Singlet Fission in Rubrene Derivatives: Impact of Molecular Packing

Christopher Sutton,*†‡ Naga Rajesh Tummala,*# David Beljonne,* and Jean-Luc Brédas*†§

†School of Chemistry and Biochemistry & Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, United States
‡Chimie des Matériaux Nouveaux & Centre d’Innovation et de Recherche en Matériaux Polymères, Université de Mons-UMONS/Materia Nova, B-7000 Mons, Belgium
§Division of Physical Science and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia

ABSTRACT: We examine the properties of six recently synthesized rubrene derivatives (with substitutions on the side phenyl rings) that show vastly different crystal structures. In order to understand how packing in the solid state affects the excited states and couplings relevant for singlet fission, the lowest excited singlet (S₁), triplet (T₁), multiexciton (TT), and charge-transfer (CT) states of the rubrene derivatives are compared to known singlet fission materials [tetracene, pentacene, 5,12-diphenyltetracene (DPT), and rubrene itself]. While a small difference of less than 0.2 eV is calculated for the S₁ and TT energies, a range of 0.50 to 1.2 eV in the CT energies and nearly 3 orders of magnitude in the electronic couplings are computed for the rubrene derivatives in their crystalline packings, which strongly affects the role of the CT state in facilitating SF. To rationalize experimental observations of singlet fission occurring in amorphous phases of rubrene, DPT, and tetracene, we use molecular dynamics (MD) simulations to assess the impact of molecular packing and orientations and to gain a better understanding of the parameters that control singlet fission in amorphous films compared to crystalline packings. The MD simulations point to a crystalline-like packing for thin films of tetracene; on the other hand, DPT, rubrene, and the rubrene derivatives all show various degrees of disorder with a number of sites that have larger electronic couplings than in the crystal, which can facilitate singlet fission in such thin films. Our analysis underlines the potential of these materials as promising candidates for singlet fission and helps understand how various structural motifs affect the critical parameters that control the ability of a system to undergo singlet fission.

INTRODUCTION

Singlet fission (SF) is a process that occurs in a limited set of molecular systems where a singlet excited state splits into two triplet excitations of about half the energy of the first excited singlet state.¹ SF has recently attracted a great deal of interest because of its potential to overcome the maximum limit of photoelectric conversion efficiency in conventional photovoltaic cells.²⁻⁴ SF has already been successfully harnessed in device applications, with an internal quantum efficiency near 200% realized in some cases.⁵⁻⁸ Materials reported to undergo SF with triplet yields above 100% now include oligoacenes,⁹⁻¹¹ functionalized acenes [e.g., trisopropylsilylethynyl (TIPS) pentacene¹²,¹³ and aza-pentacene],¹⁴,¹⁵ and covalently linked acenes;¹⁶,¹⁷ heteroacenes,¹⁸ carotenoids,¹⁹,²⁰ diphenylethyrine,²¹ perylenedimide (PDI),²² diketopyrrolopyrrole derivatives,²³ and diphenylisobenzofuran.²⁴ As is the case in these materials, efficient SF requires that the first triplet excitation energy [E(T₁)] is approximately half the energy of the first excited singlet state [E(S₁)] (i.e., ΔEₕ₅ = E(S₁) − 2 × E(T₁) ≈ 0) for the conservation of energy.¹ In addition to the optimization of the relative energies of excited states, the electronic couplings between neighboring molecules in the solid state are an important consideration in the design of materials for rapid and efficient SF.

A key (but difficult to observe) intermediate in the SF mechanism is the multiexciton (TT) state, a correlated triplet pair at approximately 2 × E(T₁) that facilitates a spin-allowed (thus, highly rapid and efficient) conversion from a spin-singlet exciton into two spin-triplet excitons.²⁵⁻²⁸ The magnitude of the coupling between the initial S₁ and TT determines whether the SF mechanism occurs directly as a two-electron process or as consecutive one-electron processes mediated through higher-lying charge-transfer (CT) states.²⁹⁻³¹

Two-electron couplings have been noted to play a role in model dimers of PDI in displaced cofacial packings with an interplanar distance of 3.5 Å; such dimers have a significant overlap of the molecular backbones, and thus, the potential for much larger one- and two-electron couplings.³²,³³ In contrast,
there is general agreement in the literature on the mechanism of intermolecular SF that for most materials the CT states play a critical role in mediating the coupling between the singlet state (populated upon photon absorption) and the TT state.29−31,34,35 Several theoretical investigations on crystalline pentacene have found a significant degree of CT character in the S1 state, which could facilitate the SF process.29−31,36,37 Large electronic couplings between the CT and TT states (~100 meV)29,30,34,35 effectively increase the strength of the S1-TT coupling, a feature rationalizing the fast formation of the TT state observed experimentally for crystalline pentacene.38,39 A recent joint theoretical and experimental study of several acenes and acene derivatives with different crystalline packings indicated that the SF rates in these materials vary by up to 2 to 3 orders of magnitude, an effect related to the degree of coupling between the neighboring molecules and the CT character in the S1 state.40 For nanoparticles of pentacene derivatives with various side-group substitutions, an increasing CT component in the S1 state was linked to a large exciton delocalization that facilitated efficient SF in these materials.41 The sensitivity of the degree of CT character in the excited state and its dependence on the molecular orientation and packing have been underscored in a recent study of covalently constrained terylenediimide (TDI) dimers; it was found that SF was promoted for specific displaced cofacial configurations because of efficient mixing of local and CT states.42 We note that the CT-mediated SF mechanism has motivated the design of oligomers and polymers with separate electron-rich (donor) and electron-poor (acceptor) segments that have a significant degree of CT character in the excited state and undergo efficient intramolecular SF.53,54 In this contribution, we examine the interplay between the molecular conformations and packings and the coupling of the S1 and CT states on the SF rates in rubrene and several rubrene derivatives.

