Molecular and Crystalline Requirements for Solid State Fluorescence Exploiting Excited State Intramolecular Proton Transfer

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Molecular and Crystalline Requirements for Solid State Fluorescence Exploiting Excited State Intramolecular Proton Transfer

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Abstract

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and exciton hopping rates. We show that in addition to the restriction of nonradiative pathways, an efficient ESIPT is essential to maximise the QE in the solid state. This extensive study of structure-property relationships for fluorophores based on the ESIPT mechanism bridges the understanding of molecular photophysics with crystal structure, accelerating the development of highly efficient solid state emitters.

Introduction

Luminescent organic materials have technological promise for applications such as light-emitting diodes, field effect transistors, imaging and detection, and solid state lasers.¹⁻⁷ Molecular organic systems offer the opportunity to tune absorption and emission characteristics for a desired application, through chromophore modification and crystal engineering. However, such control, at least from a design point of view, remains challenging due to the complex structure-property relationships in molecular crystals.

Optimising luminescence quantum efficiencies (QE) is imperative to making such devices and materials viable for use. Aggregation caused quenching (ACQ) has traditionally been the first obstacle to overcome in this process, since fluorescence quenching is highly common in conjugated aromatic systems as $\pi\pi$ interactions arise in the solid state. In past years researchers have developed a strategy to overcome ACQ *via* aggregation induced emission (AIE), where fluorescence is turned on upon molecular aggregation.^{8,9} This can require complex and laborious substituent modification to inhibit nonradiative decay, in particular due

to the difficulties in crystal structure design and the ensuing trial-and-error optimisation process.

Numerous mechanisms have been proposed to account for AIE, due to the variety of reported systems, including J-aggregate formation, suppression of Kasha’s rule of fluorescence, excimer formation, restriction of intramolecular motions (RIM), and restricted access to conical intersections (RACI).^{7,10–16} Theoretical investigation into the AIE mechanism has been led by the groups of Peng and Shuai, who have developed formalism based on the Fermi Golden Rule approach to calculate radiative and nonradiative decay rates in AIE systems.^{17–23} The work of Blancafort *et al.* has shown that S_1 - S_0 conical intersections (CIs) also play a role in the solid state.^{15,16} These theoretical frameworks have enabled researchers to understand the emitting properties of a myriad of systems.²⁴

As well as the electronic properties of the chromophore, intermolecular interactions become photophysically important in the solid state due to the dense packing in organic crystals. Since the excited state is often localised on just a few molecular units, this effect is commonly examined through Kasha’s two state exciton theory.^{7,10,25–27} Based on Kasha’s model, dimers are generally assigned as H-aggregates based on the Coulomb interaction of transition dipole moments aligning side-by-side, whilst J-aggregates arise when a slip in the x -plane (long axis) occurs. At small intermolecular distances however, the sole use of the Coulomb interaction neglects the important contribution of short-range coupling effects, resulting in interferences which cannot be described by an electrostatic interpretation alone.²⁶ Furthermore, when there is considerable perturbation between the Franck-Condon and the equilibrated excited state, Kasha’s interpretation of H- and J-aggregates is less clear.

In this work we examine both the electronic properties of the chromophore, the intermolecular relationships in the molecular crystal, and the crystal structure, to rationalise the observed fluorescence behaviour for a set of related organic materials undergoing excited state intramolecular proton transfer (ESIPT). ESIPT involves a four level photocycle between enol (E) and keto (K) tautomers triggered by electronic excitation in the E form.

ESIPT followed by emission from the resultant K^* minimum (on the excited state PES) affords a large Stokes shift, separating the absorption and emission bands. Competition between E^* and K^* emission can be tuned, for example, through substituent modification and choice of solvent.^{28–33}

Chalcone-based compounds, comprising an aromatic ketone and enone system, have found application in both technological and biological settings.^{33–48} The lasing properties of ESIPT emitters based on chalcone skeletons has aroused attention recently. In this work we investigate the properties of 2'-hydroxchalcone (**HC**) derivatives, and their mono-aryl analogues based on 2-hydroxyphenylpropenone (**HP**). The systems and properties are summarised in Table 1.^{49–51}

Table 1: Molecular structures and QEs (Φ) in the solid state^{49–51}

	R_1	R_2	Φ		R_3	R_4	Φ
HC1	H	H	0.32	HP1	H	H	0.74
HC2	CH_3	H	0.25	HP2	F	H	0.84
HC3	OCH_3	CH_3	0.26	HP3	OCH_3	H	0.77
HC4	H	CH_3	<0.01	HP4	H	F	0.72
HC5	H	OCH_3	<0.01				
HC6	F	H	0.41				
HC7	H	F	0.10				

The crystal packing, absorption and emission wavelength, and crucially the QE, are all dependent on the choice of substituent and number of aromatic rings. For structures based on **HC**, emission is dependent on the choice of substituent, which indirectly affects the packing mode.⁴⁹ Previous theoretical investigations show that fluorescence is witnessed when the conical intersection is energetically inaccessible in the solid state. Furthermore, localisation of the excited state onto one molecule in the crystal promotes the crucial ESIPT step.^{52,53}

Closely related to **HC** are the family of **HP** derivatives.⁵⁰ In contrast to **HC**, and other organic fluorophores, **HP** compounds contain only a single aryl group and have remarkable

QEs, ranging from 0.72-0.84. This has been qualitatively attributed in experimental studies to the herringbone packing mode and molecular rigidity reducing nonradiative decay. Theoretical investigation can offer insight into the factors which confer this increase in QE, enabling further understanding into how to maximise fluorescence from first principles.

Herein we investigate the factors which mediate the increased fluorescence activity for **HP** compared to **HC** systems with particular focus on the role of the crystal structure and exciton couplings. Based on our previous work, we analyse the three step mechanism to enhance radiative decay in ESIPT solid state emitters; I) localisation of excited state to one monomer, II) bias for K^* decay over E^* , III) an energetically inaccessible conical intersection.⁵³ We use quantum chemical and hybrid simulations to address each of these steps to show how the **HP** systems have an increased potency in each one with respect to their **HC** counterparts, resulting in the **HP** systems’ increased fluorescence in the solid state.

