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Competing Singlet Fission and Excimer Formation in Solid Fluorinated 1,3-Diphenylisobenzofurans

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ABSTRACT: Singlet fission (k_{SF}) and excimer formation (k_{EXC}) rate constants along with other photophysical properties of thin solid layers of 1,3-diphenylisobenzofuran and 11 of its fluorinated derivatives have been determined. The molecular properties of these compounds are similar, but their crystal packing varies widely. Most of them undergo singlet fission whereas excitation in others is trapped in excimers. The trend in rate constants k_{SF} agrees qualitatively with results of calculations by a simplified version of the frontier orbital model for a molecular pair. The main shortcoming of the model is discussed.



INTRODUCTION

Singlet fission $(SF)^{1-9}$ in an organic solid converts a singlet exciton into two triplet excitons and provides an opportunity^{10,11} to overcome the Shockley–Queisser limit¹² on the maximum efficiency of single-junction solar cells. So far, SF has only been shown to proceed with full efficiency in a small number of materials, most of them not stable enough for practical use, and many laboratories are engaged in a search for better ones. It is clear by now that the nature of the molecular chromophores and of their packing in the solid are both critically important for the yield of triplet excitons and that excimer formation can be a serious competitor to singlet fission.^{13,14} Presently, we focus on the effects of the packing.

Some experimental information on the general effects of crystal packing on the rate constant of SF (k_{SF}) and those of the equally important competing processes that codetermine triplet quantum yields has been provided by past observations on polymorphous crystalline compounds^{15–21} and on covalent dimers.²²⁻³¹ Design of efficient SF materials of either type is likely to benefit from results of a systematic examination of a series of closely related derivatives of a chromophore^{19,32,33} with nearly identical molecular photophysical properties but different crystal packing. We now compare the previously studied commercially available 1,3-diphenylisobenzofuran (1), which undergoes slightly endothermic SF,34-37 with its fluorinated derivatives 2-12 (Chart 1). The choice of the chromophore 1 is motivated both by the ease of synthesis of substituted isobenzofurans³⁸ and by the observation that SF triplet yields of the nearly identical polymorphs¹⁷ 1α and 1β differ strongly, promising a high sensitivity to packing. A

description of the synthesis and oxidation-reduction properties of all 12 compounds has been published.³⁹ Presently we report their crystal structures, photophysical properties in solution and in the solid state, and results of computation of SF rate constants. Some of the data for **2**, **10**, and **12** were described in a preliminary communication.⁴⁰

EXPERIMENTAL AND COMPUTATIONAL METHODS

Samples. Compounds 1–12 were available from prior work.³⁹ Other chemicals were used as obtained from the suppliers: toluene (Sigma-Aldrich spectroscopic grade), anthracene (Sigma-Aldrich Analytical Standard), tetraphenylporphyrin (Sigma-Aldrich >99%), anthanthrene (Sigma-Aldrich), ferrocene, zinc tetraphenylporphyrin, dibenzo[a,h]-pyrene (all three from Tokyo Chemical Industry >98%), and octaethylporphyrin (Tokyo Chemical Industry >93%).

X-ray Diffraction. Needles of **3** were grown from castor oil, while needles of **4** and **9** were grown from a solution in DMF and water. Thin plates of **6** were grown from DMF. These were twinned with single-crystalline domains roughly $5 \times 5 \times 5 \ \mu$ m in size. Crystallographic data for **3**, **4**, and **9** were collected on a Bruker APEX 2 diffractometer at Mo K α and

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Chart 1. 1,3-Diphenylisobenzofuran (1) and Its Fluorinated Derivatives (2-12)



100 K, while data for **6** were obtained at the NSF's ChemMatCARS Sector 15 Advanced Photon Source (APS) at Argonne National Laboratory on a crystal measuring just 5 \times 5 \times 5 μ m. Additional data for **3** and **4** were collected on a Bruker D8 VENTURE with Kappa Duo goniometer and PHOTON 100 CMOS detector. All single-crystal structures were solved by direct methods and refined by a full matrix least-squares approach on F^2 with hydrogen atoms fixed by a riding model. (Table S1).

Despite several attempts, 3 could not be obtained as a single crystal. High-resolution powder X-ray diffraction data were obtained at Argonne National Laboratory's Advanced Photon Source (APS) on the 11-BM (0.414176 Å, 298 K) beamline. Additional PXRD data were collected at APS on the 17-BM beamline (0.24119 Å, 289 K). Simulated annealing (TOPAS Academic V4) failed to provide a satisfactory solution.

Transient Spectroscopy in Solution. The rate of triplet energy transfer from 0.5 mM 1-12 sensitized with 0.5 mM anthracene to 20 μ M to 4 mM ferrocene was measured in a freeze-pump-thaw degassed toluene solution. The observed rate was a linear function of ferrocene concentration, and all slopes were determined at least twice from entirely independent measurements. The nanosecond-resolution instrument used was an EOS Fire transient absorption spectrometer (Ultrafast systems, Sarasota, FL) and a pump laser NT242 (Ekspla, Vilnius, Lithuania), with an OPO based system with 1 kHz repetition rate, tunable from 210 to 2600 nm. Pulse duration was 3-6 ns. The probe light source was a sub-nanosecond pulsed photonic crystal fiber based supercontinuum laser with a spectral range of 350-950 nm. The spectrometer used a linear array detector with a spectral resolution of 4 nm. The maximum time window was 400 μ s. Triplet energies of standards were obtained from the literature.41

Spectroscopy. Solution absorption spectra were measured with a Varian Cary 500 UV–vis–NIR spectrophotometer over the range of 200–600 nm. In order to account for reflectance and scattering in films, an integrating sphere attachment in an Agilent Cary 6000 UV–vis–NIR spectrophotometer was used to collect absorption spectra. Steady-state fluorescence measurements were conducted with a Horiba Yvon Model FL-1039/40 Fluorolog using a Jobin Yvon SPEX Instruments Spectrum One G35 CCD detector. The samples were typically

excited at 400 nm and spectra were collected in a detection range of 390-600 nm.

Thin solid layers were prepared by solution drop casting of a \sim 5 mg/mL solution in 50:50 chloroform and toluene. Drops of the solution were added to fill the 2.5 cm round sapphire substrate or microscope glass slide cut to a 2.5 cm square, and were subsequently allowed to dry in a N₂ glovebox. As is commonly found for drop-casting methods, films were not perfectly homogeneous and contained regions that were optically transparent and regions that were optically scattering. Films that contained few or no optically transparent regions were rejected and the films were recast. No thermal annealing was performed unless specifically indicated.