Recently, rubrene, a tetrphenyl tetracene derivative, has been the focus of many spectroscopy studies to determine whether it sustains SF.45−51 In fact, SF was determined to be the dominant decay channel of the singlet excited state in rubrene single crystals on the picosecond time scale,48,51−53 with the SF process expected to be slightly unfavorable due to an \( \Delta E_{SF} \) value of −0.07 eV (as determined from the singlet energy \( E(S_1) \)) of 2.21 eV, measured from the fluorescence maximum for crystalline rubrene,54 and the adiabatic triplet energy \( E(T_1) \) value of 1.14 eV). A different picture is obtained for the SF driving force in crystalline rubrene when the vertical \( E(S_1) \) energy of 2.32 eV is considered, which leads to a \( \Delta E_{SF} \) value of +0.04 eV.55−57

A large range of SF time scales in tetracene (10−100 ps) have been reported depending on the media.58,59 In disordered films of the tetracene derivative 5,12-diphenyltetracene (DPT), whose crystal structure shows \( \pi \)-stacking similar to rubrene, a triplet yield of 122% has been measured with two time scales of 1 and 100 ps.13 For amorphous rubrene films, a much slower SF time scale of about 200 ps has been observed compared to the ps time scale of SF in rubrene single crystals.47,54,61

In order to elucidate the impact that the interplay between packing and electronic coupling has on SF, we investigate the relative excited-state energies for a series of rubrene derivatives that have been recently synthesized62 and compare them to experimentally known SF materials (e.g., pentacene, tetracene, DPT), see Figure 1. It is useful to recall that rubrene is a benchmark material in terms of high charge carrier mobility for an organic semiconductor;63 this is due in part to the very large intermolecular couplings between the highest occupied molecular orbitals (HOMO), which we define as \( f_{BB} \) on the order of 100 meV between neighboring \( \pi \)-stacked molecules in the single crystal.64,65 Key to the understanding gained in this work, the recently published rubrene derivatives show a large variation in the intermolecular electronic couplings due to the loss of the \( \pi \)-stacking of crystalline rubrene upon functionalization.66 Therefore, these materials provide an ideal platform to analyze the interplay between the relative energies of \( E(S_1) \) versus \( 2 \times E(T_1) \), \( E(CT) \), and the electronic couplings in the solid state.

We start with an analysis of the single-molecule state energy matching condition for SF of \( \Delta E_{32} \approx 0 \), which is an energetic criterion essential for the conservation of energy.1 We then extend our study to understand the bulk crystalline and amorphous packings of the molecules of interest using molecular dynamics (MD) simulations and compare with experimental results. The resulting bulk packing and orientations within the amorphous phase are further explored to quantify the impact of intermolecular orientations on the ability of these materials to undergo SF.

**METHODOLOGY**

Neutral ground-state optimizations were carried out with Gaussian 09 using the long-range corrected density functional theory (DFT) functional \( \omega B97^{26} \) and the cc-pVDZ basis set. The vibrational frequencies of the optimized geometries were analyzed to ensure a minimum had been reached. The range-separation parameter of \( \omega B97 \) was tuned self-consistently using the IP-tuning procedure by minimizing the difference between the highest occupied orbital

![Figure 1. Molecular structures of the systems considered in this study: tetracene (I); 5,12-diphenyltetracene (II); 5,6,11,12-tetraphenyltetracene (rubrene, 1); and rubrene derivatives (2–7).](image)
The relative energy difference between the planar and twisted geometries ($\Delta E$) is also provided. All energy values are in electronVolts, and the dihedral angle, $\theta$, values are in degrees. 76 Exp. rubrene $S_1 = 2.35$ eV (solution)45,95 and $S_1 = 2.36$ eV (rubrene dispersed in a polymer matrix).92 Exp. $T_1 = 1.14–1.15$ and 1.04–1.05 eV (solution).45,47,93–95 Exp. tetracene $S_1 = 2.63$ eV (solution); $T_1 = 1.28–1.30$ and 1.35 (solution) and 1.25 eV (thin film).94–96 Exp. DPT $S_1 = 2.4$ eV (thin film).13 Exp. pentacene $S_1 = 2.19–2.28$ eV (frozen matrix)36 and 2.31 eV (gas phase).97 $T_1 = 0.86$ eV (crystalline)95 and 0.95 eV (solution).97

Table 1. Comparison of IP-Tuned oB97/cc-pVdz Optimized aT 1 and Vertical vS 1 Excitation Energies for the Planar and Twisted Gas-Phase Geometries

<table>
<thead>
<tr>
<th>system</th>
<th>$\Delta E$</th>
<th>$\theta$</th>
<th>$\alpha_{T1}$</th>
<th>$\nu_{S1}$</th>
<th>$E(S_1) - 2\times E(T_1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>rubrene</td>
<td>+0.12</td>
<td>0</td>
<td>1.11$^b$</td>
<td>2.34$^b$</td>
<td>+0.12</td>
</tr>
<tr>
<td>2</td>
<td>+0.12</td>
<td>0</td>
<td>1.11</td>
<td>2.32</td>
<td>+0.10</td>
</tr>
<tr>
<td>3</td>
<td>+0.12</td>
<td>0</td>
<td>1.11</td>
<td>2.32</td>
<td>+0.10</td>
</tr>
<tr>
<td>4</td>
<td>+0.12</td>
<td>0</td>
<td>1.11</td>
<td>2.29</td>
<td>+0.07</td>
</tr>
<tr>
<td>5</td>
<td>+0.13</td>
<td>0</td>
<td>1.07</td>
<td>2.31</td>
<td>+0.17</td>
</tr>
<tr>
<td>6</td>
<td>+0.11</td>
<td>0</td>
<td>1.11</td>
<td>2.34</td>
<td>+0.12</td>
</tr>
<tr>
<td>7</td>
<td>+0.11</td>
<td>0</td>
<td>1.12</td>
<td>2.34</td>
<td>+0.10</td>
</tr>
<tr>
<td>tetracene</td>
<td>−</td>
<td>0</td>
<td>1.29$^c$</td>
<td>2.75$^c$</td>
<td>+0.17</td>
</tr>
<tr>
<td>DPT</td>
<td>−</td>
<td>11.0</td>
<td>1.23</td>
<td>2.54$^d$</td>
<td>+0.08</td>
</tr>
<tr>
<td>pentacene</td>
<td>−</td>
<td>0.00</td>
<td>0.88$^e$</td>
<td>2.20$^e$</td>
<td>+0.44</td>
</tr>
</tbody>
</table>

The tuned values are given in Table S1.