Results and Discussion

Excited state mechanisms in the solid state are controlled by intermolecular interactions, where the crystal structure determines the free volume available for the relaxation of the chromophore in the excited state. We begin by analysing the crystal structures of the eleven compounds. Each crystal can be examined initially from the perspective of a monomeric chromophore. To this end, we use Voronoi cell volumes V_{cell} and van der Waals volumes V_{vdW} to determine a Voronoi index $V_i = V_{cell}/V_{vdW}$, a metric indicating the normalised accessible volume for a monomer in the crystal. V_i values (Figure S1) range from 1.11-1.53, showing that despite the substituent and packing differences, the each monomer in the system has between 10%-50% of its van der Waals volume to freely vibrate, rotate or translate. For the **HC** systems, the average V_i is 1.48, and 1.45 for the **HP** systems. The accessible volume for the **HC** systems shows greater variation but is overall slightly higher

than for the less varied **HP** systems. The increased volume for the **HC** systems theoretically allow for greater nuclear relaxation in the excited state. However, reorganisation energies for the **HP** systems are larger than for **HC**, showing the importance of the electronic effects over geometric considerations.

To determine the intermolecular relationships within the molecular crystals, we examine the topology of the molecular crystals of **HC** and **HP** families by considering dimer packing motifs. Crystal morphologies are commonly described qualitatively as herringbone, face-face, edge-tail, *etc.* Here we take a more quantitative approach by constructing maps of each crystal, based on a geometric description of the dimers. These maps allow the topology of the crystal to be analysed graphically, as in Figure 2.

Figure 1: Panel a), left; schematic of two monomers A and B, their centroids C , and the α , β , and γ angles used to classify dimer configurations. Panel b), right; distribution of α angles for dimers in **HC** and **HP** systems.

The dimer motifs are quantified through three angle variables, α , β , and γ . These are depicted in Figure 1, and example motifs with associated angles are given in Figure S4. Three axes, x , y , z , are defined on each molecule i and j of the dimer, where x and y are the long and short axes of the molecule, and z is the orthogonal vector. These vectors comprise an orthogonal basis to describe the dimer. The angles are then defined as:

- α : The azimuthal angle between the monomers shown as shown in Figure 1. Calculated as the angle between the z -axis located at the centroid of monomer i , and the vector connecting two centroids. α is calculated twice, once with each monomer as the reference. The smallest angle is chosen, provided $0^\circ \leq \alpha \leq 90^\circ$.

- β : The angle between the two short-axis vectors y of each molecule, shown in green in Figure 1. β ranges from 0° to 180° , tracking whether monomers are aligned cofacially parallel ($\beta = 0^\circ$, CoF-P), or cofacially antiparallel ($\beta = 180^\circ$, CoF-A), or in a herringbone edge-face manner (90° , Hb), and all configurations in between. β is commonly described as the “herringbone” angle.
- γ : The angle between the long-axis vectors x , ranging from 0° (parallel, P) to 180° (antiparallel, A). At $y = 90^\circ$, the dimer is T- or L-shaped, dependent on the x -slip.

In Figure 1b the distribution density of the α angle is shown for the **HC** and **HP** systems. The distribution is heavily skewed towards 90° , indicating that for the majority of dimers, there is little overlap between the centroids of the monomers. As such, it can be expected that in each molecular crystal there are few dimers with the perfect overlap, with most undergoing a displacement in x or y . This is common for aromatic systems.⁵⁴

Figure 2 shows the dimer distribution densities for the β and γ angles for **HC** (top row) and **HP** (bottom row). Key regions are highlighted as an example in the upper plot of panel a); for example at $\beta=90, \gamma=0$, a herringbone (Hb) stack is witnessed with the long axes arranged in parallel. For both **HC** and **HP** systems, the majority of dimers have β and γ angles close to 180° (top right of plot), indicating that the most common dimer configuration is a cofacial arrangement where the carbonyl groups align antiparallel, at opposing ends of the molecule from each other. This results in an antiparallel alignment of the S_1 transition dipole moment of each monomer.

However, as panel b) shows, when the α angle is used as a filter, the configurations with acute azimuthal angles, and therefore closest in space, are mostly herringbone in nature for **HC**, with carbonyl groups at the same ($\gamma = 0^\circ$) or opposite ends of the dimer ($\gamma = 180^\circ$). In **HC1-3** and **HC6**, the herringbone is the most common dimer, but does not occur at all in the **HP** systems, as shown in Table S2. For example, **HC1** has three herringbone-like dimers and one cofacial dimer. With the largest unit cell and the conformational flexibility of the methoxy group, **HC5** has the greatest variety of dimers, with nine herringbone, ten

T-shape, and three cofacial types.

The cofacial arrangements favoured by the Kasha model occur at large slip displacements in the x or y plane ($\alpha > 60^\circ$), and are more like edge-edge coplanar arrangements rather than the well-known π -stack. Only in **HC5** is there significant cofacial π -stacking between dimers, with other cofacial arrangements in **HC** and **HP** having larger x -slip. For **HC** compounds, 63% of the cofacially aligned dimers have a x -slip of less than half a molecule, whereas 68% of cofacially-aligned **HP** dimers have a x -slip of more than half a molecule (Figure S2). In particular, the three cofacial dimers of **HC5** have excellent alignment allowing for strong intermolecular interactions, with slip distances of less than half a molecule and all with $\alpha < 40^\circ$.

Figure 2: Panel a), left; Probability density map of the β and γ angles for **HC** (top) and **HP** (bottom) dimers. Key configurations are labelled on the axes, as explained in the text. Panel b), right; probability density for the subset of dimers where $\alpha \leq 60^\circ$.

In the **HP** systems with $\alpha \leq 60^\circ$, configurations lie on the diagonal (Figure 2)b, bottom),

indicating dimers centred around a T-shape, which move to L-shaped when $\alpha \geq 60^\circ$. Overall, the significant dimer arrangement in **HP** compounds is a T shape, with the majority of cofacial arrangements having a large x or x -slip with minimal $\pi\pi$ interactions due to the single aryl groups aligning at $y=180^\circ$. The α angle is generally larger than in **HC** with an average of 64° compared to 55° , inhibiting short-range intermolecular interactions. However, in all **HP** systems, there is at least one prominent cofacial dimer which promotes exciton coupling, as we show in the next section.

Intermolecular interactions in the molecular crystal

Competing with localisation of the excited state necessary for ESIPT is exciton hopping. This competition can delay or even prevent proton transfer.⁵³ Exciton transport can occur through coherent or incoherent hopping between molecular sites, and thus it is important to understand the possible intermolecular transport channels in the **HC** and **HP** systems. For the dimers discussed above, the exciton coupling J_{ij} between monomers i and j is calculated with Troisi’s diabaticization scheme based on the orthogonal transformation of adiabatic states to diabatic states.^{55,56} This coupling scheme incorporates both short-range and Coulombic coupling mechanisms.

