How Inter- and Intramolecular Processes Dictate Aggregation-Induced Emission in Crystals Undergoing Excited-State Proton Transfer

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Supporting Information

ABSTRACT: Aggregation-induced emission (AIE) offers a route for the development of luminescent technologies with high quantum efficiencies. Excited-state intramolecular proton transfer (ESIPT) coupled to AIE can produce devices with emission across the visible spectrum. We use a combination of theoretical models to determine the factors that mediate fluorescence in molecular crystals undergoing ESIPT. Using two materials based on 2′-hydroxycalcone as exemplar cases, we analyze how inter- and intramolecular processes determine the emissive properties in the crystal environment. This systematic investigation extends the current interpretation of AIE to polar chromophores with multiple decay pathways. We find that population of nonradiative pathways is dictated by the electronic effects of the substituents and the degree of distortion allowed in the crystal environment. Localization of the electron density is crucial to maximize fluorescence via ESIPT. Our conclusions offer design strategies for the development of luminescent molecular crystals.

A major obstacle in the fabrication of highly emissive devices such as organic lasers is aggregation-caused quenching (ACQ), a common phenomenon where highly fluorescent compounds in aqueous phase become dark in the solid state. Contrastingly, aggregation-induced emission (AIE) occurs when nonemissive chromophores in dilute solution become luminescent upon aggregation. AIE offers a route for the manufacture of organic optoelectronic devices, where highly efficient and tunable luminescence in the solid state is required for optimum performance. Proposed AIE mechanisms include J-aggregate formation, excimer emission, restriction of intramolecular motions (RIM), restricted access to the conical intersection (RACI), cis–trans isomerization, and clusteroluminescence. AIE has commonly been understood through the RIM model, where low-frequency rotational modes of phenyl rings dissipate energy nonradiatively in solution. In the solid state, the nonradiative decay channel is suppressed, increasing the quantum yield of fluorescence. Results from the RIM model, while extremely informative, are based on the vibronic coupling scheme assuming harmonic behavior, while low-frequency modes can be highly anharmonic.

As an alternative approach, the RACI model proposed by Blancafort et al. directly considers the role of the S1→S0 conical intersections (CIs), which in the solid state lie higher in energy due to environmental hindrance. RIM and RACI models have been used in combination with QM/MM methods to consider slightly polar systems. One yet unexplored question is how intermolecular and intramolecular factors can be used to tune the underlying nonradiative mechanisms.

Excited-state intramolecular proton transfer (ESIPT) systems displaying AIE have been used in laser dyes, molecular probes, and optoelectronics, where the large Stokes-shifted emission prevents self-absorption and increases efficiency. An intramolecular hydrogen bond mediates tautomerization between enol (E) and keto (K) forms in a fully reversible four-level photocycle (E → E* → K* → K). Fluorescence can occur from either or both of the E*/K* states, the ratio of which is influenced by factors such as substituents, solvent polarity, and viscosity. Because of the polarity of the molecules involved, the presence of multiple decay channels, and the role of the environment, ESIPT crystals represent ideal candidates to study the interplay between inter- and intramolecular factors in AIE chromophores.

We investigate the differing AIE behavior of two crystals based on 2′-hydroxycalcone (Figure 1). Pertinently, the identity of substituents on the 2′-hydroxycalcone skeleton determines the crystalline structure and the quantum yield of fluorescence. Compound 1 exhibits AIE and has promising properties for solid state lasers. In contrast, compound 2 is dark in both solution and the solid state. In 1, chromophores aggregate in a slip-stacking, herringbone structure in an edge to face arrangement (Figure 1). Conversely, in 2 the dominant motif is the face-to-face π–π interaction.
To simulate the long-range periodic electrostatics, we embed M15
in Ewald-derived point charges.48,49 A detailed description of all
methods, models, and codes can be found in the Supporting
Information.

Our multimodel approach ensures size consistency of the
MM region, evaluates the role of short- and long-range
interactions, explicitly models the long-range electrostatic
potential from the crystal, and determines the role of excitonic
coupling and electron transfer on the mechanistic interpreta-
tion.

