Controlling Singlet Fission with Coordination Chemistry-Induced Assembly of Dipyridyl Pyrrole Bipentacenes

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ABSTRACT: Singlet fission has the potential to surpass current efficiency limits in next-generation photovoltaics and to find use in quantum information science. Despite the demonstration of singlet fission in various materials, there is still a great need for fundamental design principles that allow for tuning of photophysical parameters, including the rate of fission and triplet lifetimes. Here, we describe the synthesis and photophysical characterization of a novel bipentacene dipyridyl pyrrole (HDPP-Pent) and its Li- and K-coordinated derivatives. HDPP-Pent undergoes singlet fission at roughly 50% efficiency ($\tau_{SF} = 730 \text{ ps}$), whereas coordination in the Li complex induces significant structural changes to generate a dimer, resulting in a 7-fold rate increase ($\tau_{SF} = 100 \text{ ps}$) and more efficient singlet fission with virtually no sacrifice in triplet lifetime. We thus illustrate novel design principles to produce favorable singlet fission properties, wherein through-space control can be achieved via coordination chemistry-induced multipentacene assembly.

Singlet fission is the organic analogue to multiple exciton generation (MEG), wherein single photon absorption by a chromophore yields one excited singlet state ($S_1$) that may relax into a correlated triplet pair ($T_1 T_1$) and, through decoherence, generate two free triplet states across multiple chromophores. Although first discovered in polyacene crystals in the 1960s, singlet fission has received renewed attention over the past 15 years following the suggestion that MEG processes could be employed in photovoltaic devices to overcome the $\sim 30\%$ Shockley–Queisser limit of efficiency in single-junction solar cells. Furthermore, the coherent properties of correlated triplet pairs suggest possible utilities of singlet fission materials in quantum information science and spintronic applications.

If novel technologies with tailored singlet fission materials are to be realized, however, the structural and electronic origins of singlet fission require further elucidation. Recently, covalently linked chromophores have arisen as an important tool to study intramolecular singlet fission, providing significant insight into the photophysics of this process. In particular, molecular bipentacenes have received great attention owing to the exergonic and efficient nature of singlet fission in pentacene systems. Systematic perturbations of the linkers as well as the position of chemical modification on the pentacene have revealed distinct fission rates and triplet pair or triplet state lifetimes. In addition, recent investigations examined the effect of through-space $\pi$-interactions on singlet fission and suggest the importance of slip-stacking geometric arrangements and Davydov splitting in the molecular excited states. While the synthetic approach of systematic variation of a covalent linker has proven very versatile toward addressing a variety of fundamental aspects of singlet fission (Figure 1), disentangling and controlling the through-bond and through-space effects that ultimately give rise to characteristic photophysical properties remain a challenge.

Herein, we demonstrate how a single molecular bipentacene scaffold may give rise to tunable singlet fission properties by means of coordination-induced structural perturbations (Figure 1). We have synthesized and studied the photophysics of a bipentacene displaying a dipyridyl pyrrole motif capable of serving as a ligand for metal ions, with the lithium and potassium complexes reported here (Figure 2). This series of complexes demonstrates the importance of designing and controlling the assembly of higher-order structures for improved singlet fission performance. While maintaining the same covalent linker between chromophores, these compounds provide new design principles for the control of singlet
RESULTS AND ANALYSIS

Synthesis and NMR Characterization. The synthesis of the bipentacene, HDPP-Pent, displaying a dipyridyl pyrrole linker was performed from a monopentacene pyridyl bromide derivative (PentPyBr, Figure 2). The $^1$H NMR spectrum of HDPP-Pent (Figure S40) is relatively broad, particularly in the 6.5–9 ppm region, in contrast to the well-resolved scalar coupling between protons on the terminal rings of the pentacene unit observed in the $^1$H NMR spectrum of PentPyBr (Figure S38). While cooling from 20 to $-80^\circ$C, the variable temperature $^1$H NMR data of HDPP-Pent display complex behavior. The aromatic region broadens considerably at $-40^\circ$C, and subsequently, a multitude of resonances grow in as the temperature is further decreased (Figure S42).

