Perylene Diimide-Based Hj- and hJ-Aggregates: The Prospect of Exciton Band Shape Engineering in Organic Materials

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Supporting Information

ABSTRACT: The exciton band dispersion in π-stacks of conjugated organic chromophores is a critical factor in determining the photophysical response and transport properties. In such stacks, the exciton band width and, in particular, the curvature at the band center, is determined by an interference between short-range coupling due to wave function overlap and long-range Coulomb coupling arising from transition dipole–dipole interactions. The interference can be completely destructive, yielding a dispersionless “flat” band resulting in an unusual situation where the aggregate displays monomer-like properties, despite having closely spaced chromophores. Coupled chromophores such as these are called “null aggregates” and the perfect balance of interactions that leads to them are referred to as “null points”. Here, we study two perylene diimide (PDI) derivatives where positive long-range coupling induces H-aggregate behavior, whereas counteracting short-range coupling induces J-aggregate behavior. As such, both derivatives display so-called Hj-aggregate properties but are shown here to straddle a null point. In N-phenyl PDI π-stacks, the stronger Coulomb coupling tilts the scales in favor of overall H-like behavior resulting in Hj-aggregates, characterized by a weak 0–0 vibronic photoluminescence (PL) peak, which increases with temperature. By contrast, in tetraphenyl PDI π-stacks, the short-range coupling dominates, resulting in hJ-aggregates, as characterized by dominant 0–0 emission. Furthermore, in tetraphenyl PDI, the 0–0/0–1 PL ratio remains approximately twice the monomer value, independent of temperature, indicating strong Peierls-like dimerization. Identifying the null points in PDI derivatives provides reference geometries for band shape engineering through, for example, chemically induced or pressure-induced changes in molecular packing.

I. INTRODUCTION

Employing organic molecular and polymeric materials for electronic device applications such as solar cells and light-emitting diodes has been an area of intense activity over the past several decades.1–7 By now, it is widely appreciated that optimal performance requires efficient design strategies that go beyond the properties of the individual molecular units and include factors related to sample morphology and, most importantly, intermolecular interactions.8 The ability to control the properties of the exciton bands (exciton band shape engineering) is particularly appealing since the band shape impacts exciton transport as well as important photophysical properties such as the optical gap and radiative cross-section. In particular, the band width dictates the speed at which an exciton can travel, with the curvature at the band center (k = 0) related to the inverse of its effective mass. The sign of the curvature also dictates the photophysical properties; as first recognized by Kasha,9–11 when the curvature is positive, the bright (k = 0) exciton lies at the bottom of the band as in the strongly emissive J-aggregates, whereas a negative curvature places the bright state at the top of the band as in the weakly emissive H-aggregates. The ability to engineer and control the shape of the exciton band is, therefore, enormously useful for the design of efficient organic light-emitting diodes (OLEDs) and solar cells.

One of the most versatile classes of molecules for the design of optoelectronics is the ubiquitous rylene,12,13 which includes the numerous perylene diimide (PDI) derivatives.13–17 Such chromophores have been extensively investigated as efficient electron-transport materials for transistor applications17,18 as

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well as materials for singlet exciton fission.\textsuperscript{19–21} PDIs can assemble to form both H- and J-aggregates\textsuperscript{22–24} based mainly on aggregation-induced spectral shifts (red-shift for J-aggregates and blue-shift for H-aggregates) consistent with the Kasha theory.\textsuperscript{9–11} Ghosh et al.\textsuperscript{25} demonstrated the control of H- and J-type π-stacking by tuning the peripheral alkyl side chains. Transformations between H- and J-aggregate morphologies involving the same PDI have also been observed by several groups\textsuperscript{25,26} by disrupting H-bond formation via control of the solvent or chemical additives.

Kasha-based design schemes are predicated entirely on the intermolecular Coulomb coupling, which is generated primarily by transition dipole–dipole interactions. For example, in a linear aggregate exhibiting a “side-by-side” orientation of transition dipoles, the dominant [nearest-neighbor (n.n.)] Coulomb coupling is positive, \( J_{\text{Coul}} > 0 \), resulting in the bright Frenkel exciton (\( k = 0 \)) residing at the top of the exciton band, as defines H-aggregates. Conversely, in the “head-to-tail” orientation the Coulomb coupling is negative, \( J_{\text{Coul}} < 0 \), so that the bright exciton resides at the band minimum, as is characteristic of J-aggregates.\textsuperscript{9–11} Such a scheme is, however, incomplete in π-stacked systems where close intermolecular contacts enable intermolecular charge transfer (CT). Here, CT gives rise to a short-range superexchange coupling, which can be competitive with Coulomb interactions but with very different dependencies on the intermolecular geometry. The simultaneous presence of both coupling sources allows for a richer array of aggregate types denoted as HJ, HH, JH, and JJ, where the relative magnitudes of both coupling sources allows for a richer array of aggregate coupling.\textsuperscript{25}

In this section, we briefly introduce the general theoretical basis for identifying null points and aggregate types from photophysical signatures, which enable one to disentangle the relative influences of long-range Coulombic coupling and short-range CT-mediated interactions in π-stacks of PDI chromophores. As is shown below, the most sensitive probe is the temperature-dependent PL line shape, which harbors a pronounced vibronic progression in the main vinyl-stretching mode with energy 0.174 eV. In particular, the 0–0/0–1 intensity ratio can accurately track the short- and long-range coupling interference through the null point, the point at which the exciton band becomes dispersionless or “flat”. In previous works,\textsuperscript{25–27,29} hybrid aggregates have been discussed in the nonresonant regime, where high-energy CT states are treated virtually leading to an effective superexchange coupling, as well as in the resonant regime, where the diabatic Frenkel superexchange coupling (i.e., \( J_h, hJ \), or \( JJ \)) or negative curvature (i.e., \( H_j, jH \), or \( HH \)) depending on the desired goal.

