

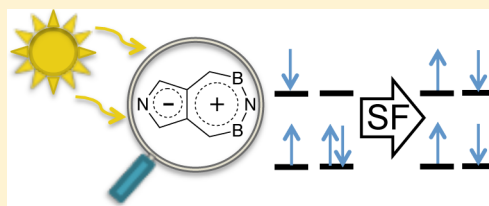
Seeking Small Molecules for Singlet Fission: A Heteroatom Substitution Strategy

Tao Zeng,* Nandini Ananth, and Roald Hoffmann

Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, United States

S Supporting Information

ABSTRACT: We design theoretically small molecule candidates for singlet fission chromophores, aiming to achieve a balance between sufficient diradical character and kinetic persistence. We develop a perturbation strategy based on the captodative effect to introduce diradical character into small π -systems. Specifically, this can be accomplished by replacing pairs of not necessarily adjacent C atoms with isoelectronic and isosteric pairs of B and N atoms. Three rules of thumb emerge from our studies to aid further design: (i) Lewis structures provide insight into likely diradical character; (ii) formal radical centers of the diradical must be well-separated; (iii) stabilization of radical centers by a donor (N) and an acceptor (B) is essential. Following the rules, we propose candidate molecules. Employing reliable multireference calculations for excited states, we identify three likely candidate molecules for SF chromophores. These include a benzene, a naphthalene, and an azulene, where four C atoms are replaced by a pair of B and a pair of N atoms.



INTRODUCTION

Singlet fission (SF) describes a process by which a photoexcited singlet exciton splits to two triplet excitons in an organic chromophore material.^{1,2} This theoretical doubling of the number of excitons, coupled with the longer lifetimes expected of triplet excitons, can lead to a greater number of charge carriers in an organic photovoltaic device. The Shockley–Queisser photoelectric conversion limit³ (~30%) for single junction solar cell efficiency may thus be circumvented,⁴ as recently demonstrated by Congreve et al.⁵

To date, a handful of molecules have been shown to undergo SF unambiguously, including tetracene,^{6–9} 5,12-diphenyltetracene,^{10,11} rubrene,^{12–15} pentacene,^{5,16–20} 6,13-bis(triisopropylsilylethynyl)pentacene,^{21,22} 1,3-diphenylisobenzofuran,^{23–26} and zeaxanthin.^{27,28} It is desirable to enhance the diversity of SF chromophores. Small chromophores are especially favorable because of the following: (1) For experimentalists, it is usually (not always though) easier to synthesize, characterize, and process smaller systems; (2) For theoreticians, the smaller size allows higher level calculations and better accuracy. The limited arsenal of SF chromophores and the advantages of small chromophores thus motivate the work described in this paper.

A systematic search to identify more SF chromophores was pioneered by Paci et al.²⁹ who proposed two conditions for the adiabatic excitation energies:

$$E(S_1) > 2E(T_1) \quad (1)$$

and

$$E(T_2) > 2E(T_1) \quad (2)$$

Here S and T stand for singlet and triplet states, the subscript denotes the ordinal energy order within the respective spin manifolds (0 being the ground state energy). For molecules

that satisfy these criteria, the second step in the overall SF process,



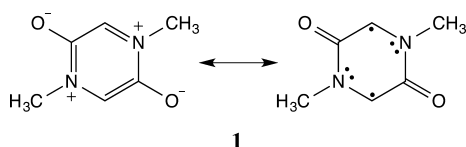
is exoergic and the recombination of the two generated triplet excitons is endoergic. The T_2 state is typically higher in energy than S_1 because it often involves intershell excitation,²⁹ making eq 1 the primary condition. Furthermore, a recent study shows that SF of molecules satisfying eq 1 is not only thermodynamically but also kinetically favorable.³⁰ Paci et al. also proposed a strategy for finding molecules that satisfy the primary SF criterion by starting with one of two classes of parent structures, alternant hydrocarbons and diradicals, and tuning their electronic structures.²⁹

More recently, Nakano et al. investigated the correlation between diradical character of a molecule's ground state and its ability to satisfy the SF criteria.^{31–34} They concluded that some, but not too much, diradical character is needed to make a good SF chromophore. In 2012, in a breakthrough in seeking small SF chromophores,³⁵ Akdag et al. proposed five heterocycles with two captodatively^{36,37} stabilized radical centers, and found one molecule (1) that theoretically satisfies the SF criteria. 1 is about half the size of tetracene, the smallest among the aforementioned chromophores. In a recent study, Wen, Havlas, and Michl continue searching in this direction and suggest more small molecule candidates for SF.³⁸

In this paper, we introduce several new small SF chromophores. Aside from size, our aim is for candidates with kinetic persistence or loosely phrased, “chemical stability.”

Received: May 26, 2014

Published: August 20, 2014



Central to their design is a realistic perturbation strategy and the beacon of moderate diradical character.

■ PERTURBATION STRATEGY: BOTH WEAK AND STRONG

A time- and experiment-honored modification of conjugated π -system is to replace two carbons (C's), not necessarily adjacent, by boron (B) and nitrogen (N). This was pioneered by M. J. S. Dewar,³⁹ and one of us (R.H.) has a special fondness for it.^{40–42} The perturbation is at the same time weak and strong, and, as we will see, particularly well-suited for stabilizing radical and diradical character.

BN substitution for carbon atoms can be considered a weak perturbation for the following reasons:

1. A 3-coordinated (3-coord) B and a 3-coord N atom, taken together, are isoelectronic and isosteric to two 3-coord C atoms.⁴³
2. B and N have Pauling electronegativities 2.0 and 3.0, respectively, sandwiching the C electronegativity of 2.5. The overall electronegativity of a BN unit is thus comparable to that of a CC unit.⁴⁴

However, introducing these heteroatoms can also be viewed as a strong perturbation in light of the subsequent considerations:

1. In a localized perspective, 3-coord N, C, and B contribute 2, 1, and 0 π electrons, respectively. BN substitutions thus introduce electron donor and acceptor centers into the π system. Among the three elements, only C, with its one electron contribution, can be a formal radical center in a completely localized picture of electron distribution.
2. The different electronegativities of the three elements lead to polarized N–C, B–C, and especially B–N bonds.^{40,45}
3. The topology of the frontier orbitals of a hydrocarbon molecule can be severely modified by the different electronegativities and bonding abilities of B and N, reflected in their α and β parameters of Hückel theory,⁴⁶ when the two atoms replace C's.⁴⁷ The HOMO (highest occupied molecular orbital)-LUMO (lowest unoccupied molecular orbital) gap may change,⁴⁸ as well as the diradical character of a molecule.³⁴

Our design strategy exploits the donor character of N and acceptor character of B. In particular, it becomes possible to position the N and B in a molecule such that they create captodatively stabilized radical centers,³⁷ and enhance the diradical character of π -conjugated hydrocarbons. The captodative concept introduced by Viehe et al.³⁶ refers to the special stabilization of radical centers substituted simultaneously (i.e., conjugated) with a π -donor and a π -acceptor. A simple orbital interaction picture for the way the effect operates was given by Fleming,⁴⁹ and a detailed theoretical analysis of this effect is in the literature.³⁷

As an illustration of the captodative effect of BN substitution, we calculate the relative frontier orbital energies of NH_3 , CH_3 , BH_3 , and the radical NH_2CHBH_2 where all 3-coord centers are assumed to be planar. The technical details of our calculations

are provided in the Computational Methods section. Figure 1 shows the orbital interaction scheme when a 3-coord C radical

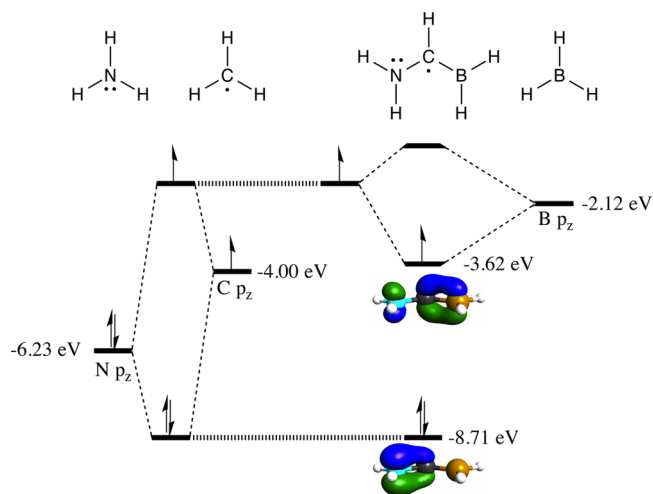


Figure 1. Orbital interaction scheme for captodative stabilization in the NH_2CHBH_2 radical. The orbital energies are obtained for the species shown on top. The hashed horizontal lines simply indicate carrying over the CN orbitals to interact with a B center, not that the orbitals at the two ends of a hashed line have the same energy. In the orbital pictures, cyan, gray, brown, and white spheres label N, C, B, and H atoms, respectively. Blue and green indicate orbital phases.

is sandwiched by a 3-coord N and a 3-coord B. The mixing of the three atomic $2p_z$ orbitals in NH_2CHBH_2 is decomposed for clarity into two sequential interactions: the N–C interaction, followed by interaction between the resulting N–C orbitals and the B $2p_z$.