“Tuning” the intermolecular electronic couplings renders the computational model of the S 1 state electronic couplings based on the wave function overlap between the molecular orbitals and the possible role of symmetry and coherence effects on SF, they provide reasonable, approximate couplings for disordered systems with localized excitations. Similar to previous studies, we also ignore the direct two-electron couplings that are negligible in comparison to the one-electron couplings. Although the π-stacked rubrene derivatives have large electronic couplings from significant overlap of the HOMO and LUMO orbitals, the twisted rubrene derivatives show negligible couplings and are therefore expected to have vanishing direct two-electron couplings. The two-electron couplings in crystalline rubrene have been previously reported to be negligible for the π-stacked material (0.0 meV).4,75 as a result of symmetry; however, closely packed materials where one-electron couplings can have large fluctuations with slight displacements are instances where the two-electron couplings might be important.34,35

It should be noted that the IP-tuning procedure used here effectively changes the amount of Hartree–Fock exchange in the functional, which affects the magnitude of the computed couplings and could lead to somewhat inconsistent values.76 Therefore, the semiempirical ZINDO method is used instead to compute the electronic couplings based on the wave function overlap between the frontier orbitals.77

To gain understanding of the solid-state packing and to compare with available experimental data, MD simulations are performed for distinct amorphous and crystalline conditions using the OPLS-AA force-field parameters4,79 with the GROMACS 4.54,80,81 package. In all simulations, the focus is on establishing the connection between packing and the magnitude of the electronic couplings. Therefore, the dihedral angle between the substituent phenyl groups and the tetracene backbone in 5,12-diphenyl tetracene (DPT) and rubrene (I) are modeled using the recently developed parameters within the OPLS-AA force-field.45 Amorphous bulk structures are generated by randomly placing 1000 [500] molecules for tetracene [DPT, rubrene, and rubrene derivatives] in a large simulation box at densities corresponding to less than 0.1 g/cm$^3$. This is followed by 1 ns of simulation in NVT [constant number of particles (N), volume (V), and temperature (T)] ensemble at 1000 K. Consequently, we perform simulations in the NPT ensemble until the density equilibrates for at least 2 ns; only the last 2 ns of the simulation trajectories after the density equilibrations are then used to compute the relevant structural properties. In this study, we try to gain an understanding of the structural differences between the acenes in the amorphous versus crystalline regions. However, our procedure to simulate amorphous bulk systems neglects the interfacial effects in the first few molecular layers observed experimentally for deposited thin films.35 Simulations of the periodic rubrene crystal35 were also performed with 600 molecules in a box of 7.99 $\times$ 7.14 $\times$ 7.11 nm$^3$ in order to compare the intramolecular twist of the backbone and intermolecular orientation for the crystalline structure with amorphous packings. Gas-phase MD simulations predominantly yield a planar backbone for tetracene and a twisted backbone for rubrene, which is consistent with the results from DFT.32,85–88

Semiempirical ZINDO electronic-structure calculations were used to compute the electronic couplings between the frontier orbitals on all of the dimers separated by a center of mass distance of less than 1.0 nm and extracted from five snapshots separated by 100 ps in the MD trajectory at 300 K. The averages for the electronic couplings are discussed rather than the probability distributions because, as proposed recently, strong couplings between a few dimers can initiate the SF process by acting as "hot-spots".13,89

Results and Discussion

1. Single-Molecule Excited-State Energies. We begin with a discussion of the computed energy levels for the isolated molecules in order to understand the energy difference in the optimized (i.e., adiabatic) aT 1 states (computed as the difference between the optimized ground state and triplet state with tuned oB97/cc-pVdz) and vertical vS 1 states (computed with TD-DFT at the same level of theory), see Table 1.
A key aspect when comparing the time scales of SF measured for rubrene in crystalline and amorphous phases is the effect of the twisted backbone on \( E(S_1) \) and \( E(T_T) \). The twisted-backbone rubrene has been determined to be the minimum energy geometry in the gas phase and is also the preferential configuration in amorphous films.\(^{86-88}\) while the backbone is planar in crystalline rubrene as a result of noncovalent interactions.\(^{88}\) The optimized-gas phase geometries have a backbone dihedral angle of \(<40^\circ\) in the rubrene derivatives; this value corresponds to the dihedral angle defined by the four atoms in the two C–C bonds on the edge of the tetracene backbone (Figure S1) (a negligible twist of 11° was computed for DPT). The planar ground-state energy \([\text{pVDZ computed} \times 1\text{ excitation energies}] = 2.20 \text{ eV}\) compares well with the experimental values (2.35/2.36 eV). A energy for the isolated (twisted) rubrene structure is 2.25 eV molecule energy levels discussed above, the energy difference between the \( E(S_0) \) for rubrene is ca. +0.1 eV higher than the twisted geometry. Therefore, it is useful to compute the optimized \( S_0 \) and \( T_T \) and the vertical TD-DFT derived \( E(S_1) \) in both twisted and planar conformations.