The thin layers were characterized by X-ray diffraction patterns, collected on a Rigaku DMAX 2500 diffractometer utilizing Cu K α ($\lambda = 1.54$ Å) radiation. After a thorough alignment procedure, scans of intensity (counts) as a function of 2θ angle ($5-30^{\circ}$) were collected and compared with the bulk crystal data. Although films deposited by thermal evaporation generally provide higher quality than those that are drop-cast, the DPIBF derivatives studied here have considerable vapor pressure, and material deposited on the walls of the chamber can contaminate subsequent thin film deposition attempts if the chamber is not extensively cleaned between depositions of different compounds. Some trial depositions were performed for a few of the compounds, and the results were qualitatively similar to those obtained with drop-cast films.

Ultrafast transient absorption measurements were performed on an Ultrafast Systems Helios/EOS setup as outlined in previous work.³⁶ In particular here, a CaF₂ crystal was used in order to generate the white light continuum probe (350-800 nm). This probe was split into two beams, one that passed through the sample to measure the excited-state absorption and one that was directed into the detector as a reference. The pump, with a spot size of about 500 μ m diameter, and probe beam (250 μ m diameter) were overlapped at the sample, and spectra were recorded at various pump-probe time delays dictated by the delay stage, which changes the path length of the probe. After passing through an optical chopper (500 Hz), the probe and reference were focused into fiber optic light guides and measured by matched photodiode arrays. For decay times longer than 5 ns, a continuum probe was generated using an electronically delayed Nd:YAG laser beam traversing a

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Figure 1. Crystal packing of 1-12.

photonic crystal fiber. The time resolution of this configuration is approximately 100 ps, with time delays to 400 μ s. The excitation beam and sample position remained unchanged for these extended scans. For films, low fluence excitation, typically <20 μ J/cm², was used to avoid singlet–singlet annihilation that can result in singlet decay kinetics that outpace singlet fission.

Mean values and standard deviations were obtained from measurement on several films (on each film, five measurements on different spots).

Computations. Reorganization energies λ were calculated according to the equation $[E(T_1,q(S_1)) + E(T_1,q(S_0)) 2E(T_1,q(T_1))]$,⁴² where *q* denotes the equilibrium geometry of the monomer in a particular state. Ground- and excited-state geometries were optimized in the ORCA⁴³ program suite with density functional theory (DFT) and time-dependent DFT (TD-DFT) with the TDA⁴⁴ using two different functionals for comparison. The $B3LYP^{45,46}$ functional was used with the Def2-TZVPP⁴⁷ basis set and Grimme's DFT-D3⁴⁸ dispersion correction. The RIJCOSX^{49,50} approximation for Coulomb and exchange integral evaluation, with the $Def2/J^{51}$ and Def2- $TZVPP/C^{52}$ auxiliary basis sets, was employed in all geometry optimizations but not in single-point evaluations. The PBE053 functional was also used with the Def2-TZVP54 basis set and the RIJCOSX approximation for Coulomb and exchange integral evaluation with the Def2/JK55 auxiliary basis. The Def2-TZVPD^{54,56} basis was used for single-point energy evaluations with analytic integral evaluation. Triplet excitation energies were calculated using the ΔSCF^{57} method. Singlet excitation energies were calculated by TD-DFT without the TDA. Frequency analysis was performed on all optimized geometries to ensure they were true minima. SIMPLE⁵⁸⁻⁶⁰ was used to calculate all singlet fission couplings, energies, and rate constants.

RESULTS

Solid Structures. 3.1.*i.* Crystals. X-ray diffraction analyses of single crystals of the two polymorphs of the parent, 1α and 1β ,¹⁷ and those of 2, 10, and 12^{40} have been published before. We have now obtained the single-crystal structures of the remaining members of the series 1-12 except for 3, where we were unable to grow a suitable single crystal (Tables S1 and S2, Figure 1, and Figures S1–S13). The high-resolution powder X-ray diffraction pattern of 3 exhibited disorder. While 2D motifs of $P2_1/c$ and $P2_1/n$ symmetry were obtained from simulated annealing (the former was chosen for the calculations below), a definitive structure solution eluded us.

The molecular structures of all these 1,3-diphenylisobenzofurans were very similar and the only significant difference was in the values of the twist angles of the two aryl substituents (Table S2). Results of DFT geometry optimization for an isolated molecule suggest that they should be about 20° when the aryl ortho positions carry hydrogens and about 40° when they carry fluorines. This is indeed observed except that in the former case the twist angles are frequently smaller, down to about 2° in **5**, and this is presumably due to crystal packing forces.

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In contrast to molecular structure, the crystal packing varies widely (Figure 1) and is discussed in the Supporting Information.

3.1.ii. Polycrystalline Thin Films. All films formed from solution drop-casting were found to possess significant crystallinity without thermal annealing. The reflections observed were well predicted from powder patterns calculated from the known crystal structures (Figure 2). The slight deviations may result from minor discrepancies between the bulk and thin-film phases and the presence of polymorph mixtures, but we have no strong indication that significant restructuring occurs in the films. Many of the expected lines are missing, making most of the diffractograms sparse and



Figure 2. X-ray diffractograms from thin films (dark lines) compared with predicted powder diffraction calculated from bulk crystal structures (thin lines, offset for clarity).

indicating significantly anisotropic orientation of the crystallites.

The effect of thermal annealing at 90 °C was examined with 1 (Figure S14A) and 2 (Figure S14B) and XRD revealed that in both cases it converted the α crystal form into the β form. This was obvious in the case of 1, where single-crystal structures and therefore also the expected XRD patterns of both forms are available.¹⁷ Since the single-crystal structures of 2α and 1α are nearly identical, as are the effects of annealing on their XRD patterns, there is little doubt that annealing converts 2α into 2β .

Solution Photophysics (Table 1). 3.2.*i. Ground-State* Absorption. We provide the normalized S_0 absorption and S_1 emission spectra of 1-12 in toluene solution (Figure 3),



Figure 3. Normalized absorption (solid) and emission (dashed) spectra of toluene solutions of 1-12. Peak molar absorption coefficients of the first band ($10^3 \text{ M}^{-1} \text{ cm}^{-1}$): 1, 16.97; 2, 18.66; 3, 17.02; 4, 19.03; 5, 18.67; 6, 20.74; 7, 19.57; 8, 22.11; 9, 20.55; 10, 20.13; 11, 20.39; 12, 22.75.

ordinary absorption spectra (Figure S15), and spectra in acetonitrile, which extend to higher energies (Figure S16). As the extent of fluorination increases, the first absorption peak shifts from ~24 500 cm⁻¹ in 1 to the red by 100–500 cm⁻¹. Only in the spectra of structures with fluorines in the ortho position of the aryl substituents is the first peak blue-shifted relative to 1, by ~1500 cm⁻¹ in 4 and 10 and by almost 3000 cm⁻¹ in 12. In Figure S17, the first singlet excitation energies $\Delta E(S_1)$ are compared with those calculated by the TD-DFT method. PBE0/def2-TZVPD//PBE0/def2-TZVPP tends to underestimate $\Delta E(S_1)$ while B3LYP/def2-TZVPP tends to overestimate it. The calculations do not reproduce the minor shifts, but they correctly account for the larger substituent

effects found with 4, 10, and 12, whose aryls are more strongly twisted.