For all models, the crystal environment shifts the bright state
to the red with respect to absorption in vacuum. The bright
state calculated for 1 with the M and D models (Table 1) is in
very good agreement with the experimental value of 3.3 eV.41
The bright state is calculated as 2.93 eV with RI-CC2/def2-
TZVP. In the case of 2, the energies predicted with all models
are in the range of 3.4 to 3.5 eV, in good agreement with the
RI-CC2/def2-TZVP value of 3.33 eV. There is no significant
intermolecular charge transfer upon excitation in either
crystal.

The electrostatic potential generated by the whole crystal (in
the Ewald model) has a negligible effect for the vertical
excitations of 1, with a convergence of 3.3 eV for the bright
state. In the case of 2, a more polar structure, the effect is more
significant, with a shift in the energy of ~0.1 eV. Because this is
on the order of the shift associated with vibrations and does not
change the nature of the excited states, even the smaller cluster
models (M7 and D7) can capture the main electrostatic
influence on the photoexcitation.50

In going from a monomer chromophore to a dimer
chromophore, the bright state shifts from S1 to S2 (Supporting
Information). For the Franck-Condon (FC) geometry, the
electronic density is delocalized over the two chromophores. As
a consequence of excitonic coupling, the bright state is blue-
shifted in 0.06 and 0.15 eV for 1 and 0.23 and 0.32 eV for 2
(M7 model as reference). This is typical of H dimers within the
Kasha excitonic coupling model, with oscillator strengths of S1
almost double those of the monomer species in S1.51 While the
splitting is more significant for 2, this does not alone explain the
different properties of 1 and 2.

Further understanding can be achieved by calculating the
excitonic couplings for the relevant dimers. We apply a
diabatization scheme that incorporates both the short-range
(exchange, orbital overlap, charge-transfer) and long-range
Coulomb interactions.52 The exciton coupling J between two
monomers in a dimer is given in the diabatic 2 × 2 Hamiltonian
matrix H(D), computed via

$$H^{(D)} = CH^4C^T$$

### Table 1. Absorption Energies from the FC Point and Emission Energies from the E* and K* Minima for QMMM Models^a

<table>
<thead>
<tr>
<th></th>
<th>Compound 1</th>
<th></th>
<th>Compound 2</th>
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<tbody>
<tr>
<td>M7</td>
<td>3.20 (1.177)</td>
<td>3.03 (1.207)</td>
<td>2.67 (1.191)</td>
</tr>
<tr>
<td>M15</td>
<td>3.30 (1.174)</td>
<td>3.10 (1.225)</td>
<td>2.61 (0.977)</td>
</tr>
<tr>
<td>Ewald</td>
<td>3.30 (1.192)</td>
<td>3.12 (1.124)</td>
<td>2.66 (1.052)</td>
</tr>
<tr>
<td>D7-P</td>
<td>3.26 (2.128)</td>
<td>3.01 (0.479)</td>
<td>2.56 (0.725)</td>
</tr>
<tr>
<td>D7-A</td>
<td>3.35 (2.063)</td>
<td>2.96 (0.119)</td>
<td>2.59 (0.616)</td>
</tr>
</tbody>
</table>

^aEnergies are presented in eV and oscillator strengths are given in parentheses, calculated at ONIOM(ωB7X-D/6-311++G(d,p)):AMBER level of theory.
where $H^A$ is the diagonal Hamiltonian of the $S_1$ and $S_0$ excitation energies and $C$ is the adiabatic--diabatic transformation matrix. The largest coupling (Table 2) in each

<table>
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<tr>
<th>Compound 1 $J$ (eV)</th>
<th>Compound 2 $J$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D7-P</td>
<td>0.060</td>
</tr>
<tr>
<td>D7-A</td>
<td>0.105</td>
</tr>
</tbody>
</table>

compound occurs when the monomers are aligned antiparallel

(A), on the order of 100 meV, which are on the order of those

obtained for some organic semiconductors.55 These couplings

result from the favorable alignment between the nitrogen of

one monomer and carbonyl group on the other monomer

($\sim4.5$ Å).