Deprotonation of HDPP-Pent with either lithium or potassium hexamethyldisilazide leads to the formation of the lithium ($\text{Li}_2(\text{DPP-Pent})_2$) or potassium (KDPP-Pent) complexes, respectively. In contrast to the broad NMR features observed in HDPP-Pent, deprotonation leads to sharp and well-defined $^1$H NMR spectra for the alkali metal complexes at room temperature (Figures S43 and S44).

Upon closer comparison of the $^1$H NMR spectra of the metal complexes, it is evident that the protons on the dipyridyl pyrroline backbone of $\text{Li}_2(\text{DPP-Pent})_2$ are significantly upfield shifted, unlike KDPP-Pent. For instance, the singlet corresponding to the pyrrole ring proton is found at 4.38 and 7.03 ppm in the $\text{Li}_2(\text{DPP-Pent})_2$ and KDPP-Pent spectra, respectively. 2D rotating frame Overhauser enhancement spectroscopy (ROESY) experiments on $\text{Li}_2(\text{DPP-Pent})_2$ also reveal through-space $^1$H–$^1$H correlation between protons on the dipyridyl pyrrole backbone at 4.38 ppm ($H_1$) and 5.14 ppm ($H_2$) and the proton on the distal side of the pentacene ring at 9.12 ppm ($H_4$) (denoted by green and blue circles, respectively, in Figure 3b). Notably, no such cross-peaks are observed in the 2D ROESY spectrum of KDPP-Pent (Figure 3c).

Structural Analysis. The broadness of the room temperature $^1$H NMR spectrum of HDPP-Pent along with the variable temperature behavior are indicative of solution-state...
conformational dynamics on the NMR time scale. These may involve rotations around aryl−aryl linkages that result in mixtures of conformers. The aromatic NMR features are resolved upon deprotonation and metal coordination of the ligand framework, as evidenced by the sharp spectra observed for Li$_2$(DPP-Pent)$_2$ and KDPP-Pent, suggesting the formation of single conformers or fast exchange processes.

The NMR data of Li$_2$(DPP-Pent)$_2$ strongly suggest a dimeric solution-state structure as proposed in Figure 3b. The π-stacking interactions between the pentacene and sandwiched dipyridyl pyrrole units are consistent with the upfield shift exhibited by the dipyridyl pyrrole protons owing to enhanced chemical shielding by perturbation of the aromatic ring currents.$^{41,42}$ Likewise, the cross-peaks in the 2D-ROESY spectrum between the pyrrole backbone protons and the protons on the far side of the pentacene support a dimeric structure. The dipolar couplings that give rise to the ROE are sensitive generally out to 5 Å, and a dimer would bring the relevant nuclei into proximity for this interaction.$^{43,44}$ Although X-ray quality single crystals of the pentacene derivatives have eluded us, we have been able to crystallographically characterize a related lithium dipyridyl pyrrolide compound with anthracenyl instead of pentacenyl substituents, Li$_2$(DPP-Anth)$_2$ (Figure 3a). This compound demonstrates the formation of a dimeric species with two lithium cations bridged by pyrrolide donors. As such, we propose that Li$_2$(DPP-Pent)$_2$ has a similar geometry.

In Figure 3b, we use CD$_2$Cl$_2$ to unambiguously assign the aromatic protons in Li$_2$(DPP-Pent)$_2$. However, the upfield shift in the pyridyl pyrrole resonances and the 2D-ROESY cross-peaks are reproduced in toluene-d$_8$, suggesting that the same dimeric complex occurs in toluene, which we employ for our transient absorption measurements (Figure S4). Additionally, $^1$H NMR spectra of Li$_2$(DPP-Pent)$_2$ were collected in toluene-d$_8$ at multiple concentrations (Figure S45). No concentration-dependence was observed for the chemical shifts of the proton resonances, suggesting that the dimerization equilibrium is biased strongly toward the dimer ($K_{eq} \gg 0$) under these conditions.