The lowest π orbital of the product is CN bonding, with little B character. The singly occupied molecular orbital (SOMO), originally on C, is delocalized over all three centers, with weak antibonding (a node) between C and N, and bonding between C and B. As Figure 1 shows, the NC π bond, the lowest molecular orbital, is substantially stabilized relative to the N lone pair (-8.71 vs -6.23 eV), more than compensating for the slight destabilization (from -4.00 to -3.62 eV) of the SOMO. Our orbital interaction picture of captodative stabilization is essentially that of Fleming.⁴⁹ The overall BN captodative stabilization of the radical is evident. Note that the resultant SOMO always has a node between the “dative” component and C, and no node between the acceptor (“capto”) substituent and C.

The BN stabilization for radical is more than a theoretical construct. Very recently a stable BCN radical was synthesized.⁵⁰ The authors focus on the spin density on the boron, but it is clearly a BN captodatively stabilized radical. With steric protection built in, this radical is exceptionally stable, with a melting point of 206 °C.

Experimentally, the first synthesis of a BN-substituted aromatic compound was reported by Dewar in 1958.³⁹ Since then, azaborine chemistry has developed rapidly;^{51–54} it is a vibrant research field and one or more BN units have been introduced into many π -conjugated hydrocarbon molecules.⁴³ The simplest representatives, with R=H in BR- and NR-substituted molecules, may not be endowed with much kinetic persistence. However, substituted compounds are generally quite stable. Experience with synthesizing BN substituted polycyclic aromatic hydrocarbons has accumulated;^{55–61} we

think that the BN-containing molecules proposed in this paper are eminently synthesizable.

PRELIMINARY EXPLORATION: BN-SUBSTITUTION IN BENZENE

We start our adventure by introducing one BN unit into benzene. The parent has little diradical character; its BN derivatives serve as a small laboratory in gaging the competence of BN substitution to generate a diradicaloid from such an inauspicious starting point. We use DFT to optimize the ground state structure of three substituent patterns, *ortho*, *meta*, and *para*. At the optimized structure we perform multireference Møller–Plesset perturbation (MRMP) theory calculations using an active space of 6 electrons distributed in 6π orbitals ($6\pi 6e$) to obtain the vertical excitation energies $E(S_1)$ and $E(T_1)$; this allows us to calculate $\Delta = E(S_1) - 2E(T_1)$, the parameter that determines whether a molecule meets the primary energy criterion for SF. In this section, as well as in Section S1 of the Supporting Information (SI), because we are after a qualitative description of the effect of BN substitution, we do not optimize the structures for S_1 and T_1 , and use vertical excitation energies to calculate Δ . The results are shown in Figure 2.

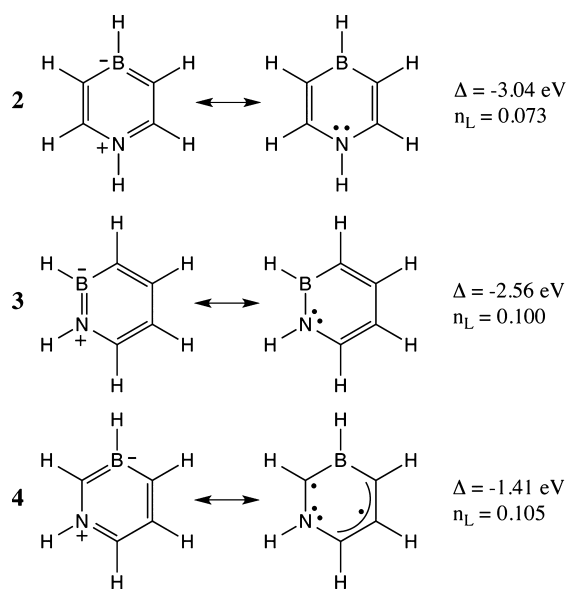
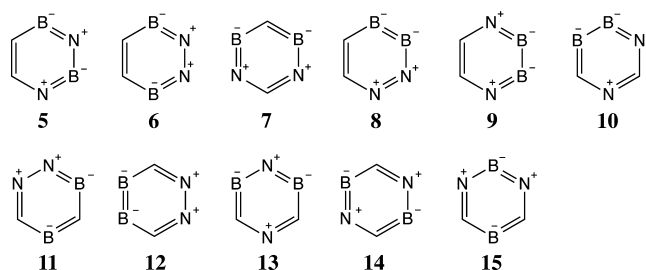


Figure 2. Mono-BN-substituted benzenes, their Δ values, and the occupation numbers of their lowest unoccupied natural orbitals. The dots near the N and C in the right-hand structures indicate the formal numbers of electrons contributed by these atoms to the π -system of the molecule. The arc and a dot in 4 indicate a delocalized π -bonding orbital and a delocalized unpaired electron over the three C atoms (i.e., an allyl group).

All three BN substituted benzene molecules have relatively large negative Δ values. However, as one moves from 2 to 4 the molecules exhibit increasing diradical character, gaged approximately by the population of the lowest unoccupied natural orbital, n_L ,^{31,34,62,63} and also come closer to satisfying the primary criterion for SF. In Figure 2, we draw one Lewis Kekulé structure for each molecule, with its attendant formal charges, as well as a Lewis structure with isolated N π -type lone pairs and nonconjugated B centers. The smaller Δ and larger n_L for the *ortho* isomer 3 compared with *para* 2 is due to the fact that a butadiene (in resonance structure 3) has a smaller HOMO–

LUMO gap and greater diradical character than the ethylene entities in 2. Uniquely, for the *meta*-substituted compound the uncharged Lewis structure is a formal diradical. B and N in 4 flank one C atom, creating two separated radical centers — one on the isolated C atom and the other an allyl-like radical. The B and N in the *meta*-substituted 4 can be viewed as captodatively stabilizing both radicals, making 4 the isomer with the largest n_L and closest to meeting the SF primary criterion energetically. We note that our MRMP methodology reproduces the experimental values⁶⁴ for $S_1 \leftarrow S_0$ vertical excitation energy of 3 within 0.1 eV. Additional details on this methodology and its accuracy are given in the Computational Methods section.

It is evident that introducing one BN unit into benzene enhances its diradical character, and this inspires us to investigate all 11 doubly-BN-substituted benzenes (5 to 15). The detailed analysis of these molecules is given in Section S1 of the SI.



None of these 11 molecules has enough diradical character to satisfy the primary energy criterion. However, 14 has the best performance among them (also better than the three monosubstituted ones) and serves as the starting point in our real search for small SF chromophores. It has the two formal radical C centers farthest apart within a six-membered ring, and both of them are subject to BN captodative stabilization. It corresponds to stitching-up two NH_2CHBH_2 radicals (Figure 1), and the head-to-end (N-to-B) alignment of the two NCB fragments (compared to 12) minimizes bonding between the two radicals.

The study of (both mono- and doubly-) BN-substituted benzenes allows us to develop a few rules of thumb for the design of small molecule SF chromophores.

1. Using charged and uncharged Lewis structures to infer diradical character is helpful.
2. The formal radical centers in a diradical resonance structure should be as separated as possible, and so situated as to avoid bonding interactions and electron transfer (formation of a zwitterionic structure; as discussed in Section S1 of the SI, this is a problem for 7, 10, and 11).
3. Captodative (donor and acceptor) stabilization of the radical centers is important.