The experimental \( S_1 \) state energy of the isolated molecule is taken from the reported absorption peak of 2.35 eV (solution)\(^{85,86}\) and 2.36 eV (for rubrene dispersed in a polymer matrix).\(^{85}\) The computed vertical single-molecule \( S_1 \) (\( vS_1 \)) energy for the isolated (twisted) rubrene structure is 2.25 eV from TD-DFT using the IP-tuned \( \omega B97 \) functional, which compares well with the experimental values (2.35/2.36 eV).\(^{87}\) A good agreement is also found between the IP-tuned \( \omega B97/\text{cc-pVDZ} \) computed \( vS_1 \) excitation energies of 2.20 eV (pentacene), 2.75 eV (tetracene), and 2.54 eV (DPT) and the experimental \( vS_1 \) values of 2.19–2.31 eV (pentacene)\(^{90,91}\), 2.63 eV (tetracene), and 2.4 eV (DPT).\(^{13}\)

If we consider the computed \( vS_1 \) energies, all rubrene derivatives would possess a positive value for \( E(S_1) - 2 \times E(T_T) \), which indicates that the SF process should be favorable (Table 1). However, a difference on the order of 0.2 eV between the \( E(S_1) \) values computed at the relaxed (adiabatic) and vertical TD-DFT level is calculated for the rubrene derivatives studied here (see Table S2). Taking the relaxed (optimized) \( aS_1 \) energies into account leads to a qualitatively different picture; for example, applying the \( E(S_1) - 2 \times E(T_T) \) equation for the \( aS_1 \) state yields a slightly negative value \( (\Delta E_{SF} = \text{ca. } -0.1 \text{ eV}) \) for the twisted rubrene conformation, which indicates that the process is slightly unfavorable (Table S2).\(^{85,86,92}\)

Many of the materials investigated here show a \( \Delta E_{SF} \) value similar to that in rubrene, and molecule \( S \) provides the largest positive value \( \Delta E_{SF} = +0.17 \text{ eV} \), which is comparable to tetracene. The solid-state couplings and energies that are important for SF are discussed below to better understand how SF will proceed in very different packing structures.

2. Crystalline Properties. As mentioned above, the change in the electronic couplings for molecules in the solid state has been used to rationalize the varying SF rates seen for different polymorphs, which indicates that orientation and intermolecular distance can significantly influence the SF dynamics.\(^{23,98}\)

An additional consideration is the impact that the solid-state packing has on the key excited-state energies for the SF mechanism: \( E(T_T) \), \( E(S_1) \), \( E(CT) \), and \( E(T_T) \). In the crystalline structure, analogous to the analysis of single molecule energy levels discussed above, the energy difference between the \( S_1 \) and \( TT \) states \( (\Delta E_{S1,T_T}) \) gives an indication of whether the process is energetically favorable, while the energy difference between the \( S_1 \) and \( CT \) states \( (\Delta E_{S1,CT}) \) is an important consideration for the overall CT-mediated superexchange SF mechanism.\(^{29-31,34} \) In particular, the mixing of singlet and charge transfer states is determined by the strength of the electronic coupling and energy difference of the excited states, which can be a determining factor in mediation SF. Indeed, the large admixture of charge-transfer character in the lowest excited state has been identified as key to the observed rapid SF in crystalline pentacene.\(^{29-31,34-37}\) The increased charge-transfer component in the lowest excited states of crystalline pentacene leads to a large stabilization of the \( S_1 \) state energy in going from the single-molecule to the crystal.

For the crystalline phase, the 0–0 vertical transition has been experimentally measured as 2.32 eV for the \( S_1 \) state in the orthorhombic crystalline rubrene structure,\(^{55-57} \) which is predicted accurately by GW-BSE calculations resulting in \( S_1 \) values of 2.28\(^{90} \) and 2.32 eV.\(^{100} \) In contrast to pentacene, these bulk values are only slightly shifted from the experimentally measured single-molecule \( S_1 \) values of 2.35–2.36 eV.\(^{55,56,92}\) A smaller bathochromic shift between the lowest optical absorption for rubrene single crystal compared to the thin film points to lower degree of exciton delocalization in rubrene versus pentacene. We note that that the SF process is measured to occur on a picosecond time scale in rubrene single crystals\(^{55,51,52} \) which is comparable to the time scale of SF in tetracene (10–100 ps).\(^{83,58,59} \) SF occurs much faster in pentacene (80–110 fs).\(^{25,101-103} \) In comparison, SF in amorphous rubrene films has been reported to occur in ~200 ps based fluorescence decay.\(^{30} \) Therefore, rubrene and rubrene derivatives offer a way to examine the role of couplings and crystalline excited-state energies in SF because these materials display very different solid-state packings that lead to a large variation in intermolecular electronic couplings.\(^{62,85}\)

In order to rationalize the large differences in the SF rates found for these systems, we will now examine the bulk properties to further understand the nature and couplings of the excited states. We begin with a comparison of the computed couplings and excited-state energies for representative dimers of rubrene and rubrene derivatives 2–7 with respect to pentacene and tetracene, which are benchmark SF materials, and DPT, which also displays \( \pi \)-stacking in the solid state.

a. Crystalline Electronic Couplings. For pentacene, we recall that the large couplings of \( \sim 100 \text{ meV} \) computed for \( t_{S1,CT} \) and \( t_{CT,TT} \) between the intermediate CT and TT states are responsible for the fast formation of the TT state.\(^{39} \) The large \( t_{S1,CT} \) and \( t_{CT,TT} \) couplings in pentacene result from the large and nearly equivalent \( t_{H/H} \) and \( t_{H/L} \) orbital couplings \( \sim 100 \text{ meV} \). We note that the ZINDO-computed \( t_{H/H}/t_{L/L} \) \( (t_{H/L}) \) values of 63/66 [53/60] meV (see Table S3) reported here for pentacene are about half the magnitude of what is reported in refs 30 and 34 because of the use of different methodologies; such differences are not surprising when considering that the computed couplings are strongly dependent on the components of the method, such as the amount of HF exchange in the density functional.\(^{1}\)

For rubrene, large intermolecular couplings for the \( \pi \)-stacking motif lead to a significant dispersion in the conduction and valence bands. Therefore, the \( t_{S1,CT} \) coupling for rubrene (67 meV, see Table 2) is equivalent to that of pentacene (65 meV) because of the very large \( t_{H/H} \) couplings in rubrene (88 meV, see Table S3). However, while the \( t_{CT,TT} \) coupling in pentacene is still large (57 meV), a vanishing value is computed for rubrene because the \( t_{H/L} \) and \( t_{L/L} \) couplings are zero due to orbital symmetry.\(^{77} \) Even though we observe negligible \( t_{CT,TT} \) in rubrene, SF in crystalline rubrene has been proposed to occur
from an increased $t_{\text{CT-}TT}$ as a result of vibronic coupling, which has been used to rationalize the large differences for triplet formation in the picosecond and femtosecond time scales between rubrene and pentacene, respectively.\textsuperscript{75} We note that vibronic coupling is not explicitly considered in the present study, though the classical MD simulations allow sampling part of the nuclear configurational space.