Considering the close packing of chromophores, we extended this method to assess the effect of a third monomer k on the exciton coupling, where the coupling J_{ij} between monomers i and j incorporates the effect of monomer k , which can be quantified through comparison of the dimeric and trimeric coupling. However, we found that this made very little difference to the coupling in **HC1**, **HC5** and **HP1** compared to the kind of coupling modulations expected due to thermal fluctuations.^{55,57} This can be attributed to the excited state being delocalised over no more than two monomers of a trimer (Figures S9 and S10).

The exciton couplings for all dimers and the identity of the dimer with the largest J are shown in Figure 3. Corroborating the robustness of the method, Figure S11a shows the coupling reproduces the supramolecular coupling of half of the energy splitting between S_1

and S_2 of the dimer. In **HC1-4**, where the closest packed dimers are herringbone in nature, similar dimer configurations are present. The largest coupling occurs in **HC1**, with $J = 108$ meV. For **HC-2**, the dimer with the largest coupling is an edge-edge stacked dimer with $\alpha = 87^\circ$, where poor alignment reduces the coupling to $J = 79$ meV. **HC3** and **HC4** have similar herringbone stacking arrangements, where the largest couplings are 80 meV and 93 meV respectively. In **HC5-7**, face-face stacked dimers are more prevalent in the crystal structure. The size of the coupling in **HC6** is reduced compared to **HC5** due to the y displacement of one of the monomers, with values of 148 meV and 113 meV. A significant drop off to 83 meV is seen for **HC7** due to an increased x -slip in the cofacial dimer.

In the **HP** compounds, the large α and x -slip values, and the smaller molecular size, reduce the average coupling compared to **HC**. In each **HP** derivative there exists one close packed, cofacial dimer which exhibits the largest coupling. For **HP1**, this is relatively small at just 48 meV due to the x -slip. However, in **HP2-3**, the crystal structures afford more efficient cofacial stacking with x -slip values of only 1 Å, resulting in the largest couplings of all investigated systems, with $J = 157$ meV for **HP2** and $J = 147$ meV for **HP3**.

Figure 3: Exciton couplings J between monomers i and j in the dimers identified in **HC** and **HP**. The mean coupling is also shown, along with the distance in angstroms between the constituent monomer centroids.

We assign the dimers as H- or J-aggregates based on the oscillator strength of the S_1 and

S₂ excitation. In the Kasha model, for a perfectly stacked dimer with no x -slip, the oscillator strength of the S₂ state should be double that of the monomer state. These systems generally fit the Kasha model, as when the x -slip is zero, a linear model (SI section S5) predicts an enhanced S₂ intensity of 2.10 for the **HCs** and 1.83 for the **HPs**. With increasing x -slip, the difference in oscillator strength between the two states decreases until the inversion to J-aggregates is witnessed ($f_{S_1} > f_{S_2}$). For the **HCs** this occurs at a x -slip of 52% of the monomer length and at 46% of the monomer length for the **HPs**.

For almost all systems, the number of H- and J-aggregates is very similar (Table S5). For **HC-4**, **HC-5** and **HC-7** the H-aggregate population grows to 78%, 66% and 100%, respectively, suggesting that an increase in H-aggregates may be a cause for the smallest quantum yields in the solid state. However, this will be relevant only if there is a significant population of the E* channel.

Exciton localisation vs. hopping: the role of nuclear reorganisation and proton transfer

Once the system is in the excited state, relaxation can happen through the K* or E* channels (or both). These mechanisms compete with exciton hopping, which prevents localisation of the electron density. For fluorescence to occur from the K* state, the exciton must localise onto one monomer to enable ESIP. ⁵³ Exciton hopping rates ν_{ij} between monomers i and j in a molecular crystal can be calculated based on a Marcus hopping scheme,

$$\nu_{ij} = \frac{J_{ij}^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp \left[-\frac{\lambda}{4k_B T} \right] \quad (1)$$

where k_B is the Boltzmann constant, $\hbar$ is the reduced Planck constant, T is the temperature (298K), and λ is the reorganisation energy. The activation energy can be approximated as

$\lambda/4$.^{58,59} The reorganisation energy λ of Equation 1 is calculated in the adiabatic regime *via*

$$\begin{aligned}\lambda_A &= \lambda_{ex} + \lambda_g \\ &= (E_{ex}^* - E_{ex}) + (E_g^* - E_g)\end{aligned}\tag{2}$$

where E_g and E_{ex} are ground state energies at the S_0 and S_1 minima, and E_g^* and E_{ex}^* are the corresponding excited state energies at respective minima. Herein, we consider the reorganisation energies involved in the relaxation to the K^* and E^* minima (Keto and Enol regimes respectively). λ can also be calculated using normal mode analysis (see SI section S2). However, for **HC1**, **HC5**, and **HP1**, it is found that λ_{NM} overestimates the reorganisation energy with respect to λ_A , so we use λ_A in the following.

Solid state reorganisation energies λ_A in keto and, when located, enol minima were calculated for (TD-) ω B97X-D/6-31G(d):UFF cluster models with a monomer chromophore using Equation 2. Figure 4 shows the coupling, reorganisation energy and the associated exciton hopping rate (using a log scale) for each dimer. The hopping rate ν is ultrafast in the enol regime (**HC1-4,6,7**), with the highest rates in the region between $1 \times 10^{13} \text{ s}^{-1}$ and $6 \times 10^{13} \text{ s}^{-1}$ due to the planar conformation conferring relatively low λ_A (244 meV on average). The highest and lowest ν for **HC1** are $4.18 \times 10^{13} \text{ s}^{-1}$ and $5.17 \times 10^{11} \text{ s}^{-1}$, while the rate of ESIPT in the molecular crystal, through time resolved spectroscopy, is $3 \times 10^{11} \text{ s}^{-1}$.³³ Intramolecular hopping is therefore expected to compete with ESIPT, which requires localisation of the excited state to one site in the molecular crystal. Due to similarity of the electronic and crystal structures, this should also be the case for **HC2-3,6,7**, hence opening nonradiative intermolecular decay channels for these systems and a source of quantum yield leak. For **HC4** and **HC5**, there is a significant bias towards proton transfer because of a larger reorganisation energy (935 meV and 978 meV respectively).