As described in an earlier much more detailed study of parent 1,⁶¹ the spectral envelope of its ground-state absorption is much broader than that of its fluorescence and shows less vibrational structure. Similar broadening is found in all 12 compounds 1-12 and is the strongest in 12. It makes it difficult to read off the excitation energies accurately. In 1, the broadening of the absorption band was attributed to the presence of two distinct but easily interconverting low-energy ground-state conformers, with conrotatory or disrotatory phenyl ring twists.⁶² Their spectra were also obtained separately and are slightly but distinctly different. According to calculations, the twist is lost upon excitation to the S₁ state, in which the aryl rotation that interconverts the conformers is essentially barrier-free, such that they are no longer distinguishable and only a single species is emitting. We expect the situation to be similar in the fluorinated derivatives, whose fluorescence spectra all exhibit clear vibrational structure. Only in 12, where both aryl substituents carry fluorine atoms in the ortho positions, can one expect both conformers to remain well defined even in the S_1 state, but they apparently still equilibrate rapidly.

3.2.ii. S_1 Fluorescence (Table 1, Figure 3). In toluene solution, fluorescence is more structured than absorption, presumably because it occurs from an essentially planar single conformer (with the probable exception of 12), and the intensity ratio of the 0–0 to 0–1 bands in the vibrational envelope is now easier to discern. It is approximately 0.9 for most compounds, with significantly lower values (~0.7) for 6, 7, and 12, and a slightly higher value (1.0) for 9. The trend in peak fluorescence position through the series mirrors that found for the absorption peak. The Stokes shift is not easily determined because the lowest absorption bands are broad but generally falls in the range 500–800 cm⁻¹.

The fluorescence quantum yield is generally above 0.9 and is slightly lower only for the three compounds with more strongly twisted aryl substituents, **4**, **10**, and **12**. Fluorescence lifetime is around 5 ns except for **10** and **12**, where it is shorter by almost a factor of 2 (Figure S21). In addition to the lower quantum yield, this is attributable to a somewhat blue-shifted and stronger absorption.

3.2.iii. Transient Absorption (Table 1). The S_1 state is characterized by a strong absorption peak near 21 000 cm⁻¹, and in the case of 10 and 12, where its lifetime falls within the overlapping experimental time ranges of our transient absorption and fluorescence equipment, it was found to be equal to that of fluorescence (Figure S22). The T_1 state was produced by sensitization with anthracene and exhibits a sharp peak at ~22 000 cm⁻¹. Its lifetime exceeds 200 μ s (Figure S23).

3.2.iv. Triplet Energy. The method reported previously⁶² for the determination of the T₁ excitation energy of 1 was adopted to obtain triplet energies of 1–12 in toluene solution from the rates of energy transfer from their triplets to ferrocene as an acceptor (Table 1, Figure S18). The triplets were produced by sensitization with anthracene. In Figure S17 the observed triplet energies $\Delta E(T_1)$ are compared with energies calculated by DFT. Similarly as in the case of singlets, minor differences are not reproduced by the calculations, which, however, correctly account for the higher triplet energies found in 4, 10, and 12, in which one or both aryl substituents are more

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Table 1	. Photophy	sics in Toluer	ne Solution (Ene	rgy Units: 10 ³	$cm^{-1})$
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cmpd	$S_0 \rightarrow S_1^a$	$S_1 \rightarrow S_0^{\ b}$	$S_1 \rightarrow S_n^c$	$\Phi_{\mathrm{F}}^{}d}$	$ au_{ m F}/{ m ns}^{e}$	$T_1 \rightarrow T_n^{f,g}$	$S_0 \rightarrow T_1^h$	$E_{\rm SF}^{i}$
1 ⁶²	24.20 (22.75)	22.07	21.2	0.99	4.7	22.0	11.8	0.8
2	24.44 (22.80)	22.28	20.7	0.94	5.0	22.0	11.7	0.7
3	24.50 (22.82)	22.17	21.3	0.98	5.6	22.1	11.7	0.6
4	25.77 (23.86)	22.33	20.9	0.87	4.0	22.2	12.6	1.3
5	24.10 (22.50)	22.12	21.2	0.89	5.3	22.1	12.2	1.8
6	23.98 (22.30)	21.83	21.1	0.89	6.4	21.8	11.9	1.4
7	23.92 (22.22)	21.79	21.2	0.98	5.2	22.0	12.0	1.8
8	24.04 (22.40)	21.93	21.1	0.99	4.3	21.4	11.9	1.4
9	24.10 (23.32)	21.79	21.1	0.96	5.0	22.1	12.0	1.6
10	25.58 (23.80)	23.20	20.7	0.88	3.1	22.3	12.5	1.2
11	24.27 (22.57)	22.12	21.3	0.94	5.2	22.0	12.0	1.4
12	27.10 (25.00)	24.52	20.4	0.86	2.7	21.7	13.0	1.0

^aMaximum of the first absorption band. Error: ± 0.12 . In parentheses, intersection of normalized absorption and emission curves. ^bThe first fluorescence peak. Error: ± 0.12 . Excitation wavelength, 400 nm. ^cProminent band in S₁ absorption. Error: ± 0.5 . ^dFluorescence quantum yield. Error: ± 0.3 . Excitation wavelength, 400 nm. ^eFluorescence lifetime. Error: ± 0.1 . Excitation wavelength, 400 nm. ^fProminent band in triplet absorption (sensitized with anthracene). Error: ± 0.5 . ^gTriplet lifetime exceeds 200 μ s in all cases. ^hTriplet excitation energy. Error: ± 0.2 . ⁱSF endoergicity expected in the absence of intermolecular interactions (S₁ excitation energy from the intersection of absorption and emission curves).

strongly twisted. The B3LYP values are in better agreement with the observed $\Delta E(T_1)$ than the PBE0 values.

Based on properties of an isolated molecule alone, all 12 compounds fall into the category that is usually considered favorable for room-temperature SF. It is endoergic by less than $\sim 0.1 \text{ eV}$ in 1-3 and never significantly more than $\sim 0.2 \text{ eV}$. The three compounds with more strongly twisted aryl substituents, 4, 10, and 12, are among the most favorable.

