Carbene derived diradicaloids – building blocks for singlet fission?

Julian Messelberger, a Annette Grünwald, a Piermario Pinter, b Max M. Hansmann c,d and Dominik Munz a,*

Organic singlet diradicaloids promise application in non-linear optics, electronic devices and singlet fission. The stabilization of carbon allotropes/cumulenes (C_1, C_2, C_4) by carbenes has been equally an area of high activity. Combining these fields, we showed recently that carbene scaffolds allow as well for the design of diradicaloids. Herein, we report a comprehensive computational investigation (CASSCF/NEVPT2, fractional occupation DFT) on the electronic properties of carbene–bridge–carbene type diradicaloids. We delineate how to adjust the properties of these ensembles through the choice of carbene and bridge and show that already a short C_2 bridge results in remarkable diradicaloid character. The choice of the carbene separately tunes the energies of the S_2 and T_1 excited states, whereas the bridge adjusts the overall energy level of the excited states. Accordingly, we develop guidelines on how to tailor the electronic properties of these molecules. Of particular note, fractional occupation DFT is an excellent tool to predict singlet–triplet gaps.

Introduction

The synthesis and spectroscopic scrutiny of organic diradicals is a vibrant area of research. These molecules are suitable for organic field-effect transistors (OFETs), non-linear optics, two-photon absorption (TPA), energy storage and organic spintronics due to their unique physico-chemical properties. Of particular importance, organic diradicals allow for the construction of solar cells based on singlet fission. Singlet fission, i.e. the conversion of one excited singlet state to two triplet states, promises a breakthrough for a new generation of photovoltaics. While current materials are typically limited to a maximum of 33% (Shockley–Queisser limit), singlet fission permits in principle quantum efficiencies of 200%. One of the major limitations for singlet fission based light harvesting is the limited number and structural similarity of chromophores currently known to undergo this process.

It has consequently been emphasized that it is “essential that additional classes of singlet fission chromophores be discovered”. One very well-known example for a Kekulé diradicaloid is Tschitschibabin’s hydrocarbon (Fig. 1). This molecule can be understood by two resonance structures, which correspond to the cumulenic closed-shell singlet state and the diradical open-shell state, which could be either an open-shell singlet or a triplet. The relative weights of these closed-shell and open-shell resonance structures are associated with the diradicaloid character of the molecule. Spectroscopic investigations of organic diradicaloids are unfortunately challenging due to their typically high reactivity. Therefore, much work has been devoted on taming these reactive compounds through the extension of the π-system, introduction of stabilizing heteroatoms and/or the kinetic stabilization by steric bulk. We introduced carbenes as suitable building blocks for the isolation of carbene–bridge–carbene ensembles with very high diradicaloid character (Fig. 2). The synthetic approach followed a straightforward and highly modular route, which allows for the combination of any stable free carbene with a large variety of different connecting bridges.

Further examples of cumulenes connected by two NHCs with saturated and unsaturated backbones were very recently reported. Equally, heterocyclic carbenes can stabilize cumulenes...
and carbon allotropes, which show unique optoelectronic properties. We conclude therefore that carbenes are very likely to find many more applications in these areas. Key for the design of singlet or triplet diradicaloids is their electronic structure, which is most prominently reflected by their degree of diradicaloid character (i.e., population of the lowest unoccupied molecular orbital (LUMO)). Computational approaches offer here a convenient method to design such molecules.

Herein, we report a detailed and comprehensive investigation using high-level CASSCF/NEVPT2 calculations on the (di)radical properties of carbene functionalized extended $\pi$-systems. We elucidate the influence of the carbene end groups and put them into perspective to other well-known diradicaloids and polyaromatic hydrocarbons (PAHs). We will quantify the effects of the cumulenic bridge and of the aromaticity. In particular, we describe which carbene leads to high diradical character. Eventually, we derive guidelines for tailoring the electronic properties of these diradicaloids for singlet fission in solar cells or two-photon absorption.

Results and discussion

Seven well-studied singlet diradicaloids were chosen as references (Fig. 3). Tschitschibabin’s diradicaloid hydrocarbon (1) is related to Thiele’s quinoid hydrocarbon (2), which was reported to be considerably more stable. Tetracene (3) and pentacene (4), which have been extensively studied in the context of singlet fission, were picked as representative for fused $\pi$-systems. Other prominent examples of this class include e.g. zethrenes, phenalenyles, quinodimethanes, or diindenyl fused $\pi$-systems. The bisnitroxide (5), bisoxoverdazyl (6) and bisquinone (7) were chosen as examples for heteroatom incorporation and supposedly very high diradical character.