In this paper, we investigate the photophysical properties of two perylene diimide (PDI) derivatives, namely, \( N, N' \)-bis(phenyl) PDI (N-phenyl PDI) and \( N, N' \)-bis(2,5,8,11-tetraethyl PDI (tetraphenyl PDI). The crystal structures of both derivatives are based on π-stacks but with slight differences in the slip–stack orientations, as depicted in Figure 1. Such differences result in dramatic changes in the photophysical response, which allow us to unequivocally classify N-phenyl and tetraphenyl PDI π-stacks as Hj and hJ-aggregates, respectively, based on their spectral signatures.\textsuperscript{35} Importantly, each derivative lies close to a particular null point but resides on opposite sides of the balance between short- and long-range couplings. In particular, in N-phenyl PDI aggregates, the Coulomb coupling is slightly dominant (Hj), whereas in tetraphenyl PDI aggregates, the short-range CT-mediated coupling is dominant (hJ). We show that temperature-dependent photoluminescence (PL) provides a reliable means for determining the proximity and bias relative to a particular null point, information that is vital in design strategies for band shape engineering.

**II. HJ-AGGREGATES IN PDI π-STACKS**

In this section, we briefly introduce the general theoretical basis for identifying null points and aggregate types from photophysical signatures, which enable one to disentangle the relative influences of long-range Coulombic coupling and short-range CT-mediated interactions in π-stacks of PDI chromophores. As is shown below, the most sensitive probe is the temperature-dependent PL line shape, which harbors a pronounced vibronic progression in the main vinyl-stretching mode with energy 0.174 eV. In particular, the 0–0/0–1 intensity ratio can accurately track the short- and long-range coupling interference through the null point, the point at which the exciton band becomes dispersionless or “flat”. In previous works,\textsuperscript{25–27,29} hybrid aggregates have been discussed in the nonresonant regime, where high-energy CT states are treated virtually leading to an effective superexchange coupling, as well as in the resonant regime, where the diabatic Frenkel

![Figure 1. Molecule structures of N-phenyl PDI (left) and tetraphenyl PDI (right). Also shown is the π-stacking organization of both chromophores in the crystal state, as determined from X-ray diffraction. N-Phenyl PDI is slipped along the short molecular axis, whereas tetraphenyl PDI is slipped along the long molecular axis.](image-url)
and CT exciton bands are close in energy. It is the latter regime that best applies to the PDIs investigated herein.

As established in several works,25,27,29,36–40 short- and long-range couplings lead to excited states consisting of an admixture of Frenkel excitons and CT excitons. For a linear aggregate (i.e., π-stack) with one molecule per unit cell, Frenkel exciton dispersion, \( E_F(k) \), is dictated by the intermolecular Coulombic coupling

\[
E_F(k) = E_{S_0} + \sum_n J_{\text{m}} \cos[k(m-n)]
\]

where \( k \) is the (dimensionless) exciton wave vector ranging from \(-\pi\) to \(\pi\). \( E_{S_0} \) is the energy of a chromophore locally excited in its first excited singlet state (including the gas-to-crystal shift) and \( J_{\text{m}} \) is the Coulombic coupling between chromophores \( m \) and \( n \), which generally derives from the atomic transition charge densities on each chromophore.\(^{41,42}\) However, in tightly packed π-stacks, a locally excited state can also undergo charge transfer, as dictated by the electron and hole CT integrals, \( t_e \) and \( t_h \), which derive from efficient LUMO–LUMO and HOMO–HOMO overlaps, respectively, between neighboring chromophores. (Here, LUMO denotes the lowest unoccupied molecular orbital, and HOMO denotes the highest occupied molecular orbital). In the simplest picture, the resulting charge-separated states are limited to nearest neighbors with energy \( E_{\text{CT}} \). When such “diabatic” (i.e., before mixing) CT states lie sufficiently above the Frenkel band (compared to \( |t_e| \) and \( |t_h| \)), they can be treated perturbatively, as virtual excitations, which mediate a short-range superexchange coupling, \( J_{\text{CT}} \).

\[
J_{\text{CT}} = \frac{-2t_et_h}{E_{\text{CT}} - E_{S_0}}
\]

The short-range coupling \( J_{\text{CT}} \) simply adds to the Coulomb coupling in a Frenkel-like Hamiltonian, thereby establishing a direct interference between the two coupling types in determining H- and J-like behavior.\(^{25,27}\) Equation 2 shows that a positive (negative) sign for the product, \(-t_et_h\), promotes H-aggregate (J-aggregate) behavior. Figure 2 demonstrates the strong sensitivity of the product \(-t_et_h\) to molecular packing in a perylene dimer based on first-principles density functional theory (DFT) calculations. The rapid oscillations in the sign are responsible for the unusual non-Kasha geometries expected for short-range-coupled J- and H-aggregates.\(^{25,27}\) For comparison, Figure 2 also shows the Coulomb coupling, \( J_{\text{Coul}} \), derived from atomic transition charge densities,\(^{44}\) which varies over much larger length scales. The yellow circle and star on each plot indicate the native orientations appropriate for N-phenyl PDI and tetraphenyl PDI, respectively, as determined from the crystal structure (see Section IV). Interestingly, both aggregates would be defined as H-aggregates based on the Coulomb coupling alone.