The NMR data for Li$_2$(DPP-Pent)$_2$ are in stark contrast to those of KDPP-Pent where the dipyridyl pyrrole backbone protons do not display either a significant upfield shift or observable cross-peaks between pyrrole and distal pentacene protons in the ROESY spectrum. As such, we conclude that Li$_2$(DPP-Pent)$_2$ and KDPP-Pent have dimeric and monomeric solution-state structures, respectively. The small ionic radius of Li$^+$ likely permits dimer formation, whereas the larger size of K$^+$ destabilizes such an interaction, enforcing a monomeric structure. We have also prepared the analogous Na complex (NaDPP-Pent) and characterized it by $^1$H NMR and 2D ROESY spectroscopy (Figures S47 and S49). Like KDPP-Pent, the data suggest that the Na complex is monomeric. However, we found this species to be more sensitive to handling and exhaustive removal of residual solvent. Our photophysical studies therefore focus on the Li and K complexes, which allow us to probe the dimeric and monomeric forms, respectively.

Steady-State Absorption and Emission. The steady-state absorption spectra of PentPyBr, HDPP-Pent, Li$_2$(DPP-Pent)$_2$, and KDPP-Pent are compared in Figure 4a. The absorption spectrum of HDPP-Pent exhibits roughly twice the intensity of PentPyBr with little difference in peak positions within the vibronic progression of the S$_1$ ← S$_0$ absorption bands. The S$_1$ ← S$_0$ absorption in Li$_2$(DPP-Pent)$_2$ is slightly broadened, and the 0–0 band is modestly red-shifted by 5 nm (∼130 cm$^{-1}$) from that of HDPP-Pent. Additionally, both
S0 from the 0 cm however, was found to be 0.43, signi
Pentacene. The absorption spectra; (b) the normalized emission spectra of PentPyBr and KDPP-Pent display similar emission pro
The Li2(DPP-Pent)2 and KDPP-Pent exhibit enhanced absorption relative to HDPP-Pent.
Figure 4. Steady-state absorption and emission spectra and time-resolved-luminescence data of the pentacene series. Shown are the (a) absorption spectra; (b) the normalized emission spectra of PentPyBr (red), HDPP-Pent (blue), L2(DPP-Pent)2 (purple), and KDPP-Pent (green) in toluene solutions; and (c) time-resolved luminescence traces and fits for PentPyBr (20 μM, toluene) and HDPP-Pent (20 μM, toluene). Note that the steady-state emission spectra are normalized by their relative emission intensities.

Li2(DPP-Pent)2 and KDPP-Pent exhibit enhanced absorption near 400–450 nm.

Steady-state emission spectra for PentPyBr and HDPP-Pent are compared in Figure 4b. Here, the 0–0 emission band of HDPP-Pent (λmax = 650 nm, ~15 400 cm−1) is red-shifted from the 0–0 band of PentPyBr (λmax = 640 nm, ~15 600 cm−1). The emission in this region is consistent with the S1 → S0 fluorescence observed in similar pentacene compounds.45 The fluorescence quantum yield of PentPyBr in toluene was determined to be 0.75, comparable to that reported for TIPS-Pentacene. The fluorescence quantum yield of HDPP-Pent, however, was found to be 0.43, significantly decreased relative to the single pentacene in PentPyBr. While L2(DPP-Pent)2 and KDPP-Pent display similar emission profiles to HDPP-Pent, the integrated emission intensity is significantly reduced relative to HDPP-Pent.

Time-Resolved Luminescence. Time-resolved luminescence traces collected at 640 and 650 nm for PentPyBr and HDPP-Pent, respectively, are presented in Figure 4c. The fluorescence decay for PentPyBr fits well to a monoexponential with a lifetime of ~15 ns. The fluorescence decay for HDPP-Pent, however, decays biexponentially with a first time constant of 0.71(4) ns and a second of 11.(8) ns, the latter of which is consistent with the intrinsic fluorescence decay of the pentacene unit.

Emission Analysis. For efficient singlet fission (i.e., triplet yields approaching 200%), we expect the prompt fluorescence intensity to vanish, as the fission pathway must deplete the excited S1 state more efficiently than emission. When singlet fission is sufficiently exothermic, which is the case for pentacene, the reverse triplet–triplet upconversion (fusion) becomes unfavorable, excluding delayed fluorescence. The observation of steady-state fluorescence intensity in HDPP-Pent already indicates that if singlet fission is occurring in this system, it is not operating at full efficiency. Nevertheless, the reduced fluorescence quantum yield for HDPP-Pent relative to PentPyBr suggests that a new, nonemissive relaxation pathway is present in the bipentacene that is not observed in the monopentacene.

