Exploiting Excited-State Aromaticity To Design Highly Stable Singlet Fission Materials

Kealan J. Fallon, †,‡,§ Peter Budden, †,¶ Enrico Salvadori, †,‖ Alex M. Ganose, †,¶ Lissa Eyre, †,‖ Simon Dowland, †,‖ Qianxiang Ai, †,‖ Stephen Goodlett, † Chad Risko, †,‡ David O. Scanlon, †,‖,†,‡ Christopher W. M. Kay, †,‖,†,‡ Akshay Rao, †,‡ Richard H. Friend, †,‡,*, Andrew J. Musser, †,‖,*,∞ and Hugo Bronstein †,‡,*,∞

1Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, U.K.
2Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, U.K.
3Department of Chemistry, University of Turin, Via Pietro Giuria 7, 10125 Torino, Italy
4London Centre for Nanotechnology, University College London, 17-19 Gordon Street, London WC1H 0AH, U.K.
5Kathleen Lonsdale Materials Chemistry, Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.
6Thomas Young Centre, University College London, Gower Street, London WC1E 6BT, U.K.
7Diamond Light Source Ltd., Diamond House, Harwell Science and Innovation Campus, Oxfordshire OX11 0DE, U.K.
8Department of Chemistry and Center for Applied Energy Research, University of Kentucky, Lexington, Kentucky 40506, United States
9Department of Chemistry, University of Saarland, 66123 Saarbrücken, Germany
10Department of Physics and Astronomy, University of Sheffield, Hicks Building, Hounsfield Road, Sheffield S3 7RH, U.K.

Supporting Information

ABSTRACT: Singlet fission, the process of forming two triplet excitons from one singlet exciton, is a characteristic reserved for only a handful of organic molecules due to the atypical energetic requirement for low energy excited triplet states. The predominant strategy for achieving such a trait is by increasing ground state diradical character; however, this greatly reduces ambient stability. Herein, we exploit Baird’s rule of excited state aromaticity to manipulate the singlet–triplet energy gap and create novel singlet fission candidates. We achieve this through the inclusion of a [4n] 5-membered heterocycle, whose electronic resonance promotes aromaticity in the triplet state, stabilizing its energy relative to the singlet excited state. Using this theory, we design a family of derivatives of indolonaphthyridine thiophene (INDT) with highly tunable excited state energies. Not only do we access novel singlet fission materials, they also exhibit excellent ambient stability, imparted due to the delocalized nature of the triplet excited state. Spin-coated films retained up to 85% activity after several weeks of exposure to oxygen and light, while analogous films of TIPS-pentacene showed full degradation after 4 days, showcasing the excellent stability of this class of singlet fission scaffold. Extension of our theoretical analysis to almost ten thousand candidates reveals an unprecedented degree of tunability and several thousand potential fission-capable candidates, while clearly demonstrating the relationship between triplet aromaticity and singlet–triplet energy gap, confirming this novel strategy for manipulating the exchange energy in organic materials.

INTRODUCTION

Phenomena that permit the generation of multiple excitons from the absorption of one photon have received large attention recently due to their potential in photovoltaic cell efficiency enhancement. One such process is singlet fission, whereby two low-energy triplet excited states are generated from one high-energy singlet excited state, allowing quantum efficiencies up to 200% and offering the potential to surpass the single junction limit in solar cells. Recent advancements in singlet fission have been materials-limited due to the rarity of molecules that meet the essential energetic requirement for the process, namely, that the energy of the lowest triplet excited state E(T1) be on the order of half the energy of the lowest singlet excited state E(S1). Known systems include rylene dyes,1−12 polynes,13−15 donor–acceptor polymers,16−18 and derivatives of the linear acenes, particularly tetracene and pentacene, which have become the focus of the field.2,19−31 The low triplet energies of the acenes are a function of their migratory Clar’s sextets resulting in their large localized

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Figure 1. Optical properties and characteristics. (a) The polycyclic aromatic hydrocarbon indolonaphthyridine thiophene (INDT) with labeled rings of interest. (b) Resonance forms of INDT showing origin of Baird [4n] ring (CS, blue). Values of NICS(1) calculations for CN-INDT are shown for S0 and T1, where a more negative value denotes greater aromaticity. (c) Solution (chloroform) steady-state absorbance spectra of the investigated family of materials. (d) Theoretical energies (eV, TD-DFT/TDA, B3LYP/6-311++G***) of S1 and T1 relative to the ground state. The ratio of these energies is given inset.