For many PDI derivatives, like the ones in the current study, the diabatic Frenkel and CT bands are sufficiently close in energy such that the superexchange picture just described is no longer valid. CT excitations need to be incorporated directly into the Hamiltonian (and not treated virtually). In the resonant regime, oscillator strength is distributed over two mixed Frenkel–CT bands. For linear aggregates (with 1 molecule/unit cell), this can be appreciated from the general dispersion relation obtained in the absence of vibronic coupling\(^{25,29,43}\)

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Table 1. Calculated Electron and Hole Transfer Integrals and Unscreened Coulombic Couplings for Both PDI Derivatives, Reported in cm$^{-1}$

<table>
<thead>
<tr>
<th></th>
<th>$t_e$</th>
<th>$t_h$</th>
<th>$J_1$</th>
<th>$J_2$</th>
<th>$J_3$</th>
<th>$J_4$</th>
<th>$J_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-phenyl PDI</td>
<td>994</td>
<td>392</td>
<td>1089</td>
<td>400</td>
<td>176</td>
<td>90</td>
<td>51</td>
</tr>
<tr>
<td>Tetraphenyl PDI</td>
<td>1316</td>
<td>953</td>
<td>457</td>
<td>59</td>
<td>-2.2</td>
<td>-9.1</td>
<td>-4.9</td>
</tr>
</tbody>
</table>

“Electron and hole integrals were evaluated using DFT with the B3LYP functional and cc-pVDZ basis set (Gaussian 16W) using the polarization-including procedure described in ref 62. Coulomb couplings were evaluated from transition densities calculated using RPA-TDDFT with omega-B97X/ma-def2svp (ORCA). The Coulomb coupling designated $J_n$ corresponds to the $n$th nearest-neighbor interaction along a $\pi$-stack. The "1" and "2" rows for tetraphenyl PDI indicate that interactions are taken with respect to the first or second molecule in the unit cell. All calculations were done in the gas phase using the crystal geometries and including all substituents.

Figure 3. (Top) A and B band dispersions (black) from eq 3 for $\pi$-stacks having one molecule per unit cell with in-phase values of the CT integrals, $t_e = 1200$ cm$^{-1}$ and $t_h = 800$ cm$^{-1}$ and taking $E_{CT} = E_{S_i}$. The dashed lines are the diabatic CT (red) and Frenkel exciton bands (blue). The nearest-neighbor Coulombic coupling, $J_{\text{Coul}}$, is positive (H-like), increasing from the left to right panel ($J_{FB} = 920$ cm$^{-1}$ using eq 4). The solid dots represent the dispersion of band A in the presence of vibronic coupling ($\omega_{\text{vib}} = 1400$ cm$^{-1}$, $\lambda^2 = 1$). Note the vibronic A band is flat in the middle panel when $J_{\text{Coul}} = J_{FB}$. The aggregate type is hJ (Hj) when $J_{\text{Coul}}$ is less than (greater than) $J_{FB}$ (Bottom) corresponding 10-mer absorption (black) and PL spectra (red, purple, blue) calculated using eqs S.9 and S.12 assuming a monomer transition with $E_{S_i} = 20000$ cm$^{-1}$ and using the Frenkel–CT Hamiltonian in eq S.1. To more easily gauge the oscillator strength distribution among the peaks, the $\omega_i$ dependence of the oscillator strength was suppressed in eq S.10 and the cubic frequency dependence was suppressed in eq S.12. Note that the PL spectra have been shifted by one vibrational quantum to the red for clarity (otherwise, the 0–0 PL peak overlaps the absorption $a_1$ peak). Finally, the “superradiant” PL spectrum in the left panel (red) is scaled by a factor of 1/N (=1/10).

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systems.22 two-band absorption structure has been observed in many PDI from the resonant Frenkel vibronically structured absorption peaks (A and B) resulting for the 10-mer stack, the Figure portrays two broad, monomer absorption (and PL) spectrum have equal intensity.

Increasing the Coulomb coupling beyond $J_{FB}$ causes band curvature inversion (the right panel of Figure 3), leading to the creation of an Hj-aggregate, where the H-promoting influence of the Coulomb coupling now outweighs the J-promoting influence of the Frenkel–CT exciton coupling.

Figure 3 also shows how the absorption and emission spectra of the vibronically coupled 10-mer π-stack respond to increasing $J_{Coul}$ through the null point. The HR factor of unity ($\lambda^2 = 1$) allows one to more clearly appreciate the effect of intermolecular interactions on the vibronic progression: when $\lambda^2 = 1$, the first two vibronic peaks (0–0 and 0–1) in the monomer absorption (and PL) spectrum have equal intensity. For the 10-mer stack, the Figure portrays two broad, vibronically structured absorption peaks (A and B) resulting from the resonant Frenkel–CT exciton interactions. Such a two-band absorption structure has been observed in many PDI systems.19,22–1,25,27,47,48 Using eq 3, the splitting (at $k = 0$) is approximately given by

$$\Delta_{AB} = 2\sqrt{2}(l_c + t_h)$$

(5)
as indicated by the double-headed arrow in the figure. Note the steady increase in the oscillator strength of the peak B with increasing Coulomb coupling due to the enhanced admixture of the optically bright $k = 0$ Frenkel exciton (the diabatic CT state is assumed to carry no oscillator strength). However, most important to what follows is the strong sensitivity of the temperature-dependent PL spectrum to the delicate balance between the two coupling influences. In Hj-aggregates (left lower panel), the emission is J-like with a dominant, superradiant 0–0 peak that diminishes with increasing temperature, whereas in Hj-aggregates (right panel), the emission is H-like with the weak 0–0 peak increasing steadily with temperature, as is also the case even for the Hj-aggregate in the right panel. As shown in ref 27, the entire absorption spectral line shape approaches that of the monomer in the limit that the diabatic CT and Frenkel bands become increasingly off-resonant (including the vanishing of band B). Hence, we rely instead on the temperature-dependent PL to determine aggregate nature and, in particular, the proximity to a null point.