The electronic and steric properties of singlet carbenes can be tuned in a straightforward fashion by adjacent $\pi$-donors, ring size, as well as aromaticity. Cyclic (alkyl)(amino) carbenes (CAACs) with one nitrogen heteroatom adjacent to the carbene (Fig. 4; 8, 10–14) allow for comparably efficient electron delocalization from the $\pi$-system of a bridge through their $\pi$-acceptor capabilities.

These derivatives were chosen in order to study the influence of the conjugated bridge, because most (10, 11, 13, 14–17) are isolable. Additionally, we included the very recently synthesized NHC congener. Olefin substituents as modeled in 15 and 16 (i.e., alkylidenes or dialkylcarbenes) and cyclic vinyl ether substituents (i.e., Fischer carbenes) 17 should lead to even stronger electron delocalization. On the contrary, bisheteroatom substituents should give rise to electron richer derivatives (18, 19). The compounds 20–23 feature moderate to comparably strong aromatic character of the respective free carbenes. The attachment of mesoionic carbenes (22) and carbenes with significant carbocarborane character (respectively bent allenes, 24) with significant population of the carbene’s $\pi$-orbital gives access to very electron rich ensembles. Note that the bentallene 24 shows only very weak aromatic character as evidenced by the experimentally observed pyramidalization of the nitrogen atoms.

Computational description of singlet diradicaloids

The computational modeling of compounds with singlet-diradicaloid character is not a straightforward task. Although...
unrestricted DFT is in principle capable of describing such systems using the broken-symmetry formalism,\textsuperscript{91–94} the multi-reference singlet state is not well modeled for small singlet–triplet gaps. Spin decontamination procedures have been proposed to address the shortcomings – however, they also do not always lead to results in agreement with the experiment.\textsuperscript{95–98}

Indeed, we observed for the bisCAAC cumulenes the description using DFT strongly underestimated the stability of the closed-shell singlet state and hence was not an appropriate method to predict the absorption spectra.\textsuperscript{29} Multireference methods like the complete active space – self-consistent field method (CASSCF)\textsuperscript{99} are suitable for properly treating such systems.\textsuperscript{100–105} Unfortunately, CASSCF is not a “black-box” procedure like DFT and the selection, i.e. quality, of the active orbitals typically determines the outcome of the calculation. The application of computational investigations using this and related methods remain therefore even for organic singlet diradicaloids comparably scarce,\textsuperscript{58–52,55,103,106–111} whereas unrestricted DFT calculations are still much more commonly applied.\textsuperscript{118–127}

A common descriptor of diradicaloid character are the diradical indices $y_0$ and $y_1$. They correspond to the natural orbital occupation number (NOON) of the lowest unoccupied natural orbital (LUNO) and LUNO+1, respectively, and are of course connected with the overall bond order.\textsuperscript{128} A population of $y_0 = 1$ and $y_1 = 0$ signifies a diradical, whereas $y_0 = 1$ and $y_1 = 1$ describes a tetraradical. Non-linear optical properties like nonlinear optical processes of triplet excitons (eqn (2)).

For practical applications, the energy of the $S_1$ and twice the $T_1$ states should be in the same order of magnitude and close or moderately higher than 2.0 eV. Furthermore, twice the energy of the excited triplet state should be smaller than the energy of the second excited triplet state in order to avoid recombination processes of triplet excitons (eqn (2)).

$$2E(T_1) \approx E(S_1) \text{ and/or } 2E(T_1) < E(S_1)$$

$$2E(T_1) < E(T_2)$$

However, note that these two requirements are obviously not necessarily sufficient for the observation of singlet fission. Additionally, intermolecular interactions for this bimolecular process (electronic coupling) as well as molecular vibrations, which are associated with relaxation processes (vibronic coupling) are important.\textsuperscript{131} Evidently, the stability of the excited states and the extinction coefficient are as well significant for light harvesting purposes. Another (computational) interpretive tool for the estimation of diradicaloid character, which relies on the fractional occupation number weighted electron density ($N^{RFO}$), was recently introduced by Grimme.\textsuperscript{137,138} Of particular interest, this method comes at an extremely low computational cost. It is based on smearing the molecule’s electrons over the molecular orbitals using finite temperature DFT and is a measure of static electron correlation. Molecules with a delocalized FOD and a large $N^{RFO}$ have multireference character.