For 5, 6, and 7, the tetracene core is planar and the π-stacking packing motif of rubrene is maintained and an increase in wave function overlap is achieved through additional noncovalent interactions provided by functionalization,\textsuperscript{85-87} which leads to large $t_{\text{s-}CT}$ couplings ranging from 69 to 100 meV that are greater than the values computed for rubrene (67 meV), pentacene (65 meV), and tetracene (58 meV), and nearly equivalent to that in DPT (83 meV) (see Table 2). However, similar to rubrene, negligible $t_{\text{CT-}TT}$ values are also found for 5, 6, and 7 because of the small $t_{\text{HL}}$ and $t_{\text{LH}}$ couplings for the π-stacking configuration.

In contrast to rubrene, 5, 6, and 7, the molecular backbone is twisted in the crystalline packing for 2, 3, and 4 and is in a way similar to that of the isolated molecule (≈40°).\textsuperscript{62,83} This feature disrupts the π-stacking motif found in crystalline rubrene and results in very small electronic couplings.\textsuperscript{85,104} For rubrene derivatives 2, 3, and 4, a significant decrease in the magnitude of $t_{\text{HL}}$ and $t_{\text{LL}}$ (0.1–14 meV, Table S3) is observed relative to rubrene, 5, 6, and 7, which leads to small $t_{\text{s-}CT}$ couplings ranging from 0–12 meV. A very small $t_{\text{CT-}TT}$ is also computed for 3 and 4, because of the small $t_{\text{HL}}$ and $t_{\text{LH}}$ couplings (0.5–3 meV, Table S3); however, in the case of 2, modest $t_{\text{HL}}$ and $t_{\text{LH}}$ couplings are obtained (18 and 5 meV, Table S3) that are comparable to DPT (12 meV), leading to $t_{\text{CT-}TT}$ couplings of 13 and 12 meV for 2 and DPT, respectively. We recall that based on the vertical (adiabatic) estimate of $v_{\text{s}}$ (at $T_T$) for the single molecule, the $E(S_1) = 2 - 2E(T_T)$ values range $+0.07$ to $+0.10$ eV for 2, 3, and 4, indicating that these twisted rubrene derivatives represent a good testbed to address whether such relatively small couplings are sufficient for SF to occur when the single-molecule energy levels point to a favorable process. Thus, the rubrene derivatives examined here indeed offer a good platform for understanding the role and magnitude of couplings in the SF process because of the broad distribution of couplings evaluated for the crystalline packings of these materials, while the single-molecule energy levels are largely consistent.

b. **Crystalline Excited-State Energies.** For the crystalline rubrene derivatives, the $S_1$ and CT states were computed using TD-DFT at the IP-tuned oB97/cc-pVDZ level for the dimers that display the largest couplings in the crystal structure. In this work, we focus on the analysis of the TD-DFT adiabatic electronic states for dimer configurations. This approach differs from several previous computational studies that employed diabatic states to investigate the energies of local and CT excitonic states and the couplings among these states. The interested reader can find in the Supporting Information pages S8–S12 a discussion of our results in the context of these previous computational examinations.

Turning now to a discussion of the $\Delta E_{S_1-CT}$ values for rubrene and rubrene derivatives, as opposed to the $\Delta E_{S_1-CT}$ value of +0.2 (+0.4) eV for crystalline pentacene [tetracene], the CT state is nearly degenerate with the $S_1$ state ($\Delta E_{S_1-CT} < 0.1$ eV) for rubrene, 5, 6, and 7, underlying that the π-stacking cofacial crystal structure leads to a large stabilization of the CT state. This result is consistent with previously reported GW-BSE calculations for crystalline rubrene that pointed to a significant CT character in the $S_1$.\textsuperscript{99,100} For the rubrene derivatives 2, 3, and 4, which display a loss of the π-stacking structure, the CT state ranges from 0.5 to 1.2 eV higher in energy than the $S_1$ state, which shows that the CT-mediated SF process should be significantly reduced in the twisted rubrene derivatives.

Next, we turn our attention to the energy separation between the triplet and singlet excited states in the solid state ($\Delta E_{S_1-CT}$). We note that the singlet-spin $^3\text{TT}$ states are difficult to calculate because of the double-excitation nature of these states and typically require multireference methods.\textsuperscript{34,75,105} Instead, the $^3\text{TT}$ energies are approximated as twice the single-molecule $T_1$ energies reported in Table 1 [i.e., $2\times E(T_1) = E(T_{\text{TT}})$]. The use of the single-molecule $E(T_1)$ is valid within the assumption that the crystalline triplet exciton is strongly localized.

Starting with crystalline pentacene, a positive value of $\Delta E_{S_1-CT} = +0.3$ eV indicates a favorable process and the energy difference should result in a larger driving force than for tetracene ($+0.14$ eV). Comparing rubrene with the rubrene derivatives, the substitution moiety has little effect on the crystalline excited-state energies, given by a range from +0.1 to +0.2 eV for $\Delta E_{S_1-CT}$, which is similar to that computed for the single-molecule $S_1$ energies. The positive and relatively large $\Delta E_{S_1-CT}$ values highlight that these materials are comparable to pentacene and tetracene in terms of the driving force to undergo SF.

