Establishing design rules for emissive materials as next generation emitters for organic light-emitting diodes: A computational perspective from the inversion of the singlet-triplet energy gap

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Abstract

The inversion of the lowest singlet and triplet excited state energy gap, in fully organic triangle-based compounds, can give rise to a new exergonic pathway to enhance the Organic Light Emitting Diodes (OLEDs) performance, going beyond the novel yet promising Thermally Activated Delayed Fluorescence (TADF) mechanism. If, on one hand, the origin of this inversion, arising from the interplay between exchange and electron correlation effects, has been extensively investigated in last years, identifying the wavefunction methods as key to predict the excited-state inversion, on the other hand a proper picture of the structure-property relationships characterizing these systems is still missing. In this work, we thus assess the effect of different symmetry point groups (D$_{3h}$, C$_{2v}$, C$_{3h}$ and C$_{3v}$) on the orbital localization to shed light on the role that the symmetry has in determining the optical features of the triangulene systems (on both S$_1$-T$_1$ inversion and oscillator strengths). The presence of the $c_2$ axis and the $\sigma_v$ plane (as it happens for the D$_{3h}$, C$_{2v}$ and C$_{3v}$ groups) turned out to be critical for ensuring the proper orbital localization aimed at minimizing the exchange interaction and therefore favouring the inversion. In particular, adopting a C$_{2v}$ (and its subgroups) symmetry, either through the proper doping pattern, by introducing substituents, or by merging two triangulene cores, is the only way to conciliate a negative $\Delta E_{ST}$ and a non-zero oscillator strength. Finally, we gathered the lessons learnt from this analysis to establish a series of design rules, aimed at helping the identification of inverted singlet-triplet (INVEST) emitters for applications in the next generation of OLEDs.
1 Introduction

Acclaimed for their brightness, lightness, as well as their potential flexibility and easy processability, Organic Light-Emitting Diodes (OLEDs) are represent an established technology in devices such as smartphones and TVs, or lighting applications, to name just a few of them. If, on one hand, these features make OLEDs more attractive than their inorganic counterpart, on the other hand the pure organic nature of these emitters severely limits the internal quantum efficiency (IQE); i.e., the ratio between the number of photons emitted upon charge injection. Indeed, in an OLED, light emission from an organic molecule takes place from the lowest singlet excited state (fluorescence) which results in a 25% IQE due to spin-statistics limit, the remaining 75% of triplet excitons decaying non-radiatively. Through the years, several design strategies have been conceived with the aim of fully harvesting both the singlet and the triplet excitons and foster IQEs beyond that 25% limit.

In the last years, a Thermally Activated Delayed Fluorescence (TADF) mechanism has represented a prominent solution to overcome the spin-statistics limit, relying on the minimization of the energy gap between the lowest singlet ($S_1$) and triplet ($T_1$) excited states, that is $\Delta E_{ST} = E(S_1) - E(T_1)$, to promote a thermally activated Reverse Intersystem Crossing (RISC) from the triplet to the singlet and reach, in theory, an IQE of ideally up to 100%. Because the $\Delta E_{ST}$ is known to be proportional to the hole-electron densities overlap, its minimization can be achieved by ensuring a spatial separation of the hole and electron densities. The initial design strategy of TADF emitters employs donor-acceptor compounds\cite{1-2}, which thus guarantees the segregation of the hole and electron densities on different parts of the molecule thus prompting excited states with a high intramolecular Charge Transfer (intra-CT) character. However, this strategy suffers from two critical drawbacks: a broad emission and a small oscillator strength (emission cross-section), both detrimental factors for the ultimate performance of a real-world OLED.

More recently, the Multi-Resonant TADF (MR-TADF) strategy proposed by Hatakeyama et al.\cite{3} solved this shortcoming through the synthesis of boron and/or nitrogen-doped organic materials\cite{4-10}, in which complementary multiple resonance effects originating from the different heteroatoms turns into a localization of the highest-occupied molecular orbitals (HOMO) and lowest-unoccupied molecular orbitals (LUMO) on alternating atomic sites. The resulting short-range intra-CT guarantees a small $\Delta E_{ST}$ along with a narrow emission and a high oscillator strength.

Generally speaking, fully organic TADF molecular compounds which all display a closed-shell ground state electronic structure are expected to obey the analogue of the Hund’s rule, which is generally assumed to lead to $T_1$ lying below $S_1$, resulting in a
positive $\Delta E_{ST}$, so that the harvesting of triplet excitons is driven by an up-conversion process.

Past experimental studies on two triangular shape compounds called cyclazine$^{[11]}$ and triazacyclazine$^{[12]}$, showed a close degeneracy of $S_1$ and $T_1$ along with a short lifetime of $T_1$, features unusual for organic molecules. Besides those initial experimental observations, which not fully conclusive, wavefunction-based quantum chemical calculations on these two molecules predicted a negative $\Delta E_{ST}$, suggesting the potential inversion of the singlet and triplet energy order and the violation of the Hund’s rule$^{[13]}$. The singlet-triplet inversion was indeed confirmed in 2019 by experimental investigations on another triangle shaped molecule called heptazine$^{[14]}$, which provided no evidence of a triplet excited state below the lowest singlet excited state, feature again supported by wavefunction-based quantum chemical calculations resulting in a negative $\Delta E_{ST}$.

Furthermore, those findings also help to understand a previous study (2013) by Adachi et al.$^{[21]}$, who reported the synthesis of a heptazine derivative (HAP-3TPA) in which the strong acceptor power of the heptazine core (HAP) and the donor power of the three triarylamino (TPA) substituents induced an intra-CT character, leading to a $\Delta E_{ST} = 0.17$ eV in oxygen-free toluene solution. Employing the HAP-3TPA as emitter in an OLED device an EQE of 17.5% was reached. More intriguing, an unusual TADF behavior was observed in the solid state, i.e. a decrease of the TADF efficiency with an increase of the temperature, which suggested a thermally promoted endergonic intersystem crossing (ISC) and thus an inverted singlet-triplet energy order.

In our previous works$^{[13,16]}$, we have investigated the electronic structure and the optical properties of a set of triangular shape compounds with different sizes and different doping patterns, either with nitrogen and/or boron atoms, by means of Time Dependent Density Functional Theory (TD-DFT) and correlated wave function methods. These studies confirmed the key role played by double and higher-order excitations as included in wave function-based methods, to promote the singlet-triplet inversion. Climbing the Jacob ladder, Local Density Approximation (LDA), Generalized Gradient Approximation (GGA) as well as hybrid functionals in combination with linear response TD-DFT are intrinsically unable to tackle the gap inversion because of the missing explicit description of double excitations. This problem can be solved when referring to double-hybrid functionals which includes a MP2-like correlation correction also extended to excited-state studies$^{[17]}$. However, the gap inversion we observed in the azaphenelene family is not systematically predicted for all double-hybrid functionals which precludes their black-box use for screening or designing new materials, and more investigations are still needed. Analogously, we carried out some tests employing the Spin-Flip TD-DFT method$^{[18,19]}$ (SF-TD-DFT) (using a triplet state as a reference) for which the strong dependency on the chosen functional, along with
the spin-contamination, precluded a systematic prediction of the negative $\Delta E_{ST}$. Besides this, we identified in our past studies three features (at least) required to have the singlet-triplet inversion, each one being accurately quantifiable: i) low to moderate radicaloid character; ii) low exchange interaction; iii) high contribution of double excitations (generally > 10%) to the $S_1$ and $T_1$ wave function.

Microscopically, the singlet-triplet inversion originates from electronic effects, namely from the interplay between the exchange interaction (Fermi correlation) acting on parallel spins and electron correlation (Coulomb correlation) interaction acting on anti-parallel spins. Whilst the former is a positive term promoting the stabilization of the triplet with respect to the singlet, the latter arises from the presence of doubly excited configurations (and/or higher order excitations) through wavefunction-based methodologies which introduce a stabilization of the singlet with respect to the triplet that, if large enough, can overcome the exchange interaction and provide a negative $\Delta E_{ST}$[15]. However, these methodologies (and others in general) do not allow to disentangle the Coulomb correlation contribution from the exchange one.

Besides, it has been historically assumed that the singlet-triplet exchange interaction ($K$) was the only magnitude to control and/or tune, being proportional to the overlap between the orbitals involved in the electronic transition ($\phi_i$ and $\phi_a$ the occupied and unoccupied orbitals, respectively). Within the two-state model (e.g. a HOMO to LUMO transition) and assuming that $S_1$ and $T_1$ share the same electronic configuration, the magnitude of this interaction can be straightforwardly quantified through the Configuration Interaction Singles (CIS) calculations, leading to $\Delta E_{ST}=2K^{[13-15]}$. That is, the smaller is the HOMO-LUMO overlap, the smaller is the exchange interaction, significantly reducing the singlet-triplet gap. As a first guess on the magnitude of the exchange integral, it follows that the (even visual or qualitative) evaluation of the shape and localization of the molecular orbitals involved in the description of the excited states can guide the minimization of $\Delta E_{ST}$ in triangulene compounds, potentially leading to singlet-triplet inversion. Previously, computational studies on the potential inversion of the singlet-triplet energy order in small conjugated hydrocarbon systems such as propalene, pentalene and heptalene pointed out on the impact of the symmetry point group variation on the orbital pattern and its effect in modulating the $\Delta E_{ST}$ from a positive to a negative value[20].

The triangulene compounds showing a negative $\Delta E_{ST}$ are characterized by the typical hole-electron pattern of the MR-TADF compounds; i.e., an alternating distribution of hole and electron densities on adjacent atomic sites so that the nature of the lower-lying singlet and triplet excited states typically displays a short-range charge transfer character. This picture is also consistent with the spatial distribution of the molecular orbitals: taking cyclazine as example, the HOMO and LUMO are mainly localized on
alternating atomic sites, favoring the minimization of their overlap (see Fig.1a and Fig.2a). This orbital distribution is dictated by the symmetry of the bare triangulene core with the most promising compounds belonging to the D$_{3h}$ symmetry point group$^{[13,16]}$. However, because $S_1$ is mainly dominated by a HOMO to LUMO transition, the oscillator strength is vanishing which involves that these compounds are not fully suitable for light-emitting applications. Note also that very recently, Pollice et al. performed a high-throughput computational screening on a large family of substituted N-doped triangulenes showing how the breaking of the D$_{3h}$ symmetry can conciliate the negative $\Delta E_{ST}$ and a non-zero $S_0 \rightarrow S_1$ oscillator strength$^{[22]}$. On the other hand, an alternative application which would benefit from the $S_1$-T$_1$ inversion is organic photocatalysis$^{[23]}$, where the zero oscillator strength do not represent necessarily a shortcoming. Computational studies carried out by Domcke at al. showed the active role played by the heptazine in photoinduced water splitting entailing the formation of a heptazine-water complex in the excited state$^{[24]}$.