**Computational methods**

All complete active-space self-consistent-field (CASSCF)\textsuperscript{99} calculations were performed with ORCA 4.0.1 [ref. 139] using the def2-TZVPP\textsuperscript{140} basis set. The resolution of identity approximation and the related basis sets for both Coulomb and HF exchange integrals were used (RI-JK).\textsuperscript{141} Tighter than default convergence criteria were chosen (tightscf). The second order perturbation theory NEVPT2 was applied to account for the effects of dynamic electron correlation.\textsuperscript{142} The reported diradical indices as well as molecular orbital plots relate to the singlet ground states for all molecules. Five roots each were calculated for the state averaged modeling of the absorption spectra for the singlet states and triplet states. For the state-averaged CASSCF(14,14) calculations, three roots were calculated for the triplet- and four roots for the singlet states. Calculations using different number of roots (e.g., 5 or 10) showed only very small deviation for the transition to the $S_1$ state and reordering of the states after the NEVPT2 correction is unproblematic when calculating at least 5 roots. Reported energies relate accordingly to vertical excitation from the $S_0$ states. Note that the geometry optimization of the excited states at the CAS level of theory is computationally extremely demanding. The structural parameters (“reorganization energy”) of the molecules change moderately upon excitation. Geometry optimizations of 13 in the triplet state, closed-shell singlet state as well as broken-symmetry open-shell singlet state (B3LYP/def2-SVP) afforded similar structural parameters. E.g., the distortion of the acetylene units differs between the calculations by only about 10°. See the ESI for CASSCF energies of the DPT optimized open-shell singlet, closed-shell singlet as well as triplet state of 13. Nevertheless, the calculated adiabatic singlet–triplet gap is 0.73 eV, while the vertical excitations $^1S \rightarrow ^3T$ for the solid state structure and the B3LYP closed-shell optimized structure are 0.80 eV and 0.98 eV, respectively. The choice of the active space for each molecule is delineated in detail in the ESI.\textsuperscript{†} For the effect of enlarging the active space from 2 electrons in 2 orbitals, see as well the ESI.\textsuperscript{†} An evaluation of basis set effects (def2-SVP, def2-TZVP, def2-TZVPP, def2-TZVPD, ma-def2-TZVPP, def2-QZVPP, cc-pVTZ, aug-cc-pVTZ)
indicates smooth convergence toward the complete basis limit and that def2-TZVPP is of sufficient quality for predicting the energies of the S1 and T1 states with a deviation of 0.04 eV from the largest basis set (ESI†). Typically, all the π-orbitals of the conjugated system were included up to 14 electrons in 14 orbitals [CASSCF(14,14)]. The NEVPT2 calculation for pentacene (4) evolved to be very time consuming for CASSCF(14,14) – therefore, the given energies relate to CASSCF(12,12). The predicted absorption wavelengths (energies of S1 states, respectively) show a root mean square deviation RMSD from the experimentally determined values of 0.19 eV (mean deviation: 0.15 eV), which we consider an excellent fit (ESI†). Time dependent DFT using the B3LYP/def2-TZVPP level of theory underestimates the energy level of the S1 state of e.g. 14 even without truncation by more than 0.5 eV. The deviation for the T1 states, which is mainly due to the constrained geometric parameters (vide supra), appears to be larger and the calculations seem to systematically overestimate the singlet–triplet gap by up to 0.3 eV. However, note that experimental energies have only been reported for tetracene and pentacene, whereas the expected error for molecules with smaller π-system like 13 is expected to be smaller (the RMSD value for these two T1 states and the calculated adiabatic singlet–triplet gap of 13 amount to 0.28 eV). The SMD implicit solvation model was applied for benchmark studies with experimental reported absorption spectra and led to moderately improved results (RMSD for S1 states: 0.18 eV).143,144 Increasing solvent polarity leads for 13 to a moderately increased level of the T1 state, whereas the effects on the S1 state appear not to follow a straightforward trend (ESI†). The absorption wavelengths reported in the manuscript are not corrected for solvation effects for comparability.

The structural parameters of 1–7, 11, 13, 14, 18 were obtained by optimization of the hydrogen atom positions from their solid state structures (B3LYP/def2-SVP). The D3 dispersion correction145 with Becke–Johnson damping146 was applied. All diisopropyl-phenyl (Dipp) groups and the methyl substituent of structure 14 were truncated by methyl substituents. The iso-propyl groups of 6 and the phenyl substituents of structure 7 were modeled by methyl groups. The structures of all the other molecules were optimized in the singlet state without symmetry or internal coordinate constrains and were verified as true minima by the absence of negative eigenvalues in the harmonic vibrational frequency analysis. The restricted formalism, which showed very good agreement with the solid state structures for the CAAC derived molecules,28 was used. The fractional occupation number weighted electron density (FOD) analysis was carried out with the default values as implemented in ORCA (TPSS/def2-TZVP; 5000 K). Calculated structures and molecular orbitals were visualized with Chemcraft, Avogadro 1.1.1147 and IBOView.148

Comparison carbene vs. non-carbene derived diradicaloids

The analysis of the electronic structure of 13 suggests strong cumulenic character and reveals that the localization of the two radicals as shown in Fig. 1 is an oversimplification (Fig. 5).

