^2$	
B_{2g}	1	-1	1	-1	1	-1	-1	1	-1	1	xy	
E_g	2	0	-2	0	2	0	0	-2	0	0	$\{xz, yz\}$	$\{l_x, l_y\}$
A_{1u}	1	1	1	1	-1	-1	-1	-1	-1	-1	$xyz(x^2 - y^2)$	
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	Z.	p_z
B_{1u}	1	-1	1	1	-1	1	1	-1	-1	1	xyz	
B_{2u}	1	-1	1	-1	-1	1	1	-1	1	-1	$z(x^2 - y^2)$	
Eu	2	0	-2	0	-2	0	0	2	0	0	$\{x,y\}$	$\{p_x, p_y\}$

Table S5: Character table for D_{4h}^{6}

Table S6: Selection rule for the electric dipole moment operator in the D_{4h} symmetry.

	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_g	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_u
A_{1g}	×	×	×	×	×	×	Z.	×	×	$\{x,y\}$
A_{2g}		×	×	×	×	Z.	×	×	×	$\{x,y\}$
B_{1g}			×	×	×	×	×	×	Z.	$\{x,y\}$
B_{2g}				×	×	×	×	Z.	×	$\{x,y\}$
E_g					×	$\{x, y\}$	$\{x, y\}$	$\{x, y\}$	$\{x, y\}$	Z.
A_{1u}						×	×	×	×	×
A_{2u}							×	×	×	×
B_{1u}								×	×	×
B_{2u}									×	×
E_u										×

	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_g	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_u
A_{1g}	×	l_z	×	×	$\{l_x, l_y\}$	×	×	×	×	×
A_{2g}		×	×	×	$\{l_x, l_y\}$	×	×	×	×	×
B_{1g}			×	l_z	$\{l_x, l_y\}$	×	×	×	×	×
B_{2g}				×	$\{l_x, l_y\}$	×	×	×	×	×
E_g					l_z	×	×	×	×	×
A_{1u}						×	l_z	×	×	$\{l_x, l_y\}$
A_{2u}							×	×	×	$\{l_x, l_y\}$
B_{1u}								×	l_z	$\{l_x, l_y\}$
B_{2u}									×	$\{l_x, l_y\}$
E_u										l_z

Table S7: Selection rule for the orbital angular momentum operator in the D_{4h} symmetry.

S2 Theory of Vibronic Coupling Density

Small diagonal and off-diagonal VCCs give rise to suppression of vibrational relaxations and nonradiative vibronic transitions, respectively. Analyses of diagonal and off-diagonal vibronic coupling densities (VCDs) enable us to design molecules with small VCCs. In this subsection, we summarise the relation between the VCCs and VCDs. For simplicity, the VCC $V_{N_1\Gamma_1\gamma_1N_2\Gamma_2\gamma_2,\alpha\Gamma_3\gamma_3}$ is written as $V_{ml,\alpha}$ hereafter, where $m = N_1\Gamma_1\gamma_1$, $l = N_2\Gamma_2\gamma_2$, and $\alpha = N_3\Gamma_3\gamma_3$.

The diagonal VCC, denoted by $V_{m,\alpha}$ with electronic state *m* and vibrational mode α , is given by the spatial integration of the VCD:⁷

$$V_{m,\alpha} = \int \eta_{m,\alpha} d^3 \mathbf{r}, \quad \text{where} \quad \eta_{m,\alpha} := \Delta \rho_m v_\alpha. \tag{10}$$

Here v_{α} is the potential derivative defined by

$$v_{\alpha}(\mathbf{r}) = \left(\frac{\partial u(\mathbf{r})}{\partial Q_{\alpha}}\right)_{\mathbf{R}_{0}},\tag{11}$$

where u denotes the one-electron nuclear-electronic potential:

$$u(\mathbf{r}) = \sum_{A} -\frac{Z_{A}e^{2}}{|\mathbf{r} - \mathbf{R}_{A}|}.$$
(12)

 $\Delta \rho_m$ is defined by the electron density difference: $\Delta \rho_m = \rho_m - \rho_0$, where ρ_m and ρ_0 are the electronic densities, for instance, for the excited state S_m and the ground state S_0 , respectively. Within the crude adiabatic (CA) approximation,⁵ the reorganisation energy in the Franck–Condon (FC) S_m state is written as

$$\Delta E_m = \sum_{\alpha} \frac{V_{m,\alpha}^2}{2\omega_{\alpha}^2},\tag{13}$$

where ω_{α} denotes the frequency for mode α . The adiabatic transition energy $E_{m,0-0}$ can be written as $E_{m,0-0} = E_m - \Delta E_m$, where E_m is the vertical transition energy. Small ΔE_m is desirable for small energy dissipation, because small ΔE_m means a small Stokes shift or vibrational relaxation.