diradical character, which compromises their chemical stability (e.g., pentacene must be stored in the dark under inert gas lest it undergo photocatalyzed dimerization or oxidation). Unfortunately, current established rationales behind synthesizing organic molecules with large singlet (S1)–triplet (T1) energy gaps—such as inducing biradicaloid character—offer the synthetic chemist little assistance in identifying or developing new chromophores for this purpose, although these rules are of very good use to check whether a structure is likely to fulfill the energetic criteria for singlet fission.34–36 Merely focusing on increasing the amount of biradical character can often involve cost to chemical stability as it can result in highly reactive localized unpaired electrons, although this can potentially be addressed with careful protection of the radical sites.37,38 There is therefore a need for a simple design approach to identify or design materials that undergo singlet fission at no expense to stability.

In the ground state, Hückel’s Rule rationalizes the enhanced stability of cyclic systems with [4n + 2] electrons and this concept of aromaticity is a fundamental pillar of chemistry. Lesser known is Baird’s Rule, which states that in the triplet state, cyclic systems with [4n] electrons are aromatic and hence stabilized.39,40 Following confirmatory modern theoretical analysis, the rule has been explored in atypical conjugated systems in the past few years.41–43 Here, we demonstrate the synthesis and characterization of highly stable, tunable organic materials that undergo singlet fission through exploitation of Baird’s aromaticity of the triplet excited state.

RESULTS AND DISCUSSION

We focus in particular on derivatives of indolonaphthyridine benzene or Cibalackrot (SI Section S1), previously proposed as a singlet fission candidate.49 Quantum chemical calculations (B3LYP/6-311G**) reveal Cibalackrot to possess a low-lying triplet state with \( E(T_1)/E(S_0) \sim 0.5 \), affirming its potential for singlet fission. This stabilized triplet state has been previously explained through the stabilized diradical nature of the indigo core.49–51 It can likewise be rationalized using Baird aromaticity, due to the presence of [4n] contribution in its resonance structure (Figure 1b and SI Section S2). We have designed a family of materials (Figure 1a) to investigate: (a) whether the indolonaphthyridine chromophore does indeed undergo singlet fission; (b) whether the optical properties and singlet fission ability could be tuned by chemical functionalization; and (c) whether contributions from an aromatic triplet state enhance chemical stability. The full synthesis and characterization of these materials is given in the SI Section S1, hereafter referred to as x-INDT where \( x \) is the atom or functional group installed at the 6,6'-positions of the INDT C6 ring (see Figure 1a).

The solution steady-state absorbance spectra (Figure 1c) demonstrate the optical tunability of this family. H-INDT and F-INDT display comparable absorbance with \( \lambda_{\text{max}} \) of 602 nm. Both Cl-INDT and Br-INDT exhibit bathochromically shifted but practically identical absorbance with \( \lambda_{\text{max}} \) of 615 nm. The addition of strongly electron withdrawing carbonitrile functional groups was achieved through a Rosenmund–von Braun reaction of Br-INDT and furnished both the asymmetric mononitrile/monobromo compound CNBr-INDT and dinitrile compound CN-INDT. The addition of each carbonitrile group narrows the optical band gap of the material significantly, yielding \( \lambda_{\text{max}} \) of 635 for the mono- and 650 nm for the dicianonitrile compound.

The energies of the S1 and T1 states of these materials were calculated using time-dependent density functional theory (TD-DFT) on DFT-optimized structures. These calculations reproduce the observed tunability of the optical energy gap and suggest that all of the molecules possess the relationship of 2T1 < S1 required for singlet fission (Figure 1d). Moreover, the ratio of calculated T1/S1 energies reveals that this parameter, and thus suitability for singlet fission, can be tuned through chemical substitution. We do note that the use of TD-DFT for the prediction of triplet state energies is problematic.52 However, whether the predicted values for the (T1/S1) ratio may be over- or underestimated as a whole, the key trends—tunability of the ratio and its relation to triplet-stated aromaticity—should remain robust. Indeed, these values are...
best taken as a guideline, since incorporation into the solid state inevitably alters the energetic structure to some degree.