The diradicaloid character is mainly associated with the two frontier orbitals, which extend over the whole π-system and show an occupation of 1.71 (highest occupied natural orbital, HONO) and 0.29 (lowest unoccupied natural orbital, LUNO), respectively. Note that the CAAC moieties show a strong contribution of their π orbitals as well as of the adjacent amine groups. The occupancies of HONO–1 (1.89) as well as the LUNO+1 (0.12) point at moderate tetradirectional contributions.

In sight of an ideal diradical index of \( y_0 = 0.36 \) for a large two-photon absorption cross section (vide supra), we conclude that 13 should be a very good candidate for two-photon absorption.5,131 The vertical excitation to the S1 state can be approximated with a double excitation (29%) from the HONO to the LUNO and smaller single excitations from the HONO and HONO–1 to the LUNO (18%) and LUNO+1 (16%), respectively. This transition is expected to have very low intensity (\( f^{\text{osc}} \approx 0.0 \)). The excitation to the S2 state, which is only slightly higher in energy, involves mainly excitation of one electron to the LUNO (44%) with strong intensity (\( f^{\text{osc}} = 0.9 \)). Hence, 13 qualifies as a class III chromophore (vide infra).11

The energy level of the S1 state shows an energy gap of 2.49 eV in relation to the S0 state, which is reasonable for applications associated with singlet fission. The vertical energy gap to the triplet state 1_t is a bit too low (0.80), whereas the level of the T2 state is sufficiently high in energy (2.90 eV). To put the carbene derived singlet diradicaloid into perspective with well-studied congeners, we compare the CAAC derived diradicaloid 13 with Tschitschibabin’s (1) as well as Thiele’s (2) hydrocarbons and tetracene (3) as well as pentacene (4). Table 1 shows the most significant parameters for an evaluation of the electronic character of these molecules. The calculated absorption bands agree very well with the experimental values (1: \( \exp E(S_1) = 576 \text{ nm} \);28 2: “orange”;28 3: \( \exp E = 475 \text{ nm} \);133 4: \( \exp E = 578 \text{ nm} \);11,151,152 13: \( \exp E = 551 \text{ nm} \)). The calculated energies of the excited T1 states appear to be a bit too high in comparison to the experimental values (e.g., 3: \( \exp E(T_1) \approx 2.61 \text{ eV} \); \( \exp E(T_2) \approx 1.34 \text{ eV} \); 4: \( \exp E(T_1) \approx 2.13 \text{ eV} \); \( \exp E(T_2) \approx 0.95 \text{ eV} \));11,151,152 which is mainly due to conformational changes associated with the transition to the T1 states (ESI†). As evidenced by \( y_0 \) and \( N^{\text{FOD}} \), the CAAC derived molecule shows significant diradicaloid character, which lies between Thiele’s and Tschitschibabin’s hydrocarbons and exceeds the one of tetracene. Note that the \( N^{\text{FOD}} \) values as well as plots (ESI†) indicate significant multireference character for all molecules. Experimentally, tetracene is well known to undergo singlet fission, although the process is slightly endergonic, i.e. \( 2E(T_1) > E(S_1) \) (“thermally activated singlet fission”).11 Tetracene
Table 1. Diradical indices $(y_0, y_1)$, $N^{\text{FCD}}$, vertical excitation energies $E(S_1, T_1, T_2)$, absorption wavelengths and oscillator strength ($f^{\text{osc}}$) for $S_0 \rightarrow S_1$ transitions. Energies are given relative to the $S_0$ state and were obtained from CASSCF$(12,12)$ calculations for 1, 3, 4 and 13 and from CASSCF$(8,8)$ for 2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y_0$</td>
<td>0.47</td>
<td>0.19</td>
<td>0.18</td>
<td>0.19$^a$</td>
<td>0.29</td>
</tr>
<tr>
<td>$y_1$</td>
<td>0.12</td>
<td>0.08</td>
<td>0.08</td>
<td>0.09$^a$</td>
<td>0.12</td>
</tr>
<tr>
<td>$N^{\text{FCD}}$</td>
<td>1.36</td>
<td>1.00</td>
<td>0.52</td>
<td>0.89</td>
<td>0.85</td>
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<tr>
<td>$E(S_1)$ [eV]</td>
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<td>2.41</td>
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<td>2.07</td>
<td>2.49</td>
</tr>
<tr>
<td>$E(T_1)$ [eV]</td>
<td>0.41</td>
<td>1.59</td>
<td>1.65</td>
<td>1.23</td>
<td>0.80</td>
</tr>
<tr>
<td>$E(T_2)$ [eV]</td>
<td>2.79</td>
<td>3.90</td>
<td>2.90</td>
<td>2.50</td>
<td>2.90</td>
</tr>
<tr>
<td>Absorption $S_0 \rightarrow S_1$ [nm]</td>
<td>581 (339 $S_0$)</td>
<td>514</td>
<td>503</td>
<td>599</td>
<td>498 (444 $S_0$)</td>
</tr>
<tr>
<td>$f^{\text{osc}} \ S_0 \rightarrow S_1$ [nm]</td>
<td>0.0 (0.01)</td>
<td>0.6</td>
<td>0.1</td>
<td>0.13</td>
<td>0.0 (0.9)</td>
</tr>
</tbody>
</table>