In contrast, the off-diagonal VCC between the S_m and S_l states for mode α , $V_{ml,\alpha}$, is given by the off-diagonal VCD:⁸

$$V_{ml,\alpha} = \int \eta_{ml,\alpha} d^3 \mathbf{r}, \quad \text{where} \quad \eta_{ml,\alpha} := \rho_{ml} v_{\alpha}. \tag{14}$$

Here ρ_{ml} denotes the overlap density between the S_m and S_l states. For the *N*-electron wave functions of states *m* and *l*, Ψ_{S_l} and Ψ_{S_m} ,

$$\boldsymbol{\rho}_{ml}(\mathbf{r}) := \frac{1}{N} \int \cdots \int \Psi_{S_l}^* (\mathbf{r}\omega_1, \mathbf{r}_2\omega_2, \dots, \mathbf{r}_N\omega_N) \Psi_{S_m}(\mathbf{r}\omega_1, \mathbf{r}_2\omega_2, \dots, \mathbf{r}_N\omega_N) d\omega_1 d^3 \mathbf{r}_2 d\omega_2 \cdots d^3 \mathbf{r}_N d\omega_N, \quad (15)$$

where $\mathbf{r}, \mathbf{r}_i (i = 2, ..., N)$ are space coordinates of electrons, and $\omega_i (i = 1, ..., N)$ are spin coordinates of electrons.

The VCD analyses enable us to discuss vibronic couplings in terms of electronic structure, $\Delta \rho_m$ or ρ_{ml} , and vibrational structure, v_{α} . The diagonal and off-diagonal vibronic couplings are characterised by the spatial distributions of $\Delta \rho_m$ and ρ_{ml} , respectively. When the overlap between $\Delta \rho_m$ or ρ_{ml} and v_{α} is small, the VCC becomes small. In addition, the symmetrical localisation of $\Delta \rho_m$ or ρ_{ml} around an atom gives rise to the cancellation of the vibronic coupling density.^{7,9} Following these guiding principles, we can reduce the VCCs under the control of $\Delta \rho_m$ and ρ_{ml} .

S3 Theory of Transition Dipole Moment Density

The oscillator strength is proportional to the square of the TDM. Since the spatial integration of transition dipole moment density (TDMD) $\boldsymbol{\tau}_{ml}^{8}$ yields the TDM $\boldsymbol{\mu}_{ml}$,

$$\boldsymbol{\mu}_{ml} = \int \boldsymbol{\tau}_{ml} d^3 \mathbf{r}, \quad \text{where} \quad \boldsymbol{\tau}_{ml} := -e \mathbf{r} \rho_{ml}, \tag{16}$$

with **r** denoting the position vector. The TDMD provides an insight into enhancing the TDM. As is the case for the off-diagonal VCD, the overlap density ρ_{ml} also plays an important role in the TDMD analysis. In our previous study, it was found that widely distributed ρ_{ml} leads to large $\boldsymbol{\mu}_{ml}$.^{8,10,11}

S4 Fundamental Structure of Anthracene Derivatives

Focusing on the $S_1 \rightarrow S_0$ transition, we compared the electron-density differences $\Delta \rho_1$ and overlap densities ρ_{10} among **1a**, **1b**, and **1c**. Their $\Delta \rho_1$ and ρ_{10} values are shown in Fig. S1. It is found that $\Delta \rho_1$ and ρ_{10} are distributed similarly among the three molecules and they do not extend to the alkyl groups.