Solid-State Photophysics. *3.3.i. Steady-State Absorption and Fluorescence.* The absorption spectra of films (Figure 4) contain broader features than those of solutions, at least in part due to intense light scattering that cannot be easily corrected for. This is most readily seen in the relatively featureless shape of the rise in absorption toward the highenergy side of the lowest absorption bands. The absorption onset is difficult to determine in many cases due to a tail of apparent absorption toward low energies. Despite these experimental complexities, some trends from solution clearly persist in films, including the significant blue shift for films of 4, **10**, and **12**. Significant deviations from solution trends include a red shift observed for the film of **3** and, to a lesser degree, **6**.

The fluorescence spectra (Figure 4) remain relatively sharp for many of the films. They often have a small Stokes shift and at least some discernible vibronic structure. However, compounds 3, 4, 5, 7, 9, and 12 emit a featureless broad strongly Stokes shifted band, which we attribute to excimer emission. The rise times are less than 150 ps, too short to be obtained with the resolution available in our fluorescence measurements, but they were determined below using transient absorption and are listed in Table 2. It is likely that weak excimer fluorescence contributes to at least some of the other emission spectra as well (e.g., in 12), but is hard to discern under the tail of stronger ordinary fluorescence. This would be compatible with the observation of biexponential and/or multiexponential decay kinetics at the emission peak (Table 2).

The film of 1β shows strong emission from S_1 but no indications of excimer emission, although we shall see below that in transient absorption an excimer is clearly present. It is possible that the film contains inclusions of 1α , which is responsible for the ordinary fluorescence and that the excimer formed in 1β itself is only weakly emissive.



Figure 4. Absorption (solid) and emission (dashed) spectra of thin solid films of 1-12. Excitation wavelength, 400 nm.

3.3.*ii.* Time-Gated Fluorescence. Figure 5 shows a decomposition of the fluorescence into early (up to 500 ps after the excitation pulse) and late (2-5 ns) emission and helps to distinguish between films that are SF vs excimer dominated. For most cases of the former, the emission profile is relatively narrow and structured, does not evolve significantly as delay time progresses, and is attributed to S₁ fluorescence (e.g., 1, 2, 10, 11). The kinetics reflect typical triplet-triplet annihilation and are dictated primarily by triplet diffusion and

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Table 2. Photoph	ysical Prop	rties of Thir	solid Films	(Energy Units:	$: 10^3 \text{ cm}^{-1})$)
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no.	$S_0 \rightarrow S_1^a$	$S_1 \rightarrow S_0^{\ b}$	$S_1 \rightarrow S_n^c$	$\Phi_{\mathrm{F}}^{}d}$	Φ_{T}^{e}	$ au_{\rm F}/{ m ns}~(\%)^f$	$k_{\rm SF}/{\rm ns}^{1g}$	$k_{\rm EXC}/{\rm n}{ m s}^{1}$ ^h	$\mathbf{T}_1 \to \mathbf{T}_n^{i}$
$1\alpha^{62}$	21.3	20.4	20.9	0.10	$1.4 \pm 0.25^{34,36}$	1.0 (52); 2.7 (42)	56 ± 6		21.5
$1\beta^{62}$	$20.7 \pm 0.3^{17,36}$	20.3	20.4	0.59	0.1 ± 0.05	1.3 (54); 3.3 (46)	10 ± 4	100 ± 20^{j}	20.8
2α	21.3	20.4	20.8	0.10	1.3 ± 0.15	1.0 (33); 2.8 (60)	50 ± 4		21.5
3	19.2	16.4	21.2	0.030	~0.3	0.9 (45); 1.8 (55)	10 ± 4	142 ± 18	21.8
4	21.4	18.1	20.8	< 0.03	<0.1	0.72 (52); 1.6 (48)		55 ± 9	
5	20.2	16.3	22.0	< 0.03	<0.1	0.74 (60); 2.2 (40)		26 ± 6	
6	19.3	19.3	20.3	0.04	k	0.4 (70); 2.0 (30)	76 ± 8		21.9
7	19.9	17.5	20.5	0.10	k	0.35 (55); 1.5 (45)	50 ± 4		20.9
8	20.0	19.4	20.3	< 0.03	j	0.71 (48); 1.2 (52)	43 ± 6		21.6
9	20.1	18.8	22.3	< 0.03	<0.1	1.0 (42); 2.2 (58)		42 ± 11	
10	22.0	20.7	21.0	0.040	k	1.4 (42); 4.9 (54)	48 ± 8		21.7
11	20.5	19.7	20.4	0.070	k	0.68 (59); 1.5 (41)	59 ± 6		22.2
12	22.9	21.8	20.7	0.035	1.5 ± 0.3	0.6 (85); 3.5 (5)	91 ± 11		23.1

^{*a*}Absorption onset (intercept of baseline with linearly extrapolated rising slope; absorption bands are distorted by scattering). Error: ± 0.5 . ^{*b*}The first peak in fluorescence. Error: ± 0.5 . ^{*c*}Prominent band in excited singlet absorption. Error: ± 0.5 . ^{*d*}Total fluorescence quantum yield (sum of ordinary and excimer emission). Error: ± 0.3 . ^{*e*}Triplet yield. ^{*f*}The two most important contributions to multiexponential fluorescence lifetime at the emission peak (% contribution in parentheses). Lifetimes also possess a small (at most a few %) component at t > 5 ns). Error: ± 0.05 . ^{*g*}Rate constant $k_{\rm SF}$ of singlet fission, given by the rate of disappearance of S₁ and equal to half the rate of appearance of T₁. Derived from a global fit in which the rate constants of S₁ decay and T₁ rise are equal (Figure S24). ^{*h*}Rate constant $k_{\rm EXC}$ of excimer formation. ^{*i*}Prominent band in triplet absorption. Error: ± 0.5 . ^{*j*}Broadened stimulated emission occurs within 1 ps of excitation and relaxes at the rate constant given to emission from a species with excimer-like absorption. ^{*k*}Triplet yield not determined due to spectral overlap.



Figure 5. Time resolved emission spectra integrated for collection delay times of 0-500 ps (dashed) or 2-5 ns (solid) for films of 1-12.

trapping. Some of the excimer-dominated films show broadened and red-shifted emission spectra that change

minimally from early to later delay times (e.g., 3, 4, 9). The films in which the emission shifts significantly at later times are 5, 6, 7, 8, and 12. The common feature of the spectral evolution is a gain in a broad and featureless emission band red-shifted from the primary band by $4000-5000 \text{ cm}^{-1}$. Both excimer and trapped exciton emission could be responsible for this red-shifted emission, as prior work on related systems has demonstrated.^{63,64} Its typical kinetic profile could reflect a combination of the delayed fluorescence that results from triplet-triplet annihilation with excimer decay pathways, making it difficult to separate the two emission types based on a global fit using exponentials. The difficulty is exacerbated by the relatively short lifetimes of triplets in the polycrystalline films, which rarely exceed 20 ns at room temperature and with fluences commonly used in TA experiments.