Up to this point, a very small energy separation of the $S_1$ and CT state ($\Delta E_{S_1-CT}$) and large $t_{\text{s-}CT}$ values but vanishing $t_{\text{CT-}TT}$ values have been computed for the π-stacked materials (i.e., DPT, rubrene, and rubrene derivatives 5, 6, and 7) in the solid state. These results point out that vibronic coupling should facilitate SF in these materials and proceed on a similar time scale as in crystalline rubrene.\textsuperscript{5} This is in

### Table 2. TD-DFT Calculated Vertical Local Excitation ($v_{\text{S}_1}$) and Charge Transfer ($v_{\text{CT}}$) States for the Strongest-Coupled Dimers Taken from the Crystal Structure, Compared with TT\textsuperscript{d} Energies\textsuperscript{b}

<table>
<thead>
<tr>
<th>crystal</th>
<th>$v_{\text{S}_1}$</th>
<th>$v_{\text{CT}}$</th>
<th>$T_T$</th>
<th>$t_{\text{s-}CT}$</th>
<th>$t_{\text{CT-}TT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>rubrene</td>
<td>2.33\textsuperscript{c}</td>
<td>2.34</td>
<td>2.22</td>
<td>0.067</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>2.28</td>
<td>2.79</td>
<td>2.12\textsuperscript{c}</td>
<td>0.012</td>
<td>0.013</td>
</tr>
<tr>
<td>3</td>
<td>2.28</td>
<td>3.41</td>
<td>2.12\textsuperscript{c}</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>4</td>
<td>2.24</td>
<td>3.20</td>
<td>2.10\textsuperscript{c}</td>
<td>0.002</td>
<td>0.003</td>
</tr>
<tr>
<td>5</td>
<td>2.35</td>
<td>2.39</td>
<td>1.46\textsuperscript{c}</td>
<td>0.100</td>
<td>0.00</td>
</tr>
<tr>
<td>6</td>
<td>2.35</td>
<td>2.38</td>
<td>2.22\textsuperscript{c}</td>
<td>0.069</td>
<td>0.00</td>
</tr>
<tr>
<td>7</td>
<td>2.35</td>
<td>2.40</td>
<td>2.24\textsuperscript{c}</td>
<td>0.091</td>
<td>0.00</td>
</tr>
<tr>
<td>tetracene</td>
<td>2.72\textsuperscript{d}</td>
<td>3.11</td>
<td>2.58</td>
<td>0.058</td>
<td>0.040</td>
</tr>
<tr>
<td>DPT</td>
<td>2.24\textsuperscript{e}</td>
<td>2.49</td>
<td>2.46</td>
<td>0.083</td>
<td>0.012</td>
</tr>
<tr>
<td>pentacene</td>
<td>2.09\textsuperscript{f}</td>
<td>2.30</td>
<td>1.76</td>
<td>0.065</td>
<td>0.057</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Estimated as 2$T_T$, of the Single Molecule. \textsuperscript{b}Absolute values for the ZINDO-computed state couplings are also reported. All values are in eV.\textsuperscript{c} Exp. single-crystal rubrene: $S_1 = 2.21$ (em.) and 2.32 (abs.) eV.\textsuperscript{d} Calc. GW-BSE $S_1 = 2.28$ eV\textsuperscript{100} and $S_1 = 2.32$ eV.\textsuperscript{100} \textsuperscript{d}Exp. single-crystal tetracene: $S_1 = 2.34$ (em.)\textsuperscript{106} and $S_1 = 2.32$ (abs.) eV.\textsuperscript{106} \textsuperscript{e}Exp. thin-film DPT: $S_1 = 2.4$ eV.\textsuperscript{13}\textsuperscript{f}Exp. single-crystal pentacene: $S_1 = 1.8$ eV.\textsuperscript{100} $\Delta T_1$ energy is computed at the optimized twisted geometry.\textsuperscript{d} $T_{1}$ energy is computed at the planar geometry.
contrast to what is evaluated for crystalline pentacene and tetracene, which have large and nearly equivalent $t_{S_1-CT}$ and $t_{CT-TT}$ couplings but larger values for $\Delta E_{S_1-CT}$ compared with $\pi$-stacking materials.

For 2, 3, and 4, a loss of the $\pi$-stacking in rubrene may have important implications for SF because of the large $\Delta E_{S_1-CT}$ energy in the range of 0.5–1.2 eV and small intermolecular electronic couplings. These rubrene derivatives are intriguing because they display the same geometry as the isolated or amorphous rubrene derivatives, where the nonplanar geometry of the tetracene backbone should be prevalent. Therefore, the amorphous bulk phase is now examined to further understand the experimental results indicating that amorphous rubrene undergoes temperature-dependent SF.47,60

3. Amorphous Phase Properties. In addition to understanding the couplings of the rubrene derivatives in the crystal structure, molecular dynamics (MD) simulations (see the Methodology section for details) were employed to model the bulk amorphous materials in order to better understand the packing for tetracene, rubrene, and DPT, which all experimentally show SF in thin films.13,47,58,109,110 The $t_{S_1-CT}$ and $t_{CT-TT}$ distributions are summarized as contour plots in Figure 2 and Figure 3 and show the absolute average of the coupling as a function of distance and orientation within the dimers; the angle reported here is computed between the vectors along the vertical axis of the two tetracene backbones used for the electronic-couplings calculations. The color code is reported in the middle panels in units of meV.

Figure 2. Average couplings computed from $t_{S_1-CT} = \sqrt{\frac{t_{HH}^2 + t_{LL}^2}{2}}$, where $t_{HH}$ and $t_{LL}$ are one-electron HOMO–HOMO and LUMO–LUMO couplings, respectively, in meV, as a function of distance and angle between neighboring molecules of (top left) amorphous tetracene, (top right) DPT, (middle left) rubrene, (bottom left) 4, (bottom right) 7, and (middle right) rubrene crystal. The angle reported here is computed between the vectors along the vertical axis of the two tetracene backbones used for the electronic-couplings calculations. The color code is reported in the middle panels in units of meV.