This is borne out by comparing the time-resolved luminescence spectra of PentPyBr and HDPP-Pent. The monoexponential decay of the fluorescence signal in PentPyBr is consistent with that expected for an emissive process. The time-resolved signal in HDPP-Pent must be fitted with at least a biexponential function with time constants τ1 = 0.71(4) ns and τ2 = 11.(8) ns and weighting coefficients of roughly 0.5 each. The latter time constant is closer to the decay observed in PentPyBr and may be associated with the intrinsic emissive relaxation within HDPP-Pent. The 0.71(4) ns exponential time constant therefore likely corresponds to the competitive nonemissive relaxation pathway.

Transient Absorption Spectroscopy—HDPP-Pent. To provide deeper insight into the nature of the competitive nonradiative relaxation process in HDPP-Pent, we performed femtosecond transient absorption (fsTA) spectroscopy on PentPyBr and HDPP-Pent. The fsTA data of PentPyBr (Figure S14) reveal a single major excited state absorption (ESA) centered at 450 nm (~22 200 cm−1), which has previously been assigned to absorption within the singlet excited state manifold (1ESA) of related pentacene compounds.25,26,45 This 1ESA decays monoexponentially over the time window, consistent with the time-resolved fluorescence data.

The fsTA data for HDPP-Pent are given in Figure 5. A 1ESA at 450 nm is observed at early time delays, but it decays across the fsTA spectrum with the concomitant rise of a new, structured absorption feature at λmax = 510 nm (~19 600 cm−1). This new feature is consistent with previous literature.

![Figure 5. Visible transient absorption spectra—HDPP-Pent.](https://dx.doi.org/10.1021/acscentsci.0c01044)
reports that assign this band to transitions arising from either the triplet pair or free triplet state (3ESA). Experiments in which anthracene is excited and undergoes triplet–triplet energy transfer with HDPP-Pent were also carried out. The long-lived spectrum of the triplet formed on HDPP-Pent in these photosensitization experiments corresponds directly to the long-lived component in the direct excitation experiments (\(\lambda_{\text{exc}} = 510\) nm), corroborating the assignment of this feature as a 3ESA (Figure S35). This triplet signal is not appreciably observed for PentPyBr. The nanosecond TA (nsTA) data for HDPP-Pent (Figure S10) reveal the full decay of the 3ESA feature. The comparison between PentPyBr and HDPP-Pent TA data suggests that the nonradiative pathway in HDPP-Pent may be associated with a transition from the S1 to the T1 or M(TT) states, as indicated by the rise of the prominent 3ESA feature.

Kinetic Modeling. Kinetic modeling was carried out via target analysis on a composite data set of the fsTA and nsTA spectra of HDPP-Pent in order to capture the complete dynamics. Using target analysis, the entire TA data set is fitted over all wavelengths and all time delays with the application of a kinetic model. The preparation of the composite data set and a full description of the model applied to HDPP-Pent is provided in the Supporting Information, Section VII, along with fits for the individual fsTA and nsTA spectra for reference.

The time-resolved luminescence data were applied as an independent probe of the S1 dynamics, leading to a four-component model in which components 1 and 2 equally reflect the 1ESA spectrum, and components 3 and 4 represent the 3ESA spectrum. Component 1 decays into components 3 and 4 equally with a rate constant \(k_{11}\); component 2 decays to the ground state with rate constant \(k_{22}\) and components 3 and 4 decay to the ground state with rate constants \(k_{13}\) and \(k_{14}\), respectively.

