Symmetry based molecular design for triplet excitation and optical spin injection

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Abstract

Spintronics, as a relatively new scientific field, is developing rapidly together with our understanding of spin related phenomena and spin manipulation. One of the challenges in the field is spin injection, which has been achieved optically in inorganic crystalline semiconductors, but not yet in organic semiconductors. Here, we introduce an approach whereby we apply group theory and computational methods to design molecular materials in which spin can be injected optically via circularly polarized light (CPL). Our approach is based on the use of group theory and double group theory to identify families of molecules whose symmetry satisfies design rules for optical excitation of triplets of particular properties. Employing such screening prior to detailed calculation can accelerate design by first identifying any structures that fail some criterion on grounds of symmetry. Here, we show using group theory and computational methods that particular families of molecules possess a low lying triplet state that can be excited with circularly polarized light causing spin polarization of an excited electron. Such structures are of potential interest for organic or molecular spintronics. We present an efficient procedure to identify candidate point groups

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and determine the excited state symmetry using group theory, before full calculation of excited states using relativistic quantum chemistry.
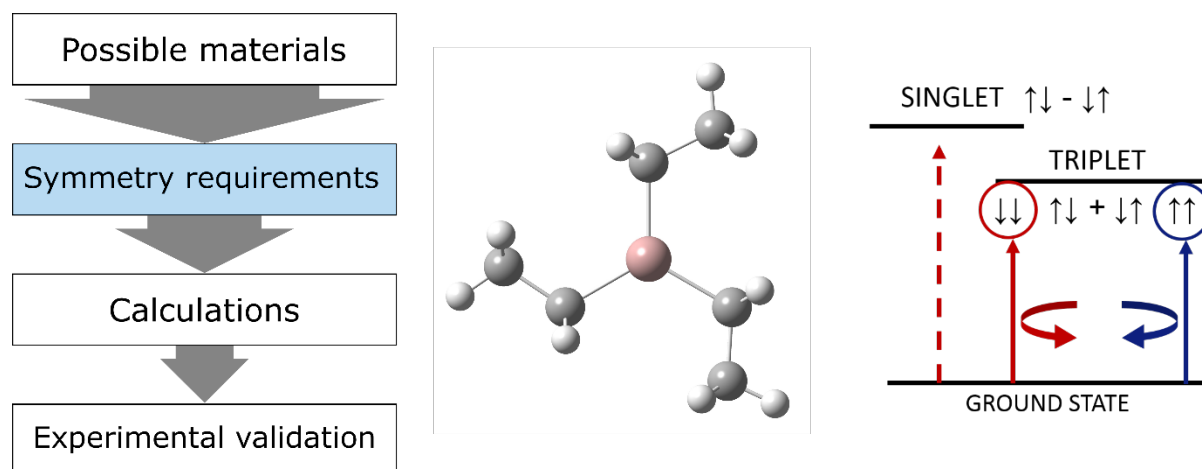
TOC FIGURE: Group theory and computational methods were applied to prepare a list of requirements for molecular materials in which spin can be injected optically via circularly polarized light.

KEYWORDS: organic spintronics, molecular design, symmetry, triplet, spin-orbit coupling, calculations

I. <u>INTRODUCTION</u>

In the last few years, we observed a significant development of material science powered by new possibilities in synthesis and manufacturing. Having more and more potential materials, selection of the best one for a specific application becomes challenging. To save time, money and effort, potential materials can be first designed theoretically using available, validated computational models. [1–5]

Computational methods are commonly used to explain experimental results in specified materials and there are plenty of publications showing this approach[6,7]. If this chronological order is reversed, that is modelling conducted first to predict the experimental results, we obtain research led by computational design of materials with desirable properties.[8] Automated molecular design can save a lot of effort and can improve the searching process. However, one should not forget about the computational cost of calculations and the enormous amount of possible materials. Especially calculating optical excited states of systems, like large organic molecules, using TDDFT or higher levels of theory is particularly expensive. For this example, it is still common, instead of calculating excited state energies, to calculate energies of HOMO and LUMO using DFT and based on those estimate the energy and the strength of the excitation of the first excited state. Moreover, quantum chemical calculations can be strongly functional dependent and do not always provide accurate quantities. For this reasons, molecular design based purely on TD-DFT calculation results might not be adequate.