To evaluate the effect of the alkyl substitution on $\Delta \rho_m$ and ρ_{ml} , the spatial integration of their absolute values were calculated. Here we call the unsubstituted unit of **1b** and **1c**, the unit of anthracene derivative **1a**, a *fundamental structure*, which has higher symmetry than the original structures. The fundamental structure is defined by the subunit of a molecule where both the electron density difference $\Delta \rho_m$ and the overlap density ρ_{ml} are mostly localised. If the fundamental structure has a higher symmetry, we can discuss the approximate selection rule based on the electronic structure of the fundamental structure. The integrations of $|\Delta \rho_m|$ and $|\rho_{ml}|$ over all space are defined as I_D and I_O , respectively. The region *R* is defined as the space constructed by the Wigner–Seitz cells¹² in the fundamental structure. The integrations of $|\Delta \rho_m|$ and $|\rho_{ml}|$ over the region *R* is defined as I_D^R and I_O^R , respectively. The definitions are summarised as follows:

$$I_D := \int |\Delta \rho_m(\mathbf{r})| d^3 \mathbf{r}, \qquad I_D^R := \int_R |\Delta \rho_m(\mathbf{r})| d^3 \mathbf{r},$$

$$I_O := \int |\rho_{ml}(\mathbf{r})| d^3 \mathbf{r}, \qquad I_O^R := \int_R |\rho_{ml}(\mathbf{r})| d^3 \mathbf{r}.$$
(17)

The ratios I_D^R/I_D and I_O^R/I_O between the S₀ and S₁ states are tabulated in Table S8. This table shows that I_D^R/I_D and I_O^R/I_O are over 98%. The small changes in $\Delta \rho_1$ and ρ_{10} caused by the alkylations lead to almost the same values of the VCCs and TDMs.

Table S8: Rates of I_D^R/I_D and I_O^R/I_O , where I_D^R, I_D, I_O^R , and I_O are defined by Eq. 17.

	1a	1b	1c
I_D^R/I_D	99.49%	99.34%	99.12%
I_O^R/I_O	99.98%	99.10%	98.51%



Fig. S1: Electron density differences $\Delta \rho_1$ and overlap densities ρ_{10} : (a1–a3) $\Delta \rho_1$ for **1a**, **1b**, and **1c**, respectively; (b1–b3) ρ_{10} for **1a**, **1b**, and **1c**, respectively. The isovalues for $\Delta \rho_1$ and ρ_{10} are both 0.001 a.u.

S5 Vibronic Coupling and Transition Dipole Moment Analyses for Pyrene and Its Derivative

S5.1 Diagonal vibronic coupling constants and densities in the Franck–Condon S₁ state



Fig. S2: Vibronic coupling constants in the Franck–Condon S_1 state: (a) pyrene **2** and (b) its derivative **2a**. The maximum-coupling modes are indicated by the arrows.

Molecule **2a** was designed to have a delocalised electron-density difference, $\Delta \rho_1$, in the pyrene unit. The diagonal vibronic coupling constants (VCCs) in the FC S₁ state, $V_{1,\alpha}$, were calculated from the force in the FC S₁ state with respect to the normal mode in the S₀ state. The VCCs of **2** and **2a** are shown in Figs. S2. The maximum-coupling mode for **2a**, shown in Fig. S4a, is smaller than that for pyrene **2**, shown in Fig. S3a. Since the VCC of the maximum-coupling mode is reduced, the reorganisation energy ΔE_1 for **2a** is smaller than that for **2**; the values for **2** and **2a** are 0.141 eV and 0.117 eV, respectively.

The reason for the reduction in the VCC for the maximum-coupling mode can be explained by the diagonal vibronic coupling density (VCD) analysis. The potential derivatives v_{α} for the maximum-coupling modes of **2** and **2a** are shown in Figs. S3b and S4b, respectively. The maximum-coupling mode for **2a** is the C–C stretching modes of the pyrene unit; the normal modes are localized on C4–C5 and C9–C10 bonds. For this reason, the potential derivative v_{α} for **2a** is localised to the pyrene unit as is the same in **2**.

The electron-density differences between the FC S₁ state and the S₀ state, $\Delta \rho_1$, of pyrene and **2a** are shown in Figs. S3c and S4c, respectively. The enlarged view of $\Delta \rho_1$ is shown in Fig. S5. It is found that $\Delta \rho_1$ for **2a** is withdrawn from pyrene unit by the 1-pyrrolylethynyl groups. In particular, $\Delta \rho_1$ in the C8–C13

and C9–C10 bond regions, which are also indicated by the red arrows in the Fig. S5, is reduced. Because the maximum-coupling mode α is localised to the pyrene unit, the overlap between $\Delta \rho_1$ and v_{α} for **2a** is smaller than that of pyrene.