Figure 3. Average couplings computed from $t_{CT-TT} = \sqrt{\frac{t_{HL}^2 + t_{LH}^2}{2}}$, where $t_{HL}$ and $t_{LH}$ are one-electron HOMO–LUMO and LUMO–HOMO couplings, respectively, in meV, as a function of distance and angle between neighboring molecules of the (top left) amorphous tetracene, (top right) DPT, (middle left) rubrene, (bottom left) 4, (bottom right) 7, and (middle right) rubrene crystal. The angle reported here is computed between the vectors along the vertical axis of the two tetracene backbones used for the electronic-couplings calculations. The color code is reported in the middle panels in units of meV.

Interestingly, the peak at 0.5 nm decreases by a factor of 4 for DPT and disappears entirely for rubrene. However, DPT shows significant couplings for a few selected pairs that also adopt a crystalline packing; the largest computed couplings occur at ca. 0 and 180 deg and are related to cofacial stackings of the backbones. The 180 degree orientation corresponds to the crystal structure packing of the tetracene backbones stacking with the side phenyl groups oriented opposite each other (see the top-right panel in Figures 2 and 3). The fact that SF is observed experimentally in disordered films of DPT13 and tetracene47 suggests that the packing densities in these materials are sufficient to allow for SF. These results support the idea that
strongly coupled dimers act as “hot-spots” for the SF process.\textsuperscript{13,59} However, we attribute this result to an increase in the couplings to an increase in $t_{\text{CT-TT}}$ (ca. $< 75$ meV) for DPT compared to what is computed for the crystal (12 meV). Indeed, an initial SF rate was reported for DPT films that is comparable to tetracene films (two SF rates of ca. 1 and 100 ps were reported for DPT),\textsuperscript{13} which is consistent with the large couplings for DPT and tetracene.

For rubrene, the lack of a peak in the $g(r)$ of rubrene at $\sim 0.5$ nm (see Figure S5) in the amorphous film points to the absence of close neighbors because of the twisting in the backbone of rubrene, in contrast to tetracene and DPT, which maintain a planar backbone in the amorphous phase. Indeed, the nearest neighbors are at least $\sim 1$ nm apart, which leads to calculated $t_{S_1-\text{CT}}$ couplings in amorphous rubrene of at most ca. 25 meV, which is substantially smaller than the $t_{S_1-\text{CT}}$ value of 67 meV computed for crystalline rubrene. However, similar to DPT, an increase in $t_{\text{CT-TT}}$ (ca. $< 25$ meV) is seen for the amorphous material relative to the crystalline value (0 meV). For the functionalized rubrene derivatives 2–7, only minor changes based on the molecular packings are indicated by the computed $g(r)$ at 0.7 nm for rubrene, 4, and 7; however, the number of planar molecules present in the amorphous films increases for 4 and 7 compared to rubrene (Figure S6, top panel). Therefore, the magnitudes of $t_{S_1-\text{CT}}$ and $t_{\text{CT-TT}}$ are comparable to those observed in rubrene (bottom panels of Figures 2 and 3). While these rubrene derivatives have not been experimentally investigated for SF, thin films of 4 and 7 have been previously measured to have large exciton diffusion lengths that point to enhanced molecular order and electronic coupling over rubrene.\textsuperscript{113}

As a complementary approach to understanding the contour plots given in Figures 2 and 3, the electronic coordination number, which can be taken as an indicator of the strength of the electronic coupling with the nearest neighbor molecules. We define the electronic coordination number as the number of nearest neighbors that have electronic couplings lesser than or equal to a threshold electronic coupling (which is plotted on the x axis). For example, an electronic coordination of 5 at 10 meV means that there are at least 5 neighbors for each molecule with at least a 10 meV electronic coupling. For a threshold of 0 meV, both the coordination number and electronic coordination would be equal because only the neighbors up to a distance corresponding to the first valley in the RDF are considered for computing the electronic coupling. The largest electronic coordination for $t_{S_1-\text{CT}}$ is computed for tetracene, followed by crystalline rubrene and then amorphous DPT, which is consistent with the conclusions already discussed based on Figures 2 and 3 (see Figure S7 in the Supporting Information). For $t_{\text{CT-TT}}$, the largest electronic coordination is computed for crystalline tetracene followed by DPT. Amorphous rubrene, 4, and 7 all have slightly larger electronic coordination for $t_{\text{CT-TT}}$ than crystalline rubrene, which is consistent with the increase in electronic coupling computed in the amorphous phases. Therefore, these results underline that SF in thin films of DPT and rubrene occurs because of a net increase in the $t_{\text{CT-TT}}$ couplings in the amorphous phase, which are nonexistent in the crystalline phase. This result is in contrast to tetracene (and by extension we speculate that it will be similar in pentacene), which still retains a high-degree of crystalline-like packings in the thin films.

Finally, we turn to a discussion of the excited-state energies computed from ZINDO for amorphous tetracene, DPT, rubrene, 4, and 7, compared to crystalline rubrene. The distribution of the $S_1$ energies is much broader for the amorphous dimers than for the crystalline dimers (see Figure S8). To understand the distribution of the $S_1-\text{CT}$ energy gaps ($\Delta E_{S_1-\text{CT}}$) in amorphous tetracene, rubrene, 4, and 7, the average, maximum, and minimum values were computed using TD-DFT for a set of ca. 100 amorphous dimers randomly selected from an equilibrated trajectory (Table S7). The CT state was identified from an analysis of the Mulliken atomic charges of the excited state.