Undoubtedly, the inversion of the singlet-triplet energy order could potentially lead to a new pathway to further improve the efficiency of OLEDs, in which the triplet harvesting is now driven by a down-conversion process. However, we still remark two main existing issues, namely: (i) the lack of a picture of the structure-property relationship characterizing the inverted singlet-triplet (INVEST) systems, and (ii) the scarce number of known INVEST emitters, who also exhibit a vanishing oscillator strength because of symmetry reasons.

Summarizing, in this article we systematically explore some INVEST molecules to gather information useful to: (i) acquire a comprehension of the structure-property relationship, and (ii) concomitantly establishing design rules aimed at guiding the identification of molecular emitters with a negative $\Delta E_{ST}$ and non-zero oscillator strength. Section 2 will describe the methodology needed to accomplish these goals, which goes beyond standard (e.g. TD-DFT) calculations, while section 3 we will assess the role of the symmetry on the orbital localization and its connection with the singlet-triplet inversion. In section 4, we will present two strategies to obtain systems with a negative $\Delta E_{ST}$ and a non-zero oscillator strength: (i) one employing substituents and (ii) one encompassing the extension of the triangulene core. In section 5, we will simulate the emission spectra from first principles for two potential INVEST emitters and in section 6 we will finally compute the fluorescence and (R)ISC rate constant as a further illustration of the possibilities arising from this study.
2 Methodology

All the molecular structures considered have been optimized at B97-3c\[^{[25]}\] level, and all real frequencies found, whereas the vertical excitation energies (S\(_n\)←S\(_0\) and T\(_n\)←S\(_0\)) have been computed at Configuration Interaction of Singles (CIS), Spin Component Scaling\[^{[26]}\] second-order approximate Coupled Cluster Singles and Doubles (SCS-CC2)\[^{[27]}\] level, State-Average Complete Active Space Self Consistent Field (SA-CASSCF) and Strongly Contracted N-Electron Valence 2\(^{nd}\)-order Perturbation Theory (SC-NEVPT2)\[^{[28-30]}\] employing the RI-JK\[^{[31]}\] approximation with the def2/JK auxiliary basis set. A (8,8) active space (eight electrons in eight molecular orbitals) were used for CASSCF and NEVPT2 calculations, ensuring a good trade-off between accuracy and computational cost. 2\(^{nd}\)-order Møller-Plesse perturbation theory (MP2) natural orbitals were used as a first guess for CASSCF calculations. All the calculations employed the def2-TZVP basis set, expected to provide negligible discrepancy with respect to larger basis set, as already observed in our previous work\[^{[16]}\]. SCS-CC2 calculations were performed using Turbomole 7.4\[^{[32]}\] package whereas the geometry optimization, frequencies, and SA-CASSCF and SC-NEVPT2 calculations were carried out with the ORCA 4.2\[^{[33]}\] package. The overlap between molecular orbitals (\(S_{ia} = \langle |\phi_{i}| |\phi_{a}| \rangle\)) and the Tozer’s diagnostic (\(\Lambda = (\sum_{i,a} c_{ia}^2 S_{ia})/\sum_{i,a} c_{ia}^2\), with \(c_{ia}\) the coefficient associated with the one-electron transition between the occupied and virtual orbitals, \(\phi_{i}\) and \(\phi_{a}\), respectively) have been computed with MultiWfn 3.6\[^{[34]}\] (for excited state dominated by only one-electron transition the Tozer’s value reduced to the orbital overlap). Note that 0 ≤ \(\Lambda\) ≤ 1, where \(\Lambda=0\) and \(\Lambda=1\) denote a pure Locally Excited (LE) and pure Charge-Transfer (CT) excitation, respectively. For the rate constants calculations, the Spin-Orbit Coupling (SOC) between S\(_1\) and T\(_n\) has been computed at S\(_0\) geometry at TD-DFT-PBE0/def2-TZVP employing the Breit-Pauli Hamiltonian within the ZORA approximation using ORCA 4.2\[^{[33]}\]. The \(k_{RISC}\) have been computed using MOMAP 2021b\[^{[57-60]}\] using the optimized geometries and frequencies computed with Gaussian16\[^{[56]}\], including the Duschinsky rotation. The absolute energies of the excited state and the respective differences have been computed at SCS-CC2/def2-TZVP level on top of the PBE0 optimized geometries.

3 Orbital localization and impact on optical properties

3.1 Impact of the symmetry point group on the \(\Delta E_{ST}\)

In symmetric compounds, the orbital localization can be systematically deduced from the symmetry point group. The Symmetry Adapted Molecular Orbitals (SAMOs) are generated as Symmetry Adapted Linear Combinations (SALCs) of \(p\) atomic orbitals (\(\chi_{i}\)) thanks to the projection operators \[^{[35]}\]. Considering a single \(p\) orbital per atomic
center as a good approximation for (nearly) planar molecular compounds, which is usually the central assumption in the Hückel method$^{36-39}$ and tight-binding approaches$^{40-42}$.

**Figure 1:** Definition of the p atomic orbitals of the triangulene systems considered in the analysis.

...the approach encompasses the following steps:

(i) Construction of the reducible representation (RR), $\Gamma_{\text{red}}$, by operating with each symmetry operator on the atomic orbitals.
(ii) Reduction of $\Gamma_{\text{red}}$ in terms of the irreducible representations (iRRs) of the point group according to equation S1.1.
(iii) Construction of the SALCs by means of the projection operators ($P^R$) according to equation S1.2.
(iv) Generation of the SAMOs.
(v) Identification of the HOMO and LUMO by ordering the SAMOs according to their energies computed at Hückel level and filling them with the $\pi$-electrons composing the system of interest (for instance in the cyclazine case, 14 $\pi$-electrons considering 13 C atoms and one central N atom).

In order to assess the effect of the presence/absence of a symmetry element on the orbital localization, the analysis has been carried out by considering the $D_{3h}$ point group, the highest point group to which most of INVEST triangulene compounds belong. We also investigated its subgroups $C_{2v}$, $C_{3h}$ and $C_{3v}$ to rationalize the impact of lowering the symmetry on the orbital localization and in the end on the $\Delta E_{\text{ST}}$.

In the following section, we present only the results of the symmetry analysis, along with the possible scenarios involving the symmetry point group at issue. For the complete analysis (generation of SALCs and SAMOs) the reader can found the details at the Supporting Information (SI).

### 3.1.1 Point group: $D_{3h}$

$D_{3h}$ is the highest order symmetry point group that can be obtained considering triangle-shape molecules. Taking as reference the structure reported in Figure 1, the reducible
representation $\Gamma^{D_{3h}}_{\text{red}}$ is written as direct sum of one- (1D) and two- (2D) dimensional iRRs: $\Gamma^{D_{3h}}_{\text{red}} = a''_1 \oplus 4a''_2 \oplus 4e''$. Optical excitations are described as (active) electronic transitions between orbitals whose iRRs direct product includes the iRR of (at least one of the components of) the transition dipole moment. So far, we have identified that both $S_1$ and $T_1$ in most of the INVEST molecules are described by electronic transitions between non-degenerate HOMO and LUMO orbitals so that these orbitals belong to $a''_1$ and $a''_2$ iRRs. Taking cyclazine as an example, we will determine the SAMOs associated with the HOMO and LUMO orbitals (see the detailed derivation in supporting information).

Starting from the iRR $a''_1$, the sole SALC obtained through the projection operator coincides with the SAMO having the following form: 

$$
\psi^{a''_1}_2 = \frac{1}{\sqrt{6}}(\chi_2 + \chi_{10} + \chi_6 - \chi_{12} - \chi_8 - \chi_4),
$$

thus a linear combination of the atomic orbitals centred on the atomic sites which do not lie on a symmetry element. By rendering $\psi^{a''_1}_2$ we obtain the molecular orbitals depicted in Fig. 2(a), which essentially matches with the orbital localization of the HOMO of the cyclazine, Fig. 2(b):

![Figure 2](image)

**Figure 2:** (a) $a''_1$- SAMO obtained by means of the projection operator; (b) HOMO of cyclazine, computed at HF/def2-TZVP level (isocontour $\sigma=0.02 \text{e} \cdot \text{Bohr}^{-3}$).