In vacuum, an E^* minimum is found on the PES for **HP** systems, where the relaxation mode is *via* partial trans-cis isomerisation about the aliphatic double bond. This minimum was optimised for **HP1** in the solid state and it was found to have a reorganisation energy

of 2.19 eV compared to 1.31 eV for the K^* state. As a direct consequence, the hopping rate for such a large λ is $1.44 \times 10^4 \text{ s}^{-1}$. For comparison, the smallest hopping rate for **HC1** is $5.17 \times 10^{11} \text{ s}^{-1}$. Exciton hopping is therefore reduced in **HP** due to the relatively small exciton coupling and the large reorganisation energy in the enol state, with the bias for ESIPT on account of the electron density redistribution rendering ESIPT the most favourable relaxation channel in the solid state.

In the K^* channel, hopping rates in **HP** are systematically lower than in the **HC** family. On average, $\nu=7.51 \times 10^8 \text{ s}^{-1}$ in the **HPs** compared to $7.61 \times 10^{10} \text{ s}^{-1}$. The highest rate in the **HP** family is $1.33 \times 10^{10} \text{ s}^{-1}$, compared to a $1.64 \times 10^{12} \text{ s}^{-1}$ in the **HCs**. This is on account of the high stability of the K^* minimum in the **HPs** producing a large reorganisation energy.

The ESIPT bias in **HP** derivatives can be understood through analysis of electronic transition densities, where a loss of electron density at the hydroxyl oxygen increases the acidity of the proton with respect to the **HC** systems, where this loss is not present, except in **HC5** (Figure S6). NBO charge analysis of the phenol oxygen shows that Δq increases from +0.01 to +0.05 to +0.09 for **HC1**, **HC5** and **HP1** respectively. This increases the bias for ESIPT in **HC5** and **HP1** due to the increased acidity of the transferring proton, as shown by the excited state PES relaxed geometry scan in Figure S9.

Figure 4: Colourmap of the exciton hopping rate ν_{ij} on a $\log_{10}$ scale, as a function of the exciton coupling J_{ij} and the reorganisation energy λ , calculated via Equation 1.

The AIE Mechanism

We compute the radiative decay rates k_r from the E^* and K^* states in ONIOM (TDDFT) by computing the fluorescence spectrum with Newton-X and calculating k_r through^{60,61}

$$k_r = \frac{1}{\hbar} \int \Gamma_r(E) dE \quad (3)$$

where Γ_r is the rate of spontaneous emission per molecule per unit of angular frequency between $E/\hbar$ and $(E + dE)/\hbar$.⁶² The spectra for **HC1**, **HC5** and **HP1**, which are the extreme cases, are given in Figure S15 and radiative rates for **HC1**, **HC5** and **HP1** are given in Table 2.

For **HC1**, k_{r,K^*} is comparable with **HP1** in both E^* and K^* . However, **HC1** exhibits lower quantum efficiency, owing to the competing exciton hopping in the enol state, which will inhibit localisation and thus ESIPT. Thus in **HC1** there is competition between delocalisation, emission from E^* , and emission from K^* . Due to the proximity of the E^* band to the absorption at 3.3 eV, only K^* fluorescence will significantly contribute to the quantum yield.

The RIM interpretation of AIE prescribes that switch-on of fluorescence upon aggregation is due to dampening of rotational modes, which dissipate the excited state nonradiatively, as witnessed by a reduction in the HR factors. While **HC1**, **HC5** and **HP1** show this effect, **HC1** and **HP1** show AIE while **HC5** is dark in both dispersed and aggregated forms. The dampening of the HR factors does not result in luminescence in **HC5**, suggesting that the excited state wavepacket decays through the MECL.⁵³ Furthermore, due to the anharmonicity of the PES, the validity of the scheme in these cases is not clear and λ_A is used in the main text.

For **HP1**, emission from E^* is negligible and emission is expected from the K^* state. The highly distorted E^* minimum, as discussed in the previous section, is expected to play little role in the photochemistry and population transfer to K^* will dominate. The radiative

rate from K^* is of similar magnitude to **HC1**, and as such the higher quantum yield of **HP1** is on account of the lower nonradiative decay rate and lack of other competitive pathways, such as exciton hopping.

Table 2: Radiative decay rates k_r in the solid state in the enol (E^*) and keto (K^*) regimes for **HC1**, **HC5**, **HP1**. All rates in s^{-1} .

System	k_{r,E^*}	k_{r,K^*}
HC1	4.68×10^8	2.99×10^8
HC5	-	9.54×10^7
HP1	5.58×10^6	1.10×10^8

For the **HP** family the stabilisation arising from ESIPT is larger than for the **HC** systems. For the **HC** systems, reorganisation energies due to ESIPT range from 532 meV (**HC3**) to 978 meV (**HC5**). However, by modifying the chromophore molecular structure through removal of the second aryl group, the bias towards ESIPT is increased for the **HP** systems due to the instability of the planar E^* conformer and the high stability of the K^* conformer. No stable planar E^* minimum can be located in the crystal such is the bias for ESIPT, with reorganisation energies ranging from 1.06 eV (**HP2**) to 1.23 eV (**HP1**). As such, in the keto state, the hopping rate is up to three orders of magnitude lower than the for the **HC** systems in the enol channel. Due to the increased organisation energy arising from tautomerism, localisation and ESIPT will be favoured over exciton hopping and a larger Stokes-shifted emission is witnessed for the **HP** family.

To achieve an efficient emissive response in the solid state, in addition to an efficient population of the K^* tautomer, nonradiative decay channels should be blocked. **HC1**, **HC5** and **HP1** show a reduction of Huang-Rhys factors and reorganisation energies associated with low-frequency motions in the solid state in contrast with the isolated chromophores (see section S2 in the SI). Consequently, the RIR model does not explain their different photochemical behaviour and we need to consider the accessibility of the conical intersections (RACI model).

It has been shown that for **HC1**, fluorescence is possible due to the high energy conical

intersection in the solid state. On the other hand, for **HC5** and **HC4**, whilst ESIPT is more efficient than in **HC1**, the QE is very small and AIE is not seen.⁴⁹ This can be attributed to dominance of nonradiative decay as a result of a low-lying MECI being classically accessible post electronic excitation.⁵³ While intermolecular factors play a role in the conformation of the MECI, the energetic accessibility is determined by the electronic structure of the chromophore. To assess the accessibility of the MECI in the solid-state in **HP1**, we construct the excitation-decay pathway in the using QM:MM cluster models. The calculated PES for **HP1** in vacuum and the solid state is shown in Figure 5.