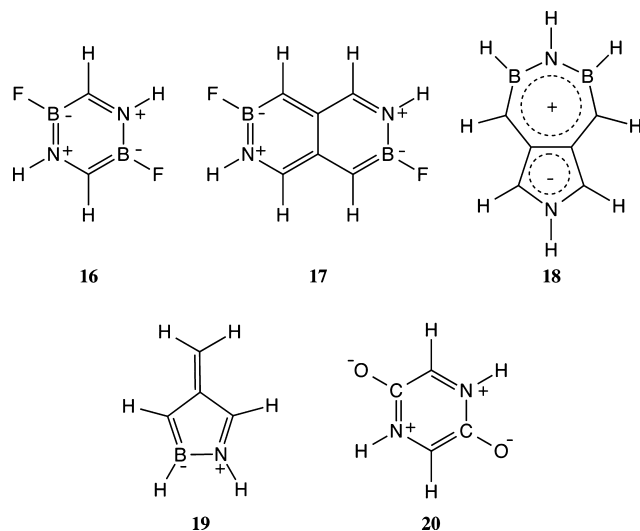
REAL SEARCH

We commence a more focused search for small SF chromophore molecules. Starting from a hydrocarbon π -system, we construct BN-substituted molecules using the rules outlined above. For candidate molecules, we obtain DFT-optimized S_0 and T_1 structures and calculate the vertical excitation energy $E(S_1)$ as well as the adiabatic excitation energy $E(T_1)$. Molecules where $E(S_1) \geq 2E(T_1)$ are considered promising candidates, and we proceed to optimize geometries for the S_0 , S_1 , T_1 , and T_2 states at the MRMP level. With the

optimized structures, we are able to identify the subset of molecules whose adiabatic excitation energies (calculated from the geometry-optimized ground and excited state energies) satisfy the criteria described in eqs 1 and 2. In the final step of the screening, we check to make sure vertical S_1 excitation energies are in the visible region of the solar spectrum, where solar photon flux is not too low.⁶⁵ Coordinates of all optimized structures are presented in Section S11 of the SI.

There are five molecules (16–20) that are found to satisfy both energy criteria. The calculated results for these are summarized in Table 1. They are all class I chromophores, as

Table 1. Summary of Calculated Results for 16–20.^a



	16	17	18	19	20
symmetry	C_{2h}	C_{2h}	C_{2v}	C_s^b	C_{2h}
S_0 label	1A_g	1A_g	1A_1	$^1A'$	1A_g
S_1 label	1B_u	1B_u	1B_1	$^1A'$	1B_u
T_1 label	3B_u	3B_u	3B_1	$^3A'$	3B_u
T_2 label	3A_u	3A_g	3B_1	3A	3B_g
adiabatic $E(S_1)$	3.01	1.99	2.03	1.28	1.74
adiabatic $E(T_1)$	1.34	0.97	0.84	0.51	0.77
adiabatic $E(T_2)$	5.29	2.82	3.00	2.71	2.73
vertical $E(S_1)$	3.15	2.08	2.10	1.92	1.85
f^c	0.229	0.138	0.069	0.014	0.073
HOMO–LUMO gap	3.21	2.34	2.36	2.43	2.41
n_L	0.216	0.267	0.295	0.167	0.289

^aAll reported energies are in eV. ^bThe T_2 of 19 has a C_1 symmetry. ^c f is the oscillator strength for the $S_1 \leftarrow S_0$ vertical excitation.

defined by Michl et al.;^{1,2} that is, their S_1 and T_1 states are well-represented by HOMO-to-LUMO excitation. Overall, the strategy of tuning diradical character is devised for this class of chromophores. The lines of thought that led us to those molecules are described below—the path to them is as important as the quality of the molecules as SF chromophores.

Further Tinkering with Boron. 16 evolves from the good starting point 14. Inspecting the HOMO and LUMO of 14, shown in Figure 3a,b, we conclude that the introduction of two π -donor substituents on the B atoms will result in an antibonding interaction that raises the energy of the HOMO. The LUMO should remain unchanged, because it has no contribution from the B atoms, leading to a decrease of the HOMO–LUMO gap and a corresponding increase in diradical character. Our initial choice of π -donor is fluorine, the most

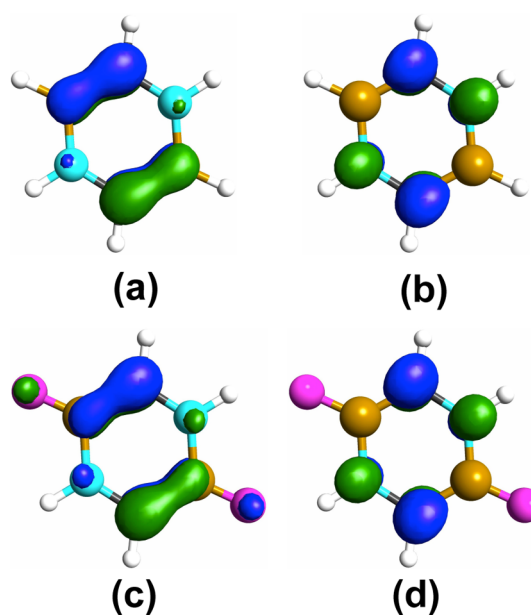


Figure 3. (a) HOMO; (b) LUMO of 14; (c) HOMO; (d) LUMO of 16. Purple, cyan, gray, brown, and white spheres label F, N, C, B, and H atoms, respectively. Blue and green indicate orbital phases.

effective π -donor for boron among halogens (see Section S2 of the SI). This F-substitution leads to molecule 16. We note that halo-substitution on B is known to increase stability—whereas BH_3 dimerizes readily, BX_3 , X = F, Cl, Br, and I are monomeric (see, for instance, Section 6.7.1 of ref 66).

As anticipated, the HOMO of 16 (Figure 3c) gains some antibonding character between F and B, whereas the LUMO (Figure 3d) remains unchanged. The HOMO–LUMO gap thus decreases from 3.65 eV in 14 to 3.21 eV in 16, along with an increase of n_L from 0.150 to 0.216. With its stronger diradical character, 16 has an excess energy of $\Delta = 0.33$ eV when its adiabatic S_1 and T_1 energies are substituted in eq 1. We calculate the oscillator strength of the $S_1 \leftarrow S_0$ transition $f = 0.229$ and the vertical excitation energy $E(S_1) = 3.15$ eV. The vertical $S_1 \leftarrow S_0$ transition of 16 is, thus, sufficiently bright, and its absorption frequency corresponds to a blue photon. The T_2 of 16 involves HOMO–1 to LUMO excitation, and the HOMO–1 can be seen in Figure S7 in the SI.

The fairly large (0.33 eV) adiabatic excess energy suggests that part of the photoexcitation energy dissipates as vibrational energy (heat). We address this apparent inefficiency in the material by comparing the energetics of tetracene and pentacene. Adiabatic excitation energies for tetracene molecule are $E(S_1) = 2.64$ eV and $E(T_1) = 1.27$ eV,^{67,68} and for pentacene molecule, they are $E(S_1) = 2.31$ eV and $E(T_1) = 0.87$ eV.^{69,70} Both molecules satisfy the primary criterion, but tetracene would seem a better candidate with a lower excess energy (0.10 vs 0.57 eV). However, the excitation energies in tetracene crystal are $E(S_1) = 2.32$ eV and $E(T_1) = 1.25$ eV,⁷¹ whereas in the pentacene crystal, they are $E(S_1) = 1.83$ eV and $E(T_1) = 0.86$ eV.^{72,73} Crystalline tetracene thus turns out to be unsatisfactory for SF, although crystalline pentacene has $E(S_1) > 2E(T_1)$ by 0.11 eV. In moving from molecules to their crystals, typically a relatively large red-shift in $E(S_1)$ is observed, whereas the $E(T_1)$ is largely unchanged. This S_1 red-shift is a common phenomenon in organic molecular crystals and is attributed to the Coulomb effect of neighboring molecules and a Davydov splitting.⁷⁴ The T_1 exciton is typically more localized

in a crystal and experiences less of an energy shift.⁷⁵ Without further calculation, we cannot predict the S_1 shift in a hypothetical crystal of **16**. However, we recognize that when screening molecules for good SF efficiency, $E(S_1) \approx 2E(T_1)$ is not an essential criterion. Even in solids, having zero adiabatic excess energy is not as ideal as it appears to be. Indeed, matching the excess energy and the peak frequency of the phonon spectrum is more desired.^{76–79}