For amorphous tetracene, the minimum $\Delta E_{S_1-\text{CT}}$ value of $+0.3$ eV is similar to what is found for crystalline tetracene ($+0.4$ eV); however, the average $\Delta E_{S_1-\text{CT}}$ value of 0.9 eV is much larger, which potentially explains the large range of SF time scales measured for tetracene depending on the media (10–100 ps).\textsuperscript{38,58,59} For amorphous rubrene, the average of the $\Delta E_{S_1-\text{CT}}$ values is +1.2 eV [with a min. (max.) of +0.7 (+1.4) eV], which is significantly larger than the $\Delta E_{S_1-\text{CT}}$ value of 0.01 eV for crystalline rubrene. We assign the much longer SF time scales measured for amorphous rubrene films of ca. 200 ps\textsuperscript{50} compared to the measured picosecond time scale of SF in rubrene single crystals to this difference in the $S_1-\text{CT}$ gap.\textsuperscript{45,51,52}

We recall that for the crystalline rubrene derivatives, the $\Delta E_{S_1-\text{CT}}$ values range from a few meV [1, 5, 6, and 7] to ca. 0.5–1.2 eV [2, 3, and 4]. In contrast to the crystalline materials, the energy distributions of the amorphous packings of the two rubrene derivatives examined display comparable ranges: for amorphous 4, the avg. $\Delta E_{S_1-\text{CT}}$ value is +1.0 eV [min. (max.) $\Delta E_{S_1-\text{CT}} = +0.5 (+1.3)$ eV]; for amorphous 7, the avg. $\Delta E_{S_1-\text{CT}}$ value is +1.0 eV [min. (max.) $\Delta E_{S_1-\text{CT}} = +0.5 (+1.3)$ eV], see Table S7. Therefore, the SF rates in thin films of these materials should all display similar SF rates. We note that these $\Delta E_{S_1-\text{CT}}$ distributions do not account for the potential stabilization of the environment that would act to decrease the $S_1-\text{CT}$ energy gap.

\section*{Conclusions}

Six recently synthesized rubrene derivatives were investigated as potential SF materials and compared to tetracene, DPT, rubrene, and pentacene. All six rubrene derivatives examined here have comparable state energies to that of rubrene, with calculated $E(S_1) - 2 \times E(T_1)$ values ranging from +0.07 to +0.17 eV, indicating that SF should occur in all of these materials.

From an examination of the energy separation of the $S_1$, CT, and TT states and couplings between these states for select solid-state dimers, some conclusions can be made toward understanding the mechanistic details of CT-mediated SF: (1) the computed crystalline energy separation of $S_1$ and TT ($\Delta E_{S_1-\text{CT}}$) is similar in all of the rubrene derivatives and slightly more favorable than that of tetracene, indicating that the driving force provided by the relative energies of TT and $S_1$ would be similar in the solid state. (2) For all $\pi$-stacked rubrene derivatives (e.g., rubrene, 5, 6, and 7), while the $S_1$ and CT states are nearly degenerate (ca. < 0.1 eV) and the $t_{S_1-\text{CT}}$ couplings (67–100 meV) are large, which should result in rapid
SF, the $t_{\text{CT-}}$couplings are vanishingly small. Thus, SF should be facilitated by vibronic coupling in these materials, which is similar to what has been proposed for rubrene in order to rationalize the much slower experimental SF rates for rubrene compared to pentacene. (3) For those vibronic derivatives that do not display π-stacking in the solid state (2, 3, and 4), the CT energies range from ca. 0.5 to 1.2 eV higher than the $S_1$ energy and small $t_{\text{CT-}}$ and $t_{\text{CT-}}$ values are computed; SF should thus proceed inefficiently if these parameters indeed control the SF process as opposed to just the single molecule energy levels. (4) Crystalline 2, 3, and 4 are interesting cases because $t_{\text{CT-}}$ is on the order of 0.5−13 meV. Experimental validation of the SF rates in 2, 3, and 4 could help elucidate the exact role of these couplings compared with a large driving force of $E(S_1) - 2 \times E(T_1)$ ranging from +0.07 to +0.10 eV for SF efficiency. (5) Molecular dynamics (MD) simulations of the amorphous SF process as opposed to just the single molecule energy levels. (6) Also, the bulk packing properties of rubrene and its derivatives differ from those in DPT and tetracene thin films where large intermolecular couplings are found for pairs with specific orientations and do not occur with equal probability for all disordered sites.

The results discussed here underline that the comparison of SF in amorphous versus crystalline phases can prove to be a useful means to elucidate key aspects of the SF mechanism in these systems.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b04633.

Tuned-ω values for IP-tuned ωB97; optimized excited state TD-DFT calculations; orientation distributions for molecules in the amorphous MD simulations; amorphous and crystalline rubrene backbone distributions; radial distribution functions and coordination numbers from amorphous films; contour plots of various orbital couplings ($t_{\text{HH}}, t_{\text{HP}}, t_{\text{PP}}$ and $t_{\text{LH}}$); comparison of E(CT) using various methods; plots of excited-state distributions of $S_1$ ($S_2$) for monomer and dimers; and electronic coordination numbers based on $t_{\text{S-S}}$ and $t_{\text{CT-CT}}$ (PDF)

### AUTHOR INFORMATION

#### Corresponding Authors

*E-mail: sutton@fhi-berlin.mpg.de.*

*E-mail: jean-luc.bredas@chemistry.gatech.edu.

#### ORCID

Naga Rajesh Tummala: 0000-0001-9957-6330

Jean-Luc Brédas: 0000-0001-7278-4471

#### Present Address

*Department, Fritz Haber Institute of the Max Planck Society, Berlin 14195, Germany.

#### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by the National Science Foundation through the MRSEC Program under Award DMR-0819885 with computing resources provided by the CRIF Program under Award CHE-0946869. We thank Dr. Sukrit Mukhopadhyay for helpful discussions. D.B. is a FNRS Research Director.

## REFERENCES


(4) Nozik, A. J.; Ellingson, R. J.; Micie, O. I.; Blackburn, J. L.; Yu, P.; Murphy, J. E.; Beard, M. C.; Rumbles, G. In Unique Approaches to Solar Photon Conversion Based on Semiconductor Nanostructures and Novel Molecular Chromophores; Dynamics of Electron Relaxation, Interfacial Charge Transfer, and Carrier Multiplication, Twenty-Seventh DOE Solar Photochemistry Research Conference, Warrenton, Virginia, 2004; pp 63−64.