$^a$ The diradical indices relate to CASSCF$(14,14)$, whereas the energies were only calculated with CASSCF$(12,12)$ due to prohibitive computational demand for the NEVPT2 correction.

(note $f^{\text{osc}} = 0.1$) shows typically a very slow singlet-fission rate, which underlines the need for the development of novel materials.\cite{153,154} Oxygen sensitive pentacene on the contrary shows experimentally slightly exoergic singlet fission.

Comparison of carbene derived diradicaloids

The CAAC (8) and NHC (9) derivatives of Thiele’s hydrocarbon 2 (Table 2) are predicted to show a quite similar diradicaloid character (2: $y_0 = 0.19$; 8: $y_0 = 0.16$; 9: $y_0 = 0.13$). The energy levels of the excited T1 states are moderately elevated [2: $E(T_1) = 1.59$ eV; 8: $E(T_1) = 1.70$ eV; 9: $E(T_1) = 1.78$ eV]. Interestingly, the diradical character of 2, 8 and 9 is much smaller than the one of the nitroxide 5 or oxoverdazyl 6. Both these compounds are almost perfect diradicals with energetically degenerate open-shell singlet and triplet ground states. The unpaired electrons are essentially localized on the heteroatoms with only very small contribution of the phenyl rings (ESI). The quinone congener 7 is predicted to show a diradical index, which is in between ($y_0 = 0.32$).

Table 3 collects all data for the carbene analogues of 13. Olefin substitution by a “diphenylalkylidene” substituent (15) leads to quite low lying $S_1$ and $T_1$ states [$E(S_1) = 1.59$ eV; $E(T_1) = 0.54$ eV] and a high diradical index $y_0$ of 0.41 (Table 3). It is interesting to note that the “dialkylalkylidene” substituted diradicaloid 16 shows comparably elevated $S_1$ and $T_1$ states and reduced diradical character [$E(S_1) = 2.56$ eV, $E(T_1) = 0.86$ eV, $y_0 = 0.30$]. The very $\pi$-electron deficient “dialkylmethylidene” group stabilizes accordingly the closed-shell cumulene. The high diradical character of 15 in comparison to 16 is - as also evidenced by electron delocalization of the relevant orbitals onto the phenyl rings - due to the radical-stabilizing influence of the aromatic phenyl substituents.

Dialkylcarbenes in their (excited) singlet state are of course more $\pi$-acidic than a Fischer carbene or CAAC with one $\pi$-electron donating oxo substituent or amine group, respectively. Decreasing the $\pi$-acceptor properties through introduction of an oxygen atom (17) reduces the diradical character as well as energy of the $S_1$ state very slightly [$y_0 = 0.29$, $E(S_1) = 2.55$ eV].