The diagonal vibronic coupling densities $\eta_{1,\alpha} = v_{\alpha} \times \Delta \rho_1$ for pyrene and **2a** are shown in Figs. S3d and S4d, respectively. Because of the small $\Delta \rho_1$ in the pyrene unit, $\eta_{1,\alpha}$ for **2a** is reduced. Therefore, the VCC for the maximum-coupling mode for **2a** is smaller than that for pyrene. Thus, it is shown that introducing the 1-pyrrolylethynyl groups to pyrene gives rise to delocalised $\Delta \rho_1$ and to the small VCCs.



Fig. S3: Diagonal vibronic coupling density analysis for pyrene **2**: (a) maximum-coupling mode $\omega_{62} = 1684.69 \text{ cm}^{-1}$ with carbon atom labels; (b) derivative of the electronic-nuclear potential v_{62} ; (c) electron-density difference between the S₁ and S₀ states $\Delta \rho_1$; (d) diagonal vibronic-coupling density $\eta_{1,62}$; and The isovalues for v_{62} , $\Delta \rho_1$, and $\eta_{1,62}$ are 0.01, 0.002, and 1×10^{-5} , in atomic units, respectively.



Fig. S4: Diagonal vibronic coupling density analysis for pyrene derivative **2a**: (a) maximum-coupling mode $\omega_{166} = 1660.31 \text{ cm}^{-1}$; (b) derivative of the electronic-nuclear potential v_{166} ; (c) electron-density difference between the S₁ and S₀ states $\Delta \rho_1$; and (d) diagonal vibronic-coupling density $\eta_{1,166}$. The isovalues for v_{166} , $\Delta \rho_1$, and $\eta_{1,166}$ are 0.01, 0.002, and 1×10^{-5} , in atomic units, respectively.



Fig. S5: Enlarged view of electron-density differences between the S₁ and S₀ states $\Delta \rho_1$ for (a) pyrene 2 and (b) its derivative 2a. The isovalues for $\Delta \rho_1$ are 0.001, in atomic units.

S5.2 Off-diagonal vibronic coupling constants and densities between the S₁ and S₀ states



Fig. S6: Off-diagonal vibronic coupling constants between the S_1 and S_0 states: (a) pyrene 2 and (b) its derivative 2a.

In order to calculate the off-diagonal vibronic couplings in the internal conversion $S_1 \rightarrow S_0$, we obtained the adiabatic state by carrying out the geometrical optimisation in the S_1 state. The off-diagonal VCCs were calculated using the normal modes in the S_0 state at the optimised structure for the S_1 state.

In the adiabatic S₁ state, the off-diagonal VCCs between the S₁ and S₀ states, $V_{10,\alpha}$, of **2** and **2a** are shown in Figs. S6. The VCC for the maximum-coupling mode of **2a** is smaller than that of pyrene. The suppressed off-diagonal VCCs come from a delocalised overlap density ρ_{10} for **2a**.

It should be noted that the number of active modes in **2a** is smaller than that in a molecule with the same size that has a lower symmetry than D_{2h} . Because the irreducible representation (irrep) of the S₁ state is B_{1u} , only b_{1u} modes are active in the off-diagonal vibronic couplings between the S₀ and S₁ states. For pyrene **2**, 12 b_{1u} modes of all 72 modes are active:

$$\Gamma_{\rm vib}(D_{2h}) = 13a_g + 4b_{1g} + 7b_{2g} + 12b_{2g} + 5a_u + 12b_{1u} + 12b_{2u} + 7b_{3u},\tag{18}$$

for pyrene derivative **2a**, 32 b_{1u} modes of all 192 modes are active:

$$\Gamma_{\text{vib}}(D_{2h}) = 33a_g + 14b_{1g} + 17b_{2g} + 32b_{2g} + 15a_u + 32b_{1u} + 32b_{2u} + 17b_{3u}.$$
(19)

From the symmetry viewpoint, internal conversion is suppressed with the small number of radiationless channels.

The off-diagonal VCCs are analysed by the off-diagonal VCDs. The maximum-coupling modes for pyrene **2** and its derivative **2a** are depicted in Figs. S7a and S8a, respectively. The maximum-coupling modes of **2a** are localised to the pyrene unit. The potential derivatives v_{α} for **2** and **2a** are shown in Figs. S7b and S8b, respectively. Both of the v_{α} on the C2 and C7 atoms are large because of the localisation of the normal modes.