Biexponential or multiexponential decay is, however, observed even for compounds whose emission spectra are devoid of any evidence for a broad excimer emission band, such as 1 or 2. Some of this could be due to trapping in disorder sites, but the absence of significant dependence on the choice of the spot observed on the thin film sample does not support this notion.

3.3.iii. Transient Absorption at Room Temperature (Figures S24 and S25). Fitted rate constants are listed in Table 2. In Figure 6 we display the spectra associated with the slowest decaying time component of the TA map. The spectra of 1α , 2, 10, and 12 have been previously identified as due primarily to the T_1-T_6 and T_1-T_7 transitions overlapped with ground-state bleach.³⁴ The triplet features rise on a time scale equal to that of S_1 disappearance and the two rate constants were set equal in the fitting procedure (a global fit with two decay components, one for S_1 decay and T_1 rise and one for T_1 decay, captures the essential kinetics across the spectrum without significant residuals). Films of 6, 7, 8, and 11 also possess similar but somewhat distorted long-lived features that rise on this time scale and are also attributed to T₁ absorption (Table 2). The triplets of 1β and 3 become detectable only after much of the excimer has decayed and $k_{\rm T}$ has been inferred from k_{EXC} and Φ_{T} .



Figure 6. Decay associated spectra of long-lived species (>1 ns) for solid films, derived from transient absorption.

In a partially oriented sample, the relative intensities of the overlapping observed triplet absorption and ground-state bleach depend on the angle between the T_1-T_n and S_0-S_1 transition dipole moments and on the second moments of the molecular orientation distribution function (orientation factors).⁶⁵ The comparison of XRD patterns obtained on our thin films with those expected from single-crystal structures (Figure 2) showed that the films are partially oriented, and it is known from earlier work⁶² that in 1 the S_0-S_1 transition is polarized along the vertical axis in Chart 1, whereas the $T_1 - T_n$ band that overlaps it is of mixed polarization since it contains two strongly allowed transitions, one polarized in the vertical and the other in the horizontal direction in Chart 1. In view of the strong general similarity of the spectra of all these derivatives, it is safe to assume that the same situation will prevail in all of them. Since differently fluorinated derivatives of 1 have different crystal structures, it is essentially guaranteed that their partial orientation in the film will exhibit different orientation distributions and that they will produce nonidentical spectral envelopes in the observed triplet absorption region. Fortunately, all these envelopes have in common a relatively sharp peak at 21 000-23 000 cm⁻¹, which identifies the transitions as arising from triplets. Note that the partial orientation of crystallites in the samples affects the spectral shapes but not the kinetics of the reactions that proceed within them, which are the subject of current interest.

The decay of the triplet absorption is slow and occurs beyond the 5 ns time delay range of the measurements used here. It was only investigated at longer delays in the case of 1, where it is multiexponential, with fluence-dependent lifetimes ranging from 5 to 10 ns, likely attributable to triplet-triplet annihilation, and a weak component with 50-100 ns decays, probably related to trapping. The film of 7 is exceptional in that it shows rapid formation of a triplet, yet predominantly forms an excimer. A likely explanation is that it is heterogeneous and contains two different crystal phases, the minor one giving mostly triplet and the dominant one giving mostly excimer.

In contrast, the longest-lived species observed in the films of 1β , 3, 4, 5, and 9 largely possess broad and relatively unstructured bands below 20 000 cm⁻¹, which we assign to excimers. The rising rate constants of these broad bands are also listed in Table 2. Figure 7 shows a magnified comparison of the absorption spectra of the two types of long-lived species observed.



Figure 7. (A) Decay associated spectra of 1α , composed primarily of triplet (blue), and of 3, composed primarily of excimer (red) contributions. (B) Primary decay associated spectra for 2 before (blue) and after (red) thermal annealing.

3.3.iv. Transient Absorption at Low Temperatures. Films of 10, dominated by triplet formation (though no quantitative yield could be measured due to spectral overlap) showed an increase in relative triplet yield of roughly 25% from room temperature to 150 K, followed by a further ~10% increase at 77 K (Figure 8A). The shape of the transient absorption features did not change discernibly with temperature. The rate constant for triplet formation decreased from 48 ns⁻¹ at room temperature to 38 ns⁻¹ at 150 K and to 33 ns⁻¹ at 77 K.

Films of 3 are dominated by excimer formation at room temperature, with only about 30% triplet yield. The yield, judged by the strength of the triplet absorption at 21 800 cm⁻¹, increases at 150 K and then decreases again at 77 K. The strength of the excimer absorption, a broad feature peaking near 18 000 cm⁻¹, follows the opposite trend to that of the triplet (Figure 8B). If all else is equal, the triplet yield goes from ~0.3 at room temperature to ~0.7 at 150 K and to ~0.5 at 77 K. The interplay between the intensities of triplet



Figure 8. Long-lived (>10 ns) decay associated spectra derived from transient absorption upon 25 000 cm⁻¹ excitation for (A) 10 and (B) 3 at the temperatures indicated.

absorption and excimer absorption is thus similar to that found for films of alkyl substituted 1.38

Computed SF Rate Constants k_{SF} . The SIMPLE^{58–60} model and program, originally developed for the identification of molecular pair geometries that maximize k_{SF} , have been used as the simplest tool for estimating relative values of k_{SF} in

molecular crystals. The input parameters are (i) one (or more) geometries of the pairs of neighbors for which the calculated value of the squared matrix element for SF T^2 is the largest (Table S3), (ii) the intrinsic energy balance of SF [$\Delta E^0(SF) = 2\Delta E(T_1) - \Delta E(S_1)$], where $\Delta E(T_1)$ and $\Delta E(S_1)$ are the observed solution values (Table 1), (iii) the reorganization energy λ for SF, calculated by DFT (Table S4), and (iv) the energy separation of the charge transfer and locally excited states [$\Delta E(CT) = E(CT) - \Delta E(S_1)$], which is set at 2 eV. In a slight modification of the model, in the evaluation of SF rate we do not assume that $\Delta E^0(SF) = 0$.