The same analysis carried out on the $a''_2$ iRR leads to four SALCs that result in four $a''_2$-SAMOs. Among the $a''_2$-SAMOs the one labelled as $\psi^{a''_2}_3$, proportional to the linear combination of the atomic orbitals written as $0.4\chi_1 - 0.01\chi_2 - 0.4\chi_3 - 0.01\chi_4 + 0.4\chi_5 - 0.01\chi_6 - 0.4\chi_7 - 0.01\chi_8 + 0.4\chi_9 - 0.01\chi_{10} - 0.4\chi_{11} - 0.01\chi_{12} + 0.16\chi_{13}$, represents the $a''_2$-SAMO depicted in Figure 3(a), which is consistent with the orbital localization of the LUMO of cyclazine, Figure 3(b).
As it can be seen, while the HOMO is defined by atomic orbital centered on non-adjacent atomic sites (non-bonding character), but all $p$ atomic orbitals contribute to the LUMO instead. Among them, the ones bringing the largest weights are centered on the atomic sites on which there is no weight on the HOMO orbital ($\chi_1, \chi_3, \chi_5, \chi_7, \chi_9, \chi_{11}, \chi_{13}$), whereas a smaller contribution derives from atomic orbitals centered on the atomic sites where the HOMO weight is different than zero ($\chi_2, \chi_4, \chi_6, \chi_8, \chi_{10}, \chi_{12}$). It follows that, even though the HOMO and LUMO are mainly localized on alternating atomic sites, there is a non-negligible, yet small overlap involving the latter set of atomic orbitals, leading to a non-vanishing HOMO-LUMO overlap ($S_{HL} = 0.509$, and consequently a non-vanishing exchange interaction term. Further decreasing the LUMO weight on $\chi_2, \chi_4, \chi_6, \chi_8, \chi_{10}, \chi_{12}$ atomic sites and forcing its localization on the remaining atomic sites would further decrease the exchange interaction leading to an even more negative $\Delta E_{ST}$. A related example is the B-doped parent compound of cyclazine (2T-B, Figure S2), in which the nitrogen is replaced by a boron atom, for which the MOs localization is opposite with respect to the nitrogen counterpart, i.e. HOMO and LUMO being now represented by the $a''_2$- and $a''_1$-SAMOs, respectively. Starting from this compound and introducing the more electronegative N atoms on $\chi_1, \chi_5$ and $\chi_9$ atomic sites (2T-B-3N, Figure S3); i.e., by concentrating the HOMO density on the atomic sites not covered by the LUMO, the exchange interaction can be reduced from 0.155 eV ($S_{HL} = 0.453$) to 0.114 eV ($S_{HL} = 0.393$) and a reduced $\Delta E_{ST}$ value from -0.280 eV to -0.454 eV and from -0.200 eV to -0.176 eV at the SCS-CC2 and NEVPT2 level, respectively. In addition, it is worth noting how this strategy leads to an increase of the $S_1$ and $T_1$ excitation energies of 2T-B-3N with respect to 2T-B (Table S4), a behavior originating from the stabilization of the HOMO orbital with respect to the LUMO thanks to the introduction of the nitrogen atoms. We also applied this strategy to N centered triangulenes, introducing the B atom on the vertices; however, it turns out into a distorted molecular structure providing a positive $\Delta E_{ST}$ (Figure S4).
The D$_{3h}$ point group can give rise to a second scenario, in which the MOs involved in the lower-lying singlet and triplet excited states are two degenerate orbitals, either occupied or unoccupied and thus belonging to the 2D iRR. Figure 4 shows two triangulene derivatives doped with three nitrogen atoms, reported in ref. 16 both of the same dimension and both belonging to the D$_{3h}$ point group. In the triangulene (a) (4T-a) both the HOMO and LUMO are not degenerate and associated with the $a_1''$ and $a_2''$ iRRs as in cyclazine with an orbital localization sharing similarities with cyclazine, i.e. HOMO and LUMO mainly localized on alternating atomic sites ($S_{HL} = 0.471$), with consequently a small exchange interaction of 0.147 eV computed at the CIS level, together with a negative $\Delta E_{ST}$ (-0.275 eV and -0.260 eV at SCS-CC2 and NEVPT2 level, respectively). The different positions of the nitrogen atoms in the core of the triangulene (b) (4T-b) leads to the same HOMO pattern, but induces an inversion of the $a_2''$ and $e''$ unoccupied MOs (Figure S5) so that the LUMO is defined by two degenerate orbitals. In this case, a larger orbital overlap is observed ($A_{HL} = 0.545$) with a much larger exchange interaction of 0.551 eV as computed at the CIS level within a two-state model which translates in a positive and large $\Delta E_{ST}$ (0.296 eV and 0.290 eV at SCS-CC2 and NEVPT2 level, respectively).

![Figure 4](image)

**Figure 4**: HOMO and LUMO computed at HF/def2-TZVP, exchange interaction, $\Delta E_{ST}$ and oscillator strength computed at SCS-CC2/def2-TZVP of the two triangulenes doped with nitrogen atoms (isocontour $\sigma=0.02$ e·Bohr$^3$).

This larger HOMO-LUMO overlap is a consequence of the orthogonality between the degenerate LUMO orbitals which impose a spatial localization of the LUMO orbitals at atomic sites with high HOMO weights resulting in a larger exchange interaction.

Moreover, whilst in the (a) case the iRRs of the HOMO and LUMO lead to a symmetry forbidden transition ($f_{OSC} = 0$), in the (b) case the 2D iRR of the LUMO ($e''$)
guarantees a $f_{\text{OSC}}$ different from zero (0.144 at SCS-CC2 level), suggesting the critical role played by the doping pattern in modulating the optical properties of these triangle-shape systems. It is worth noting that systems with a high symmetry such as $D_{3h}$ are prone to undergo Jahn-Teller distortions in the excited state\cite{43}, which could release the symmetry constraints and open a radiative pathway for the excited state. However, this effect occurs when a degeneracy in the excited states is observed, which in turn encompasses a degeneracy in the molecular orbitals. By optimizing the $S_1$ geometry of the triangulenes in Figure 4, we observed no lowering of the symmetry in compound (a) while compound (b) is characterized by a degeneracy in the vertical excitation energy of $S_1$ and $S_2$, seen its symmetry is reduced to $C_{2v}$. The singlet-triplet gap remains almost unaffected ($\Delta E_{ST} = -0.276$ eV) for compound (a) whilst it remains positive for compound (b) ($\Delta E_{ST} = 0.265$ eV, see Figure S6).

Referring to compounds reported in the literature, the TABNA-1 compound\cite{44} (Figure 5), a triangulene MR-TADF emitters doped with nitrogen and boron exhibits a $D_{3h}$ symmetry in the ground state. In this case, the doping pattern involves the degeneracy of the HOMO orbitals, whereas the LUMO is non-degenerate, with a $\lambda_{HL} = 0.628$ and a positive $\Delta E_{ST}$ of 0.167 eV at SCS-CC2 level and a degeneracy of $S_1$ and $S_2$ excited states that are symmetry-allowed with $f_{\text{OSC}}$ of 0.189. By optimizing its $S_1$, the symmetry is reduced to $C_{2v}$ and $\Delta E_{ST}$ increases to 0.248 eV while $f_{\text{OSC}}$ decreases to 0.164.

\[ K = 0.775 \text{ eV} \]
\[ \Delta E_{ST}^{\text{SCS-CC2}} = 0.167 \text{ eV} \]
\[ f_{\text{OSC}}^{\text{SCS-CC2}} = 0.189 \]

**Figure 5:** HOMO and LUMO computed at HF/def2-TZVP, exchange interaction, $\Delta E_{ST}$ and oscillator strength computed at SCS-CC2/def2-TZVP for TABNA-1 (isocontour $\sigma=0.02$ e\text{-Bohr}^{-3}).

A third scenario would involve the simultaneous degeneracy of the HOMO and LUMO orbitals. This case has been recently investigated by Domcke *et al.*\cite{45} in a B- and N-doped triangulene composed by three benzene rings on the rim. Interestingly, $S_1$ and $T_1$ excited states belong to two different iRRs, namely $A'_2$ and $E'$, respectively. In this
case a negative $\Delta E_{ST}$ was obtained, even though the $S_0 \rightarrow S_1$ oscillator strength remains equal to zero.

3.1.2 Point group: $C_{2v}$

Lowering the symmetry to the $C_{2v}$ point group, i.e. removing the $C_3$ rotation axis, leads to the loss of the 2D iRRs, resulting in the absence of degeneracy. The $I_{red}^{C_{2v}}$ is reduced to the direct sum of two iRRs: $8b_2 \oplus 5a_2$. It can be noted that these two iRRs give rise to three possible direct products: $b_2 \otimes b_2 = b_1$, $a_2 \otimes a_2 = a_1$, $b_2 \otimes a_2 = b_1$, i.e. the same iRRs of the $z$ ($a_1$) and $x$ ($b_1$) component of the transition dipole moment. It follows that, assuming the $A_1$ iRR for $S_0$, the two possible iRRs of $S_1$ are always compatible with a symmetry allowed $S_0 \rightarrow S_1$ transition. In light of this, by lowering the symmetry to $C_{2v}$, the two major issues encountered with the $D_{3h}$ symmetry are solved: (i) degenerated MOs are now no longer present, and (ii) a non-zero oscillator strength is now achievable.

The application of the projection operators of $a_2$ ($P^{a_2}$) and $b_2$ iRRs ($P^{b_2}$ results in five and eight SALCs, respectively, which are then combined to generate five $a_2$-SAMOs and eight $b_2$-SAMOs. The corresponding SAMOs $\psi_3^{a_2}$ and $\psi_5^{b_2}$ patterns (see Figure S7) are consistent with the HOMO and LUMO of cyclazine. However, while displaying the same phase alternation of the atomic orbitals as the $a_2''$-SAMO of the $D_{3h}$ symmetry point group, the $\psi_5^{b_2}$ SAMO exhibits slightly different weights on the different $\chi_i$ atomic sites. This confirms that the sole change of the point group symmetry dictate a different shape of the orbitals. Substituting cyclazine on site $\chi_1$, we lowered its symmetry to the $C_{2v}$ point group and obtained the compound represented in Fig. 6a (2T-2N). The orbital localization is in line with the ones of $\psi_3^{a_2}$ and $\psi_5^{b_2}$ SAMOs (see Figure S7). The slight changes in orbitals patterns result in an increase with respect to cyclazine of the HOMO-LUMO overlap ($S_{HL} = 0.523$) and exchange energy to 0.223 eV with the $\Delta E_{ST}$ of -0.174 and -0.120 eV, at SCS-CC2 and NEVPT2 levels of theory respectively. In addition, the symmetry lowering results in an increase in the oscillator strength close to $10^{-3}$. 
As for the D\textsubscript{3h} structure, relying on a B-centered triangulene substituted with N atoms (2T-B-N, see Figure 6b), retaining the C\textsubscript{2v} symmetry can help to further reduce the HOMO-LUMO overlap ($S_{HL} = 0.458$) and exchange interaction (0.132 eV), leading to a more negative $\Delta E_{ST}$ along with a non-zero oscillator strength (Figure 6b). Again in this case, the 2T-B-N shows a blue-shift of the S\textsubscript{1} and T\textsubscript{1} excitation energy with respect to 2T-2N (Table S7), thanks to the stabilization of the HOMO due to the N-doping on $\chi_1$ site.