Table 2. Diradical indices $(y_0, y_1)$, $N^{\text{FCD}}$, vertical excitation energies $E(S_1, T_1, T_2)$, calculated absorption wavelengths and oscillator strength ($f^{\text{osc}}$) for $S_0 \rightarrow S_1$ transitions. Energies are given relative to the $S_0$ state and were obtained from CASSCF$(8,8)$ for 8 and CASSCF$(12,12)$ for the other compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nitro</th>
<th>5</th>
<th>Oxo-verdazyl</th>
<th>6</th>
<th>Quinone</th>
<th>7</th>
<th>CAAC</th>
<th>8</th>
<th>NHC</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y_0$</td>
<td>1.0</td>
<td>1.0</td>
<td>0.09$^a$</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.13</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$y_1$</td>
<td>0.16</td>
<td>0.14</td>
<td>0.32$^a$</td>
<td>0.16</td>
<td>0.16</td>
<td>0.16</td>
<td>0.13</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$N^{\text{FCD}}$</td>
<td>2.14</td>
<td>2.10</td>
<td>1.34$^a$</td>
<td>0.47</td>
<td>0.47</td>
<td>0.47</td>
<td>0.69</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E(S_1)$ [eV]</td>
<td>2.30</td>
<td>3.09</td>
<td>2.19$^a$</td>
<td>2.74</td>
<td>2.74</td>
<td>2.74</td>
<td>2.46</td>
<td></td>
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<tr>
<td>$E(T_1)$ [eV]</td>
<td>0.0</td>
<td>0.0</td>
<td>0.75</td>
<td>1.70</td>
<td>1.70</td>
<td>1.70</td>
<td>1.78</td>
<td></td>
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<tr>
<td>$E(T_2)$ [eV]</td>
<td>2.2</td>
<td>2.97</td>
<td>2.90$^a$</td>
<td>2.90</td>
<td>2.90</td>
<td>2.90</td>
<td>2.79</td>
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<td></td>
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<tr>
<td>Absorption $S_0 \rightarrow S_1$ [nm]</td>
<td>538</td>
<td>400</td>
<td>566$^a$</td>
<td>461</td>
<td>461</td>
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<td>503</td>
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<tr>
<td>$f^{\text{osc}} \ S_0 \rightarrow S_1$</td>
<td>0.02</td>
<td>0.2</td>
<td>1.3$^a$</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.9</td>
<td></td>
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</tr>
</tbody>
</table>
For S0 – T1. Our calculations suggest accordingly that other non-aromatic carbene derivatives with a single HONO – LUNO excitation. The CAAC stabilized compound 14 shows a very high diradical index of \( y_0 = 0.78 \) (Table 4), which is well reflected in the reduced electron density on the linker in the HONO and LUNO (Fig. 7). The singlet-triplet gap of this molecule becomes consequently very small \( \Delta E(T_1) = 0.21 \text{ eV} \). The calculated absorption spectrum is well in line with the experiment, where a band of small intensity was observed at 767 nm and a band of strong intensity at 653 nm.\textsuperscript{163} The transition to \( \text{S}_2 \) (\( \text{FOD} = 1.0 \)) is mainly associated with a promotion of one electron from the HONO to the LUNO, whereas the \( \text{S}_1 \) state \( (\text{FOD} = 0.001) \) corresponds to the double excitation as was obtained for 13 (vide supra). This chromophore qualifies accordingly also as a class III chromophore featuring a “doubly excited singlet state”.\textsuperscript{11} It is interesting to note that polyenes are typical class III chromophores, whereas aromatics usually belong to either class I or class II.\textsuperscript{11}

The other compounds 8–12 on the contrary are class I chromophores, where the transition to the \( \text{S}_1 \) state is due to a single HONO–LUNO excitation. The CAAC stabilized carbon(0) allene, respectively 10 shows of course only negligible diradicaloid character. Surprisingly, already the \( \text{C}_2 \) derivative 11 has an energetically low-lying triplet state \( \Delta E(T_1) = 1.4 \text{ eV} \) and is significantly diradical \( (y_0 = 0.22, \text{FOD} = 0.5) \). Its diradical character is comparable to Thiele’s hydrocarbon and tetracene (vide supra).

This unexpected diradical character has not been noticed in previous calculations,\textsuperscript{43,164} but is equally reflected by the overall trend when going from 8 \( (y_0 = 0.16, \text{FOD} = 0.5) \) to “\( \text{C}_2 \)” extended” 13 \( (y_0 = 0.29, \text{FOD} = 0.8) \). Equally, it explains perfectly why the NHC congener 21, which is according to Tables 3 and 4 expected to show even larger diradicaloid character, could not be isolated in a previous synthetic study.\textsuperscript{165} Note furthermore that 11, which has been reported to be even stable at temperatures as high as 240 °C,\textsuperscript{41} appears to be a good candidate for singlet fission \( \Delta E(\text{S}_1) = 2.88 \text{ eV}, E(T_1) = 1.41 \text{ eV} \) with a reasonable \( \text{FOD} = 0.63 \) for the relevant transition from the \( \text{S}_0 \) to the \( \text{S}_1 \) state.