Thus far, the model shows that by making subtle modifications to the aggregate structure, one can effect changes through a null point that have dramatic consequences for the photophysical properties of molecular aggregates. In what follows, we will show how the coupling between Frenkel and CT excitons in the presence of Coulomb coupling impacts the exciton band shape in both PDI derivatives, leading to the unusual hybrid (hj and Hj) aggregate types.

### III. EXPERIMENTAL ABSORPTION AND EMISSION SPECTRA

To validate our theoretical prediction of the switching between hj and Hj behaviors, we have carried out absorption and photoluminescence (PL) spectroscopy in solution-grown tetraphenyl and N-phenyl PDI microcrystals. Sample preparation methods are detailed in the SI, along with optical microscopy and fluorescence microscopy images of the as-grown microcrystals (Figure S1). Figure 4 summarizes the steady-state absorption and PL spectra of the two derivatives in the solution and crystalline phases. The monomer absorption
spectra (Figure 4a,d, black dash) are very similar for the two derivatives: both monomers exhibit pronounced vibronic progressions in their absorption line shapes resembling most PDI families resulting from coupling between the main S0 → S1 electronic transition and the symmetric vinyl-stretching mode with frequency near 1400 cm⁻¹ and HR factor λ² = 0.6 (see Figure S5). The monomer PL spectrum closely mirrors that of the absorption spectrum.

Compared to monomeric solutions, the absorption spectrum of many PDI aggregates displays two asymmetrically broadened absorption bands with one red-shifted and the other blue-shifted relative to the main monomer peak. A similar two-band structure is observed in tetraphenyl and N-phenyl PDI aggregates in Figure 4a,d, with the lowest energy electronic transition red-shifted by more than 1000 cm⁻¹ relative to the monomer peak. As indicated in Figure 2, the long-range Coulomb coupling alone supports H-aggregates for both PDI derivatives and, therefore, blue-shifted absorption bands (compared to the monomer), entirely at odds with the reported spectra in Figure 4a,d. As we show here, the band splitting behavior observed in both PDI aggregates is primarily a result of the coupling between Frenkel and CT excitons in the resonant regime, driven by intermolecular electron and hole transfer, and not long-range Coulomb coupling. In general, however, both effects play an important role in determining the exciton band shape and the overall hybrid “HJ” nature of the photophysical response, as already indicated in Figure 3.

More clues to the H/J-behavior can be gathered from the temperature-dependent PL measurements. Figure 4b,e shows the steady-state PL spectra obtained from 5 to 280 K for the crystalline phases of both PDI derivatives. Measurements were performed on thin crystals to eliminate reabsorption effects, and all spectra were normalized to the dominant vibronic peak (the 0–1 peak in N-phenyl PDI and the 0–0 peak in tetraphenyl PDI). As can be appreciated from Figure 4b,e, the difference between the two PDI derivatives is striking: in the N-phenyl derivative, the 0–0 PL intensity (relative to the 0–1 intensity) almost vanishes at the lowest temperature but grows steadily with increasing temperature until it eventually surpasses the 0–1 peak. Such behavior is characteristic of weakly coupled H-aggregates where the 0–0 peak is thermally activated, as discussed in greater detail in the following section. By contrast, in the tetraphenyl derivative, the 0–0 peak remains dominant and several times larger than the 0–1 peak over the entire temperature range. The 0–0/0–1 intensity ratio is about twice that for the monomer, a strong indication of J-aggregation, but with a coherence limited to only a couple of chromophores, as the 0–0/0–1 ratio is approximately Ncoh times greater than for the monomer in J-aggregates. Here, Ncoh is the number of coherently connected chromophores. In Section IV, we show that the temperature-stable ratio of approximately two is likely due to Peierls-like dimerization.

We further investigated the possible creation of excimmers, which are quite common in PDIs by obtaining the time-resolved emission spectrum using a streak camera. Results are shown in the SI, where we demonstrate that, for tetraphenyl PDI, a slowly decaying red-shifted shoulder peak at ~730 nm (Figure S2 in the SI) with <20% of the peak intensity of the main peak may be attributable to an excimer. This excimer spectral position is red-shifted from a previous report, which suggested excimer-like emission at 675 nm from defect sites within a polycrystalline film of tetraphenyl PDI grown from physical vapor deposition but falls well within the reported range of 650–850 nm. The discrepancy in the excimer emission could result from a different defect type due to different growth methods (solution-grown microcrystal in our case vs physical vapor deposited thin film in ref 19). Because the steady-state PL spectra are dominated by the exciton component and the ~730 nm feature (13 600 cm⁻¹) is low enough in energy, the two main vibronic features present in Figure 5 should not be seriously impacted by the excimer. For N-phenyl PDI, no obvious excimer feature has been observed.

The temperature dependence of the time-resolved PL lifetimes is also consistent with overall J- and H-like behaviors for tetraphenyl- and N-phenyl PDI aggregates, respectively. The experimental temperatures were varied from 5 to 280 K, and the experiments were conducted at low pump fluence to avoid exciton–exciton annihilation, as described in the SI. In the aggregate form, both PDIs display multieponential PL decay dynamics. N-Phenyl PDI aggregates exhibit a 4-fold increase in the lifetime upon cooling to 5 K (τ1 = 5.7 ns and τ2 = 20.7 ns) in comparison to the lifetimes at 280 K (τ1 = 1.6 ns and τ2 = 5.1 ns), which could be attributed to the decreased population of the bright state at low temperature (Figure S3). In comparison, the PL lifetime of the tetraphenyl aggregates is several times shorter than N-phenyl PDI, possibly due to a faster-decaying (superradiant) radiative component. The lifetimes are also nearly temperature-independent between 40 and 280 K, suggesting a flat energy band, which we discuss further in Section IV.