Figure 5: Calculated energies and geometries at critical points on PES. Crystal geometries obtained with ONIOM((TD)- ω B97X-D/6-31G(d):AMBER), with energies calculated at MS-3-CASPT2(12,11):AMBER. Vacuum geometries obtained with (TD)- ω B97X-D/6-311++G(d,p) and energies obtained with MS-3-CASPT2(12,11). The average energy of the S_1 and S_0 states is shown for the MECI.

At the MS-3-CASPT2(12,11)/6-31G(d):AMBER level, absorption for **HP1** is calculated at 3.67 eV ($f=0.868$), in fair agreement but blue-shifted by 0.41 eV compared with the crystalline absorption maximum of 3.26 eV.⁵⁰ Post photo-excitation, relaxation in S_1 *via* ESIPT is expected to be dominant relaxation channel in **HP1** due to the negligible oscillator strength ($f=0.016$) of the S_2 state, which is $n\pi^*$ in character. Fluorescence in the molecular crystal is centred at 2.34 eV, thus displaying a Stokes shift of 0.94 eV. The emission wavelength predicted at CASPT2 is 2.73 eV, again in fair agreement and with similar

blue-shift as calculated for absorption.

The MECI in **HP1** lies 1.46 eV above the K^* minimum and 1.08 eV above the bright absorption state. As such, it is classically inaccessible and **HP** emission can be attributed to the trapping of the excited state at the K^* minimum, followed by radiative decay. The degeneracy of the S_1 and S_0 states on going from CASSCF to CASPT2 is lifted, with a gap of 0.2 eV at CASPT2 level. As the substituent effects in the crystalline samples are minor in the **HP** samples, it can be assumed that this mechanism can be applied to all four systems in the family. It would be of interest to synthesise a **HP** system to assess its AIE behaviour with a methoxy group the *para* position, as in **HC5**.

In Figure 6, the MECI geometries of **HC1**, **HC5**, and **HP1** are compared. All three involve the pyramidalisation of the protonated carbonyl group combined with torsional rotation of the deprotonated phenol moiety. In **HC1** and **HP1**, the compounds which undergo AIE due to the high energy of the MECI, the torsional angles are 49.6° and 53.3° . In **HC5**, where the MECI is energetically accessible, the pyramidal distortion is only 26.7° . The same effect is seen in vacuum, where the MECI of **HC5** is also onset at lesser distortion than the other systems, as discussed above and shown in Figure S13. Therefore the high energy MECIs of **HC1** and **HP1**, are inherent to the electronic effects of the chromophore. Rather, the role of the packing and the crystalline environment as a whole is to promote efficient localisation of the excited state at the expense of exciton hopping the enol state. A largely increased QE is witnessed as a result of the high propensity for ESIPT in **HP** and the high energy MECI.

Figure 6: Overlaid structures of the MECI for **HC1** (blue) and **HC5** (black), and **HP1** (green), shown from three viewpoints. Only the atoms shared by all three compounds are shown.

Conclusions

In this work we have systematically evaluated the photo behaviour of a range of solid-state emitters based on the ESIPT mechanism. In the **HC** family of compounds, AIE is witnessed for five of the seven compounds, with QEs ranging from 0.1 to 0.41. In the **HP** systems, which differ by containing only one aryl ring, all reported compounds are emissive in the solid state with QEs of 0.72-0.84. In each crystal structure, there exist a range of dimer motifs each with their own excitonic profile. In the **HC** systems, with the exception of **HC5**, the herringbone stacking is prominent, with exciton coupling enhanced by the two aryl rings promoting $\pi\pi$ interactions which are mostly absent in their **HP** counterparts,

In the **HC** compounds (except **HC5**, after photoexcitation to the S_1 state, exciton hopping in the enol tautomer will compete with ESIPT on account of minimal electron density loss on the phenol oxygen and the stability of the planar enol tautomer, which results in only a small reorganisation energy. Here the the hopping rate is several orders of magnitude larger than in the K^* state and will allow nonradiative dissipation of the excited state. Conversely in the **HP** compounds, and **HC5**, the electron density loss is increased on the oxygen and ESIPT is more favourable, coupled with the planar E^* tautomer being unstable. The stability of the K^* state increases the reorganisation energy λ of the chromophore and subsequently will increase the population of the ESIPT channel in these systems. The K^* state will be highly localised with minimal hopping. In **HC1**, emission from E^* will increase unfavourable self-absorption and contribute to the lower quantum yield compared to **HP1**.

The K^* minimum takes a planar conformation in the solid state, with considerable oscillator strength for emission back to S_0 . **HP1** has an energetically inaccessible MECI, like **HC1**, whereas in **HC5** the MECI is energetically accessible. As for **HC1**, the MECI for **HP1** in the crystal takes a distorted, pyramidalised geometry and is energetically inaccessible in the decay path. As such, emission will occur from the planar K^* minimum for the **HP** compounds and with larger QE, due to the increase in the population of the K^* channel. Such is the similarity in absorption and emission spectra in the **HP** family, this mechanism

is expected to be independent of the substituents present in this study.

At this point, we can say that incorporation of the following features into the next generation of ESIPT emitters can move the field forward, based on the remarkable properties of the **HP** derivatives:

1. To maximise the population of the ESIPT channel, chromophore design should encourage a highly labile proton, where electronic excitation destabilises the E^* state.
2. Packing modes should limit π - π interactions, which enable exciton coupling and delocalisation. However, if the ESIPT is favourable enough, the localisation inherent to the K^* state can overcome unfavourable stacking arrangements.
3. In the K^* form, solid state conical intersections are accessed *via* a combination of pyramidalisation and rotation. This can be made more unfavourable by tethering and chromophore design, where we have shown that simple measures such as scanning coordinates in vacuum can predict K^* stability.

This work connects the electronic, molecular picture with the crystalline regime for organic, light-emitting materials. In these ESIPT emitters, the intermolecular interactions dominate in the Franck-Condon regime at photoabsorption. Subsequently the electronic structure and the character of the excited state, inherently molecular properties, become dominant. The deconstruction of intra- and intermolecular factors here, connecting the chromophore with its crystal structure, offers a step forward in first principles design of solid state luminescent materials.

Computational Methods

Crystal structures of compounds **HC1-7** and **HP1-4** were obtained from the CCDC as described in references 49–51. Monomers of **HC1-5** and **HP1-4** were optimised in vacuum in

the S_0 and S_1 enol and keto states at the (TD-) ω B97X-D/6-311++G(d,p) level of theory. Relaxed geometry scans of the torsional rotation angle in the keto S_1 state (K^*) were performed for the same compounds. Proton migration scans of the ESIPT process were also performed in vacuum for **HC1** and **HP1**. All scans were calculated at TD- ω B97X-D/6-31G(d).