Moving to carbene stabilized tetracarbon (12) or a phenylene (8) bridge reduces the energies of the \( \text{S}_1 \) states and elevates the energies of the \( \text{T}_1 \) states slightly [8: \( E(\text{S}_1) = 2.74 \text{ eV}, E(T_1) = 1.70 \text{ eV}; 12: E(\text{S}_1) = 2.82 \text{ eV}, E(T_1) = 1.68 \text{ eV}] . The \( \text{T}_1 \) energy levels
Table 4  Diradical indices \((\gamma_0, \gamma_1)\), \(N^{\text{FOD}}\), vertical excitation energies \(E(S_1, T_1, T_2)\), calculated absorption wavelength and oscillation strength \(\langle F^{\text{osc}} \rangle\) for \(S_0 \rightarrow S_1\) transitions. Energies are given relative to the \(S_0\) state and were obtained from CASSCF(4,4) for 10 and 11, CASSCF(6,6) for 12, CASSCF(8,8) for 8, CASSCF(12,12) for 13 and CASSCF(14,14) for 14.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bridge</th>
<th>(\gamma_0)</th>
<th>(\gamma_1)</th>
<th>(N^{\text{FOD}})</th>
<th>(E(S_1)) in [eV]</th>
<th>(E(T_1)) in [eV]</th>
<th>(E(T_2)) in [eV]</th>
<th>Absorption (S_0 \rightarrow S_1 (S_2)) in [nm]</th>
<th>(f^{\text{osc}} S_0 \rightarrow S_1 (S_2))</th>
</tr>
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<tbody>
<tr>
<td>10</td>
<td>(C_1)</td>
<td>0.07</td>
<td>0.04</td>
<td>0.06</td>
<td>5.38</td>
<td>4.27</td>
<td>4.54</td>
<td>231 (430) (442) (461) (498) (784)</td>
<td>0.0 (0.6) (0.0) (0.6) (0.0) (0.0)</td>
</tr>
<tr>
<td>11</td>
<td>(C_2)</td>
<td>0.22</td>
<td>0.07</td>
<td>0.50</td>
<td>2.88</td>
<td>1.41</td>
<td>5.62</td>
<td>430 (442) (461) (498 (444) (784) (610)</td>
<td>0.6 (0.0) (0.0) (0.0) (0.0) (0.0)</td>
</tr>
<tr>
<td>12</td>
<td>(C_4)</td>
<td>0.16</td>
<td>0.07</td>
<td>0.47</td>
<td>2.82</td>
<td>1.68</td>
<td>4.4</td>
<td>442 (461) (498 (444) (784) (610)</td>
<td>0.0 (0.0) (0.0) (0.0) (0.0) (0.0)</td>
</tr>
<tr>
<td>13</td>
<td>(C_6H_4)</td>
<td>0.16</td>
<td>0.09</td>
<td>0.47</td>
<td>2.74</td>
<td>1.70</td>
<td>3.51</td>
<td>461 (498 (444) (784) (610)</td>
<td>0.0 (0.0) (0.0) (0.0) (0.0) (0.0)</td>
</tr>
<tr>
<td>14</td>
<td>(CC)</td>
<td>0.29</td>
<td>0.12</td>
<td>0.85</td>
<td>2.49</td>
<td>0.80</td>
<td>2.90</td>
<td>498 (444) (784) (610)</td>
<td>0.0 (0.0) (0.0) (0.0) (0.0) (0.0)</td>
</tr>
<tr>
<td>15</td>
<td>(CC)</td>
<td>0.78</td>
<td>0.11</td>
<td>1.43</td>
<td>1.58</td>
<td>0.21</td>
<td>2.10</td>
<td>784 (610)</td>
<td>0.0 (1.0)</td>
</tr>
<tr>
<td>16</td>
<td>(CC)</td>
<td>0.81</td>
<td>0.36</td>
<td>0.03</td>
<td>0.36</td>
<td>0.0</td>
<td>0.04</td>
<td>784 (610)</td>
<td>0.0 (1.0)</td>
</tr>
<tr>
<td>17</td>
<td>(CC)</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.0</td>
<td>0.04</td>
<td>784 (610)</td>
<td>0.0 (1.0)</td>
</tr>
<tr>
<td>18</td>
<td>(CC)</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.0</td>
<td>0.04</td>
<td>784 (610)</td>
<td>0.0 (1.0)</td>
</tr>
<tr>
<td>19</td>
<td>(CC)</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.0</td>
<td>0.04</td>
<td>784 (610)</td>
<td>0.0 (1.0)</td>
</tr>
<tr>
<td>20</td>
<td>(CC)</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.0</td>
<td>0.04</td>
<td>784 (610)</td>
<td>0.0 (1.0)</td>
</tr>
<tr>
<td>21</td>
<td>(CC)</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.0</td>
<td>0.04</td>
<td>784 (610)</td>
<td>0.0 (1.0)</td>
</tr>
<tr>
<td>22</td>
<td>(CC)</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.0</td>
<td>0.04</td>
<td>784 (610)</td>
<td>0.0 (1.0)</td>
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<tr>
<td>23</td>
<td>(CC)</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.0</td>
<td>0.04</td>
<td>784 (610)</td>
<td>0.0 (1.0)</td>
</tr>
</tbody>
</table>