In the following section we show how the disparate behaviors exhibited by the two PDI derivatives are consistent with the formation of hJ- and Hj-aggregates in tetraphenyl PDI and N-phenyl PDI, respectively.

**IV. STRADDLING A NULL POINT: HJ-AGGREGATE BEHAVIOR IN N-PHENYL VS TETRAPHENYL PDI**

In this section, we show how the packing details of the two PDI derivatives contribute to their opposing emission behaviors, i.e., their Hj and Hj behaviors. Figure 5 shows selected views of N-phenyl PDI and tetraphenyl PDI π-stacks,
as determined from their known crystal structures. The n.n.
separation in both cases is approximately 3.5 Å, but the relative
orientations are quite different; in N-phenyl PDI, there is just
one chromophore per unit cell (within a single π-stack) with
the two n.n. chromophores shifted along the short molecular
axis by approximately 1.8 Å. Conversely, tetraphenyl PDI has
two molecules in a unit cell (within a π-stack), with neighbors
displaced mainly along the long molecular axis by as much as
3.6 Å. The relative orientations are indicated in the contour
plots of $-t_e t_h$ and $J_{\text{Coul}}$ in Figure 2, which provides a qualitative
assessment of the coupling interference. Interestingly, for both
derivatives, the two CT integrals are in-phase, thereby
supporting J-like short-range coupling, whereas the long-
range coupling is positive and, therefore, H-promoting. The
overall destructive interference leads to their hybrid HJ-
aggregate nature, similar to what was found for TAT
nanopillars.26 As we will show, it is the competition between short-
and long-range couplings, which is responsible for
diverse emission behaviors observed for the two PDI
derivatives.

In Table 1, we report results from more detailed calculations
of the short-range and long-range couplings, which go beyond
the perylene core approximation of Figure 2 and employ the
full atomistic detail obtained from the X-ray diffraction
data.19,61 Care was taken to ensure a consistent phase
assignment for transfer integrals and Coulomb integrals, as
discussed in detail in the SI and ref 29. For N-phenyl PDI, the
Coulomb couplings are uniformly positive and H-promoting,
whereas the electron and hole transfer integrals, calculated via
the method described in ref 62 are in-phase and J-promoting.
Because there are two molecules in a unit cell for tetraphenyl
PDI, there are two sets of electron and hole CT integrals
labeled 1 and 2 in the Table. The former applies to the two
molecules in a given unit cell, whereas set 2 applies to electron
and hole transfer between two chromophores in neighboring
unit cells. Hence, for tetraphenyl PDI, charge transfer differs to
the “right” or “left” of a given chromophore. However, in both
cases, $t_e$ and $t_h$ remain in-phase (J-promoting). The strong
asymmetry in the short-range coupling leads to interesting
dimer-like behavior, which results in band splitting, as
explained in greater detail in the SI. The Coulomb couplings
in tetraphenyl PDI are also divided into two sets, as shown in
the table, to account for asymmetric couplings on each side of
a chromophore; they remain dominantly positive (H-like),
and, unlike in N-phenyl, are mostly confined to the nearest
neighbors due to the very significant long-axis slip between
neighboring molecules. The latter is also responsible for
an eventual sign change in the coupling for chromophores beyond
nearest neighbors.

In what follows, we analyze in detail the absorption and
emission spectral line shapes for the two PDIs in turn, using
the calculated values of $t_e$ and $t_h$, the extended Coulomb
interactions from Table 1 and the vibronic parameters deduced
from the monomer absorption spectra in Figure 4a,d, see
Figure S5. Spectral simulations are based on $\pi$-stacks
containing 10 chromophores utilizing the Frenkel–CT/
Holstein Hamiltonian, which treats vibronic coupling quantum
mechanically. The Hamiltonian is represented in a two-particle
basis set and numerically diagonalized to yield the eigenstates
and eigenenergies, which are then used to construct the
absorption and emission spectra. Details can be found in the
SI.

IV.J. N-Phenyl PDI. To demonstrate the interference
between short- and long-range couplings in N-phenyl PDI,
Figure 7. Calculated band dispersions (left), associated absorption spectrum (middle), and temperature-dependent PL spectra (right) for tetraphenyl PDI π-stacks as a function of increasing Coulombic coupling in going from top to bottom rows. Insets on the right panels show a magnified version of the band A dispersion indicating activation energy for 0–0 emission. Electronic coupling parameters are taken from Table 1 but with Coulombic couplings reduced by a factor of $\varepsilon = 3$ due to dielectric screening. The Coulombic couplings are multiplied by a scaling factor, starting with $s = 0$ in the top row (no Coulomb coupling) and increasing to $s = 1.6$ in the bottom row. Band dispersions are evaluated without vibronic coupling. Spectral simulations were conducted on 10-mers including vibronic coupling with $\omega_{ob} = 1400 \text{ cm}^{-1}$ and $\lambda^2 = 0.6$, values which best fit the solution-phase spectrum in Figure 4, with anionic and cationic HR factors each equal to 0.3. $E_{CT} - E_n$ was set to $900 \text{ cm}^{-1}$. Spectra are evaluated using the Frenkel–CT/Holstein Hamiltonian, as described in the SI. The solid circle in the $A_h$ band (left panels) indicates the bright $k = 0$ exciton, from which 0–0 emission derives. Note that the $k$ values are referenced to an aggregate with two molecules per unit cell.