This model was applied in two cases: one in which \(k_{1}\) and \(k_{2}\) were allowed to vary freely, and one in which \(k_{1}\) and \(k_{2}\) were fixed to 1.4 and 0.08 ns\(^{-1}\), respectively, as obtained directly from the time-resolved fluorescence fits. The results of the free and fixed fittings are shown in Tables S1 and S2, respectively. Of note, the results for \(k_{1}\), \(k_{2}\), and \(k_{4}\) are remarkably consistent between the two fits. Even when allowed to vary, the fit of \(k_{1}\) gives a time constant \(\tau_{1}\) of 0.74(6) ns, consistent with the \(\tau \sim 0.71\) ns obtained from the emission data. This \(k_{1}\) corresponds to the nonradiative transition from S1 to T1 within our model. \(k_{2}\) shows the largest divergence in the two fits: \(\tau_{2} \sim 1.5(5)\) ns when allowed to vary from the fixed value of 11.8(8) ns. Both values are consistent with the radiative lifetime, though the error may come from the convolution of spectral features in the combined fs/nsTA data.

Triplet Yield Estimation—HDPP-Pent. The triplet yield after direct excitation of HDPP-Pent was estimated from the TA data and the target kinetic modeling. First, the extinction coefficient of the 3ESA at 510 nm was determined by the triplet energy transfer method using a donor of known triplet molar absorptivity (anthracene) under pseudo-first-order kinetic conditions (Supporting Information, Section VIII). From this, we approximate the 3ESA molar absorptivity of HDPP-Pent at 510 nm to be 49,000 M\(^{-1}\) cm\(^{-1}\) (Figure S36).

As is shown explicitly in Section IX of the Supporting Information, the target model can be used to decompose the maximum AOD into its contributions from the 1ESA and 3ESA as 2.8 and 10.0 mOD, respectively. Thus, after direct excitation of HDPP-Pent in toluene solution, the value of 10.0 mOD for the effective 3ESA intensity provides an estimated triplet yield of \(\sim 100\%\).
which the $S_1$ decays in two pathways and supports the assignment of the nonrelaxative observation in the time-resolved luminescence to be associated with singlet to triplet conversion.

Finally, the triplet yield of HDPP-Pent is estimated to be 100% out of a maximum of 200%. As previously noted, the fluorescence quantum yield of HDPP-Pent is 43%. The weighting coefficients of the exponential decays observed in the time-resolved luminescence data are also $\sim 0.5$ each. Taken together, these data are self-consistent with a model in which nearly half of the photogenerated singlets give rise to twice the number of triplets. The nonradiative transition in HDPP-Pent may thus be assigned as intramolecular singlet fission.

Li$_2$(DPP-Pent)$_2$ and KDPP-Pent. The HDPP-Pent analysis provides a foundation to understand the dynamics exhibited by the alkali metal complexes. The fsTA data for Li$_2$(DPP-Pent)$_2$ are shown in Figure 6a–c. At early time delays, there is a $^3$ESA feature at $\lambda_{\text{max}} = 450$ nm that decays and gives rise to a strong $^1$ESA centered at $515$ nm ($\sim 19400$ cm$^{-1}$). The composite fs/nsTA data of Li$_2$(DPP-Pent)$_2$ can be kinetically modeled with either a three- or four-component model (Tables S5 and S6).

In the three-component model, the $S_1$ state is converted into the triplet manifold with a time constant $\tau_1$ of 96.2 ps; the triplet feature is then fitted to a biexponential decay with time constants $\tau_2$ and $\tau_3$ of 23.3 ns and 35.0 (0) $\mu$s, respectively. In the four-component model, the $S_1$ state is converted to the triplet manifold with a time constant $\tau_1$ of 0.11 (1) ns, and the triplet feature is fitted to a triexponential decay ($\tau_2 = 10.7 (7)$ ns, $\tau_3 = 0.1 (3)$ $\mu$s, and $\tau_4 = 50.1 (1)$ $\mu$s).

Biexponential triplet decays are not uncommon in singlet fission-active bipentacenes, and the two decay components are typically ascribed to geminate triplet pair recombination and free/decorrelated triplet decay processes, respectively. Triexponential triplet decays have also been observed, notably in related adamantane-derived bi- and tetra-pentacene systems reported by Hetzer et al. In that study, the authors correlated the transient absorption data to time-resolved EPR experiments on the bipentacene species, assigning the three decay components to $^3(T_1;T_1)$, $^3(T_1;T_3)$, and free $T_1$.