A well-known triangulene with a C\textsubscript{2v} core is the pentaazaphenalene (5AP), obtained through the introduction of nitrogen atoms on $\chi_4$, $\chi_6$, $\chi_8$, $\chi_{10}$ and $\chi_{13}$ atomic sites, following the enumeration of Figure 1, widely used as a building block for the synthesis of emitting conjugated polymers\cite{46,47} and as Near-Infrared (NIR) absorber, exploiting the spatial localization of the HOMO and LUMO and the combined effect of Electron-Donating Groups (EDGs) and Electron-Withdrawing Groups (EWGs)\cite{48}. The HOMO and LUMO are, in fact, mainly localized on different atomic sites, but in contrast to the triangulenes so far explored, the non-bonding character of the HOMO is no longer provided, with the electron density extended over the bonds (Figure 7). As a consequence, the HOMO and LUMO overlap ($S_{HL} = 0.562$) leading to a higher exchange interaction (0.341 eV, twice the one of cyclazine), favouring a less negative $\Delta E_{ST}$. The different HOMO pattern arises from the introduction of the heteroatoms on the atomic sites composing the $a_2$-block of the Hückel Hamiltonian, which is now characterized by two different values of the site-energy term ($\alpha_C$ and $\alpha_N$) and the resonance integral ($\beta_C$ and $\beta_N$), which, in turn, generate a different set of eigenvectors. This can be straightforwardly observed by computing the Hückel MOs, which are consistent with the HOMO and LUMO patterns of 5AP (Figure S8). Despite of that, SCS-CC2 calculations provided a $\Delta E_{ST} = -0.233$ eV, in clear contrast to higher

$K = 0.223$ eV

$\Delta E_{ST}^{\text{SCS-CC2}} = -0.174$ eV

$\Delta E_{ST}^{\text{NEVPT2}} = -0.120$ eV

$\gamma_{\text{osc}}^{\text{SCS-CC2}} = 8 \cdot 10^{-4}$

$\gamma_{\text{osc}}^{\text{NEVPT2}} = 7 \cdot 10^{-4}$

$K = 0.132$ eV

$\Delta E_{ST}^{\text{SCS-CC2}} = -0.293$ eV

$\Delta E_{ST}^{\text{NEVPT2}} = -0.174$ eV

$\gamma_{\text{osc}}^{\text{SCS-CC2}} = 2 \cdot 10^{-3}$

$\gamma_{\text{osc}}^{\text{NEVPT2}} = 1 \cdot 10^{-3}$

Figure 6: HOMO and LUMO computed at HF/def2-TZVP, exchange interaction, $\Delta E_{ST}$ and oscillator strength computed at SCS-CC2/def2-TZVP and NEVPT2/def2-TZVP of the C2v triangulene core (isocontour $\sigma = 0.02 \text{ e \cdot Bohr}^3$).
correlated wavefunction methods such as ADC(3)/def2-SVP, resulting in a less negative $\Delta E_{ST} = -0.072$ eV, or NEVPT2 calculations, spanning from a negative to a positive $\Delta E_{ST}$ gradually increasing the active space: -0.089 eV, 0.034 eV and 0.036 eV for a (8,8), (10,10) and (12,12) active space. This discrepancy might derive from the inclusion of the double excitations only up to the 0th order by SCS-CC2, leading to a less accurate description of the electron-correlation contribution and the consequence overestimation of the $S_1$-$T_1$ inversion, suggesting that a proper validation by means of higher correlated calculations is necessary for molecules like 5AP, lying at the edge between INVEST and TADF systems.

![Figure 7: HOMO and LUMO computed at HF/def2-TZVP for 5AP (isocontour $\sigma=0.02$ e·Bohr$^{-3}$).](image)

A further example on the importance of the heteroatoms position in determining the MOs localization is the compound DABNA-1 (Fig.8), a (nearly) C$_2v$ MR-system, in which both the HOMO and LUMO are clearly extended over the bonds with a $S_{HL} = 0.609$, leading to a large exchange interaction and a positive $\Delta E_{ST}$.

![Figure 8: HOMO and LUMO computed at HF/def2-TZVP, exchange interaction, $\Delta E_{ST}$ and oscillator strength computed at SCS-CC2/def2-TZVP for DABNA-1 (isocontour $\sigma=0.02$ e·Bohr$^{-3}$).](image)

If, on one hand, the C$_2v$ symmetry prevents the presence of orbital degeneracy and allows obtaining a non-zero oscillator strength of the $S_0\rightarrow S_1$ transition, on the other
hand, the last two examples demonstrate that within this point group a negative $\Delta E_{ST}$ is not guaranteed, suggesting that the heteroatoms position has to be carefully chosen, paying attention to not (or slightly) perturb the orbital localization of the MOs. The substitution with nitrogen atoms could result in different scenarios depending on the targeted atomic sites. On one hand, substitution on a node of the HOMO orbital leads to no impact on its pattern. On the other hand, substitution on an atomic site corresponding to an anti-node leads to a decrease of the weight of the HOMO on that particular site. We observed a redistribution of the electron density towards the other atomic sites which is the consequence of the release of the symmetry constraints on orbital localization imposed by the $D_{3h}$ symmetry point group. The latter case is readily explained in terms of the Hückel model. By adding nitrogen (i.e. heteroatoms) atoms, we introduced different $\alpha$ and $\beta$ values. The HOMO orbital spreads preferentially between identical atomic sites since they have exactly the same $\alpha$ values and larger $\beta$ values giving us a hint on how the HOMO pattern could be affected. A similar conclusion also holds for the LUMO orbital.

Overall, a reasonable choice to minimize the impact of electron-donating atom doping on the non-bonding character of the HOMO would be inserting the heteroatoms on the atomic sites which do not contribute to the $a_2$-SALC, i.e. the ones sitting on symmetry elements. As it can be seen in Figure 6a, the introduction of the N atom on $\chi_1$ preserves, in fact, the non-bonding nature of the HOMO.

### 3.1.3 Point group: $C_{3h}$

As compared to $D_{3h}$, the $C_{3h}$ group does not include the $C_2$ axis and the $\sigma_v$ plane among its symmetry elements. The resulting $I_{\text{red}}^{C_{3h}}$ is reduced to give the direct sum of iRRs, $5a'' \oplus 4e''$. The symmetry analysis focused on the sole 1D iRR ($a''$), since it has been already confirmed that degenerate MOs are disadvantageous for the singlet-triplet inversion (see section 3.1.1). It can be firstly noted that there is only one 1D iRR, $a''$, i.e. moving from $D_{3h}$ to $C_{3h}$ the iRRs $a''_1$ and $a''_2$, associated with HOMO and LUMO, respectively, converge to the same iRR. The application of the projection operator of the $a''$ iRR ($P a''$) leads to five SAMOs and none of them renders the orbital localization of the HOMO and LUMO encountered with the $D_{3h}$ and $C_{2v}$ point groups. Interestingly, by forcing a $C_{3h}$ symmetry for the cyclazine, the HOMO and LUMO patterns (see Figure S9) are consistent with the orbital localization dictated by the SALCs $\psi_{3''}^a$ and $\psi_{4''}^a$, in which the atomic sites on the edge are two by two characterized by the same phase (Figure 9), i.e. both the MOs bear a bonding character, and thus expected to enhance the orbital overlap and increase the exchange interaction.
In light of this, it is not surprising that by forcing the C$_{3h}$ symmetry, e.g. by using substituents (2T-N-3NH2), this orbital localization is promoted, with consequently a large HOMO-LUMO overlap ($S_{HL} = 0.687$), exchange interaction energy and positive $\Delta E_{ST}$, as shown in Figure 10.

\[ K = 0.564 \text{ eV} \]
\[ \Delta E_{ST}^{SCS-CC2} = 0.475 \text{ eV} \quad f_{OSCC}^{SCS-CC2} = 0.000 \]
\[ \Delta E_{ST}^{NEVPT2} = 0.267 \text{ eV} \quad f_{OSCC}^{NEVPT2} = 0.000 \]

**Figure 10:** HOMO and LUMO computed at HF/def2-TZVP, exchange interaction and $\Delta E_{ST}$ computed at SCS-CC2/def2-TZVP and NEVPT2/def2-TZVP for the substituted cyclazine (C$_{3h}$ symmetry) (isocontour $\sigma=0.02 \text{ e·Bohr}^{-3}$).

It is worth mentioning the case of the triazacyclazine (Figure S10), in which the position of the nitrogen atoms in the core leads to a C$_{3h}$ symmetry. Despite the increase of the bonding character of the HOMO and LUMO, inducing a $S_{HL} = 0.552$, their patterns do not change drastically from their patterns within the D$_{3h}$ symmetry point group and do not appear to be pronounced as compared to the compound in Figure 10. The exchange interaction for triazacyclazine is larger than cyclazine (0.342 eV and
0.168 eV, respectively), inducing a less negative $\Delta E_{ST}$ at SCS-CC2 and NEVPT2 level (-0.084 eV and -0.082 eV, respectively).

It is clear that a $C_{3h}$ symmetry, due to the unfavorable orbital localization of both the HOMO and LUMO which increases the exchange interaction, can hardly promote the singlet-triplet inversion. In addition, the lower singlet excited state oscillator strength will be vanishing since the HOMO and the LUMO (the dominant expected one-electron transition involved in $S_1$) belongs to the same iRR while the transition dipole moments components are associated with the $a''$ and $e'$. Summarizing, compounds with a $C_{3h}$ symmetry are not expected to be good candidates as INVEST materials for OLED applications.

3.1.4 Point group: $C_{3v}$

Going to the $C_{3v}$ point group involves losing the $C_2$ axis and the $\sigma_h$ symmetry elements. The reduction of the $\Gamma_{red}^{C_{3v}}$ gives the direct sum of iRRs: $4a_1 \oplus a_2 \oplus 4e$. As in sections 3.1.1 and 3.1.4, we focused only on the 1D representations.