BN-Substituted Naphthalenes. The idea of creating formal radical centers through BN substitution can be readily extended to other aromatic structures, such as naphthalene. We screened a good number of mono- and doubly-BN-substituted naphthalenes and identified **17**, the naphthalene analogue of **16**, as the best candidate. Compared to the two isolated C atoms in **16**, the formal radical centers in the diradicaloid resonance structure of **17** are the two allyl groups on its upper and lower edges (Figure 4a). **17** can thus be considered as a bis-

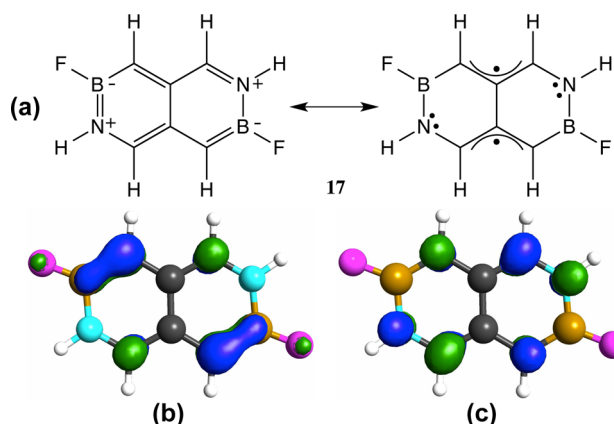


Figure 4. (a) Kekulé structure and the diradicaloid structure of **17** in resonance; (b) HOMO; (c) LUMO of **17**.

allyl diradical (See Figure S8 in the SI for the Lewis structure and frontier orbitals of bis-allyl) connected via two BN units that serve to captodatively stabilize the bis-allyls.

The two SOMO's of bis-allyl are nearly degenerate (exactly so in a Hückel calculation). In the HOMO and LUMO of **17** (Figure 4b,c), one can see that one of the bis-allyl SOMO is stabilized by bonding with B's (HOMO) and the other destabilized by antibonding with N's (LUMO). The pseudodegeneracy of the two SOMO's is thus lifted, resulting in a HOMO–LUMO gap of 2.45 eV and $n_L = 0.267$. The stronger diradical character of **17** over **16** is consistent with the trend that longer acenes are more diradicaloid.⁶³

In addition to satisfying the energy criteria, **17** has S_1 and T_1 energies that match the respective optimal energies, ~ 2 eV and ~ 1 eV, ideal for SF efficiency.¹ The T_2 of the molecule involves 44% HOMO-to-LUMO+1 and 35% HOMO–1-to-LUMO excitations (see Figure S9 in the SI for the sketches of HOMO–1 and LUMO+1). Finally, **17** has a vertical excitation energy $E(S_1) = 2.08$ eV and the oscillator strength for this transition $f = 0.138$, corresponding to a fairly strong red absorption.

Azulene. Is it possible to avoid F substitution? Replacing F atoms in **17** by H atoms leads to a molecule that fails to satisfy the primary energy criterion. We then turn to an isomer of naphthalene, azulene (Figure 5(a)). Azulene has a smaller HOMO–LUMO gap than naphthalene (3.33 eV vs 4.79 eV), and is likely to have more diradical character, making it a better starting structure.

The HOMO and LUMO of azulene are shown in Figure 5b,c. Replacing the C atoms where the HOMO has large amplitudes by less electronegative B atoms will lead to an increase in the HOMO energy.⁴⁶ Similarly, if the C atoms where the LUMO has large amplitudes are replaced by N atoms, the LUMO energy will decrease. Based on this first order perturbation theory argument, we are led to substituted azulene **18**.

In an uncharged resonance structure shown in Figure 6a, **18** can be viewed as a bis-allyl diradical with the radical extremities connected by a BNB fragment on “top” and an N atom on “bottom”. The parentage of the bis-allyl SOMO's (shown in Figure S8 in the SI) are clearly seen in the HOMO and LUMO of **18** (Figure 6b,c). One SOMO is stabilized by tiny bonding interaction with the two B atoms, whereas the other is destabilized by antibonding interaction with the N at the bottom. The HOMO–LUMO gap of **18** is 2.36 eV, smaller than both those of **17** and azulene. The larger n_L (0.295) indicates a stronger diradical character than **17**. Correspondingly, both energy criteria are better satisfied by **18**, eliminating the need for fluorination.

The T_2 of **18** involves 41% HOMO–1-to-LUMO and 38% HOMO-to-LUMO+3 excitations. The HOMO–1 and LUMO+3 are shown in Figure S10 in the SI. The vertical excitation energy $E(S_1) = 2.10$ eV and the oscillator strength $f = 0.069$. The S_1 and T_1 energies of **18** are very similar to those of pentacene, a good SF chromophore.^{5,17,80}

A possible competing process for SF is S_1/S_0 radiationless decay — by shortening the lifetime of S_1 , this decay process can hinder the efficiency of SF. For instance, indigo, which satisfies eq 1,⁸¹ is an unsuitable SF chromophore for this reason.^{1,82} Azulene is known to undergo an S_1/S_0 radiationless decay in

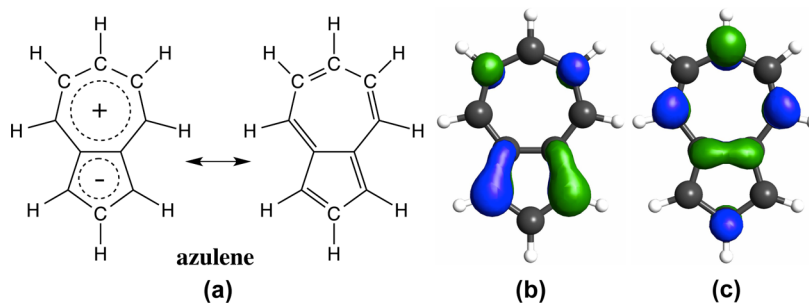


Figure 5. (a) Resonance structures of azulene, (b) its HOMO, and (c) LUMO. Gray and white spheres label C and H atoms, respectively. Blue and green indicate orbital phases. The molecule has C_{2v} symmetry.

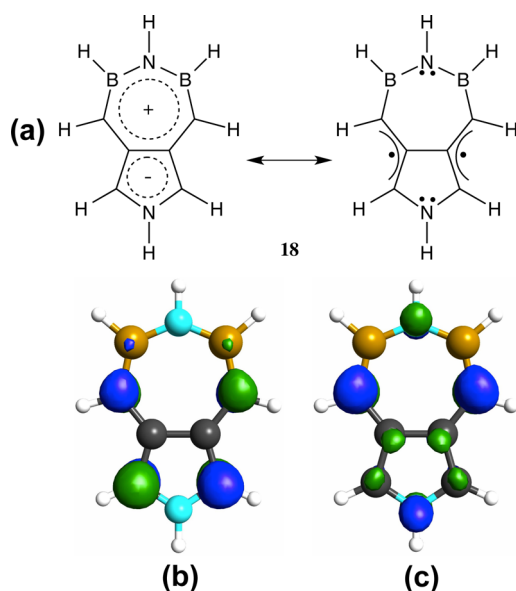
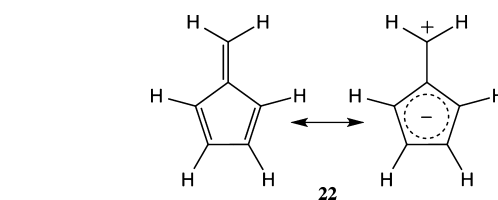
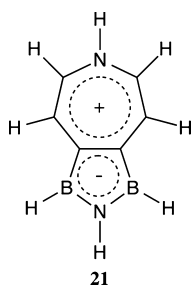


Figure 6. (a) Aromatic and diradicaloid resonance structures of **18**; (b) HOMO; (c) LUMO of **18**. Cyan, gray, brown, and white spheres label F, N, C, B, and H atoms, respectively. Blue and green indicate orbital phases.

femtoseconds.⁸³ In order to make sure **18** does not inherit this decay pathway from azulene, we search (see Section S7 of the SI for details) for its S_1/S_0 conical intersection geometry with minimum energy and found that it lies 3.90 eV higher than the vertical $E(S_1)$. The decay is thus not a likely event. For comparison, a similar calculation for unsubstituted azulene finds its S_1/S_0 conical intersection minimum energy to be 0.04 eV lower than the vertical $E(S_1)$, confirming an active decay channel.⁸³

We also investigated another BN-substituted azulene, **21**, with two B's in the five-membered ring. Unfortunately, the perturbation of this substitution pattern is "too strong", that is, it gives rise to too much diradical character; the molecule has a triplet ground state.