we show in Figure 6 the impact of increasing the Coulomb coupling on 10-mer π-stacks using the electronic couplings from Table 1 (the Coulomb couplings from the table were reduced by a factor of $\varepsilon = 3$ to account for dielectric screening). In Figure 6, the Coulomb coupling is increased in going from top to bottom, whereas the CT integrals remain constant; all of the screened Coulomb couplings from Table 1 are scaled by a factor, $s$, beginning with $s = 0$ (top), i.e., no Coulomb coupling, and increasing in even increments to $s = 1.5$ (bottom). In addition, we take the diabatic CT band to be offset by, $E_{CT} - E_{S_1} = 1000 \text{ cm}^{-1}$, a reasonable value in agreement with previous works.\textsuperscript{26} We note that since $l_{e} + t_{h}$ remains much greater than the offset, we are well within the (near) resonance regime of Frenkel–CT coupling.

As observed from the panels in the topmost row, in the limit of no Coulombic coupling, the dispersionless, diabatic Frenkel, and CT exciton bands interact to create bands A and B with maximum splitting at $k = 0$, as follows from the in-phase relationship between $t_e$ and $t_h$. Hence, a $k = 0$ exciton resides at the bottom of band A, as defined J-aggregates. Based on the values of $t_e$ and $t_h$ for N-phenyl (see Table 1), the predicted band splitting from eq 5 is

$$\Delta_{AB} = 2\sqrt{2}l_e + t_h \approx 4000 \text{ cm}^{-1}$$

in good agreement with the actual splitting in the presence of vibronic coupling, as determined from the absorption spectrum (middle panel). The large splitting is responsible for a substantial red-shift of peak A by about $1000 \text{ cm}^{-1}$ from the monomer peak (at approximately $19,000 \text{ cm}^{-1}$). Moreover, the ratio of the vibronic intensities $a_i/a_g$ is noticeably larger than the monomer value of approximately $1/2^2 = 1.67$, as is characteristic of J-aggregates.\textsuperscript{35} Also, note the significant asymmetry between peaks A and B. The greater oscillator strength in peak A is due mainly to the ordering of the diabatic Frenkel and CT bands. Since the Frenkel band is lower in energy, the band A excitons have slightly more Frenkel character, giving peak A slightly more oscillator strength (the diabatic CT excitons are assumed to carry no oscillator strength). Turning to the PL spectrum, we again see clear J-like behavior: the 0–0 component is dominant, with the 0–0/0–1 ratio exceeding the monomer ratio by about a factor of $N$ ($=10$) at very low temperatures.\textsuperscript{51} The ratio decreases with the increasing temperature, as the $k = 0$ exciton, the only one which can source 0–0 emission, is thermally depleted.\textsuperscript{35,51}

Increasing the Coulomb coupling to half-strength (second row in Figure 6) already shows evidence of the destructive interference between the two coupling sources. The positive Coulombic couplings result in a diabatic ("before-mixing") Frenkel band shown in blue with negative curvature, i.e., the $k = 0$ Frenkel exciton is on top of the band, as defines Kasha H-aggregates. However, subsequent mixing with the dispersionless CT band (in red) produces an unusual mustache-shaped dispersion for band $A_h$ in which the $k = 0$ exciton now lies within the band, approximately $100 \text{ cm}^{-1}$ above the band bottom. The intermediate position of the $k = 0$ exciton is a hallmark characteristic of the destructive interference inherent to HJ-aggregates\textsuperscript{29} and follows from eq 3 when using extended Coulomb interactions. Thermal activation is now required to populate the $k = 0$ exciton to provide 0–0 emission. The PL spectrum, therefore, shows hybrid HJ behavior, an initial H-
like growth with increasing temperature, which eventually rolls over and undergoes a J-like decay with further temperature increases. Finally, note that the A–B band splitting in the absorption spectrum hardly changes with the increase in Coulomb coupling to $s = 0.5$, since the splitting is mainly sensitive to the sum $|t_1 + t_2|$. Peak B does, however, acquire greater oscillator strength compared to the case when Coulomb coupling is absent (top row) due to the enhanced resonance between the $k = 0$ diatomic CT and Frenkel excitons observed in the left panel.

Further increasing the Coulomb coupling (last two rows in Figure 6) results in a continued increase in peak B intensity so that it becomes the dominant band. The increased Coulomb coupling also results in a diminishing $a_1/a_2$ ratio as the H-character continues to increase, for example, when $s = 1.5$ (last row) $a_1/a_2$ is approximately 1.2, substantially less than the monomer value of $1/\sqrt{2} = 0.71$. Moreover, the increased activation energy for populating the $k = 0$ exciton within the mustache-shaped dispersion band leads to a monotonic H-like increase in the 0–0 peak relative to the 0–1 peak in the PL spectrum with no roll-over to J-like behavior as is observed when $s = 0.5$. Note that when $s = 1$ the spectral characteristics are qualitatively very similar to what was obtained experimentally for N-phenyl, see Figure 4c. When we fine-tune the couplings for optimal agreement between the simulated and measured spectra (as described in the caption of Figure 4) we obtain the spectra shown in Figure 4a,c, which agree well with experiment.