We assessed the relative aromaticity of the molecular structures through a variety of computational methods. The aromaticity of the five-membered (CS) ring in the triplet state was assessed using nucleus-independent chemical shift calculations (NICS(1)); this data is given in full in the SI Section S3 and the data for CN-INDT is shown in Figure 1b. Importantly, the NICS calculations demonstrate how the aromaticity in the CS ring is significantly increased in the triplet state in accordance with Baird’s rules.

Figure 2 shows ACID (anisotropy of the induced current density) plots for the F-INDT in the S0 and T1 states (see SI for further details).

Figure 2. ACID plots for F-INDT in the S0 (left) and T1 (right) states. The isovalue of the isosurface was set to 0.05. The induced current density vectors are denoted by the arrows with the length limited to 0.3–1.5. Larger images available in SI.

As shown in Figure 3, we observe a distinct photoinduced absorption band at ~680 nm (Br-INDT) or ~740 nm (CN-INDT). This species, which persists out to the μs time scale with little spectral evolution, should therefore only originate from charges or triplet excitons. Triplet sensitization in solution (green dashed)53 yields a similar spectral signature, after taking into consideration the difference in underlying ground-state bleach and a slight bathochromic shift of the T1 → T0 transition in the solid state which is consistent with other organic systems.54,55,56 Thus, we assign the μs excited-state absorption to triplet excitons. This is further confirmed via electron paramagnetic resonance (EPR), discussed below. We detect similar evolution in CI-INDT and CNBr-INDT, while in F-INDT the spectral signature we attribute to triplets decays faster, with a lifetime of 300 ns. In contrast, we do not find evidence for triplets in H-INDT. The primary signature we observe in H-INDT (Figure S4.3) in this temporal regime is a set of positive peaks that match the ground-state absorption and can be assigned to bleaching of the ground state. These are accompanied by a weak photoinduced absorption (ΔT/T < 0) from 650 nm to the near-infrared which decays on an instrument-limited time scale and is assigned to the singlet. There is no triplet-like absorption in this film, and there are evidently no significant long-lived electronic states in this film. The positive features that outline the photoinduced absorption are due to thermal modulation of the absorption and reflectivity and are commonly observed in measurements in the ground-state absorption region.54,57,58

These measurements provide clear evidence of sub-ns triplet formation, but it is difficult to distinguish the mechanism—intersystem crossing or singlet fission—from optical spectroscopy alone. We therefore characterized the sublevel populations of the triplet states using time-resolved EPR, which is a powerful tool for probing singlet fission materials.59-65 In frozen dilute solution, singlet fission—being an intermolecular process—is inactive, and the zero-field sublevel populations of triplet states in these conditions are attributed to intersystem crossing. The frozen solution EPR spectra (Figure 3c) of Br- and CN-INDT exhibit emission/absorption polarization patterns EEEAAA. In thin film, singlet fission becomes possible and may out-compete intersystem crossing. In such a case, the presence of a new channel for triplet formation would manifest as changes in the triplet absorption onsets display similar trends to the solution measurements; however, we remind the reader that direct comparison of theoretical (gas phase) energetics to solid state experimental results is unwise as each molecule will experience different intermolecular coupling.

Evidence for Singlet Fission. We investigated the ability of INDT films to undergo singlet fission using time-resolved optical and spin-resonance techniques. In transient absorption spectroscopy, the sample is excited with a short laser pulse and then interrogated with a broadband probe pulse at a controllable time delay (100 fs to 1 ms). Changes in the transmission of the probe reflect the depopulation of the ground state, the absorption spectrum of photoexcited states, and stimulated emission from allowed optical transitions. Full details of the experimental setup are presented in the SI Section S4. Representative transient absorption spectra are shown in Figure 3b for Br-INDT and CN-INDT acquired using a ns–μs system (λex = 532 nm, ~1 ns). A broader probe spectral range and equivalent measurements for the remaining molecules are presented in the SI Section S4.

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sublevel populations. The polarization pattern of Br-INDT films is EAEAEA, which cannot be caused by the same intersystem crossing pathway active in dilute solution. The absence of other potential mechanisms allows us to attribute triplet formation in these films to singlet fission. The spectrum of CN-INDT films is more complex—at least two components with different zero-field splitting parameters are present. One component has zero-field splitting parameters similar to those observed in solution but with AEEAE polarization (SI Section S5). Importantly, this polarization pattern, previously observed in TIPS-tetracene and pentacene dimers,\textsuperscript{59,60} is a signature of singlet fission.\textsuperscript{59} On the basis of this direct evidence of fission in Br-INDT and CN-INDT and the similar sub-ns triplet formation observed in Figure 3b, we conclude that singlet fission is active in all of the reported INDT derivatives except H-INDT.