Crystal structures of all **HC** and **HP** compounds were optimised using Quantum Espresso in the periodic DFT framework.⁶³ Optimisation of each unit cell was carried out with DFT-D2 (PBE) with a plane-wave cutoff of 30 Ry and ensuring Monkhorst-Pack k-point convergence in each case.

Exciton couplings J_{ij} were calculated for dimers in each optimised crystal structure. A 2x2x2 supercell was constructed for each system, starting from the optimised unit cell, and all unique dimers were identified and extracted. A dimer was defined as any molecular pair with an interatomic distance less than or equal to the van der Waals radii of the atoms plus a distance of 1.5Å. This selection criterion has previously been used in similar applications.⁶⁴ The coupling J_{ij} between monomers i and j in unique dimers are calculated in Troisi’s diabaticization scheme based on the orthogonal transformation of adiabatic states to diabatic states based on the transition dipole moments.^{55,56}

Crystalline emission spectra for **HC1**, **HC5** and **HP1** in E^* and K^* minima were simulated using the nuclear ensemble method as implemented in the NEWTON-X software suite.⁶⁰ 100 initial conditions were sampled from the harmonic frequencies calculated at ONIOM(TD- ω B97X-D/6-31G(d)):AMBER level from 7Å cluster models. The S_1 - S_0 energy gap was computed for each initial condition in embedded point charges to reflect the positions of the MM charges. No MM-level energies were computed, and as such the fluorescence spectra are of only the electronic energies.

To calculate solid state reorganisation energies in the adiabatic approximation (λ_A), for each compound we generated cluster models based on the 2x2x2 supercell, where all molecules which lay within 20Å of the central chromophore were included in the cluster. Geometries were optimised in S_1 and S_0 states within the ONIOM protocol at ω B97X-D/6-

31G(d):UFF using electronic embedding. MM charges were derived automatically using the QEq method.⁶⁵ The UFF forcefield was chosen here due to the automatic charge assignment, allowing the highthroughput generation of structures and input files. In the cases of **HC1-4** and **HC6-7**, λ_A was calculated for both enol and keto pathways. For **HC5** and **HP1-4**, only the λ_A associated with keto relaxation was used since no E^* minimum was located in the monomer QM:MM relaxation. Reorganisation energies in the normal-mode approximation (λ_{NM}) were calculated using the DUSHIN program for **HC1**, **HC5** and **HP1**.⁶⁶ Frequencies for an ONIOM-optimised monomer chromophore were calculated in an array of point charges representing the molecular crystal, at TD- ω B97X-D/6-31G(d) level. This lead to one imaginary frequency in each case.

The radiative rates k_r in the molecular crystals of **HC1**, **HC5** and **HP1** were calculated by simulating the fluorescence spectrum using the nuclear ensemble method. Excited state frequencies at the E^* (where located) and K^* minimum for a monomer chromophore were calculated at ONIOM(TD- ω B97X-D/6-31G(d):AMBER) level of theory and used to generate 100 initial conditions using a Wigner distribution. For each initial condition the S_1 - S_0 energy gap was calculated in a bed of point charges representing the MM atoms at TD- ω B97X-D/6-31G(d) level. Integration of the spectrum gives k_r as described in reference 61.

For **HP1**, the full excited state decay mechanism was established through QM:MM cluster models using density functional and multireference methods. A monomer and trimer chromophore at the centroid of the 20Å cluster were optimised in the ground and excited states at (TD-) ω B97X-D/6-31G(d):AMBER level of theory. The S_1/S_0 MECI in both monomer and trimer cluster models were calculated using a modified version of the CIOpt algorithm.^{67,68}

The MECI in the monomer cluster models was also obtained with the state-averaged complete active space self-consistent field method, employing the S_0 and S_1 states in the averaging. The active space consisted of 12 electrons in 11 orbitals (SA-2-CASSCF(12,11)), shown in Figure S11. The 6-31G(d) basis set was using for the QM region and the AMBER forcefield was used to describe the MM region. Calculating the MECI with CASSCF:MM ensures the

validity of the TD-DFT:MM-calculated MECI. The potential energy profile was refined with multistate complete active space second-order perturbation theory (MS-3-CASPT2(12,11)/6-31G(d):AMBER), incorporating the S_0 , S_1 , and S_2 states. The TD-DFT:MM geometries from the trimer models at the Franck-Condon, S_1 minimum, and MECI were taken as the reference geometries, where the central molecule was taken for the CASPT2 calculation and the remaining two molecules of the trimer were added to the MM region. A three state average was used due to include the S_2 electronic state at the Franck-Condon geometry. The orbitals chosen for the active space are shown in Figure S11. All density functional calculations were performed in the Gaussian 09 suite of programs.⁶⁹ CASSCF and CASPT2 calculations used OpenMolcas with the Tinker v.6.3.3 interface.⁷⁰

To analyse the spatial environment for the monomers at the centre of the cluster models in the each crystal, Voronoi cells partition the crystal into molecular regions. These cells define all the points in space which are closer to the reference molecule than an exterior molecule. Dividing the Voronoi cell volume by the van der Waals volume gives a molecule-independent Voronoi index V_i for each crystal structure. To generate the Voronoi cells, a cluster of molecules was extracted from its crystalline positions. A real space grid was generated at an arbitrary resolution and at each point of this grid, the distance to each atom was calculated and scaled by the corresponding van der Waals radius. All voxels with the lowest scaled distance belonging to an atom of the central molecule were marked as belonging to the accessible of the molecule, resulting in an irregular polyhedron of finite volume. The analysis of volumes and dimer motifs is implemented in the package **fromage**.⁷¹

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Supporting Information Available

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Supporting Information For:

Molecular and Crystalline Requirements for Solid

State Fluorescence Exploiting Excited State

Intramolecular Proton Transfer

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S1 Crystal Packing Properties

Figure S1: Voronoi cell volumes (V_{cell}), van der Waals volumes (V_{vdW}) and the index ($V_i = V_{\text{cell}}/V_{\text{vdW}}$)

Figure S2: The density of slip distances for each molecular dimer in the x -plane (long axis) for cofacial dimers. The slip is normalised by the length of the long axis x for each molecule, such that slip is molecule independent.