Here, in the absence of additional corroborating evidence, we err on the side of caution and discuss the data in the context of both models. The singlet fission rate is not significantly altered between the two fits. When including a third triplet decay component, though, the fastest triplet lifetime shortens slightly from 23 to 11 ns. In addition, we note that an additional singlet component that decays in parallel to the productive fission pathway could be added to each model; however, the fitted results for each component were not substantially different from the original model, and the rate constants corresponding to the added singlet component had substantially higher standard errors from the fit.

As with HDPP-Pent, concentration-dependent sensitization experiments were carried out on mixtures of anthracene and Li$_2$(DPP-Pent)$_2$, giving a $^3$ESA extinction coefficient at 515 nm of $\sim 52000$ M$^{-1}$ cm$^{-1}$. Applying this value to the fsTA spectrum after direct excitation at 550 nm approximates a triplet yield of 195%. Ground state bleach analysis via the method of Eaton et al. gives a triplet yield estimate of 186%. Using these two methods, we place the triplet yield of Li$_2$(DPP-Pent)$_2$ in the range 186–195%, considerably higher than in HDPP-Pent (Supporting Information, Sections X and XI).

In the case of KDPP-Pent, the fsTA data show the decay of the $^3$ESA to a broad feature suggestive of the overlapping singlet and triplet absorption bands observed in HDPP-Pent (Figure 6d–f). The nsTA data reveal a structured $^3$ESA that decays biexponentially in the KDPP-Pent sample. The kinetics could be fitted with both the three-component model applied to the Li$_2$(DPP-Pent)$_2$ data set and a four-component model used for HDPP-Pent (Tables S9 and S10). There is some absorption intensity in the 400–500 nm region in the singular value decomposition of the residual data matrix of the three-component fit that is adequately accounted for in the four-component model. With regards to the two models, the fittings place a singlet fission time constant in KDPP-Pent around 400–600 ps. Despite the qualitative similarity between the K- and HDPP-Pent TA data, little emission intensity was observed from the K complex, and no time-resolved luminescence could be acquired, which suggests that KDPP-Pent may represent an intermediate case between HDPP-Pent and the Li complex.

**DISCUSSION**

**Comparisons within the DPP-Pent Series.** HDPP-Pent undergoes intramolecular singlet fission with a time constant $\tau_{SF}$ of $\sim 730$ ps with an estimated 100% triplet yield. In contrast, singlet fission in Li$_2$(DPP-Pent)$_2$ ($\tau_{SF} \sim 100$ ps) is nearly 7-fold faster than HDPP-Pent and occurs with higher efficiency (i.e., 186–195% triplet yield). KDPP-Pent, on the other hand, demonstrates a rate of fission ($\tau_{SF} \sim 400–600$ ps) more akin to HDPP-Pent.

There are several considerations for the origin of the rate enhancement in Li$_2$(DPP-Pent)$_2$. First, the NMR data demonstrate temperature-dependent conformational dynamics in HDPP-Pent, which suggests that a heterogeneity of conformations are excited in solution during the TA experiment, some of which may be less favorable for intramolecular singlet fission than others. Deprotonation and complexation may rigidify the linker, leading to more efficient singlet fission in solution. However, the Li and K complexes both display well-resolved $^1$H NMR spectra, unlike the spectrum of HDPP-Pent, and therefore, the structural rigidification alone does not explain the rate enhancement in Li$_2$(DPP-Pent)$_2$.

Second, the ion-π-stacking interaction introduces an electric dipole in the vicinity of the pentacene subunits, where a potential Stark effect could influence singlet fission within the system. The Li and K complexes would likely exhibit distinct electric field influences, but at this point it is unclear the extent to which this would differentiate the two.

Third, NMR data support the assignment of dimeric and monomeric solution-state structures for Li$_2$(DPP-Pent)$_2$ and KDPP-Pent, respectively. The Li complex is thus distinct from the K structure, as it exhibits π-stacking interactions between the pentacene subunits and also has four pentacene rings in a single molecular unit as opposed to two (Figure 3). It is likely that these structural perturbations lead to a pronounced rate enhancement in Li$_2$(DPP-Pent)$_2$ relative to KDPP-Pent. The interactions established via π-stacking may promote favorable electronic coupling, leading to efficient fission.