Among the resulting SAMOs, the sole $a_2$-SAMO ($\psi_3^{a_2}$, corresponding to the HOMO, and the third $a_1$-SAMO ($\psi_3^{a_1}$), corresponding to the LUMO, show the same pattern as $a_1''$-SAMO and $a_2''$-SAMO of $D_{3h}$, respectively. It follows that the two point groups dictate the same orbital localization and thus they are expected to provide similar order of magnitude for the exchange interaction. To corroborate this statement we computed the MOs, at the HF level, exchange interaction, at the CIS level, and $\Delta E_{ST}$ with SCS-CC2 and NEVPT2 methods for a triangulene having a phosphorus atom in the center (2T-P). The introduction of a phosphorus atom within the triangulene core induces a distortion of the molecular geometry leading to a $C_{3v}$ symmetry (Figure 11). As inferred, the HOMO and LUMO patterns provided a moderately small overlap ($S_{HL} = 0.461$), small exchange interaction (0.273 eV) and a negative $\Delta E_{ST}$ at both SCS-CC2 (-0.182 eV) and NEVPT2 (-0.095 eV). Unfortunately, as for the $D_{3h}$, the symmetry of the HOMO and LUMO leads to a symmetry forbidden $S_0 \rightarrow S_1$ transition.
3.1.5 Conclusion on orbital localization

In this section, we basically found that a non-bonding character and strong orbital localization can be induced to both the HOMO and the LUMO when a compound bears either a D$_{3h}$, a C$_{2v}$, or a C$_{3v}$ symmetry. Note that the HOMO (LUMO) in N (B)-centered is expected to belong to the $\alpha_1''$ iRR for the D$_{3h}$ symmetry point group and the $\alpha_2$ iRR for the C$_{2v}$ and C$_{3v}$ symmetry point groups. Focusing on N-centered compound, the HOMO pattern is generated through the application of the projection operator associated with the $\alpha_1''$ iRR for the D$_{3h}$ symmetry point group and the $\alpha_2$ iRR for the C$_{2v}$ and C$_{3v}$ symmetry point groups, and it is determined from a Hückel calculation as the highest occupied SAMO. The HOMO in these point groups displays nodes on some atomic sites. For these iRRs from the above-mentioned point groups, the number of characters associated with the different symmetry operators exhibiting a “-1” and “+1” values are identical. Summing over the product of these characters by the action of the projectors associated with each symmetry elements cancels out for the atomic sites laying on a symmetry element, resulting in the nodes in the HOMO (see equation S1.2 and sections 1.1, 1.2 and 1.3 in the supporting information). We observed that these nodes on the HOMO only appear when the HOMO belongs to a iRR where the rotation (C$_2$ in D$_{3h}$ and C$_{2v}$, or C$_3$ in C$_{3v}$) and the plane operator have opposite character sign. We evidenced here that symmetry is key in order to impose constraints on orbital localization in these triangular-shape molecules which results in a minimization of the HOMO-LUMO overlap and thus favors a small exchange interaction.
4 Design INVEST compounds with a non-zero oscillator strength

Working in the substitution pattern of the core, it turned out that the only way to conciliate a negative $\Delta E_{ST}$ and a non-zero oscillator strength requires a core with a $C_{2v}$ symmetry with substitution at atomic sites compatible with the frontier orbitals. However, even though ideal features for INVEST emitters are achieved for the sole core, from a practical point of view, polyaromatic hydrocarbons such as triangulene derivatives are prone to aggregation which causes emission quenching and likely affects $\Delta E_{ST}$. This requires a proper choice of bulky substituents to avoid these shortcomings.

4.1 Substituent effects

We decided to start the computationally guided molecular design by taking as reference the cyclazine core. The symmetry can be easily reduced to $C_{2v}$ by inserting the same number of substituents on the two sides of the molecule defined by one of the $\sigma_v$ planes. Figure 12 shows a possible scenario, in which the $-R_1$ and $-R_2$ substituents sit on the atomic sites with a large HOMO and LUMO weight (see Figures 2 and 3), respectively. For the sake of illustration, we selected amino and cyano groups as model electron donating (EDGs) and withdrawing groups (EWGs). We report in Table 1 the impact of either EDGs, EWGs or their combination on the optical features.

![Figure 12: substitution pattern.](image)

**Table 1**: Excitation energies, $\Delta E_{ST}$, oscillator strength and CT-distance computed at SCS-CC2/def2-TZVP for the substituted cyclazine.

<table>
<thead>
<tr>
<th></th>
<th>$S_1$ [eV]</th>
<th>$T_1$ [eV]</th>
<th>$\Delta E_{ST}$ [eV]</th>
<th>$f_{OSC}$</th>
<th>$D_{CT}$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclazine</td>
<td>R$_1$ = H, R$_2$ = H</td>
<td>1.109</td>
<td>1.334</td>
<td>-0.225</td>
<td>0.00</td>
</tr>
<tr>
<td>2T-a</td>
<td>R$_1$ = NH$_2$, R$_2$ = H</td>
<td>0.920</td>
<td>1.069</td>
<td>-0.213</td>
<td>8 $\cdot$ 10$^{-4}$</td>
</tr>
<tr>
<td>2T-b</td>
<td>R$_1$ = H, R$_2$ = NH$_2$</td>
<td>1.684</td>
<td>1.907</td>
<td>-0.223</td>
<td>3 $\cdot$ 10$^{-3}$</td>
</tr>
<tr>
<td>2T-c</td>
<td>R$_1$ = H, R$_2$ = CN</td>
<td>0.909</td>
<td>1.075</td>
<td>-0.166</td>
<td>4 $\cdot$ 10$^{-4}$</td>
</tr>
<tr>
<td>2T-d</td>
<td>R$_1$ = CN, R$_2$ = H</td>
<td>1.397</td>
<td>1.590</td>
<td>-0.193</td>
<td>8 $\cdot$ 10$^{-4}$</td>
</tr>
<tr>
<td>2T-e</td>
<td>R$_1$ = NH$_2$, R$_2$ = CN</td>
<td>0.681</td>
<td>0.796</td>
<td>-0.115</td>
<td>1 $\cdot$ 10$^{-4}$</td>
</tr>
<tr>
<td>2T-f</td>
<td>R$_1$ = CN, R$_2$ = NH$_2$</td>
<td>2.084</td>
<td>2.214</td>
<td>-0.130</td>
<td>9 $\cdot$ 10$^{-3}$</td>
</tr>
</tbody>
</table>
Interestingly, the vertical excited state energies can be easily tuned by introducing the EDGs and EWGs in the proper position. Moving the NH$_2$ group (EDG) from R$_1$ (high HOMO weight, compound 2T-a) to R$_2$ (high LUMO weight, compound 2T-b) results in an increase of both S$_1$ and T$_1$ energies while $\Delta E_{ST}$ remains constant. Analogously, the excited state energies can be increased by moving the CN group (EWGs) from R$_2$ (compound 2T-c) to R$_1$ (compound 2T-d). This behaviour is in line with the destabilizing (stabilizing) effect of the EDGs (EWGs) on the energy of the frontier MOs (Figure 13).

\[ \text{Figure 13: Effect of the EDGs and EWGs on the HOMO and LUMO energy computed at HF/def2-TZVP level.} \]

Moreover, the HOMO-LUMO gap can be further decreased or increased by combining EDGs and EWGs, allowing the shift of the excitation energy from the low to the high energy regions of the spectra. This is evident with 2T-f compound, in which the excitation energies of the lower-lying singlet and triplet excited states are dramatically blue-shifted with respect to cyclazine (from 1.109 eV to 2.084 eV and from 1.334 eV to 2.214 eV for S$_1$ and T$_1$, respectively).

Remarkably, it can be noticed that by moving the NH$_2$ group from a site with a high HOMO coefficient to a site with a high LUMO coefficient, the oscillator strength increases from $8 \cdot 10^{-4}$ (compound 2T-a) to $3 \cdot 10^{-3}$ (compound 2T-b). Analogously, by moving the CN group from a site with a high LUMO coefficient to a site with a high HOMO coefficient, the oscillator strength increases from $4 \cdot 10^{-4}$ (compound 2T-c) to $8 \cdot 10^{-4}$ (compound 2T-d). An even higher oscillator strength can be obtained by combining the EDGs and EWGs group, as shown with compound 2T-f in which the oscillator strength is almost two orders of magnitude increased ($f_{osc} = 9 \cdot 10^{-3}$). This behavior can be rationalized by inspecting the hole-electron distribution by means of two descriptors: the CT delocalization volume and the CT distance. The former is defined as the integral over the whole space of the difference between the (relaxed) real space electron density of the excited state (electron) and the ground state (hole) \( \int |\Delta \rho(r)| dr \), with \( \Delta \rho(r) = \rho_{ES}(r) - \rho_{GS}(r) \) and quantifies the spatial extension of the electron density reshuffling upon the excitation$^{[44]}$, whereas the latter represents the
distance between the barycenters of the ground and the excited state electron densities. As it can be seen, the increase of the oscillator strength is systematically accompanied by an increase of both the CT distance $D_{CT}$ and the CT delocalization volume (Table S14), which arises from a more spatially extended excitation due to the delocalization of the HOMO and the LUMO orbitals on the EWG and an EDG, respectively. This is coherent with the definition of the transition dipole moment, i.e. $M = \langle \Psi_{ES} | \hat{\mu} | \Psi_{GS} \rangle = -e\langle \Psi_{ES} | \hat{\rho} | \Psi_{GS} \rangle$: larger the spatial rearrangement of the electron density upon the excitation, larger is the hole-electron distance and, consequently, larger will be the transition dipole moment. Even though this statement might seem in contradiction with the necessity of ensuring a good overlap between the hole and the electron to maximize the magnitude of the transition dipole moment, it is important having in mind that in these systems the hole-electron overlap is ensured by short-range \textit{intra-}CT that guarantees the overlap between the tail of the hole and electron wavefunctions, similarly as observed in MR-TADF emitters\cite{49}. The effect of the substituents is just introducing an asymmetry in the hole and electron distribution, without breaking their alternating localization, as it can be clearly seen with the difference density plots in Figure S11. $D_{CT}$ appears as a measure of how much symmetry breaking from the $D_{3h}$ point group occurs.

Interestingly, this strategy turned out to be effective regardless of the substitution pattern employed, provided that the EDGs and the EWGs are placed on sites with a high LUMO and a high HOMO weight, respectively (Figure S12).

4.2 Extension of the triangulene core

An alternative way for decreasing the symmetry encompasses the extension of the triangulene core by merging two (or more) triangular units with the loss of the $C_3$ axis and thus reducing the point group from $D_{3h}$ to either $C_{2v}$, $C_{2h}$ or their subgroups. This strategy was used previously when extending DABNA-1 into v-DABNA\cite{50}, DiKTA to DDiKTA\cite{51}, and ICzMes$_3$ to DiICzMes$_4$\cite{52}. Depending on the relative orientation of the triangulene units, the emerging structures can be considered the hetero-doped derivatives of graphene nanoribbons such as zethrene and uthrene, the latter rising attention in the last years being the smallest non-planar polycyclic biradical obtained from graphene\cite{53}.