Table S3 provides the energy values and SF couplings for the excised pairs calculated with the observed $\Delta E(S_1)$ and $\Delta E(T_1)$ values and compares the observed values of $k_{\rm SF}$ with those obtained from SIMPLE. This model assumes that the initial singlet excitation is delocalized across both partners in the pair, resulting in two excitonic singlet states, S* at lower and S** at higher energy. The Davydov splitting is their energy difference $[\Delta E_{\text{DS}} = E(S^{**}) - E(S^{*})]$ and the endoergicity of SF is the energy difference between the biexciton TT* and the S* or S^{**} state $[\Delta E_{SF}(S^*) = E(TT^*) - E(S^*), \Delta E_{SF}(S^{**}) =$ $E(TT^*) - E(S^{**})$]. The SF electronic matrix elements T^* and T^{**} are the couplings between the initial S^{*} or S^{**} and the final singlet biexciton state TT* [$T^* = \langle S^* | \hat{H} |^1 TT^* \rangle$, $T^{**} =$ $\langle S^{**}|\hat{H}|^{1}TT^{*}\rangle$]. The biexciton binding energy ΔE_{BB} is the energy difference between two noninteracting triplets and the biexciton state $[\Delta E_{BB} = 2E(T_1) - E(TT^*)]$. Its physical origin is the disappearance of stabilization of the singlet biexciton by configuration interaction with charge-separated states at higher energy when the two molecules are separated.

In SIMPLE, rate constants for SF from the S* and S** states are calculated by Marcus theory^{66–69} and averaged according to two-level Boltzmann statistics⁷⁰ to obtain k_{SF} , using both the observed and the calculated $\Delta E(T_1)$ for comparison. The reorganization energies calculated with the B3LYP and PBE0 functionals are similar. Since B3LYP is better than PBE0 for calculating triplet energies for this set of compounds (Figure S17), B3LYP reorganization energies were used to calculate

Tabl	e 3.	Calculated	and	Observed	Relative	Singlet	Fission	Rate	Constants
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pair ^a geom	$k_{\rm SF}/k_0^{\ b}$	$k_{\rm SF}/k_0^c$ B3LYP	$k_{\rm SF}/k_0^d \exp$	pair ^a geom	$k_{\rm SF}/k_0^{\ b}$	$k_{\rm SF}/k_0^c$ B3LYP	$k_{\rm SF}/k_0^d \exp$
1α			1.0	9			$(0.08)^{e}$
Α	1.0	1.0		А	0.00	0.00	
В	0.08	0.08		В	0.05	0.14	
1 <i>β</i>			0.18	С	0.00	0.00	
Α	0.99	0.99		D	0.08	0.23	
В	0.08	0.08		10			0.86
2			0.89	А	3.9	2.3	
Α	1.3	1.2		В	0.08	0.05	
В	0.08	0.07		11			1.05
3	0.03	0.02	0.18	А	14	58	
4	1.0	0.15	$(0.10)^{e}$	В	0.17	1.0	
5	0.00	0.00	$(0.05)^{e}$	12			1.63
6	9.8	11	1.36	А	45	3.8	
7	0.02	0.06	0.89	В	0.06	0.01	
8			0.77				
Α	8.8	20					
В	0.70	1.5					

^{*a*}See Figures S19 and S20 for pair geometries. ^{*b*}Predicted rate constant ratio using observed singlet and triplet excitation energies. $k_0 = 4.84 \times 10^7$ s⁻¹. ^{*c*}Predicted rate constant ratio using observed singlet and calculated triplet excitation energies. $k_0 = 4.84 \times 10^7$ s⁻¹. ^{*d*}Ratio of measured rate constants of SF; $k_0 = 56$ ns⁻¹. ^{*e*}Ratio with maximum possible SF rate, estimated at 10% of excimer formation rate.

the rates of SF. The predicted and observed ratios $k_{\rm SF}/k_0$ of the SF rate constant for each pair in each crystal relative to that of the slip-stacked pair A in the parent crystal 1α ($k_0 = 4.84 \times 10^7$ s⁻¹) are provided in Table 3, using both the observed and the B3LYP calculated $\Delta E(T_1)$ values.

Figures S19 and S20 show multiview projections of all neighboring pairs with non-negligible predicted $k_{\rm SF}$ values that can be excised from the crystal lattices of the 12 compounds examined (for 3, whose crystal structure could not be determined, the $P2_1/c$ structure obtained from simulated annealing was used). Each crystal also contains pairs that are mirror images of those reported here.

Figure 9 plots the calculated against the observed SF rate constant on a logarithmic scale. For compounds 4, 5, and 9,



Figure 9. Plot of log $k_{\rm SF}$ (calcd) vs log $k_{\rm SF}$ (obsd). The width of the ovals represents the experimental uncertainty. Open-ended bars represent possible values for the unobserved $k_{\rm SF}$, assuming they are less than 10% of the excimer formation rate. The blue and red points represent compounds with one and two perfluorinated phenyls, respectively.

which only formed excimers, only the upper limit is available. It is estimated from the assumption that triplet formation would have been observed if $k_{\rm SF}$ exceeded 10% of the observed excimer formation rate constant $k_{\rm EXC}$.

DISCUSSION

The striking separation of the 12 compounds 1-12 with very similar molecular properties into triplet formers ($k_{\text{SF}} > k_{\text{EXC}}$, 1α , 2α , 6-12) and excimer formers ($k_{\text{SF}} < k_{\text{EXC}}$, 1β , $2\beta-5$) illustrates the importance of crystal packing for the properties of solids. We hope that the measured rate constants k_{SF} and k_{EXC} will serve as a test bed for increasingly elaborate theories aimed at the prediction of SF triplet quantum yields. A starting point is provided by the SIMPLE method, used presently. Even this cheap and primitive method that estimates relative values of k_{SF} and makes no attempt to evaluate k_{EXC} is capable of providing a rough classification of the dozen compounds into two classes, triplet formers and excimer formers.

Singlet Fission versus Excimer Formation. The data are most complete for the parent 1α , where the temperature dependence of k_{SF} and Φ_{T} in films has been reported in

detail.^{17,36} The rate constant is weakly temperature dependent, decreasing by less than a factor of 2 as temperature is lowered to 10 K. The yield first increases from roughly 1.3 at room temperature to near 2.0 at about 80 K, followed by a decrease toward 1.5 at 10 K. The increase of triplet yield as temperature is lowered toward 80 K was rationalized as due to a thermally activated nonradiative decay channel, such as excimer formation. The decrease below 80 K was thought to be related to the presence of a small activation barrier for SF. The similarity between trends for films of 1 and 10 offers no reason to revise the earlier hypotheses.