In Section S8 of the SI, we analyze the ground state natural orbitals of fulvene and conclude that its low-lying T_2 is related to the biradical character of the molecule. Armed with this understanding, we propose molecule **19**, where the BN substitution is chosen such that there is only one dominant diradicaloid resonance structure for the ground state.

19 is effectively a trimethylenemethane connected to a BN, and its diradical character comes from the Lewis structure shown in Figure 7a. The two radical centers are stabilized by

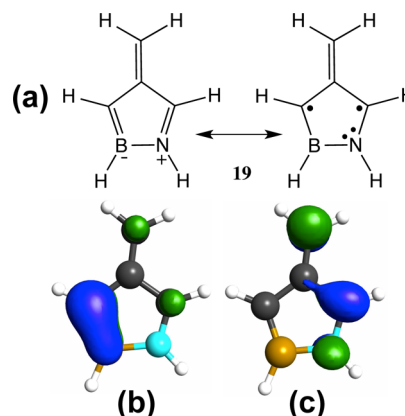


Figure 7. (a) Conjugated and diradicaloid resonance structures of **19**; (b) HOMO; (c) LUMO of **19**.

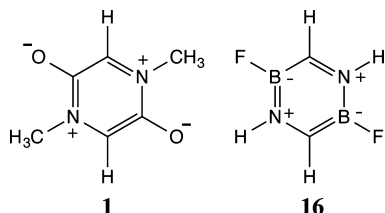
the B "capto" and N "dative" effects, respectively. Unlike the molecules discussed earlier, where individual radical centers were subject to the captodative effect, here the whole diradical unit is stabilized. This is indicated by the HOMO and LUMO of **19** shown in Figure 7b,c — the HOMO features bonding between one of the radical C centers and B, whereas the LUMO shows antibonding between the other C and N. Resonance structures which place the formal radicals at any other place within the trimethylenemethane unit do not benefit from this overall captodative stabilization. With its uniquely dominant diradical character, **19** has a larger separation in energy between T_1 and T_2 , satisfying eq 2. The diradical character determines that the S_1 state only involves excitation among the two radical centers (HOMO-to-LUMO), leaving the exocyclic π bond intact. This feature allows **19** to evade the S_1/S_0 radiationless decay of fulvene (see Section S9 of the SI for a detailed analysis of this issue).⁷⁹

Although it satisfies both energy criteria and has an absorption of red photon (vertical $E(S_1) = 1.92$ eV), **19** has two demerits. The $S_1 \leftarrow S_0$ oscillator strength is too weak, $f = 0.014$, weaker than those of all other chromophores designed here. Additionally, the adiabatic excitation $E(T_1)$ (0.51 eV) is rather low, and may lead to dimerization when the molecules are close to each other in solution or in a crystal. Even if the crystal of **19** existed, the large excess energy ($E(S_1) - 2E(T_1) = 0.90$ eV) would be unlikely to be reached by the phonon spectrum.^{76–79} These drawbacks make **19** less promising than **16–18**. We note that tuning the energy of the lowest triplet

Fulvene. The success of **18** encourages us to follow a similar strategy with a smaller nonalternant hydrocarbon, fulvene (**22**), a π -conjugated and much less stable isomer of benzene. Fulvene satisfies eq 1 with adiabatic excitation energies $E(S_1) = 3.33$ eV and $E(T_1) = 1.59$ eV. Therefore, creating and stabilizing radical centers as such are not our primary aim. Instead, we will focus on ameliorating the two problems that fulvene has. First, fulvene has a low-lying T_2 state; with a constraint of C_{2v} symmetry for all states, we find $E(T_2) - 2E(T_1) = -0.62$ eV for the calculated adiabatic excitation energies of fulvene. Also, fulvene can undergo efficient S_1/S_0 radiationless decay.^{84–90} We address these two problems in designing a candidate chromophore based on fulvene.

state of fulvene is an interesting subject, conventionally effected through substituting the exocyclic or endocyclic H's with electron-donating or electron-drawing groups.⁹¹ We show here that BN substitution for carbon atoms is also a viable tuning method.

Chromophore without BN Substitution. At the beginning of the paper, we showed the small molecule **1**



designed by Akdag et al.³⁵ Through a BN-substitution strategy, we came up with **16**. Ignoring the methyl substituents, these two molecules are related through the isoelectronic nature of BF and CO. A question then naturally arises: are the two methyl groups in **1** necessary to make it a good chromophore?

Our calculation shows that the molecule (**20**, Figure 8a) with the two methyls of **1** being replaced by H atoms satisfies both

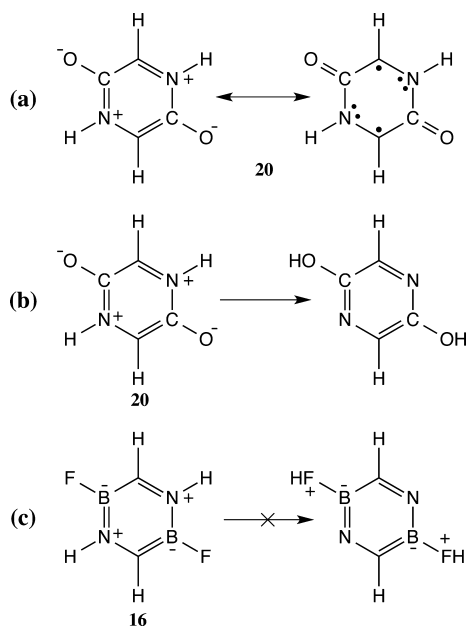


Figure 8. (a) Kekulé and the diradicaloid resonance structures of **20**; (b) tautomerization of **20**; (c) hypothetical (and unlikely) tautomerization of **16**.

energy criteria and has a fairly strong absorption of red photons. The two methyls thus seem to be unnecessary to make a good chromophore. However, an author (J.M.) of ref 35, pointed out that the methyls are needed to maintain the stability of **1**.⁹² With two H atoms instead of two methyls on the N's, the proton migration (tautomerization) from N to O is likely to be facile, to yield a more stable aromatic product without attendant formal charges, 2,5-dihydropyrazine (Figure 8b). The lack of diradical character in the six-membered-ring aromatic structure makes 2,5-dihydropyrazine unlikely to be an SF chromophore.

We note that nonionic F's in **16** and **17** rarely form hydrogen bonds.⁹³ The lone pair electrons on F are more tightly bound, and thus less basic than those on N and O. Therefore, the

tautomerization in Figure 8c is not likely to occur; **16** and **17** are safe.

We realize that two molecules, **19** and **20**, which satisfy both energy criteria and have $S_1 \leftarrow S_0$ absorptions in visible spectrum, ultimately turn out to be not so promising. This serves to emphasize that the highlighted criteria are necessary but not sufficient conditions for good SF chromophores. We focus further discussion on the three good molecules, **16**–**18**.

SOME FURTHER CONSIDERATIONS

The arrangements of **16**–**18** in their crystals remain unknown and are of considerable importance in determining their utility as SF chromophores.⁹⁴ In this paper, we do not explicitly calculate any crystal structures (we intend to do this in the future) but provide a short, speculative discussion of the likely intermolecular orientation based on available parent crystal structures.