The boron and nitrogen-doped uthrene-like structures were obtained by merging two cyclazine units (2N-uthrene) and two boron-centered triangulene units (2B-uthrene), respectively. Their ground state geometries have been optimized at the PBE0/def2-SVP level to be consistent with the following simulation of emission spectra (\textit{vide infra}). The resulting structures belong to the $C_2$ point group due to the distortion caused by the steric hindrance of the hydrogen atoms, leading the $S_0 \rightarrow S_1$ transition to be symmetry allowed with an oscillator strength of $6 \cdot 10^{-3}$ and $4 \cdot 10^{-3}$ at the SCS-CC2
level for 2N-uthrene and 2B-uthrene, respectively. A more interesting aspect characterizing this compound is that both $S_1$ and $S_2$ lie below $T_1$, with a $\Delta E(S_1-T_1) = -0.089$ eV and a $\Delta E(S_2-T_1) = -0.063$ eV for 2N-uthrene and a $\Delta E(S_1-T_1) = -0.187$ eV and a $\Delta E(S_2-T_1) = -0.076$ eV at SCS-CC2 level. These values are confirmed by NEVPT2 calculations providing a $\Delta E(S_1-T_1) = -0.141$ eV and a $\Delta E(S_2-T_1) = -0.084$ eV for 2N-uthrene and a $\Delta E(S_1-T_1) = -0.192$ eV and a $\Delta E(S_2-T_1) = -0.025$ eV for 2B-uthrene. Indeed, this is the first case in which the singlet-triplet inversion involves two singlet excited states. From Figure 15, it can be seen that for both the compounds $S_2$ is also a short-range charge transfer excited state as $S_1$ and $T_1$, an aspect that can be easily rationalized by looking at the orbitals involved in the dominant transitions defining $S_2$, i.e. HOMO$\rightarrow$LUMO+1 and HOMO-1$\rightarrow$LUMO. It can be noted that these four dimeric MOs can be easily written as linear combinations of the HOMO and LUMO of the isolated cyclazine (Figure S13), and consequently preserve the orbital pattern which guarantees the alternating localization of the hole and electron. This is further confirmed by the one-electron difference density plot of $S_2$ (Figure S14), obtained as $(\sum c_i^2 \varphi_i^2) - (\sum c_i^2 \varphi_i^2)$ with $c_i$ the coefficients associated with a given one-electron transition describing a given excited state and $\varphi_i$ the MOs, providing the same pattern as the difference density plot obtained through the ground state and excited state relaxed electron density shown in Figure 14. However, because the $S_2$ arises from a different electronic configuration than $T_1$, the approximation $\Delta E_{ST}(\text{CIS}) \approx 2K$ is no longer valid and the inversion may be explained assuming strong correlation effects which stabilize $S_2$ bringing it below $T_1$.

Contrarily, the zethrene-like structures, belonging to the $C_{2h}$ point group, show positive energy gaps considering both $S_1$ and $S_2$: $\Delta E(S_1-T_1) = 0.128$ eV and $\Delta E(S_2-T_1) = 1.647$ eV for 2N-zethrene and $\Delta E(S_1-T_1) = 0.202$ eV and $\Delta E(S_2-T_1) = 0.848$ eV for 2B-zethrene at the SCS-CC2 level. CASSCF(8,8)/NEVPT2(8,8) brings the $\Delta E(S_1-T_1)$ to -0.032 eV and -0.049 and closes the $S_2$-$T_1$ gap to 0.634 eV and 0.505 eV for 2N-zethrene and 2B-zethrene, respectively. Increasing the CASSCF active space to (10,10) leads to a positive $\Delta E(S_1-T_1) = 0.018$ eV for 2N-zethrene and $\Delta E(S_1-T_1) = 0.004$ eV for 2B-zethrene, suggesting that these compounds might lay at the edge of the INVEST and TADF systems, similarly to 5AP (section 3.1.2). The discrepancy between SCS-CC2 and NEVPT2 may again originate from the treatment of the double excitations at the 0-th order by the former method. An analysis of the CASSCF(8,8) wavefunction shows that the percentage of double and higher order excitations in $S_1$ and $T_1$ wavefunction is $> 10\%$ for the uthrene-like structures, while it is $< 8\%$ for the zethrene-like structures (see Table S15).

Overall, the $S_0\rightarrow S_1$ transition bears a non-zero oscillator strength ($4\cdot10^{-3}$ and $1\cdot10^{-3}$ for 2N-zethrene and $3\cdot10^{-3}$ and $3\cdot10^{-4}$ for 2B-zethrene at SCS-CC2 and NEVPT2 level, respectively) again due to symmetry lowering.
As for the isolated triangulenes the application in OLED devices of the extended structures would require the introduction of bulky substituents, both to preclude the aggregation in the solid state and increase the magnitude of the oscillator strength. Nevertheless, there is no doubt that these doped nanographene-like compounds deserve further investigations as materials for OLEDs with a closed-shell ground state and an inverted singlet(s)-triplet energy gap.
5 Emission spectra simulation

INVEST compounds share a large number of common features with MR-TADF emitters such as a rigid structure and an alternating hole-electron localization which would suggest that the INVEST materials photophysical properties would also display a narrow emission spectra ensuring the color purity. In order to corroborate this hypothesis, we simulated the emission spectra of the mono- and di-substituted cyclazine defined in Table 1 with the highest oscillator strength, i.e. the compounds 2T-b, 2T-d and 2T-f.

The vibronic structure of the spectra has been simulated by using Q-Chem 5.4 package\cite{54} employing different levels of approximation: the undistorted Displaced Harmonic Oscillator (DHO), in which the frequencies and normal modes of the ground state and excited state are considered identical (Duschinsky rotation neglected), the Franck-Condon (FC) approximation including the normal modes mixing (Duschinsky rotation included) and the Herzberg-Teller (HT) approximation, i.e. accounting for the modulation of the transition dipole moment along each vibrational normal mode (see supporting information). All the spectra have been simulated at 300 K. The optimization of the S\(_0\) and S\(_1\), along with the respective frequencies calculation, have been carried out at TD-DFT (with PBE0) level. The resulting emission spectra has been then shifted so that the E\(_{00}\) vibronic transition (S\(_1\)(\(\nu=0\))→S\(_0\)(\(\nu=0\)), with \(\nu\) the vibrational quantum number), corresponds to the \(\Delta E_{S0-S1}\) adiabatic energy computed at SCS-CC2 level based on the TD-DFT S\(_1\) optimized geometry. All the calculations employed the def2-TZVP basis set.

\textbf{Figure 16}: Simulated emission spectra at 300K of the compounds 2T-b (a), 2T-d (b) and 2T-f (c). Stick spectra (straight lines), DHO spectra (dashed lines), FC spectra (solid pale coloured lines) and FC + HT spectra (solid coloured lines).

As it can be seen, both the DHO and FC spectra are characterized by the highest-intensity narrow band centered at the E\(_{00}\) transition, accompanied by a weaker band at lower energy arising from the vibronic progression. The inclusion of the Duschinsky rotation does not affect the shape of the spectra for 2T-d and 2T-f, while it leads to an increase of the intensity of the shoulder band of 2T-b, whose Duschinsky rotation matrix is not diagonal (Figure S15). Consequently, this translates into an increase of
the Full Width at Half Maximum (FWHM) moving from DHO to FC spectra for 2T-\(b\), while it remains constant for 2T-\(d\) and 2T-\(f\) (Table 2). The Huang-Rhys (HR) factor analysis allows identifying the normal modes at 459 cm\(^{-1}\), 1535 cm\(^{-1}\) and 279 cm\(^{-1}\) as the ones mainly involved in the vibronic coupling in 2T-\(b\), 2T-\(d\) and 2T-\(f\), respectively, and giving rise to the weaker vibronic band at lower energy. While for 2T-\(b\) and 2T-\(f\) these modes are torsional and bending modes mainly involving the substituents, thus retaining unmodified the triangulene core, the 2T-\(d\) one is associated with the stretching of the C-C bonds, as shown in Figure 17.

![Figure 17](image_url)

**Figure 17:** visualization of the normal modes at 459 cm\(^{-1}\) (HR=0.1927), 1535 cm\(^{-1}\) (HR=0.2067) and 279 cm\(^{-1}\) (HR=0.3615) for 2T-\(b\) (a), 2T-\(d\) (b) and 2T-\(f\) (c), respectively.

**Table 2:** FWHM of the DHO, FC and FC+HT simulated spectra and ratio in FWHM between FC+HT and FC approaches for 2T-\(b\), 2T-\(d\) and 2T-\(f\) compounds.

<table>
<thead>
<tr>
<th>FWHM</th>
<th>DHO [cm(^{-1})]</th>
<th>FC [cm(^{-1})]</th>
<th>FC+HT [cm(^{-1})]</th>
<th>(FC+HT)/FC</th>
</tr>
</thead>
<tbody>
<tr>
<td>2T-(b)</td>
<td>960</td>
<td>1120</td>
<td>2100</td>
<td>1.9</td>
</tr>
<tr>
<td>2T-(d)</td>
<td>640</td>
<td>640</td>
<td>2280</td>
<td>3.6</td>
</tr>
<tr>
<td>2T-(f)</td>
<td>1060</td>
<td>1060</td>
<td>1160</td>
<td>1.1</td>
</tr>
<tr>
<td>2N-Uthrene</td>
<td>800</td>
<td>800</td>
<td>880</td>
<td>1.1</td>
</tr>
<tr>
<td>2B-Uthrene</td>
<td>1840</td>
<td>1840</td>
<td>1840</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The introduction of the Herzberg-Teller effect leads to the systematic increase of the low-energy band intensity with respect to the main peak, inducing the consequent broadening of the FWHM for all the compounds, as shown in Table 2. In particular, for 2T-\(d\), the lower-energy band increases its intensity equaling the one of the \(E_{00}\) transition, leading to the largest increase of the FWHM moving from FC to FC+HT spectra for this compound. The normal modes with high contributions to the Herzberg-Teller effect are mainly located in the 1000-1700 cm\(^{-1}\) frequencies window, as shown in Figure 18 with the highest contributions for each molecule coming from two stretching modes leading to a distortion of the molecular core which break the C\(_{2v}\) symmetry (Figure S16).
It is worth comparing the FWHM values obtained from the simulated spectra with those of some MR molecules recently synthesized, namely Mes$_3$DiKTa [55] (FWHM=1306 cm$^{-1}$ in toluene), ν-DABNA [50] (FWHM=645 cm$^{-1}$ in toluene) and DABNA-1 [3] (FWHM=1048 cm$^{-1}$ in toluene). While the FWHM values obtained with the FC spectra are comparable to the ones of the MR-systems, with 2T-$d$ reaching a value smaller than ν-DABNA, the inclusion of the Herzberg-Teller effect inevitably increases the FWHM to values much larger than the reference compounds for 2T-$b$ and 2T-$d$, representing, in fact, a detrimental effect for the color purity. Interestingly, the 2T-$f$ compound presents a similar FWHM that is comparable to DABNA-1 and Mes$_3$DiKTa making it a suitable candidate for OLED applications.