Notably, despite the 7-fold rate enhancement in Li$_2$(DPP-Pent)$_2$, there is little sacrifice in terms of triplet lifetimes. Compared to the $\sim 38$ ns and 36 $\mu$s lifetimes observed in HDPP-Pent, we find lifetimes of 23 ns and 35 $\mu$s in Li$_2$(DPP-
Pent)₂ when fitted with a biexponential decay. The faster decay lifetime in Li₂(DPP-Pent)₂ does shorten to 11 ns when including a triexponential, with intermediate and long lifetimes of 100 ns and 50 μs.

Comparison to Previously Reported Bi- and Poly-pentacenes. The present results find themselves in distinction from many of the reported bipentacene systems in which there is typically an increase in the rate of triplet decay when stronger coupling between pentacene units results in faster rates of fission (Table S14). The series of phenylene-linked dimers initially reported by Zirzlmeier et al. displays increasing rates of singlet fission going from meta- (63 ps) to para- (2.7 ps) to ortho- (500 fs) and shows a related decrease in triplet pair lifetimes (2.2 ns, 17.3 ps, and 12 ps, respectively). Likewise, the oligophenylene-bridged bipenta-

cenes linked in the 2,2’ position reported by Sanders et al. show an analogous increase in singlet fission rate with concomitant reduction in triplet pair lifetime with decreasing linker units (τ₃₉ from 220 to 20 ps to 760 fs; τ₅ from 270 to 16.5 ns to 450 ps). In these cases, conjugated linkers permit strong electronic coupling between pentacenes, which can be modulated via substitution patterns on the linker or by increased linker length. Nonconjugated linkers have also been explored, as these systems tend to attenuate the interpentacene electronic coupling. Nevertheless, similar trends (increased singlet fission rate with decreased triplet/triplet pair lifetime) have also been observed in such species.

In the DPP-Pent series reported here, the pentacene units are linked in the 6,6’-position by the DPP ligand scaffold. The optimal geometry for the pentacene units is likely orthogonal to the pyridine rings due to steric constraints. This, in addition to the length of the linker, likely weakens the through-bond coupling via the conjugated dipyridyl pyrrole or pyrrolide in comparison to more directly linked systems such as the ortho-, meta-, para-phenylene dimers or the oligophenylene systems. This is reflected in the relatively slower rate of fission in HDPP-Pent. In Li₂(DPP-Pent)₂, through-space π-interactions via the intermediary dipyridyl pyrrolide moiety provide an alternative coupling pathway. The rate of singlet fission in Li₂(DPP-Pent)₂ (τ₅₉ ~ 100 ps) is still slower than other bipentacenes displaying strong direct pentacene–pentacene π-interactions (typically less than 1 ps). These through-space coupled systems tend to have fast triplet pair annihilation pathways, whereas Li₂(DPP-Pent)₂ exhibits ns–μs triplet pair/triplet lifetimes.

Another important point of comparison is having four pentacene units in the dimeric Li complex, which may favor a faster rate of singlet fission and slower rate of triplet annihilation. For example, by comparing adamantyl-linked bi- and tetra-pentacene systems, Hetzer et al. suggested that additional chromophores may effectively delocalize the triplet pair state, providing a favorable entropic factor to the rate of fission. The authors report that the tetra-pentacene species likewise shows very little deviation in triplet lifetimes from the bipentacene system, despite the faster rate of fission.

In Li₂(DPP-Pent)₂, the higher-order structure enforced by lithium coordination likely impacts the photophysics of the system in several ways. First, the through-space π-interactions establish an important coupling pathway that leads to the rate enhancement from HDPP-Pent and KDPP-Pent; however, because the coupling is via the dipyridyl pyrrole, this interaction is tempered such that the generated triplet pair is longer lived than in other π-stacked bipentacenes. This is in conjunction with the entropic favorability of having four pentacene rings within a single molecular dimer.

In summary, with HDPP-Pent and its alkali metal derivatives, we have demonstrated the ability to tune singlet fission via supramolecular assembly promoted by metal coordination. The π-stacking interactions and dimeric structure revealed in Li₂(DPP-Pent)₂ are critical to its increased singlet fission efficiency compared to the parent HDPP-Pent. This approach highlights the importance of through-space, geometric perturbations that influence singlet fission beyond strict through-bond interactions. Controlling the orientation and interaction of multiple pentacene motifs through coordination chemistry is demonstrated as a new, impactful tool for improving singlet fission performance.