Figure S3: Probability density map of β and γ angles for each of the systems under study

Table S1: Dimer classification definitions

	α Condition	β Condition	γ Condition
Herringbone	$\alpha \leq 60^\circ$	$45^\circ \leq \beta \leq 135^\circ$	$\gamma \leq 45^\circ \vee (135^\circ \leq \gamma \leq 225^\circ)$
Parallel T	$\alpha \leq 60^\circ$	$\beta \leq 45^\circ \vee (135^\circ \leq \beta \leq 225)$	$45^\circ \leq \gamma \leq 135^\circ$
Perpendicular T	$\alpha \leq 60^\circ$	$45^\circ \leq \beta \leq 135^\circ$	$45^\circ \leq \gamma \leq 135^\circ$
CoFacial	$\alpha \leq 60^\circ$	$\beta \leq 45^\circ \vee (135^\circ \leq \beta \leq 225)$	$\gamma \leq 45^\circ \vee (135^\circ \leq \gamma \leq 225^\circ)$

Table S2: Dimer classifications in each molecular crystal for $\alpha \leq 60^\circ$. Significant increase in **HC5** dimers due to rotational flexibility of the methoxy group.

System	Herringbone	Parallel-T	Perpendicular-T	CoFacial
HC1	3	0	0	1
HC2	4	0	0	0
HC3	3	0	0	0
HC4	1	0	4	0
HC5	9	6	4	3
HC6	3	0	0	1
HC7	0	3	0	0
HP1	0	0	3	1
HP2	0	0	0	2
HP3	0	0	2	1
HP4	0	3	0	1

Herringbone Parallel

α : 56° β : 68° γ : 18°

Herringbone Antiparallel

α : 18° β : 112° γ : 162°

CoFacial Parallel

α : 16° β : 5° γ : 3°

CoFacial-Antiparallel

α : 11° β : 180° γ : 180°

Parallel T

α : 41° β : 3° γ : 111°

Perpendicular T

α : 22° β : 58° γ : 80°

Figure S4: Example dimer packing modes and associated α , β and γ angles in **HC1**, **HC5**, and **HP1**.

S2 Huang-Rhys Factors

Normal modes can be correlated between different electronic states using the the Duschinsky rotation matrix, yielding the Huang-Rhys factors S between the electronic states for each frequency ω

$$S_j = \frac{\omega_j D_j^2}{2\hbar} \quad (\text{S1})$$

where D_j is the displacement of mode j between the equilibrium geometry in the considered electronic states. Summation of each Huang-Rhys factor yields the normal mode reorganisation energy for the system

$$\lambda_{NM} = \sum_{j=1}^{3N-6} \hbar \omega_j S_j \quad (\text{S2})$$

In this section, we calculate the HR factors for **HC1**, **HC5**, and **HP1**.

The Huang-Rhys (HR) factors in vacuum and molecular crystals were calculated for **HC1**, **HC5**, and **HP1**. In vacuum, ground and excited states were optimised at (TD-) ω B97X-d/6-31G(d) level. In the molecular crystal, a cluster model consisting of a central chromophore and all molecules within a 7Å, taken from the optimised unit cell for each system (see main text for unit cell optimisation details). Ground and excited states were optimised at ONIOM((TD-) ω B97X-d/6-31G(d):AMBER) level, and frequencies were calculated at (TD-) ω B97X-d/6-31G(d) level using point charge embedding. The DUSHIN program was used to calculate the Huang-Rhys factors and the associated reorganisation energies (λ_{NM}).

Figures S5-S7 show the Huang-Rhys (HR) factors in vacuum and solid state for **HC1**, **HC5** and **HP1**. The different y-axis scales for the Huang-Rhys factors between plots should be noted. Each system is discussed in turn below.

Figure S5: Huang-Rhys factors associated with each normal mode calculated *via* the Duschinsky rotation matrix between the E* and S₀, and K* and S₀ electronic states for **HC1**. Frequencies 0-500 cm⁻¹ in the solid state are shown in the inset.

Figure S6: Huang-Rhys factors associated with each normal mode calculated *via* the Duschinsky rotation matrix between K* and S₀ electronic states for **HC5**. Frequencies 0-500 cm⁻¹ in the solid state are shown in the inset.

Figure S7: Huang-Rhys factors associated with each normal mode calculated *via* the Duschinsky rotation matrix between K^* and S_0 electronic states for **HP1**. Frequencies 0-500 cm^{-1} in the solid state are shown in the inset.

For **HC1** in vacuum (Figure S5, left), the geometric similarity between the planar E^* excited state minimum and the ground state equilibrium geometry yields negligible HR factors. This leads to λ_{NM} of 0.08 eV, which underestimates the λ_A of 0.36. For K^* , the PES in vacuum is highly anharmonic, and intramolecular rotation leads to a highly distorted geometry with respect to the ground state. As a consequence, the HR factors are extremely large and the harmonic approximation is non-applicable for determining the reorganisation energy, as shown by a value of 99 eV ($\lambda_A=3.64$ eV). Moving to the molecular crystal (Figure S5, right), in E^* the HR factors are of similar magnitude as in vacuum but in K^* they are markedly reduced and suppressed to fractional values. The largest K^* HR factor is the O-H stretching mode, since the geometry remains planar and has the largest displacement between S_0 and S_1 as it is the ESIPT coordinate. The K^* λ_{NM} is 4.67 eV, with $\lambda_A=0.59$ eV.

In **HC5** there is no stable E^* minimum in either vacuum or the solid state for the monomer chromophore. In vacuum, the HR factors are much less than in **HC1** due to the rotation angle at the minimum being less distorted. The molecule is more planar and is closer in structure and vibrational signature. At larger rotation angles the MECI is reached (see Section S6). HR factors are reduced in the solid state, in particular for the rotational modes, but with the O-H stretch HR factor increasing.

For **HP1**, large reorganisation energies, and correspondingly large HR-factors, are associated with low-frequency rotational modes. Indeed, such is the displacement between

modes in the ground and excited states, the total reorganisation energy is 41 eV, whereas the adiabatic value 3.89 eV. As such, the harmonic approximation is invalid here due to the excited state potential energy surface anharmonicity. In the solid state, the normal modes associated with rotation are significantly reduced, whilst the largest HR factor is associated with the stretching of the phenol oxygen. This is to be expected, since it is along this coordinate that ESIPT occurs, and hence it has the largest HR-factor. In solid state, λ_{NM} is 2.19 eV, compared with λ_A of 1.24 eV.

In the case of the **HC** and **HP** systems, the AIE behaviour can not be directly attributed to the reduction of the HR factors in the solid state compared to vacuum. Such is the complexity of the PES, where ESIPT and rotation occur in the excited state (in vacuum), the surfaces are highly anharmonic and the validity of the HR scheme via Duschinsky is not clear. As such, it is not the focus of our investigation into the AIE behaviour of these systems.