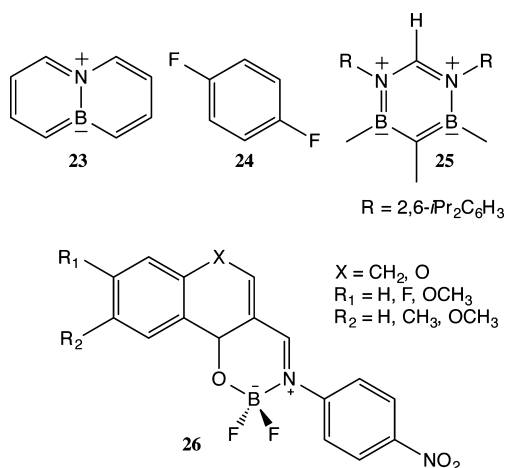
A BN-substituted naphthalene, **23**, has been shown to have a herringbone crystal structure similar to that of naphthalene.⁹⁵ This suggests that BN substitution may not alter the relative orientation of molecules in a crystal significantly, a manifestation of BN being a weak perturbation. We, therefore, expect the BN-substituted molecule **16** to have a slip tilted-stacked structure (an arrangement that particularly favors SF in class I molecules¹) that resembles the packing configuration of its parent 1,4-difluorobenzene (**24**) crystal.⁹⁶

On the basis of the related herringbone structures of benzene and naphthalene crystals,^{97,98} we believe that the crystal structure of molecule **17** will closely resemble that of **16** as well. We further suggest a herringbone structure for **18**, based on its parent azulene.^{99,100}

To the best of our knowledge, none of the molecules we propose have been synthesized; however, molecules with related structures have been reported. Introducing two BN units into a benzene ring has been achieved (see ref 53 and the references therein). **25**, which has **7** as its central structure and is closely related to **16**, has been synthesized.¹⁰¹ Mono-BN-substituted naphthalene was made soon after the dawn of azaborine chemistry;¹⁰² however, we do not find any reports of doubly-BN-substituted naphthalenes or BN-substituted azulenes. Recently, there has appeared a synthesis of a family of BN compounds (**26**) that show promising triplet quantum yields through SF.¹⁰³ Although the authors of ref 103 focus more on the phosphorescence of those compounds than on their photovoltaic properties, this is a positive sign of the emerging overlap between azaborine chemistry and organic photovoltaics.

CONCLUSIONS

We endeavor to design small molecules that are computationally convenient and experimentally realistic from the point of view of chemical stability. To the end, we propose three new small singlet fission chromophores, on the basis of a careful tuning of their diradical character. Quantum chemical calculations at an appropriate level shows that these candidate structures all satisfy the two energy criteria for SF and are likely to absorb visible photons with reasonable oscillator strength. BN substitution is shown to be a viable way of introducing propitious diradical character into π -conjugated hydrocarbons, through its captodative effect. We also take into consideration escape channels for chromophores: our calculation excludes the possibility of S_1/S_0 radiationless decay for two molecules that



might have inherited this deactivation channel from their parent structures.

For the three molecules, we speculate that they will adopt in the solid-state crystal structures similar to those of their unsubstituted parent species, packing modes which are believed to facilitate singlet fission. We hope that our present work will lead to the synthesis of these small molecules and thus supplement the limited arsenal of singlet fission chromophores.

COMPUTATIONAL METHODS

We use density functional theory (DFT) with the B3LYP functional^{104,105} and the cc-pVTZ basis set¹⁰⁶ to preliminarily optimize ground state structures for all molecules investigated. These calculations are the sources of the illustrated canonical molecular orbitals (HOMO, LUMO, HOMO-7, etc.) and their energies, for example, HOMO-LUMO gaps. For radicals like CH₃, a restricted-open-shell scheme is employed. All species in Figure 1, BH₂CHBH₂, and NH₂CHNH₂ in Figure S1 in the SI are all optimized with a planar symmetry constraint. This is to emphasize their π interactions. Only qualitative results are pursued for them.

The structures of each state of **16–20** are optimized at the level of multireference Møller–Plesset perturbation (MRMP) theory. Both nondynamical and dynamical electron correlations are covered. We use a Slater-determinant-based perturbation scheme for easy implementation. The conventional shifting parameter of 0.02 E_H² is introduced to avoid the intruder state problem.¹⁰⁷ Chemical core electrons are excluded from the perturbation treatment. As the first step, all MRMP geometry optimizations are performed with the highest symmetry of the molecules (Table 1). We subsequently use time-dependent DFT (TDDFT) to optimize structures for the S₀'s, S₁'s, and T₁'s and calculate their Hessians. No imaginary frequencies are obtained, confirming that the symmetry constraints do not lead to saddle point structures for those states. For the T₂'s, we distort the optimized structures slightly to have C₁ symmetry and reoptimize. Except **19**, all species return to the previously found structures. **19** turns out to have no symmetry for T₂.

Another MRMP scheme, the general multiconfigurational quasidegenerate perturbation theory (GMC-QDPT) developed by Nakano et al.,^{108–110} is used to calculate excited state energies, with the same treatments of core electrons and the intruder states. For state-averaged MRMP calculations, Granovsky's zeroth order Hamiltonian is employed to generate the zeroth order states that are subsequently perturbed.¹¹¹

The accuracy of this MRMP scheme of optimization and excited state energy calculation is promising. Using this scheme, a 6 π e active space, and a state-specific manner, we calculate the vertical E(S₁) to be 4.49 eV (276 nm) for **3**, in reasonable agreement with the 4.61 eV (269 nm) experimental absorption.⁶⁴ The calculated value is improved to 4.70 eV (264 nm) with an equally weighted state-averaged treatment over S₀ and S₁. Note that both states transform as the same irreducible representation (A' of the C_s point group) and the state-specific treatment cannot guarantee orthogonality between them. The underestimated vertical E(S₁) = 4.49 eV results from mixing some S₀ component in S₁. For **16–18**, and **20**, all related states are orthogonal by symmetry and state-specific treatment is more accurate.

For the calculated properties of pentacene mentioned in the text, please refer to ref 70 for computational details. All calculations are done with the GAMESS-US quantum chemistry program package.^{112,113} All orbital pictures are prepared using the associated graphical software MacMolPlt.¹¹⁴ For further computational details, especially the choice of active space in our MRMP calculations, please refer to Section S10 of the SI.

ASSOCIATED CONTENT

Supporting Information

Figures S1–S14; Discussion on doubly-BN-substituted benzenes; Discussion on F being the best π -donor for B in the halogen series; Lewis structure and frontier orbitals of bis-allyl; Discussion on the S₁/S₀ minimum energy crossing point of **18**; Discussion of the biradical character in fulvene's ground state; Discussion of the unlikely S₁/S₀ radiationless decay of **19**; All interesting coordinates of molecules **16–20**. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

AUTHOR INFORMATION

Corresponding Author

E-mail: tzeng@cornell.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Josef Michl and David Reichman for enlightening discussions. We are grateful to Mark Gordon and Michael Schmidt for their continuing development of the GAMESS-US program suite. T.Z. is thankful to the Natural Sciences and Engineering Research Council (NSERC) of Canada for the Banting postdoctoral fellowship (201211BAF-303459-236530). N.A. thanks the support of a start-up grant from Cornell University. R.H. thanks the National Science Foundation (NSF) for its financial support (CHE-1305872).

REFERENCES

- (1) Smith, M. B.; Michl, J. *Chem. Rev.* **2010**, *110*, 6891–6936.
- (2) Smith, M. B.; Michl, J. *Annu. Rev. Phys. Chem.* **2013**, *64*, 361–386.
- (3) Shockley, W.; Queisser, H. J. *J. Appl. Phys.* **1961**, *32*, 510–519.
- (4) Hanna, M. C.; Nozik, A. J. *J. Appl. Phys.* **2006**, *100*, 074510.
- (5) Congreve, D. N.; Lee, J.; Thompson, N. J.; Hontz, E.; Yost, S. R.; Reuswig, P. D.; Bahlke, M. E.; Reineke, S.; Van Voorhis, T.; Baldo, M. A. *Science* **2013**, *340*, 334–337.
- (6) Burdett, J. J.; Müller, A. M.; Gosztola, D.; Bardeen, C. J. *J. Chem. Phys.* **2010**, *133*, 144506.
- (7) Burdett, J. J.; Gosztola, D.; Bardeen, C. J. *J. Chem. Phys.* **2011**, *135*, 214508.

