

Organic molecules with the excited-state singlet-triplet inversion: Beyond BN-based structures

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2. Vertical transition

The most straightforward way to determine the singlet-triplet energy gap of a molecule is to compute 'vertical' energies of the lowest singlet (S_1) and triplet (T_1) states (Δ_{ST}^{ν}) at the equilibrium geometry of the ground state with the appropriate theoretical method. With respect to OLED applications not only the negative Δ_{ST} matters but also fluorescence from the S_1 state has to be allowed. Unfortunately, in InvST molecules with three-fold symmetry axis the S_1 - S_0 transition is forbidden by symmetry. The oscillator strength of this transition can be enlarged by the triangle symmetry breaking due to chemical substitutions. However, symmetry breaking also influences value of Δ_{ST}^{ν} . The correlation between Δ_{ST}^{ν} and oscillator strength of the S_1 - S_0 transition for the studied class of molecules with different number of nitrogen atoms in the outer ring is illustrated in Fig. 2. Additionally, number of nitrogen atoms in the ring modifies energy of the lowest excited states of the system (Fig. 3).

Fig 1. (a) Mechanism of TADF 3^{rd} generation OLEDs, and (b) the new generation OLEDs based on emitters with the inverted S_1 - T_1 excited states.

In most optoelectronic materials, voltage-generated charge carriers recombine to form excitons in a singlet-to-triplet state ratio of 1:3, as per spin statistics. This limits the luminescence quantum yield of standard OLEDs to a maximum of 25%. However, the recent discovery of organic molecules (see inset in (b)) with an inverted ordering of the lowest singlet and triplet excited states (InvST) has paved the way for a new generation of OLED materials [1,2]. These molecules, with a negative S_1 -T₁ energy gap (Δ_{ST}), can efficiently down-convert the triplet to the singlet population through reverse intersystem crossing (RISC). The potential of carbon nitrides and boron carbon nitrides to exhibit this unique property has been extensively studied in recent computational works [3-5], the space of novel structures, however, is still largely unexplored. In the following we present a novel theoretically designed boron-free class of InvST organic molecules and analyze their optoelectronic properties.

3. Excited-state geometry optimization

In most of InvST molecules theoretically designed over the years, only the 'vertical' Δ_{ST}^{ν} was considered. However, from the point of view of OLED applications, the adiabatic energy of the S₁ and T₁ states matters. To achieve this, geometry optimization of a molecule in these states is necessary. Since in trigonal InvST systems the S₂-T₂ energy gap is generally positive, the 'vertically' T₂ states may become adiabatically the lowest triplet state (T₁) of the system. This effect is illustrated in Fig. 4 for selected nitrogenand sulfur- substituted systems.



Fig. 2. (a) Correlation between vertical excitation energy (Δ_{ST}^{ν}) and oscillator strength (f) of the nitrogen derivatives of the structure inserted in figure. X=O - blue dots, X=NH - orange squares, X=S - grey triangles. (b) examples of some of the molecules and their nitrogen derivatives plotted in (a). Numbers denote energy in electronvolts.





Fig. 3. Absorption energy (E_{abs} blue dots) and vertical S_1 - T_1 energy (Δ_{ST}^{ν} - red stars) dependence on the number of nitrogen atoms symmetrically inserted into the first structure shown in Fig. 2. (b)

Methods

Ground electronic state geometry optimizations were performed with the second-order Møller-Plesset (MP2) method. Vertical electronic excitation energies of singlet (S_1) and triplet (T_1) states along with geometry optimization were done using algebraic-diagrammatic construction of second order (ADC(2)) method. All the calculations employed the cc-pVDZ basis set.

Fig. 4. Correlation diagrams of the energies (eV) computed for the chosen systems of the first singlet (orange) and triplet (blue) states with schematic potential energy curves driven through the computed energies. Arrows denote emission from the lowest excited states. Numbers denote energy in electronvolts.

Conclusions

- In some of the InvST systems discussed here, the geometry of the triplet state is largely stabilized by symmetry breaking that causes single/double-bondlength defferentiation, making the singlet and triplet states nearly degenerate adiabatically.
- Thus, a simple computation of vertical excitation energies are not sufficient to predict novel molecules with the negative Δ_{ST}.
- Nevertheless, nitrogen insertion into these systems both shifts the emission towards shorter wavelengths, and in some cases preserves the negative Δ_{ST} upon the excited-state geometry optimization.

References

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