Fig. 7 Frontier orbitals of 14 as obtained from CASSCF(14,14) calculation.

Fig. 8 Suitability of 8, 10–14 for singlet fission according to energy matching condition of the \(S_1\) and \(T_1\) states. Error bars relate to the root mean square deviation for the \(S_1\) states from the experimentally available values.

Fig. 9 Suitability of investigated diradicaloids for singlet fission according to energy matching condition of \(S_1\) and \(T_1\) states (left; 10 has been omitted for clarity) and the value of the diradical indices \(\gamma_0\) and \(\gamma_1\) (right). Error bars relate to the root mean square deviation for the \(S_1\) states from the experimentally available values.

The molecules 8, 11, 12, 13, 16–21, 23 appear to be overall most promising for singlet fission, whereas 13, 15–23 should be good targets for two-photon absorption. Equally note that many of these molecules (16–21, 23) show comparably (in relation to their \(S_1\) states and the values obtained for pentacene and especially tetracene) low lying \(T_1\) states, which allows for considerably exoergic singlet fission. Of particular interest, we obtained an exponential relation \([\ln(N^{\text{FOD}}) = -0.81E(T_1) + 0.68]\) between the \(N^{\text{FOD}}\) and the energies of the excited \(T_1\) states with a very good \(R^2\) value of 96% (Fig. 10). The correlation of the \(N^{\text{FOD}}\)
with the energies of the $S_1$ states, the population of the LUNO ($\eta_0$), or the correlation between $\eta_0$ and the energies of the $T_1$ states appears to be weaker (ESI†). We conclude therefore that the $N_{FOD}$ is a reliable and time-efficient method for the estimation of the singlet–triplet gaps of these molecules.

Conclusions

Detailed CASSCF/NEVPT2 computations outline how to design carbene derived diradicaloids with tailored electronic properties for optoelectronic applications. Non-aromatic carbones allow mainly for a tuning of the energies of the $T_1$ states. Aromaticity of the carbene groups has a very strong influence and reduces especially the energy level of the $S_1$ states. Overall, π-electron poor carbones are predicted to lead to comparably low diradicaloid character, whereas π-electron rich C-donor ligands like bent allenes lead to “pristine” diradicals. The design of the bridge (“insulator”) permits for an adjustment of the energy levels of both the first excited singlet and triplet states $S_1$ and $T_1$. Surprisingly, even very short bridges like carbene stabilized dicarbon ($C_2$) is predicted to show quite strong diradicaloid character. We observe that the capability of saturated NHCs to stabilize organic radicals appears to be stronger than commonly believed in the literature.

The fractional occupation number weighted electron density ($N_{FOD}$) is correlated with the energy levels of the $T_1$ state. Hence, it is an excellent predictive tools for the singlet–triplet gap.

Overall, the computations suggest that a considerable number of molecules studied herein are good candidates for application in singlet fission considering the energy matching criteria whereas some are suitable candidates for two-photon absorption. Our findings delineate how to obtain diradicaloids with desired electronic properties and give guidelines for merging carbene chemistry with singlet diradicaloid synthesis. We are convinced that diradicaloids derived from CAACs and NHCs with a saturated backbone are excellent candidates for optoelectronic applications and are therefore currently investigating their experimental behavior.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

68 J. Ma, J. Liu, M. Baumgarten, Y. Fu, Y.-Z. Tan, K. S. Schellhammer, F. Ortmann, G. Cuniberti,
Note that the morphology is of course very important in the solid state.


161 Note that the experimental UV-Vis spectrum relates to a mixture of E and Z isomers.


164 Compounds 7, 9, 21, 22 (which have NOT been omitted from the fit) appear to be outliers. Exploratory calculations suggest that enlarging the active space beyond CASSCF(14,14) leads to a better fit for these compounds.