**Rapid Triplet Formation.** For further insight into the mechanism of singlet fission, we examine the initial decay of S\textsubscript{1} in Br-INDT and CN-INDT using fs–ps transient absorption spectroscopy ($\lambda_{exc} = 530$ nm, $\sim 250$ fs, 37 kHz repetition rate). Representative transient absorption spectra at a high excitation density are shown in Figure 4a and 4b for the same molecules presented in Figure 3. At early times there is a broad photoinduced absorption ($\Delta T/T < 0$) spectrally overlapped with the ground state absorption (making the spectra highly congested in this region) and extending to a peak in the near-infrared. From comparison of the steady-state absorption and photoluminescence spectra, we can attribute much of the complex structure of this spectrum to overlapping $\Delta T/T > 0$ signatures from bleaching of the ground-state absorption and stimulated emission from S\textsubscript{1}.

As the strong initial photoinduced absorption decays, the underlying triplet signal is revealed (685 nm in Br-INDT, 745 nm in CN-INDT), corresponding well with the ns TA experiment (Figure 3b). Due to the overlapping signals, it is not possible to definitively distinguish the formation time of this signal; however, it is certainly present by 2–3 ps in CN-INDT, effectively ruling out the formation of these triplets from ISC, and confirming the result from EPR that triplets are originating from singlet fission.

We observe that the dynamics of the loss of the initial photoinduced absorption peaked at 850 nm are strongly dependent on excitation density. In Br-INDT, at high excitation densities comparable with those required to measure ultrafast photoluminescence\textsuperscript{64} (Figure 4c), the decay is $\sim 7$ ps. This rapid decay is likely due to singlet–singlet annihilation. At the lowest excitation densities at which TA was measured, annihilation is not significant, and the decay (biexponential: 58 and 990 ps) is in agreement with the intrinsic 1 ns lifetime from time-correlated single-photon counting (Figure 4c). This agreement with photoluminescence measurements in both high- and low-annihilation regimes firmly establishes the initially decaying spectral features, peaked at 850 nm, as signatures of S\textsubscript{1} and indicates that the INDTs are similarly sensitive to singlet–singlet annihilation as perylenediimides.\textsuperscript{65}

Given that the S\textsubscript{1} lifetime is so strongly affected by singlet–singlet annihilation, we would expect that the triplet yield and formation kinetics are also power dependent. Curiously, when
formed rapidly via singlet measurements using di ff from the hot spots cannot undergo singlet
Meanwhile, a parallel population of singlets formed too far fi e r e n ts o l v e n t so r
be tuned through processing (seeSI Section S4.12). PLQY is
quantum yield (PLQY), suggesting the density of hot spots can
conditions reveal considerable changes in photoluminescence
−
−
due to singlet
mobile enough to show a strong excitation density dependence
The ultimate goal of exploiting excited state aromaticity to generate singlet fission-capable materials is to
access triplet states without cost to the chemical stability. The
ambient stability of each INDT material was compared to TIPS-pentacene. Thin films were identically prepared and stored in individual clear Perspex boxes on a shelf, in air, in a well-lit area, but out of direct sunlight, and the steady state absorption was measured periodically over 31 days (see SI Section S6). Under these ambient conditions TIPS-pentacene showed total degradation after 4 days, while the INDT materials exhibited excellent ambient stability and CN-INDT maintained over 80% of its original absorbance after 31 days (Figure 5c). The high chemical stability of the INDTs showcases their robust ground and excited states despite fission occurring readily (and hence a high concentration of triplets being present) in the material. By exploiting triplet aromaticity, not only is the energy of the triplet state lowered such that it can undergo singlet fission, but the delocalized nature of the unpaired electrons means they are less susceptible to photodegradation reactions, in an analogous way that ground state aromaticity increases the stability of organic compounds. Triplet-mediated photodegradation of acenes and other polyaromatic hydrocarbons is well-documented, thus introducing some aromatic character into excited states could lead to a generalized method to enhance the photoactivity of organic materials.

We note that the increase in triplet-state aromaticity does come at some slight cost to ground-state aromaticity, but this effect is negligible as the materials also possess significant ground state aromaticity as evidenced by their high stability in the ground state as well.