- (8) Burdett, J. J.; Bardeen, C. J. *J. Am. Chem. Soc.* **2012**, *134*, 8597–8607.
- (9) Chan, W.-L.; Ligges, M.; Zhu, X.-Y. *Nat. Chem.* **2012**, *4*, 840–845.
- (10) Robert, S. T.; McAnally, R. E.; Mastron, J. N.; Webber, D. H.; Whited, M. T.; Brutchey, R. L.; Thompson, M. E.; Bradforth, S. E. *J. Am. Chem. Soc.* **2012**, *134*, 6388–6400.
- (11) Mastron, J. N.; Robert, S. T.; McAnally, R. E.; Thompson, M. E.; Bradforth, S. E. *J. Phys. Chem. B* **2013**, *117*, 15519–15526.
- (12) Najafav, H.; Lee, B.; Zhou, Q.; Feldman, L. C.; Podzorov, V. *Nat. Mater.* **2010**, *9*, 938–943.
- (13) Rysanyanskiy, A.; Biaggio, I. *Phys. Rev. B* **2011**, *84*, 193203.
- (14) Ma, L.; Zhang, K.; Kloc, C.; Sun, H.; Michel-Beyerle, M. E.; Gurzadyan, G. G. *Phys. Chem. Chem. Phys.* **2012**, *14*, 8307–8312.
- (15) Jankus, V.; Snedden, E. W.; Bright, D. W.; Arac, E.; Dai, D.; Monkman, A. P. *Phys. Rev. B* **2013**, *87*, 224202.
- (16) Lee, J.; Jadhav, P.; Baldo, M. A. *Appl. Phys. Lett.* **2009**, *95*, 033301.
- (17) Chan, W.-L.; Ligges, M.; Jailaubekov, A.; Kaake, L.; Miaja-Avila, L.; Zhu, X.-Y. *Science* **2011**, *334*, 1541–1545.
- (18) Rao, A.; Wilson, M. W. B.; Hodgkiss, J. M.; Albert-Seifried, S.; Bässler, H.; Friend, R. H. *J. Am. Chem. Soc.* **2010**, *132*, 12698–12703.
- (19) Rao, A.; Wilson, M. W. B.; Albert-Seifried, S.; Di Pietro, R.; Friend, R. H. *Phys. Rev. B* **2011**, *84*, 195411.
- (20) Wilson, M. W. B.; Rao, A.; Clark, J.; Kumar, R. S. S.; Brida, D.; Cerullo, G.; Friend, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 11830–11833.
- (21) Ramanan, C.; Smeigh, A. L.; Anthony, J. E.; Marks, T. J.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2012**, *134*, 386–397.
- (22) Walker, B. J.; Musser, A. J.; Beljonne, D.; Friend, R. H. *Nat. Chem.* **2013**, *5*, 1019–1024.
- (23) Schwerin, A. F.; Johnson, J. C.; Smith, M. B.; Sreearunothai, P.; Popović, D.; Černý, J.; Havlas, Z.; Paci, I.; Akdag, A.; MacLeod, M. K.; Chen, X.; David, D. E.; Ratner, M. A.; Miller, J. R.; Nozik, A. J.; Michl, J. *J. Phys. Chem. A* **2010**, *114*, 1457–1473.
- (24) Johnson, J. C.; Nozik, A.; Michl, J. *J. Am. Chem. Soc.* **2010**, *132*, 16302–16303.
- (25) Johnson, J. C.; Akdag, A.; Zamadar, M.; Chen, X.; Schwerin, A. F.; Paci, I.; Smith, M. B.; Havlas, Z.; Miller, J. R.; Ratner, M. A.; Nozik, A. J.; Michl, J. *J. Phys. Chem. B* **2013**, *117*, 4680–4695.
- (26) Schrauben, J. N.; Ryerson, J. L.; Michl, J.; Johnson, J. C. *J. Am. Chem. Soc.* **2014**, *136*, 7363–7373.
- (27) Wang, C.; Schlamadinger, D. E.; Desai, V.; Tauber, M. J. *ChemPhysChem* **2011**, *12*, 2891–2894.
- (28) Wang, C.; Tauber, M. J. *J. Am. Chem. Soc.* **2010**, *132*, 13988–13991.
- (29) Paci, I.; Johnson, J. C.; Chen, X. D.; Rana, G.; Popović, D.; David, D. E.; Nozik, A. J.; Ratner, M. A.; Michl, J. *J. Am. Chem. Soc.* **2006**, *128*, 16546–16553.
- (30) Yost, S. R.; Lee, J.; Wilson, M. W. B.; Wu, T.; McMahon, D. P.; Parkhurst, P. R.; Thompson, N. J.; Congreve, D. N.; Rao, A.; Johnson, K.; Sfeir, M. Y.; Bawendi, M.; Swager, T. M.; Friend, R. H.; Baldo, M. A.; Van Voorhis, T. *Nat. Chem.* **2014**, *6*, 492–497.
- (31) Minami, T.; Ito, S.; Nakano, M. *J. Phys. Chem. Lett.* **2012**, *3*, 2719–2723.
- (32) Ito, S.; Minami, T.; Nakano, M. *J. Phys. Chem. C* **2012**, *116*, 19729–19736.
- (33) Minami, T.; Nakano, M. *J. Phys. Chem. Lett.* **2012**, *3*, 145–150.
- (34) Minami, T.; Ito, S.; Nakano, M. *J. Phys. Chem. Lett.* **2013**, *4*, 2133–2137.
- (35) Akdag, A.; Havlas, Z.; Michl, J. *J. Am. Chem. Soc.* **2012**, *134*, 14624–14631.
- (36) Viehe, H. G.; Janousek, Z.; Merenyi, R.; Stella, L. *Acc. Chem. Res.* **1985**, *18*, 148–154.
- (37) Pasto, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 8164–8175.
- (38) Wen, J.; Havlas, Z.; Michl, J. *J. Am. Chem. Soc.*, submitted.
- (39) Dewar, M. J. S.; Kubba, V. P.; Pettit, R. *J. Chem. Soc.* **1958**, 3073–3076.
- (40) Hoffmann, R. In *Advances in Chemistry*; Niedenzu, K., Ed.; American Chemical Society: Washington, DC, 1964; Chapter 8, pp 78–86.
- (41) Hoffmann, R. *J. Chem. Phys.* **1964**, *40*, 2474–2480.
- (42) AlKaabi, K.; Dasari, P. L. V. K.; Hoffmann, R. *J. Am. Chem. Soc.* **2012**, *134*, 12252–12258.
- (43) Campbell, P. G.; Marwitz, A. J. V.; Liu, S.-Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 6074–6092.
- (44) Niedenzu, K.; Dawson, J. W. In *The chemistry of boron and its compounds*; Muetterties, E. L., Ed.; John Wiley and Sons, Inc.: New York, 1967; Chapter 7, pp 377–442.
- (45) Liu, Z.; Marder, T. B. *Angew. Chem., Int. Ed.* **2008**, *47*, 242–244.
- (46) Heilbronner, E.; Bock, H. *The HMO-Model and its Application, Basis and Manipulation*; Verlag Chemie, GmbH: Weinheim, 1968.
- (47) Velinova, M.; Georgiev, V.; Todorova, T.; Madjarova, G.; Ivanova, A.; Tadjer, A. *J. Mol. Struct. (Theochem)* **2010**, *955*, 97–108.
- (48) Ghosh, D.; Periyasamy, G.; Pati, S. K. *Phys. Chem. Chem. Phys.* **2011**, *13*, 20627–20636.
- (49) Fleming, I. *Molecular orbitals and organic chemical reactions*; Wiley: UK, 2009.
- (50) Bissinger, P.; Braunschweig, H.; Damme, A.; Krummenacher, I.; Phukan, A. K.; Radacki, K.; Sugawara, S. *Angew. Chem., Int. Ed.* **2014**, *53*, 7360–7363.
- (51) Michl, J.; Jones, R. *Collect. Czech. Chem. Commun.* **1971**, *36*, 1233–1247.
- (52) Michl, J. *Collect. Czech. Chem. Commun.* **1971**, *36*, 1248–1278.
- (53) Bosdet, M. J. D.; Piers, W. E. *Can. J. Chem.* **2008**, *86*, 8–29.
- (54) Braunschweig, H.; Hörl, C.; Mailänder, L.; Radacki, K.; Wahler, J. *Chem.—Eur. J.* **2014**, *20*, 9858–9861.
- (55) Jaska, C. A.; Emslie, D. J. H.; Bosdet, M. J. D.; Piers, W. E.; Sorensen, T. S.; Parvez, M. *J. Am. Chem. Soc.* **2006**, *128*, 10885–10896.
- (56) Bosdet, M. J. D.; Piers, W. E.; Sorensen, T. S.; Parvez, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4940–4943.
- (57) Abbey, E. R.; Zakharov, L. N.; Liu, S.-Y. *J. Am. Chem. Soc.* **2010**, *132*, 16340–16342.
- (58) Neue, B.; Araneda, J. F.; Piers, W. E.; Parvez, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 9966–9969.
- (59) Xu, S.; Zakharov, L. N.; Liu, S.-Y. *J. Am. Chem. Soc.* **2011**, *133*, 20152–20155.
- (60) Braunschweig, H.; Damme, A.; Jimenez-Halla, J. O.; Pfaffinger, B.; Radacki, K.; Wolf, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 10034–10037.
- (61) Xu, S.; Haefner, F.; Li, B.; Zakharov, L. N.; Liu, S.-Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 6795–6799.
- (62) Yamaguchi, K. In *Self-consistent field: theory and applications*; Carbó, R.; Klobukowski, M., Eds.; Elsevier B. V.: The Netherlands, 1990; Chapter 20, pp 727–823.
- (63) Hachmann, J.; Dorando, J. J.; Avilés, M.; Chan, G. K.-L. *J. Chem. Phys.* **2007**, *127*, 134309.
- (64) Marwitz, A. J. V.; Matus, M. H.; Zakharov, L. N.; Dixon, D. A.; Liu, S.-Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 973–977.
- (65) Würfel, P.; *Physics of Solar Cells: From Basic Principles to Advanced Concepts*; WILEY-VCH Verlag: Weinheim, 2009.
- (66) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Elsevier B. V.: Amsterdam, 1997.
- (67) Petrenko, T.; Krykova, O.; Neese, F.; Sokolowski, M. *New J. Phys.* **2009**, *11*, 015001.
- (68) McGlynn, S. P.; Azumi, T.; Kasha, M. *J. Chem. Phys.* **1964**, *40*, 507–515.
- (69) Heinecke, E.; Hartmann, D.; Müller, R.; Hese, A. *J. Chem. Phys.* **1998**, *109*, 906–911.
- (70) Zeng, T.; Hoffmann, R.; Ananth, N. *J. Am. Chem. Soc.* **2014**, *136*, 5755–5764.
- (71) Tomkiewicz, Y.; Groff, R. P.; Avakian, P. *J. Chem. Phys.* **1971**, *54*, 4504–4507.
- (72) Sebastian, L.; Weiser, G.; Bässler, H. *Chem. Phys.* **1981**, *61*, 125–135.