The presently observed temperature dependence for the excimer forming film 3 provides further insight. The anticorrelation between trends in the intensities of triplet and excimer absorption with temperature suggests a competition for excited-state population between these two species. As temperature is initially lowered from 298 K, the triplet yield increases as excimer formation is more strongly thermally activated than SF. The requirement for molecular motion to decrease the intermolecular distance to form the excimer state is likely the driving force behind the temperature dependence. As temperature is lowered further, the loss of excimer absorption saturates, and triplet yield turns over toward lower values. This behavior of triplet yield may be related to the previously invoked slowing of SF due to its thermal activation, while the lack of further decline in excimer absorption may be due to densification of the unit cell that is known¹⁷ to occur at 100 K for 1α and 1β and is likely to occur for the fluorinated derivatives as well. The smaller intermolecular distance achieved upon unit cell densification may counteract the loss of thermal energy and restore excimer formation as the dominant pathway.

It is likely that the same type of competition between the SF process and the formation of an excimer occurs in all of the compounds 1-12. The excimer apparently represents a deep enough trap to render singlet fission from it too endothermic and noncompetitive, and it decays to the ground state by combined radiative and nonradiative processes. The data in Table 2 show that within the series 1-12 it is both a variation in the observed values of $k_{\rm SF}$ by a factor of 9 and in the observed values of k_{EXC} by a factor of 6 that determine whether a compound is primarily a triplet or an excimer producer. Given that some of the rate constants were too small to be detectable, the variation is likely even larger. This observation makes it clear that a predictive theoretical procedure for triplet yields in this set of compounds requires a computation of k_{EXC} just as much as a computation of k_{SF} , and the conclusion may be general. As discussed next, the rapid SIMPLE procedure yields a rough estimate of the relative value of the latter, but a similar facile procedure for the former still needs to be developed.

Although in 1-12 excimer formation is the primary competitor for singlet fission, different processes are likely to play this role in other groups of compounds and will require the development of a simple theoretical treatment if extensive searches for optimal candidates for singlet fission are to be made. For instance, in solid cibalackrot⁶⁶ and diaminoquinones,⁷¹ the main competing process is the formation of a charge-separated state, which then undergoes intersystem crossing to the triplet, most likely not by singlet fission but by the radical pair mechanism. Intersystem crossing does not allow the triplet yield to exceed 1.0. Calculation of Singlet Fission Rate Constants by the SIMPLE Procedure. The collection of rate constants k_{SF} for singlet fission and k_{EXC} for excimer formation provided in Table 2 is meant as a testing ground for computational methods. We start the testing by examining the performance of the public domain SIMPLE algorithm^{58–60} for k_{SF} . As noted above, this method was originally developed for a different purpose, the identification of all local maxima of k_{SF} in the six-dimensional search space of possible geometries of a pair of rigid chromophores, but it also has the ability to compute k_{SF} for any choice of a pair geometry in which the two molecules do not interpenetrate. Because of the approximations used, only relative rates are meaningful.

We start by acknowledging the main weakness of the procedure, which is the pair additive approximation: the method only considers a pair of molecules at a time instead of a whole infinite crystal simultaneously, and it chooses the most strongly interacting pair or at most a few. This may cause serious problems, best exemplified by the crystal structures of 1α and 1β . They are nearly identical in that each molecule has almost exactly the same environment of nearest neighbors in both polymorphs, and the calculation thus produces nearly equal $k_{\rm SF}$ values. Yet, the observed values differ by a factor of ~5.5 (Table 2).⁴⁰ The difference between 1α and 1β is the relation of next nearest neighbors and is worth considering in some detail.

In both crystal polymorphs, each column of molecules is offset from the neighboring identical columns by 10.1 Å, with the difference between the two forms being the angle of the offset (see a discussion in the SI and Figure 1). In 1α , the offset is always at +16.2°, while in 1β , the offset angle alternates between $+16.4^{\circ}$ and -16.4° . The result of this is that all nearest neighbor pairs in 1β are also found in 1α and only the next-nearest neighbor pairs are different between the two. In SIMPLE the next-nearest neighbors are too far apart to be competitive in the calculation of T^2 and Davydov splitting, and only nearest neighbor pairs matter in the evaluation of the SF rate constants. Since the SIMPLE procedure focuses on the largest pair interactions, it predicts nearly identical values for $k_{\rm SF}$ in the two polymorphs of 1, in disagreement with observations (Table 2, cf. the positions of 1α and 1β in Figure 8).

The constraint to the largest pairwise interaction can lead to incorrect values of T, incorrect Davydov splitting, or both. Since T for a molecular pair falls off exponentially with distance, only indirect contributions mediated by a third molecule could possibly contribute to a difference between 1α and 1β , and these are difficult to extract from observations. Excitonic interactions fall off more slowly with distance, and their effects are easier to observe directly. Although it is difficult to determine the singlet excitation energies and Davydov splittings from the spectra of 1α and 1β solids exactly, the S₁ excitation energy of 1α is clearly higher than that of 1β (Figure S14A). The difference could be as little as 200 and as much as 900 cm⁻¹, depending on how it is evaluated. If the solution S_1 excitation energy is used for 1α and the difference between the solid S1 excitation energies of 1α and 1β is added to the solution excitation energy to obtain an S₁ excitation energy for $\mathbf{1\beta}$, the resulting $k_{\rm SF}$ values for $\mathbf{1\beta}$ are quite sensitive to the difference value chosen (Table 4). The values 600-900 cm⁻¹ have been suggested as the most likely,¹⁷ and reference to Table 3 then produces a ratio $k_{\rm SF}(\mathbf{1\beta})/k_{\rm SF}(\mathbf{1\alpha})$ of 0.07–0.18, which includes the value

Table 4. Observed vs Calculated $k_{\rm SF}(1\beta)/k_{\rm SF}(1\alpha)$ Ratio as a Function of Difference in Endoergicity

		calcd; addition to endoergicity (cm^{-1})						
ratio	obsd	0	200	600	900			
$k_{ m SF}(\mathbf{1eta})/k_{ m SF}(\mathbf{1eta})$	0.18	0.99	0.58	0.18	0.07			
^a Calculated with Sl given.	F more end	oergic ir	1 1β than	1α by the	amount			

observed. It is thus possible and perhaps even likely that the different $k_{\rm SF}$ in 1α and 1β are not due so much to a difference in the SF matrix element *T*, but to a difference in excitonic interactions. This is not accounted for by the SIMPLE model, in which only interactions within a pair of nearest neighbors matter.

We have checked whether a consideration of a larger crystal domain would change the situation, but it did not. We performed SIMPLE calculations of singlet excitation energies for two nanocrystals excised from the crystal structures of both 1α and 1β . The first nanocrystal comprised 32 molecules contained in two unit cells in each dimension, and the second contained 64 molecules, four molecules in each dimension. A matrix of excitonic interactions between all pairs of molecules, including local S₁ excitations on each molecule and all charge transfer excitations, was constructed using the approximations inherent to SIMPLE and diagonalized. The results for 1α and 1β were essentially identical, with excitation energy differences of a few tens of cm⁻¹, an order of magnitude less than that observed.