Expanding the Chemical Space. The experimental proof of singlet fission in INDT-based materials and their photochemical stability benchmarks the essential validity of our approach: increasing triplet aromaticity through chemical functionalization results in more energetically favorable singlet fission, into more stable triplet states. We now return to our design principle to explore the scope of materials tunability and identify robust trends linking excited-state energetics and triplet aromaticity. To widen our analysis, theoretical energies of \(S_1\) and \(T_1\) and NICS(1) aromaticity for 9920 indolophthryidene candidates were calculated using TD-DFT incorporating the Tamm–Dancoff approximation (TDA) at the B3LYP/6-311G** level of theory (rationale of these methods given in the SI Section S7). The results and codes used to generate and perform all calculations detailed in this report are provided online in a publicly available repository (https://github.com/SMTG-UCL/singlet-fission-screening).

In this wider sample group (Figure 5a), the correlation of increased excited state aromaticity and reduced \(T_1/S_1\) is unequivocally clear. It demonstrates that, through appropriate chemical substitution to increase the aromaticity of the triplet state, its energy can be lowered without affecting the energy of the singlet—the red bar highlights candidates with \(S_1 = 2.1\) eV and with \(T_1\) ranging from 1.5–0.5 eV. We can directly visualize this tuning by plotting the calculated \(S_1–T_1\) energy gap as a function of triplet-state aromaticity (Figure 5b). These results directly demonstrate that exploiting Baird-type aromaticity is a powerful approach for manipulating the singlet–triplet energy gap. Independent manipulation of the singlet and triplet energies in such a manner has never been demonstrated and has implications across many areas of science such as light emitting diodes, photovoltaics, photocatalysis, photochemistry, spintronics, and magnetism. In the context of singlet fission, this data has allowed us to identify 2616 new singlet fission candidates with a wide range of optical band-gaps and T/S ratios. These are all based on straightforward substitution of the indolophthryidine chromophore, which is itself well-known for photochemical robustness and large oscillator strength—both ideal properties for applications of singlet fission.

Applicability to Other Systems. In order to demonstrate the application and generalizability of the proposed methodology we demonstrate here that excited state aromaticity can be used to rationalize the energetic position of alternative non-aceene singlet fission candidates and also as a predictive tool to search for new materials which fulfill the energetic design criteria. Diketopyrolopyrole (DPP) has been suggested to undergo singlet fission but thus far there has been no explanation for its unusually large \(S_1–T_1\) energy gap.66 Similarly to our Cibacular derivatives, we propose that the presence of [4n] resonance structures induces aromaticity of the triplet excited state, resulting in a widening of the \(S_1–T_1\) energy gap such that fission becomes energetically feasible.

Figure 6 shows amide bond resonances which result in a core which has an electronic structure similar to pentacene, which has an aromatic triplet state.62 This aromaticity of the triplet state of DPP is confirmed by NICS calculations (each central-ring has NICS(1) ~ 3.96 using DFT/TDDFT B3LYP/6-311G**). As detailed earlier, we suggest this is responsible for its energetic stabilization and potentially also explains the superior stability toward photodegradation of this chromo-
phore (the unpaired electrons are delocalized rendering them less reactive to photodegradation reactions).

Implementation of the proposed design rules to identify and design new chromophores as singlet fission candidates or merely as a tool to predict and rationalize the relative excited state energetics is demonstrated below. Table 1 shows the structures and calculated vertical excited state energies (using DFT/TDDFT, B3LYP 6-311G**) of two sets of molecules A and B and their two regioisomers (5 or 6) based on the size (and connectivity) of the lactam ring. It can clearly be seen that within each set of isomers (i.e., A5 vs A6) virtually all parameters that could affect excited state energies (e.g., torsion angles, conjugation paths, atom connectivity) are identical with the exception of the core ring size.

It should be noted that all calculations are performed at the ground state geometry where the amide-containing cores are completely planar. Similarly to INDT and DPP, in both cases where a 5-membered cyclic amide is present (A5 and B5) it is possible to draw resonance structures (see Figure S2.5) that contain [4n] electrons suggesting that the triplet excited state will have aromatic character. In both cases where the central core is comprised of 6-membered rings (A6 and B6) the resulting resonance structures have [4n + 2] electrons, suggesting that the excited states will have antiaromatic character. Therefore, one can simply predict without even the aid of theoretical calculations that the compounds with 5-membered cyclic amides will have narrower optical energy gaps, and larger S1−T1 energy gaps, making them singlet fission candidates. Both of these predictions, alongside confirmation of the reversal of aromaticity are completely supported by the theoretical calculations (Table 1).