Recently, the effect of excitonic couplings on the non-
radiative constants for AIE was evaluated.54 For a set of five

highly aromatic conjugated molecules, with $J$ values on the

order of 10 meV, the authors found that excitonic coupling

always increases the nonradiative decay constants. On the basis

of these vibronic models, in the $E^*$ form, a larger $J$ on the

nonradiative vibrational decay should be expected for 2.

Relaxation to either $E^*$ or $K^*$ minima will follow

photoexcitation. Because of the short-range interactions in

the dimer models, oscillator strengths for emission are smaller

than those obtained for the monomer models (Table 1). In the

case of 1, significant reabsorption is expected due to the small

Stokes shift for the $E^*$ minimum. This has been recently

confirmed experimentally.56 For 2, oscillator strengths from $E^*$

are extremely small. In this context, no significant emissive

response is expected from the $E^*$ state of either material. For 1,

relaxation in $E^*$ involves localization of the electronic density

on one molecule, whereas delocalization is observed for 2. In

vacuum and monomer models, $E^*$ is not stable for 2.

Geometries of the $E^*$ and $K^*$ minima are planar in the solid

state. Because no double proton transfer $K^*$ minimum was

found for 1, emission is expected from a localized $K^*$ state. The

experimental emission spectrum for 1 can be assigned to the

$K^*$ state ranging from 1.5 to 2.1 eV. The predicted values are

blue-shifted to 2.7 eV (CC2/def2-TZVP predicts emission at

2.2 eV). The blue-shifted to 2.7 eV (CC2/def2-TZVP predicts emission at

2.2 eV). The

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effects provided by the methoxy substituent, aided by the electrostatic potential discussed above. As a result, 2 has enough energy to deactivate through the conical intersection and return to the ground state via the nonradiative pathway, a channel infeasible for compound 1. In summary, the analysis of two materials with contrasting emissive properties illustrates how the balance of intermolecular and intramolecular factors can control the radiative and nonradiative mechanisms underlying their light response (Schemes 1 and 2). Considering the radiative mechanisms, emission from E* is unlikely from the delocalized state in 2 but still possible from K*. The crystal environment also significantly affects the population distribution between of the nonradiative pathways. For both crystals, deactivation through the E* channel is blocked due to a significant increase in the energy of the MECI. For the K* channel, the crystal changes the relative energy of two conical intersections present in gas phase, stabilizing a structure where the carbonyl group pyramidalizes. While being structurally similar to the MECI of 1, the MECI of 2 is lower in energy due to the difference in electronic density distribution in S1 on account of the methoxy group. The \( \pi-\pi \) stacking interactions in 2 increase the excitonic coupling. On the contrary, an effective localization of the electronic density is required for the ESIPT process. Our calculations show that either nonradiative delocalized electron-transport processes (E* channel) or localized deactivation through the ESIPT (K* channel) are more likely in 2 than in 1. The interplay of all discussed factors results in an enhance emissive response of 1 and a switch-off of fluorescence in 2 in the solid state.

From our results, some design principles can be proposed for more efficient solid-state emitters. As strong electrostatic interactions aid the deactivation through nonradiative pathways, it is clear why many of the reported AIE fluorophores are nonpolar. For the ESIPT chromophores, stabilizing E* over K* minima could be favorable because the E* nonradiative pathway is hampered in the solid state. For this, the nature of the E* state must be altered to induce a larger Stokes shift. Alternatively, if the E* state is made more unstable by increasing the lability of the transferring proton, then the population of the K* channel will increase. To maximize returns, access to the pyramidal K* MECI can be further hindered by imposing further geometrical restrictions, such as introducing fused rings to the molecular structure. Torsional restraint can also be achieved by coordination to metals.\(^{57}\) We think that this mechanistic understanding has the potential to contribute to the design of more efficient highly emissive ESIPT materials.

**ASSOCIATED CONTENT**

\*S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b02893.
Computational details, model descriptions, excitation and emission energies, critical point energies, analysis of conical intersections, visualizations of the potential energy surfaces, and crystal structure analysis. (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