For the 2N-Uthrene and 2B-Uthrene, the S$_0$ and S$_1$ geometries have been optimized at the PBE0/def2-SVP level, to keep the computational affordable, while the SCS-CC2 calculations have been carried out with a def2-TZVP basis set, for the sake of accuracy. The emission spectra for the 2N-Uthrene compound is shown in Figure 19. As for the substituted triangulenes, the spectra is characterized by a high peak centered at the E$_{00}$ transition (1.418 eV) along with a weak shoulder at lower energies. The normal modes with the highest Huang-Rhys factor are the ones at 55 cm$^{-1}$ and 247 cm$^{-1}$, both involving a torsional motion of the molecular core, while the mode giving rise to the weaker band is a stretching motion at 1581 cm$^{-1}$ (Figure 20). Because the Duschinsky matrix between S$_0$ and S$_1$ normal modes is diagonal (Figure S17), the DHO and FC spectra show the same shape and consequently the same FWHM of 800 cm$^{-1}$. Despite the introduction of the Herzberg-Teller effect leads to an increase of the intensity of the weaker shoulder, the FWHM remains as small as 880 cm$^{-1}$, below the values obtained experimentally for DABNA-1 and Mes$_3$DiKTa. The mode providing the highest contribution to the Herzberg-Teller mechanism is a stretching mode at 1638 cm$^{-1}$, shown in Figure 22b. For 2B-Uthrene, the DHO, FC and FC-HT spectra result in the same emission profile, with the main peak centered at the E$_{00}$ (1.041 eV). The resulting FWHM = 1840 cm$^{-1}$, larger than 2N-Uthrene but still comparable to the values of some
MR-systems. This is in line with the much larger $S_0$ relaxation energy of 2B-uthrene than 2N-uthrene (0.162 eV and 0.084 eV, respectively), along with the larger average $S_0$-$S_1$ bond-length variation (0.015 Å and 0.007 Å, respectively). The normal modes with the highest HR-factors are located in the low-frequency region, i.e. 59 cm$^{-1}$, 104 cm$^{-1}$ and 157 cm$^{-1}$ involving torsional motions of the core (Fig.21 a-c). The weaker shoulder arises from high frequency modes, in particular the ones at 782 cm$^{-1}$ and 1325 cm$^{-1}$ (Fig.21 d-e), the latter representing the mode with the highest contribution to the HT mechanism (Fig.22 c). Note that the narrowing of the emission by extending the size of the molecular core is an effect that has already been observed with increasing the molecular size from DABNA-1 to ν-DABNA (FWHM 1048 cm$^{-1}$ and 645 cm$^{-1}$) and recently with a new compound synthesized by Hatakeyama et al. called V-DABNA$^{[61]}$, obtained by merging three DABNA-1 core, and reaching a FWHM = 564 cm$^{-1}$ in toluene. It follows that the extension of the molecular core represents as well a promising strategy to enhance the color purity in INVEST compounds.

**Figure 19:** DHO (dashed line), FC (blue line) and FC-HT (red line) simulated spectra for 2N-Uthrene (left) and 2B-Uthrene (right).

(a)  
(b)  
(c)

**Figure 20:** visualization of the normal modes at 55 cm$^{-1}$ (HR = 0.590), 247 cm$^{-1}$ (HR = 0.261) and 1581 cm$^{-1}$ (HR = 0.152) for 2N-Uthrene.
Figure 21: visualization of the normal modes as 59 cm\(^{-1}\) (HR = 0.739), 104 cm\(^{-1}\) (HR = 1.044), 157 cm\(^{-1}\) (HR = 0.251), 782 cm\(^{-1}\) (HR = 0.230) and 1325 cm\(^{-1}\) (HR = 0.156) for 2B-Uthrene.

Figure 22: a) contributions of the Herzberg-Teller effect associate with each normal mode \(\frac{\partial \mu_f}{\partial Q_{fk}}v_i | Q_{fk} | v_f\); b) normal mode at 1638 cm\(^{-1}\) for 2N-Uthrene compound; c) contributions of the Herzberg-Teller effect associate with each normal mode for 2B-uthrene.

6. Rate constants calculation

In this section, we finally evaluated the potential of these materials in light-emitting devices by computing the magnitude of the radiative decay rate \(k_F\) and (R)ISC (\(k_{(R)ISC}\)) rate, for the compounds 2T-b, 2T-d and 2T-f.

From Table 3 it can be seen that the \(S_1-T_1\) inversion is retained considering the adiabatic energies. The SOC between \(S_1\) and \(T_1\), \(\langle \psi_{S_1} | H_{SOC} | \psi_{T_1} \rangle\) vanishes for 2T-b, 2T-d and 2T-f. This can be easily rationalized in terms of symmetry (see supporting information for further details) within the \(C_{2v}\) point group. The spatial part of the \(S_1\) and \(T_1\) excited states wavefunctions is both dominated by a HOMO (\(a_2\)) \(\rightarrow\) LUMO (\(b_2\)) transition, leading the two excited states belonging to a \(b_1\) iRR. Since the representations of the spin wavefunctions of the different triplet sublevels (\(T_1^x\), \(T_1^y\) and \(T_1^z\)) correspond to the
ones of the rotation \( R_{x,y,z} \) namely \( b_2, b_1 \) and \( a_2 \), respectively, the direct product of the iRRs, \( \Gamma(S_1) \otimes \Gamma(T_1) \otimes \Gamma(R_{x,y,z}) \) does not contain the totally symmetric iRR, leading to a vanishing SOC. On the contrary, \( T_2 \) is dominated by HOMO (\( a_2 \)) \( \rightarrow \) LUMO+1 (\( a_2 \)) transition, thus bearing a \( a_1 \) symmetry, leading the direct product \( \Gamma(S_1) \otimes \Gamma(T_1) = a_1 \), compatible with the iRR of \( R_y \). As a consequence, the integral \( \langle S_1|\hat{\Delta}S\rangle|T_2 \rangle \neq 0 \). It follows that the \( k_{\text{ISC}} \) and \( k_{\text{RISC}} \) between \( S_1 \) and \( T_1 \) for \( 2T-b \), \( 2T-d \) and \( 2T-f \) vanish while acquire a value different than zero for the \( S_1\rightarrow T_2 \) (R)ISC, suggesting that involving the higher lying \( T_2 \) states might be necessary for the harvesting of the triplet excitons. The RISC rate from \( T_2 \) to \( S_1 \) computed without accounting from spin-vibronic effect leads to a range of values compatible with MR-TADF emitters (see Table 3). However, recently, Marian et al.\textsuperscript{[62]} pointed out the critical role played by aHerzberg-Teller mechanism in promoting a non-vanishing SOC for mediating an efficient \( S_1-T_1 \) interconversion in heptazine and its derivative leading to an increase in RISC rate resulting from symmetry lowering. Furthermore, a similar mechanism likely also enhances \( S_1-T_n \) (R)ISC mechanism.

Table 3: \( S_1 \) vertical excitation energy and oscillator strength at \( S_1 \) geometry, \( S_1-S_0 \), \( S_1-T_1 \) and \( S_1-T_2 \) adiabatic energies, \( S_1-T_1 \) and \( S_1-T_2 \) SOC, fluorescence rate (without and with the Herzberg-Teller contribution), ISC and RISC for \( S_1-T_1 \) and \( S_1-T_2 \) transitions computed at 300 K, including Duschinsky rotation of the normal modes for \( 2T-b \), \( 2T-d \) and \( 2T-f \) compounds.

<table>
<thead>
<tr>
<th></th>
<th>( 2T-b )</th>
<th>( 2T-d )</th>
<th>( 2T-f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( aS_1^{eq} ) vert. exc. [eV]</td>
<td>1.506</td>
<td>1.250</td>
<td>1.750</td>
</tr>
<tr>
<td>( b_f^{\text{OSC}} )</td>
<td>3\cdot10^{-3}</td>
<td>9\cdot10^{-4}</td>
<td>9\cdot10^{-3}</td>
</tr>
<tr>
<td>( b_f^{\text{FC+HT}} )</td>
<td>5\cdot10^{-2}</td>
<td>5\cdot10^{-2}</td>
<td>0.1</td>
</tr>
<tr>
<td>( a\Delta E_{S_1-S_0} ) [eV]</td>
<td>1.533</td>
<td>1.287</td>
<td>1.808</td>
</tr>
<tr>
<td>( a\Delta E_{S_1-T_1} ) [eV]</td>
<td>-0.206</td>
<td>-0.202</td>
<td>-0.132</td>
</tr>
<tr>
<td>( a\Delta E_{S_1-T_2} ) [eV]</td>
<td>-0.874</td>
<td>-0.863</td>
<td>-0.721</td>
</tr>
<tr>
<td>SOC(_{S_1-T_1} ) [cm(^{-1})]</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>SOC(_{S_1-T_2} ) [cm(^{-1})]</td>
<td>0.010</td>
<td>0.020</td>
<td>0.032</td>
</tr>
<tr>
<td>( k_F ) [s(^{-1})]</td>
<td>2.7\cdot10^5</td>
<td>6.0\cdot10^4</td>
<td>1.2\cdot10^6</td>
</tr>
<tr>
<td>( k_F^{\text{FC+HT}} ) [s(^{-1})]</td>
<td>5.2\cdot10^6</td>
<td>3.2\cdot10^6</td>
<td>1.9\cdot10^7</td>
</tr>
<tr>
<td>( k_{\text{ISC}}^{S_1\rightarrow T_1} ) [s(^{-1})]</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>( k_{\text{RISC}}^{T_1\rightarrow S_1} ) [s(^{-1})]</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>( k_{\text{ISC}}^{S_1\rightarrow T_2} ) [s(^{-1})]</td>
<td>0.820</td>
<td>1.620</td>
<td>0.810</td>
</tr>
<tr>
<td>( k_{\text{RISC}}^{T_2\rightarrow S_1} ) [s(^{-1})]</td>
<td>5.3\cdot10^3</td>
<td>7.6\cdot10^3</td>
<td>3.6\cdot10^4</td>
</tr>
</tbody>
</table>