**IV.II. Tetraphenyl PDI**. As reported in Table 1, in tetraphenyl PDI π-stacks, the n.n. Coulomb coupling is positive (H-promoting) but rapidly decreases (and even becomes negative) for more distant neighbors due to the significant longitudinal shift between neighboring chromophores. The short-range coupling is J-promoting ($t_1$ and $t_3$ are in-phase) but is strongly asymmetric due to the slightly different shifts experienced by the right and left nearest neighbors (see Figure 5) and the extreme sensitivity of both electron and hole transfer integrals to sub-angstrom shifts in geometry, see Figures 2 and 5. The calculated electron and hole transfer integrals are largest between the two chromophores in a unit cell ($t_{11}, t_{33}$) and much weaker between chromophores in different (but neighboring) unit cells ($t_{12}, t_{34}$). In what follows it is convenient to view the π-stack as a linear array of coupled dimers, where each dimer is comprised of the two strongly coupled molecules within a unit cell.

To understand how the asymmetry in the short-range coupling affects the exciton band structure, we first examine the simplest case where there is no Coulomb coupling (row 1 in Figure 7). The strong asymmetry in the CT transfer integrals create a Peierls-like band splitting within both the lower and upper adiabatic Frenkel–CT bands, leading to the creation of the lower-energy bands $A_L$ and $A_{LU}$ as well as the higher-energy bands $B_L$ and $B_{LU}$ as demonstrated in the left panel of Figure 7. The A band (and B band) splitting depends mainly on the interference between the short-range coupling induced by the large intradimer transfer integrals (compared to the interdimer transfer integrals) and the intradimer Coulomb coupling. The case in which $t_1$ and $t_3$ are in-phase, as occurs in tetraphenyl PDI, the short-range coupling is J-promoting, so that when $J_{\text{Coul}} = 0$, oscillator strength is deposited in the lowest energy state, the $k = 0$ exciton in the band $A_L$, with the band $A_{LU}$ remaining optically dark to absorption. By contrast, in the higher-energy band, the oscillator strength is consumed by the $k = 0$ exciton in $B_L$ (which is optically dark). Hence, the absorption spectrum retains the two-band structure with a red-shifted peak $A_L$ accompanied by a blue-shifted peak $B_{LU}$ with a band splitting $\Delta_{A_L B_{LU}}$ of about 4600 cm$^{-1}$ from Figure 7 (top middle panel). The splitting agrees well with the exact expression derived for two molecules per unit cell in the absence of vibronic coupling

$$\Delta_{A_L B_{LU}} = 2\sqrt{(t_1 + t_{33})^2 + (t_2 + t_{34})^2}$$

Note that eq 6 reduces to eq 5 when there is no asymmetry ($t_1 = t_2$ and $t_3 = t_4$).

The temperature dependence of the PL spectrum ultimately arises from the shape of the lower band $A_L$, which, in the absence of Coulomb coupling, maintains a positive curvature (J-like) with the bright $k = 0$ state at the band minimum. Hence, as observed in Figure 7 (top right panel), the emission is J-like, with the 0–0/0–1 PL ratio significantly larger than that of the monomer at low temperatures but decreasing significantly with increasing temperature (as the bright $k = 0$ population is depleted). Note that even at the highest temperature, the 0–0/0–1 PL ratio is about twice the monomer value, as in a J-dimer (see the SI), because $k_0T$ is still much smaller than the $A_L$–$A_{LU}$ band splitting.

As the Coulomb coupling increases, the two-band absorption spectrum in Figure 7 is almost an invariant. Here, the H-like Coulomb coupling is not strong enough, even at its highest setting ($s = 1.6$), to significantly alter the intradimer splitting between the $A_L$ and $A_{LU}$ bands induced by the short-range interactions. Therefore, the intradimer interactions remain dominantly J-like in all cases, where the lowest energy band ($A_L$) possesses the bright $k = 0$ state. However, the Coulomb coupling does eventually invert the curvature of the (emitting) $A_L$ band, since it can more easily destructively interfere with the weaker interdimer short-range couplings. This is reflected in the temperature dependence of the PL spectra: when the $A_L$ band is almost completely rendered flat ($s = 0.8$), the PL line shape is practically temperature-independent resembling that of a J-dimer at all temperatures, i.e., what one would expect from a system of uncoupled dimers. For larger Coulomb couplings, the $A_L$ band curvature becomes negative, and the PL spectrum becomes H-like with the 0–0/0–1 peak ratio now increasing with temperature. Note that at the highest temperatures, for all Coulomb couplings considered in Figure 7, any small curvature in the lower band is overcome by $k_0T$, and the PL spectrum evolves into the J-dimer line shape, where the 0–0/0–1 ratio is about twice that of the monomer.

The experimental PL spectrum of tetraphenyl PDI in Figure 4e exhibits almost no temperature dependence of the 0–0/0–1 ratio, with a 0–0/0–1 ratio about twice as large the monomer, consistent with a positive (H-promoting) Coulomb coupling, which is strong enough to nullify the interdimer short-range coupling, resulting in emission akin to non-interacting J-dimers. Hence, tetraphenyl PDI forms J-aggregates. When we fine tune the couplings (as reported in the caption of Figure 4) for optimal agreement between the simulated and measured spectra, we obtain the spectra shown in Figure 4df. The simulated absorption spectrum agrees well with the experiment and manages to account for the vibronic structure spread over the two main (A, B) peaks. Interestingly, as for N-phenyl PDI, the electron and hole integrals require a scaling by 0.8 to accurately reproduce the A/B splitting. Most
importantly, the temperature independence and shape of the PL spectrum agree well with the experiment.