The overlap densities between between the S₁ and S₀ states, ρ_{10} , of **2** and **2a** are shown in Figs. S7c and S8c, respectively. One can see that **2a** has smaller ρ_{10} than **2** does. The small ρ_{10} in the pyrene unit originates from the extended π conjugation to the 1-pyrrolylethynyl groups. That is, the orbital overlap density between the HOMO and LUMO, which is the main component of ρ_{01} , is delocalised with small density in the pyrene unit. Because of the small ρ_{10} , $\eta_{10,\alpha}$ for **2a** is decreased in the pyrene unit, as shown in Figs. S7d and S8d for **2** and **2a**, respectively.

The VCCs $V_{10,\alpha}$ are also decomposed into the atomic vibronic coupling constants (AVCCs), $V_{A,10,\alpha}$ ⁹:

$$V_{10,\alpha} = \sum_{A} V_{A,10,\alpha},\tag{20}$$

where *A* indicates the atoms. The AVCCs of the maximum-coupling modes of **2** and **2a** are shown in Fig S9. It is found that the AVCCs of the 1-pyrrolylethynyl group is small and the main contribution comes from pyrene group. The absolute value of AVCC for the C2 atom of **2a** decreases largely. This is because the large ρ_{10} on the C2 atom of pyrene is reduced by introducing the 1-pyrrolylethynyl groups. Thus, an extension of π conjugation can be one way to reduce the off-diagonal VCCs.



Fig. S7: Off-diagonal vibronic coupling density analysis for pyrene **2**: (a) maximum-coupling mode $\omega_{19} = 694.61$ cm⁻¹ with carbon atom labels; (b) derivative of the electronic-nuclear potential v_{19} ; (c) overlap density between the S₁ and S₀ states ρ_{10} ; and (d) diagonal vibronic-coupling density $\eta_{10,19}$. The isovalues for v_{19} , ρ_{10} , and $\eta_{10,19}$ are 0.01, 0.002, and 1×10^{-5} , in atomic units, respectively.



Fig. S8: Off-diagonal vibronic coupling density analysis for pyrene derivative **2a**: (a) maximum-coupling mode $\omega_{70} = 687.59 \text{ cm}^{-1}$ with carbon atom labels of the pyrene unit; (b) derivative of the electronic-nuclear potential v_{70} ; (c) overlap density between the S₁ and S₀ states ρ_{10} ; and (d) diagonal vibronic-coupling density $\eta_{10,70}$. The isovalues for v_{70} , ρ_{10} , and $\eta_{10,70}$ are 0.01, 0.002, and 1×10^{-5} , in atomic units, respectively.



Fig. S9: Off-diagonal atomic vibronic coupling constants between the S₁ and S₀ states, in 10^{-5} atomic units: (a) pyrene **2**, $V_{10,19}$, and (b) its derivative **2a**, $V_{10,70}$.

S5.3 Transition dipole moment densities between the S_1 and S_0 states

The delocalised distribution of overlap density ρ_{10} gives rise to a large transition dipole moment (TDM). The product of overlap density ρ_{10} and position vector **r** yields the transition dipole moment density (TDMD) τ_{10} . Because of the selection rule, *x*- and *y*-component of TDMs are zero, and the *z*-component of TDMDs can be non-zero.

The *z*-component of TDMD, $\tau_{z,10}$, for pyrene **2** and its derivative **2a** are shown in Figs S10. It is found that the overlap density is polarised in the *z*-direction. For pyrene **2**, $\tau_{z,10}$ on the C1, C3, C6, and C8 atoms are large, in accordance with the large ρ_{10} on these atoms.

On the other hand, large $\tau_{z,10}$ appears on the 1-pyrrolylethynyl groups in **2a**. This is because the introduced groups are so distant from the pyrene that the overlap of *z*-value and ρ_{10} . As the result of the spatial integration of $\tau_{z,10}$, **2a** has much larger TDM $\mu_{z,10}$ than pyrene; The values of **2a** and **2** are 4.4465 and 1.9393, in atomic units, respectively. Thus, the delocalised distribution of ρ_{10} increases the TDMs and then enhances fluorescence process.



Fig. S10: Transition dipole moment densities in the *z*-direction between the S₁ and S₀ states $\tau_{z,10}$: (a) pyrene 2 and (b) its derivative **2a** The isovalue for $\tau_{z,10}$ is 0.01, in atomic unit.

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