- (73) Burgos, J.; Pope, M.; Swenberg, C. E.; Alfano, R. R. *Phys. Status Solid. B* **1977**, *83*, 249–256.
- (74) Schwoerer, M.; Wolf, H. C. *Organic Molecular Solids*; WILEY-VCH Verlag GmbH and Co. KGaA: Weinheim, 2007.
- (75) Tiago, M. L.; Northrup, J. E.; Louie, S. G. *Phys. Rev. B* **2003**, *67*, 115212.
- (76) Busby, E.; Berkelbach, T. C.; Kumar, B.; Chernikov, A.; Zhong, Y.; Hlaing, H.; Zhu, X.-Y.; Heinz, T. F.; Hybertsen, M. S.; Sfeir, M. Y.; Reichman, D. R.; Nuckolls, C.; Yaffe, O. *J. Am. Chem. Soc.* **2014**, *136*, 10654–10660.
- (77) Berkelbach, T. C.; Hybertsen, M. S.; Reichman, D. R. *J. Chem. Phys.* **2013**, *138*, 114102.
- (78) Berkelbach, T. C.; Hybertsen, M. S.; Reichman, D. R. *J. Chem. Phys.* **2013**, *138*, 114103.
- (79) Berkelbach, T. C.; Hybertsen, M. S.; Reichman, D. R. *J. Chem. Phys.* **2014**, *141*, 074705.
- (80) Wilson, M. W. B.; Rao, A.; Ehrler, B.; Friend, R. H. *Acc. Chem. Res.* **2013**, *46*, 1330–1338.
- (81) de Melo, J. S. S.; Burrow, H. D.; Serpa, C.; Arnaut, L. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 2094–2096.
- (82) de Melo, J. S. S.; Raodão, R.; Burrow, H. D.; Melo, M. J.; Navaratnam, S.; Edge, R.; Voss, G. *ChemPhysChem* **2006**, *7*, 2303–2311.
- (83) Bearpark, M. J.; Bernardi, F.; Clifford, S.; Olivucci, M.; Robb, M. A.; Smith, B. R.; Vreven, T. *J. Am. Chem. Soc.* **1996**, *118*, 169–175.
- (84) Bearpark, M. J.; Bernardi, F.; Olivucci, M.; Robb, M. A.; Smith, B. R. *J. Am. Chem. Soc.* **1996**, *118*, 5254–5260.
- (85) Dreyer, J.; Klessinger, M. *J. Chem. Phys.* **1994**, *101*, 10655–10665.
- (86) Asmis, K. R.; Allan, M.; Schafer, O.; Fülischer, M. *J. Phys. Chem. A* **1997**, *101*, 2089–2095.
- (87) Deeb, O.; Cogan, S.; Zilberg, S. *Chem. Phys.* **2006**, *325*, 251–256.
- (88) Sicilia, F.; Bearpark, M. J.; Blancafort, L.; Robb, M. A. *Theor. Chem. Acc.* **2007**, *118*, 241–251.
- (89) Mendive-Tapia, D.; Jasorne, B.; Worth, G. A.; Bearpark, M. J.; Robb, M. A. *Phys. Chem. Chem. Phys.* **2010**, *12*, 15725–15733.
- (90) Jenkins, S.; Blancafort, L.; Kirk, S. R.; Bearpark, M. J. *Phys. Chem. Chem. Phys.* **2014**, *16*, 7115–7126.
- (91) Ottosson, H.; Kilså, K.; Chajara, K.; Piqueras, M. C.; Crespo, R.; Kato, H.; Muthas, D. *Chem.—Eur. J.* **2007**, *13*, 6998–7005.
- (92) Michl, J. *Private communication*.
- (93) Dunitz, J. D.; Taylor, R. *Chem.—Eur. J.* **1997**, *3*, 89–98.
- (94) Johnson, J. C.; Nozik, A. J.; Michl, J. *Acc. Chem. Res.* **2013**, *46*, 1290–1299.
- (95) Fang, X.; Yang, H.; Kampf, J. W.; Holl, M. M. B.; Ashe, A. J., III *Organometallics* **2006**, *25*, 513–518.
- (96) Thalladi, V. R.; Weiss, H.-C.; Bläser, D.; Boese, R.; Nangia, A.; Desiraju, G. R. *J. Am. Chem. Soc.* **1998**, *120*, 8702–8710.
- (97) Cox, E. G. *Rev. Mod. Phys.* **1958**, *30*, 159–162.
- (98) Robertson, J. M. *Proc. R. Soc. London A* **1933**, *142*, 674–688.
- (99) Robertson, J. M.; Shearer, H. M. M.; Sim, G. A.; Watson, D. G. *Acta Crystallogr.* **1962**, *15*, 1–8.
- (100) Bräuniger, T.; Poupko, R.; Luz, Z.; Gutsche, P.; Meinel, C.; Zimmermann, H.; Haebleren, U. *J. Chem. Phys.* **2000**, *112*, 10858–10869.
- (101) Forster, T. D.; Krahulic, K. E.; Tuononen, H. M.; McDonald, R.; Parvez, M.; Roesler, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 6356–6359.
- (102) Dewar, M. J. S.; Dietz, R. *J. Chem. Soc.* **1959**, 2728–2730.
- (103) Koch, M.; Perumal, K.; Blacque, O.; Garg, J. A.; Saiganesh, R.; Kabilan, S.; Balasubramanian, K. K.; Venkatesan, K. *Angew. Chem., Int. Ed.* **2014**, *53*, 6378–6382.
- (104) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (105) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
- (106) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- (107) Witek, H. A.; Choe, Y.-K.; Finley, J. P.; Hirao, K. *J. Comput. Chem.* **2002**, *23*, 957–965.
- (108) Nakano, H.; Uchiyama, R.; Hirao, K. *J. Comput. Chem.* **2002**, *23*, 1166–1175.
- (109) Miyajima, M.; Watanabe, Y.; Nakano, H. *J. Chem. Phys.* **2006**, *124*, 044101.
- (110) Ebisuzaki, R.; Watanabe, Y.; Nakano, H. *Chem. Phys. Lett.* **2007**, *442*, 164–169.
- (111) Granovsky, A. A. *J. Chem. Phys.* **2011**, *134*, 214113.
- (112) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. *J. Comput. Chem.* **1993**, *14*, 1347–1363.
- (113) Gordon, M. S.; Schmidt, M. W. In *Theory and Applications of Computational Chemistry: The First Forty Years*; Dykstra, C. E., Frenking, G., Kim, K. S., Scuseria, G. E., Eds.; Elsevier: Amsterdam, 2005.
- (114) Bode, B. M.; Gordon, M. S. *J. Mol. Graphics Mod.* **1998**, *16*, 133–138.