It is important to note that although these dyes have been previously reported, neither A5 nor B5 have been investigated for singlet fission, indicating the ease with which new candidates that fulfill the energetic criteria for singlet fission can be identified using this theory. Additionally, the ease with which [4n] vs [4n + 2] cyclic motifs can be identified adds an extremely powerful tool for the synthetic chemist to predict and rationalize optical energy gaps.

The inclusion of some ground-state antiaromaticity need not compromise stability of these chromophores as all the materials presented here have substantial overall aromatic character, and experimentally both DPP and Cibalackrot are extremely stable chromophores. As seen in Figure 4, the magnitude of the S1−T1 energy gap can be tuned and we suggest that in order to control this value through chemical design it is necessary to investigate the relative contributions of the excited states (both S1 and T1) to the aromatic [4n] core as Baird’s rules formally applies to both types of excited states, which is beyond the scope of this investigation. Additionally, we again note that our calculations are performed at a relatively low level of theory, but the predicted values of the compounds presented in Table 1 are in good agreement with experiment.67,68 Finally, we note that solid-state intermolecular interactions play a very significant role in the process of the singlet fission.12,27,51,69,70 These are not considered in our theoretical analysis of new core chromophores, but where the intermolecular coupling motifs are known it should be possible to optimize the geometry either experimentally12,57,70 or computationally.11,69,71

Table 1. Structures and Theoretical Excited State Properties of Two Molecules A and B, and Their Two Isomers 5 (Bridged C5 Lactam Rings) and 6 (Fused C6 Lactam Rings) Calculated at the TDDFT/B3LYP 6-311G** Level of Theory

| Molecule | A5 (eV) | A6 (eV) | B5 (eV) | B6 (eV) |
|----------|---------|---------|---------|---------|
| S1       | 2.29    | 3.11    | 2.20    | 3.22    |
| T1       | 1.04    | 1.94    | 0.73    | 2.11    |
| T1/S1    | 0.45    | 0.62    | 0.33    | 0.66    |
| S1−T1    | 1.25    | 1.31    | 1.47    | 1.10    |
| Triplet NICs(1) | −3.1 | +5.2 | −3.4 | +4.7 |

CONCLUSIONS

Though our experimental exploration has been limited to a single family of materials, the wide tunability we have demonstrated, our preliminary calculations on alternative [4n] containing dyes, and previous investigations of Baird-type aromaticity41−43,72 indicate that the same principles can be readily applied to other materials systems. In practical terms, the requirement of a [4n] cyclic contribution to a molecule’s resonance structures translates into a simple design rule for targeting singlet fission systems. Examples of these (beyond INDT) are structures such as DPP (which has been proposed to undergo singlet fission, but no rationale for its large singlet-triplet energy gap has been suggested), indigo, isoindigo,74,75 pechmann dyes, and fulvalenes. Ground state aromaticity is a fundamental cornerstone of synthetic organic chemistry, providing stability and tunability to unsaturated systems, underpinning the entire development of the field of organic electronics. The work we present here demonstrates that excited-state aromaticity plays an equally important role in both the energetic position and the stability of photoexcited...
triplet states. More broadly, we envisage the same approach may be used to tune the exchange energy in organic systems where triplets play a critical role, to mitigate losses in photovoltaics, harvest additional carriers in light-emitting diodes, enhance the stability of novel open-shell systems, or broaden the materials library for photon up-conversion and singlet fission.

ASSOCIATED CONTENT

Supporting Information
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Synthetic methods and characterization, spectroscopic data and analysis (PDF)

AUTHOR INFORMATION

Corresponding Authors
*rfh10@cam.ac.uk
*ajm557@cornell.edu
*hab60@cam.ac.uk

ORCID
Kealan J. Fallon: 0000-0001-6241-6034
Christopher N. Savory: 0000-0002-9052-7484
Chad Risko: 0000-0001-9838-5233
David O. Scanlon: 0000-0001-9714-8601
Christopher W. M. Kay: 0000-0002-5200-6004
Akshay Rao: 0000-0003-4261-0766
Richard H. Friend: 0000-0001-6565-6308
Andrew J. Musser: 0000-0002-4600-6606
Hugo Bronstein: 0000-0003-0293-8775

Present Address
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