METHODS

Steady-State Emission Spectroscopy. Corrected room temperature emission spectra were collected in the Beckman Institute Laser Resource Center using a modified Jobin Yvon Fluorolog-3 instrument. Samples were excited with a xenon arc lamp, employing a monochromator for wavelength selection, and emission was detected at 90° using two Ocean Optics ECDPro CCD spectrometers spanning 300–930 nm.

Fluorescence quantum yields were determined via the comparative method in which the experimental quantum yields were measured relative to a known standard under the same excitation conditions. Rhodamine-6G in EtOH was used as a standard (Φₓ = 0.95). All samples were diluted such that the maximum absorbance values were less than 0.1. Pentacene samples of unknown quantum yield were prepared in toluene, added to 1 cm glass emission cuvettes, and sealed with a Kontes plug under N₂(g) atmosphere. Samples were excited at λₐₓ = 530 nm. The unknown quantum yields (Φₓ) were calculated with eq 1 using the absorbance values A(λₐₓ) and the integrated fluorescence intensities F(λₐₓ), and correcting for the differing indices of refraction between EtOH and toluene.

Φₓ = Aₓ(λₐₓ) Fₓ(λₐₓ) nₓ² Fₛ / Aₛ(λₛ) Fₛ(λₛ) nₛ² Φₛ

(1)

Time-Resolved Luminescence Spectroscopy. The 1064 nm output of a Nd:YAG laser (Spectra Physics Vanguard) was regeneratively amplified (Continuum) and frequency doubled using a potassium dihydrogen phosphate (KDP) crystal to 532 nm excitation pulses (~10 ps, 10 Hz). Luminescence was collected 90° from the excitation, passed through a polarizer oriented at the magic angle, and then directed onto the entrance slit of a monochromator for wavelength selection. Detection was achieved using a streak camera (Hamamatsu C5680) in photon-counting mode, and data were collected over a 50 ns time window. Samples were prepared in sealed 1 cm quartz cuvettes under N₂(g) and were stirred during data acquisition.

Transient Absorption Spectroscopy. The 800 nm output of a S W, 1 kHz pulsed Ti:sapphire amplifier (Coherent Astella) was partitioned with a 50:50 beamsplitter. One half was fed into an OPerA Solo optical parametric amplifier tuned to 550 nm output, which was used as the excitation pump and routed through a chopper and into a joint femtosecond and nanosecond HELIOS FIRE/EOS transient absorption (TA) spectrometer (Ultrafast Systems). For femtosecond experiments, a small portion of the other half of the Ti:sapphire output was routed into the spectrometer and used to generate...
broadband probe light of the appropriate wavelength region (visible or near-infrared). For nanosecond experiments, a separate white light fiber laser was employed as the probe light. Samples were prepared in sealed 2 mm glass cuvettes under \( \text{N}_2(\text{g}) \) and were stirred during data acquisition. Data were processed using Ultrafast Systems Surface Xplorer software for chirp and time zero corrections. The rest of the data workup was performed in MATLAB. For fsTA data sets, pretime zero spectral vectors were averaged and subtracted from the rest of the data set to remove background pump scatter. Pretime zero spectral vectors were similarly averaged in the nsTA data sets and then subtracted up to 20 \( \mu \text{s} \) delay times as pump scatter is not detected beyond this threshold by the EOS.

**ASSOCIATED CONTENT**

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.0c01044.

Synthetic procedures, NMR characterization, steady-state and time-resolved absorption and emission spectra, target kinetic modeling of the transient absorption data, a detailed description for the triplet yield estimation for HDPP-Pent and \( \text{Li}_x(\text{DPP-Pent})_y \), and a comparison of HDPP-Pent, \( \text{Li}_x(\text{DPP-Pent})_y \), and KDPP-Pent singlet fission and triplet lifetime rates with the broader literature (PDF)

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**Notes**

The authors declare no competing financial interest.

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