V. DISCUSSION/CONCLUSIONS

We measured the steady-state absorption and emission spectra of the solution (unaggregated) and crystal phases of two PDI derivatives, \( \text{N,N}^\prime\text{-bis}(\text{n-octyl})-2,5,8,11\)-tetraphenyl PDI and \( \text{N,N}^\prime\text{-bis(phenyl)-PDI} \), and analyzed the spectral line shapes theoretically using the Frenkel–CT/Holstein Hamiltonian. Both derivatives show convincing evidence of an effective destructive interference between the H-promoting Coulomb couplings and the J-promoting short-range couplings derived from intermolecular charge transfer between neighboring chromophores within a \( \pi \)-stack. Interestingly, the two derivatives straddle a null point, the point at which the destructive interference is so efficient as to create a flat dispersionless exciton band, but appear on opposite sides, as determined primarily by the temperature-dependent steady-state PL line shapes. Hence, \( N \)-phenyl PDI, with slightly dominant Coulomb interactions, forms Hj-aggregates, whereas tetraphenyl PDI with slightly dominant short-range interactions, forms a chain of Hj-dimers.

Both PDI derivatives produce similar absorption spectra in the crystal phase, characterized by two main bands, A and B. The band splitting is reflective of strong resonant coupling between the \( k = 0 \) Frenkel and CT excitons, driven by the in-phase electron and hole transfer integrals (\( t_{\text{eh}} > 0 \)). The stronger Coulomb coupling in \( N \)-phenyl PDI leads to a slightly larger oscillator strength in the higher-energy band (B) versus the lower-energy band (A), whereas in the more J-like tetraphenyl PDI, the oscillator strength is larger in the band (A). However, a far more dramatic difference exists in the PL spectra. \( N \)-Phenyl PDI displays classic H-like emission behavior, with the 0–0/0–1 PL ratio increasing monotonically with increasing temperature, whereas tetraphenyl PDI displays a J-like PL spectrum with a dominant 0–0 peak. In tetraphenyl PDI, the 0–0/0–1 ratio exceeds the monomer value by about a factor of 2 and is practically independent of temperature, indicative of dimer localization caused by the presence of two strongly coupled molecules per unit cell. The opposing PL spectral behaviors best reflect the competition between the H-promoting Coulomb coupling and the J-promoting CT-mediated coupling. In \( N \)-phenyl PDI \( \pi \)-stacks the larger Coulomb coupling, arising from the more efficient (side-by-side) overlap between neighboring chromophores, tilts the scales in favor of H-like PL behavior (Hj-aggregates). Conversely, in the Hj-aggregates (\( \pi \)-stacks) of tetraphenyl PDI, neighboring chromophores are longitudinally displaced by more than 3 Å, leading to a much weaker (but still positive and, therefore, H-promoting) Coulomb coupling, which is overwhelmed by the stronger J-promoting CT-mediated coupling within the unit cell “dimers”.

Despite the overall good agreement between the calculated and measured spectra, there remain some notable discrepancies. For example, in the PL spectrum for \( N \)-phenyl PDI, the 0–0 peak retains a small but significant intensity down to the lowest temperatures, \( \approx 5 \) K. This is very likely the result of static disorder in the form of site imperfections, such as vacancies, chemical impurities, and localized stress, or, from longer-range structural imperfections, such as stacking faults and dislocations. Such defects have been studied theoretically in oligoacenes as well as oligothiophene and oligophenylene–vinylene herringbone lattices but have not been included in the present work. Disorder breaks the translational symmetry, causing the band states to mix. As a result, the lowest energy (emitting) state, which is a \( k \neq 0 \) exciton in \( N \)-phenyl PDI, borrows 0–0 oscillator strength from the bright \( k = 0 \) state, which exists at slightly higher energies (see the exciton band shapes in Figure 6). Energy transfer within a disordered landscape also enhances the Stokes shift; in both PDI derivatives, the Stokes shift is larger in the solid phase (1200–1400 cm\(^{-1}\)) versus the solution (300–400 cm\(^{-1}\)). In future work, we will test these hypotheses by averaging over disorder ensembles with varying degrees of spatial correlation.

Future work will also focus on exciton dynamics in the Hj versus Hj PDI systems. We expect that dimer trapping in tetraphenyl PDI will lead to a diminished diffusion constant for exciton transport along the \( \pi \)-stacking direction. Such trapping and subsequent ultrafast, intradimer relaxation has been suggested in several works. We also plan to evaluate exciton—excitation annihilation in both PDI derivatives, hoping to reveal further differences due to the destructive relationship between short- and long-range couplings. The proximity to a null point means that relatively small perturbations, such as the application of hydrostatic pressure or chemical tuning, can cause Hj and Hj interconversions as revealed through changes in temperature-dependent PL line shapes and possibly changes in exciton diffusion coefficients. The ability to direct such changes would represent a significant step in furthering our goal of band shape engineering for targeted applications.

ASSOCIATED CONTENT

Supporting Information

Sample preparation and details of the optical measurements, the Frenkel–CT Hamiltonian and its parameterization, expressions for the absorption and emission spectra, dimer analysis and an in-depth discussion of the phase convention for the intermolecular interactions (PDF)

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(44) Note that the energy scale for the contour plot of the Coulombic coupling in Figure 2 has been corrected from ref 25. The unscreened Coulomb coupling between two perfectly eclipsed perylenes separated by 0.35 nm is about 1000 wavenumbers. (In Figure 4f of ref 25 the eclipsed value is approximately 350 wave numbers because the Coulomb couplings, although reported as unscreened, were actually scaled by a factor of 1/e, with the relative dielectric constant, ε = 3.)

(45) There is also a third band of degenerate CT excitons with energy E_{CT} which do not couple to the Frenkel excitons and hence carry no oscillator strength, see ref 25.