Returning to the comparison of the measured and calculated $k_{\rm SE}$ values for 1–12, we note that they differ significantly among nearest neighbor pairs in the same crystal and among pairs in different crystals. The most strongly interacting pairs to be considered based on an evaluation of T^2 and the SF energy balance for all nearest neighbors are shown in Figures S19 and S20. Based on only these pairs with the calculated values of λ and of state energy shifts due to intermolecular interaction (Table 3), Marcus theory yields $k_{\rm SF}$ values that are 3 orders of magnitude too small, and only the relative values are meaningful. We take the rate constant $k_0 = 4.84 \times 10^7 \text{ s}^{-1}$ predicted for pair A in 1α as standard. The order of the predicted relative rates $k_{\rm SF}/k_0$ for the 11 derivatives (Table 3 and Figure 9) actually agrees moderately well with the experimental rate constants of SF relative to that in 1α (Table 3), but the variation in the SF rate constant that is predicted is much larger than the variation observed. The predicted SF rate constants are very sensitive to the intrinsic energy balance of SF, $\Delta E^0(SF)$, and the use of accurate S₁ and T₁ excitation energies appears to be vital. Inadequacies in these values may well be responsible for the discrepancies between the predicted and experimental results. The calculated relative rates differ significantly from the observed rates for 1β , 4, and 7 (Figure 9), and it is reasonable to suspect that the reason for the failure in the cases of 4 and 7 is a poor description of excitonic interaction, as outlined above for the pair 1α , 1β . It is to be hoped that the present identification of the likely problem will help in the development of the next generation of models.

In the absence of any calculations for the rate constant k_{EXC} of the competing excimer formation and knowing that in 1α SF competes very well, as a first guess we could postulate that the computed ratio k_{SF}/k_0 should be no less than some limiting value for SF to compete well in other derivatives. If we choose

this cutoff value to be 0.25, we obtain a good prediction of the SF triplet formers among the 12 compounds examined, with only two (4 and 7) classified incorrectly. This is satisfactory considering the crude nature of the SIMPLE model, which was designed for a different purpose, and the absence of any attempt to calculate k_{EXC} . The pair geometries of 4 and 7 are very similar, with one C_6H_5 ring nearly in the isobenzofuran plane and the fluorinated phenyl twisted out of that plane. For 4, the k_{SF} values calculated with the observed and B3LYP triplet energy disagree, with the former incorrectly predicting SF. For 7, SIMPLE predicts that SF will not be observed, but it is.

Finally, we offer a few comments on the desirable packing of 1,3-diphenylisobenzofurans for achieving high triplet formation rate constants through SF. In a previous study,⁷² the SIMPLE program and model were used to optimize thousands of candidate geometries of four pairs of rotamers of 1 (C_2 , C_2 , C_3 , and C_1) for a local maximum of k_{SF} and then rank them. Some relevant pairs are shown in Figure 10, and we can comment on



Figure 10. Multiview projections of some optimized SF pairs for 1, using the standard third angle projection method. The main view of the *xy* plane is located in the lower right; the top view of the *xz* plane is above it (it results when the main view is rotated 90° clockwise about the *x* axis, with the horizontal axis pointing right). The left side view of the *yz* plane is to the left (this view would result if the main view were rotated 90° clockwise about the *y* axis, with the vertical axis pointing up).

their relation to the packing actually observed in the crystals of 1-12. The pair structures predicted to be best for SF are slipor twist-stacked. The primary pairs found in the parent 1 are the slip-stacked pair 1A and herringbone pair 1B, and 2 is nearly identical (Figure S19). The primary SF pair in 3 is also slip-stacked but partner B (in red) is slipped parallel to the 2fold axis y of the isobenzofuran core of partner A (in blue) as well as its other in-plane axis x. The SF pair in 3-8 (Figures S19 and S20) are all also slip-stacked. Interestingly, the SF pair in 5 is slipped almost exclusively along the y axis of partner A, with only a very slight slip along *x*. Compound 9 (Figure S20) has a less regular crystal packing, containing four similar yet distinct twist-stacked pairs. The four pairs have similar structures to the 19th ranked $1(C_{2\nu})$ pair in Figure 10 and pairs 9B, 9C, and 9D are very similar to each other yet their predicted energetics and rate constants in Table 3 and Table **S3** are distinct.

The SF pair in **10** (Figure S20) has an interesting structure where one partner's fluorinated phenyl ring overlaps the nonfluorinated ring of the other, causing the isobenzofuran cores to avoid each other and not overlap. The structure of pair

11A is similar to the fourth ranked optimized $1(C_{2v})$ pair in Figure 10 except that the red partner is slipped further along the *y* axis of the isobenzofuran core of the blue partner in the **11** pair. Being similar to the fourth best optimized pair, it is not too surprising that this pair structure has the largest predicted rate constant ratio. The last and most fluorinated derivative **12** (Figure S20) has two primary pairs in its crystal and they have structures that are somewhat similar to the third and fifth ranked optimized pairs for $1(C_s)$ in Figure 10.

CONCLUSIONS

The primary outcome of the present study is a set of rate constants $k_{\rm SF}$ and $k_{\rm EXC}$ for thin solid layers of the closely related compounds **1–12**, collected in Table 2. It is hoped that it will be useful for further development and testing of computational procedures aiming to guide the design of solar cell materials capable of overcoming the Shockley–Queisser limit. The results suggest that a consideration of more than two molecules at a time is unavoidable but that it might be possible to limit this to the evaluation of the energies of states that result from excitonic interactions. Accurate evaluation of these energies is essential.

The SIMPLE model suffers from its limitation to pairwise chromophore interactions but nevertheless provides a first approximation to (i) properly rendering relative rates of SF within a group of structurally closely related compounds very differently packed in the solid state and (ii) separating those that produce good yields of triplets from those in which excitation is trapped in the form of excimers and subsequently wasted. The need for simple theories that would permit an identification of crystal packing that promotes processes capable of competing successfully with singlet fission factors is emphasized.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c06712.

Details of X-ray diffraction results, discussion of crystal packing, observed and calculated absorption spectra, determination of triplet excitation energies, full transient absorption spectral maps, views of molecular pairs excised from crystal structures, information on SIMPLE calculations, and DFT (PBE0/Def2-TZVP) optimized geometries for the S₀, S₁, and T₁ states of **1–12** and for molecular pairs excised from crystals, Cartesian coordinates (PDF)

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Notes

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