Table S3: Reorganisation energies (eV) in the adiabatic regime for each system in the enol (where located) and keto minima

System	E*	K*
HC1	0.233	0.786
HC2	0.246	0.804
HC3	0.249	0.668
HC4	0.250	0.935
HC5	-	0.978
HC6	0.210	0.533
HC7	0.213	0.649
HP1	-	1.238
HP2	-	1.059
HP3	-	1.120
HP4	-	1.204

S3 Electronic excitations

Figure S8: Electron density difference maps for the first three excitations of **HP1**. Blue regions represent electron density loss from the ground state and red represent electron density gain in the excited state, with isovalue of 0.002. Calculated at TD- ω B97X-D/6-311++G(d,p) in vacuum.

Figure S9: Electron density difference maps for the first nine excited state of the **HP1** trimer. The same colour scheme is used as in Figure S8

S4 Exciton Coupling in Trimers

The exciton coupling in trimers was calculated for **HC1**, **HC5**, and **HP1**. The results are given in Table S4, and shown schematically in Figure S9, where the couplings obtained in a dimer scheme are compared to those obtained when an additional molecule is included.

It is found that the addition of a third molecule has only a small effect on the dimer coupling in **HP1** and **HC1**, where the increased coupling in one dimer is compensated for by the decreased coupling in the other dimer, with difference of less than 0.02 eV. The largest effect is seen in **HC5** due to the cofacial packing of the trimer system, where the central monomer is sandwiched by two cofacially stacked monomers, one parallel and one antiparallel. In this system, the parallel dimer ($\gamma = 0$) has its coupling increased by 0.04 eV with the addition of the third molecule, which is aligned antiparallel ($\gamma = 180$). Conversely, the antiparallel coupling is reduced by 0.07 eV due to the parallel stacked monomer.

Table S4: Exciton coupling comparison for dimer and trimer in **HC1**, **HC5**, and **HP1**

System	Dimer Coupling (eV)	Trimer Coupling (eV)
HC1	0.108	0.090
	0.108	0.125
	0.061	0.063
	0.061	0.052
HC5	0.116	0.157
	0.142	0.085
	0.004	0.001
HP1	0.056	0.066
	0.005	0.014

Figure S10: Schematic of the trimer motifs extracted from unit cells of **HC1**, **HC5** and **HP1**. Exciton couplings for dimer pairs (shown in brackets) and then for the full trimer are shown. Calculated at ω B97X-D/6-311++G(d,p) level of theory using the diabaticization described in the main text.

S5 H- and J-Aggregates

Figure S11: Panel a), top; Correlation between the energy splitting of the dimer states and the diabatic exciton coupling. Panel b), bottom; Linear regression of the x -slip against the difference in oscillator strength between the S_2 and S_1 states in dimers. The definition of Δf_{Norm} is given in Equation S3

As shown in Figure S11a, the coupling J correlates linearly with half of the energy splitting for the S_1 and S_2 states of the dimer. The energy splitting is perhaps the simplest way to obtain the exciton coupling in the Kasha regime, although it is more expensive than using atomic-centred transition charges, or the PDA approximation, since the supermolecular calculation must be done rather than one monomer calculation. At small intermolecular distances ($<4\text{\AA}$), these computationally efficient metrics can underestimate the couplings

due to them only considering the Coulomb interaction.¹ The linear correlation here shows that the general Kasha interpretation of the coupling applies here and that the diabaticization method to obtain the couplings reproduces the supramolecular coupling.

Table S5: Dimer types located for each molecular crystal. Significant increase in **HC5** dimers due to rotational flexibility of the methoxy group

System	H-aggregates	J-aggregates	Total
HC1	4	4	8
HC2	5	4	9
HC3	4	5	9
HC4	7	2	9
HC5	19	10	29
HC6	4	3	7
HC7	6	0	6
HP1	5	5	10
HP2	5	6	11
HP3	4	5	9
HP4	5	5	10

In the Kasha model, for a perfectly stacked dimer with no x -slip, the oscillator strength of the S_2 state should be double that of the monomer state. Figure S11b shows the relationship between the x -slip in the dimers and the oscillator strength, namely the difference in oscillator strength between the S_2 and S_1 states in the dimer, normalised by the corresponding monomer oscillator strength

$$\Delta f_{Norm} = \frac{f_{S_2}^{dimer} - f_{S_1}^{dimer}}{f_{S_1}^{monomer}}. \quad (S3)$$

These systems generally fit the Kasha model, as when the x -slip is zero, the line of best fit predicts an enhanced S_2 intensity of 2.10 for the **HCs** and 1.83 for the **HPs**. With increasing x -slip, the difference in oscillator strength between the two states decreases until the inversion to J-aggregates is witnessed ($f_{S_1} > f_{S_2}$). For the **HCs** this occurs at a x -slip of 52% and at 46% for the **HPs**. However, there is some significant noise in the model, which is understandable given the simplicity of the model and the complex electronic structure of the dimer. The largest group of outliers are cofacially stacked dimers, where a larger shift is

seen at lower slip distances due to the minimal x -slip and archetypal stacking.²

S6 Bias for ESIPT

Figure S12: Relaxed geometry scan of the phenol hydrogen to carbonyl oxygen distance for **HC1**, **HC5** and **HP1**, calculated at TD- ω B87X-D/6-31G(d). Electron density difference maps are also shown, with same labelling as for Figure S8.

Figure S13: Relaxed geometry scan of the torsional angle (shown inset) for **HC1**, **HC5** and **HP1** in vacuum, calculated at TD- ω B87X-D/6-31G(d). For **HC5**, the scan cannot proceed further than 60° due to the convergence of the two electronic states.

S7 Orbitals in CASPT2 Calculations

Figure S14: Orbitals in the active space for the CASPT2 calculations, where the active space consists of 12 electrons in 11 orbitals. Orbitals shown for each of the Franck-Condon (FC), keto S₁ (KS₁) and minimum energy conical intersection (MECI) calculations.

S8 Crystalline Emission Spectra

Figure S15: Emission spectra in molecular crystal for 7 Å clusters for **HC1**, **HC5** and **HP1**, calculated at TD- ω B97X-D/6-31G(d) in point charges. Single point energies were calculated for 100 initial conditions based upon a Wigner distribution of the excited state frequencies calculated at ONIOM(TD- ω B97X-D/6-31G(d):AMBER) level.

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