\( ^{a}\text{computed at SCS-CC2/def2-TZVP level}; ^{b}\text{computed at TDDFT-PBE0/def2-TZVP level.} \)

We next evaluate the \( S_1-S_0 \) fluorescence rate constants. The \( k_F \) has been calculated according to the following expression:

\[
k_F = \frac{f_{\text{OSC}}\Delta E^2}{1.499}
\]

(1)
with $\Delta E$ the vertical excitation energy at $S_1$ geometry in cm$^{-1}$. In order to account for the Herzberg-Teller effect contribution on the fluorescence rate, the value of the sum $\sum_k \langle \partial \mu_i / \partial Q_{fk} \rangle |v_i| Q_{fk} |v_f\rangle$ has been added to the unperturbed transition dipole moment ($\mu_{if}^0$) (equation S2.3) and the resulting oscillator strength ($f_{\text{OSC}}^{\text{FC+HT}}$) has been calculated according to the following expression (note that for the sake of consistency the $\mu_{if}^0$ obtained at TD-DFT level has been considered):

$$f_{\text{OSC}}^{\text{FC+HT}} = \frac{2}{3} \hbar \nu \mu_{if}^2$$

with $\hbar \nu$ the vertical excitation energy at $S_1$ geometry in hartree and $\mu_{if}$ the new transition dipole moment including the Herzberg-Teller term in e·bohr. The final fluorescence rate ($k_F^{\text{FC+HT}}$) has been calculated according to the following expression (note that for the sake of consistency the $\mu_{if}^0$ obtained at TD-DFT level has been considered):
**Table 4:** \(S_1\) vertical excitation energy and oscillator strength at \(S_1\) geometry, \(S_1-S_0\), \(S_1-T_1\), \(S_1-T_2\), \(S_2-T_1\) and \(S_2-T_2\) adiabatic energy difference, \(S_1-T_1\), \(S_1-T_2\), \(S_2-T_1\) and \(S_2-T_2\) SOC, fluorescence rate (without and with the Herzberg-Teller contribution), ISC and RISC for \(S_1-T_1\), \(S_1-T_2\), \(S_2-T_1\) and \(S_2-T_2\) and IC for the \(S_2-S_1\) transitions computed at 300 K, including Duschinsky rotation of the normal modes for \(2B\)-Uthrene.

<table>
<thead>
<tr>
<th></th>
<th>2B-Uthrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>(s^e_{S_1})</td>
<td>0.923</td>
</tr>
<tr>
<td>(\Delta E_{S_1-S_0}) [eV]</td>
<td>1.041</td>
</tr>
<tr>
<td>(\Delta E_{S_1-T_1}) [eV]</td>
<td>-0.202</td>
</tr>
<tr>
<td>(\Delta E_{S_1-T_2}) [eV]</td>
<td>-0.497</td>
</tr>
<tr>
<td>(\Delta E_{S_2-T_1}) [eV]</td>
<td>0.015</td>
</tr>
<tr>
<td>(\Delta E_{S_2-T_2}) [eV]</td>
<td>-0.279</td>
</tr>
<tr>
<td>(\Delta E_{S_2-S_1}) [eV]</td>
<td>0.218</td>
</tr>
<tr>
<td>(k_F) ([s^{-1}])</td>
<td>4.2 \cdot 10^4</td>
</tr>
<tr>
<td>(k_{FC+HT}) ([s^{-1}])</td>
<td>1.6 \cdot 10^6</td>
</tr>
<tr>
<td>(k_{ISC}^{S_1-T_1}) ([s^{-1}])</td>
<td>9.1 \cdot 10^2</td>
</tr>
<tr>
<td>(k_{ISC}^{S_1-T_2}) ([s^{-1}])</td>
<td>2.8 \cdot 10^4</td>
</tr>
<tr>
<td>(k_{ISC}^{S_2-T_1}) ([s^{-1}])</td>
<td>2.4 \cdot 10^1</td>
</tr>
<tr>
<td>(k_{ISC}^{S_2-T_2}) ([s^{-1}])</td>
<td>8.7 \cdot 10^6</td>
</tr>
<tr>
<td>(k_{RISC}^{S_1-T_1}) ([s^{-1}])</td>
<td>7.9 \cdot 10^5</td>
</tr>
<tr>
<td>(k_{RISC}^{S_1-T_2}) ([s^{-1}])</td>
<td>3.9 \cdot 10^7</td>
</tr>
<tr>
<td>(k_{RISC}^{S_2-T_1}) ([s^{-1}])</td>
<td>6.0</td>
</tr>
<tr>
<td>(k_{RISC}^{S_2-T_2}) ([s^{-1}])</td>
<td>4.2 \cdot 10^4</td>
</tr>
<tr>
<td>(k_{IC}^{S_2-S_1}) ([s^{-1}])</td>
<td>2.5 \cdot 10^13</td>
</tr>
</tbody>
</table>

\(^a\)computed at SCS-CC2/def2-TZVP level; \(^b\)computed at TDDFT-PBE0/def2-TZVP level.

Overall, the inclusion of the Herzberg-Teller effect induces a systematic increase of the fluorescence rate constant, promoting a higher fluorescence quantum yield which can potentially outcompete the non-radiative decay process, i.e. Internal Conversion (IC), the latter expected to be negligible thanks to the rigidity of the molecules.
7 Conclusion

The systematic and detailed symmetry analysis carried out in this work has proved to provide results in line with those obtained through *ab initio* methods, suggesting that they can be used to have a first and qualitatively hint on the magnitude of the orbital overlap and the exchange interaction term.

At this stage, it is useful to formulate and summarize the lessons learnt so far, to write down a series of rules to design an INVEST emitter:

1. The symmetry dictates the localization of the HOMO and LUMO, which in turn leads to the alternating hole-electron pattern of the INVEST compounds.
2. A non-bonding character on the HOMO and LUMO can be obtained by imposing either a $D_{3h}$, a $C_{2v}$ or a $C_{3v}$ symmetry point group to triangular-shape compounds. Moreover, it is possible to induce vanishing weights on the HOMO (LUMO) of nitrogen or phosphor (boron)-centered triangular-shape compounds. We observed that these nodes on the HOMO only appear when the HOMO belongs to a iRR where the rotation ($C_2$ in $D_{3h}$ and $C_{2v}$ or $C_3$ in $C_{3v}$) and the plane operator have opposite character sign. This is crucial in order to minimize the overlap with the LUMO and thus favors a small exchange interaction.
3. The orbital degeneracy, either involving the occupied or unoccupied MOs, increases the exchange interaction and thus it is detrimental for the $S_1$-$T_1$ inversion.
4. The doping pattern should be carefully chosen to avoid perturbing the non-bonding orbital localization. In light of this, a good choice might be introducing the heteroatoms on the atomic sites lying on the symmetry elements (e.g. Fig.6).
5. The negative $\Delta E_{ST}$ can be achieved even with a distorted molecular structure ($C_{3v}$), provided that the $\sigma_v$ plane is retained.
6. The $S_1$ and $T_1$ energy can be tuned through the proper choice of EDGs and EWGs, ensuring that the substitution pattern does not affect the orbital localization and a negative $\Delta E_{ST}$ is still retained (see ref 14 as well).
7. A $C_{2v}$ point group (and subgroups), obtained either by the doping pattern, substituents or extension of the triangulene core, can promote a negative $\Delta E_{ST}$ along with a non-zero oscillator strength, keeping in mind that this condition is however not sufficient to ensure the $S_1$-$T_1$ inversion.
8. The oscillator strength can be increased by inserting EWGs and EDGs on the positions bearing a high HOMO and LUMO density, respectively.
9. Narrow emission can be ensured for INVEST compounds with a proper choice of the EWGs and EDGs positions on triangular-shape compounds or with extended triangular-shape, uthrene-like compounds.
The peculiar features of the INVEST compounds can certainly open the way for fostering the performances of light-emitting devices. The growing *in silico* studies, from electronic structure investigations to high-throughput screenings, demonstrate how the theoretical prediction is essential to achieve a detailed understanding of this new family of molecules. We are confident that this work can represent a further guideline useful to create the joining link between theory and experiment to make a step forward towards the applications of these systems in the next generation of Organic Light Emitting Diodes.

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**Supporting Information**

Detailed symmetry analysis (generation of SALCs and SAMOs) of the four point-groups (D$_{3h}$, C$_{2v}$, C$_{3h}$ and C$_{3v}$), excited state (S$_1$ and T$_1$) energies, $\Delta E_{ST}$ at SCS-CC2/def2-TZVP and NEVPT2(8,8)/def2-TZVP and molecular orbitals computed at Hartree-Fock/def2-TZVP level for the compounds mentioned in the main text, hole-electron difference density plots of the cyclazine derivatives (section 4.1), charge transfer delocalization volume, percentage of double- and higher-order excitations in S$_1$ and T$_1$ computed at CASSCF(8,8)/def2-TZVP for 2N-Uthrene and 2N-Zethrene, Duschinsky rotation matrices and vibrational normal modes contributing to the Herzberg-Teller mechanism for the cyclazine derivatives (section 5), derivation of the Thermal Vibration Correlation Functions (TVCF) for the radiative and non-radiative decay processes.
References