The cost of calculations can be reduced by limiting the amount of materials that need to be modelled by using symmetry requirements. In one prior study taking this approach, point group theory was successfully applied to materials for thermally activated delayed fluorescent (TADF) OLEDs.[9] The authors identified the best symmetry point group for a

molecule in which high rate of reverse intersystem crossing (RISC) is expected. Having chosen the D_{4h} point group based on the character table, the authors could focus only on molecules possessing that symmetry. To the best of our knowledge, this is the only reported research that exploits molecular symmetry using group theory for more efficient molecular discovery. Here, we study a symmetry-based approach to design a material for organic spintronics.

Since the discovery of giant magnetoresistance in 1988[10], the field of spintronics has developed rapidly, underpinning applications for memory storage and spin based quantum computing. The most commonly studied mode of spin injection into a non-magnetic material is via electrical spin injection from a ferromagnetic electrode. However, this is not the only way of injecting spin. For example spin polarized electron populations can be achieved in inorganic crystals, such as GaAs, also by optical excitation using circularly polarized light.[11] So far, optical spin injection in organic molecular compound has not been reported.

The symmetry of the crystal structure is the foundation and the essential criterion of the optical spin injection in GaAs and other III-V crystals.[12] The origin of this phenomenon lies in the basic band structure of GaAs, the lack of an inversion point between Gallium and Arsenic atoms in the primitive unit cell of the zincblende crystal structure and high spin-orbit coupling (SOC), causing mixing and splitting of heavy and light holes' bands.

Symmetry properties can also be fundamental for spin injection into organic compounds. However, inorganic crystals and organic molecular materials need to be considered differently. In the first case electronic states are delocalized and close in terms of their energy, due to the crystal periodicity and the high electron density, so they form bands, valence (VB) and conduction (CB) bands. An electron excited from VB to CB can be treated as an independent particle with spin of ½. In the case of a closed shell molecular material, an

excited electron is coupled to the hole and forms a singlet or triplet excited state. Even though open-shell molecules are widely investigated for spintronics application, we choose to focus on closed-shell molecules, as their optical properties are better understood.

Here we report symmetry-based molecular design rules for molecules for optical spin injection via excitation of spin polarized triplets with m_S equal +1 or -1 selectively with left and right circularly polarized light. We also prepare a list of requirements for the geometry and the electronic structure of the molecule that would enable spin injection.

II. THEORY

First we use point group theory to identify allowed dipole transitions induced by circularly polarized light to the triplet. Subsequently we apply double group theory to check if the triplet excitation corresponds to two separate transitions: left and right circularly polarized. Finally, we apply double group theory to molecular orbitals in order to assign circularly polarized transitions to spin-polarized final excited states. Additionally, we include simple calculations of the energy splitting of doubly degenerate triplet state due to SOC.

We first review the basic requirements for optical excitation of triplets. In a molecular material, an optically excited electron is coupled to a hole and forms singlet or triplet exciton. Due to a requirement for the excited state wavefunction to be antisymmetric, the singlet and the triplet with $m_S = 0$ are not spin polarized. Only triplets with m_S equal -1 or 1 possess a non-zero spin. [13] Because of the antisymmetric spatial part of the wavefunction, excitation of a triplet directly from a singlet ground state is not allowed unless SOC mixes singlet and triplet states. It has been shown that in molecules containing heavy elements, which will provide SOC, the triplet becomes optically accessible.[14] Exciting states with m_S equal -1 or 1 requires increase or decrease in spin angular momentum, which can only be achieved with circularly polarized light (CPL). [15] In our analysis we focus on spin and do not explicitly

consider selection rules based on parity, because these should already be accounted for in the analysis based on symmetry considerations.

Based on the properties of excited states of molecular materials, we propose that to obtain spin polarized population of excited electrons we have to directly excite a triplet excited state, which: (a) corresponds to quantum number m_S equal +1 or -1, (b) has a circularly polarized symmetry. We discuss the conditions for these two requirements.

Obtaining direct triplet state excitation requires significant SOC in the molecule (internal effect). SOC mixes singlets and triplets having the same total symmetry. When SOC is included in a model, states no longer have pure character, as singlets or triplets. The amount of singlet character states mixed into a state determines the oscillator strength of the optical excitation. Triplet excitation can also be enhanced via the external heavy-atom effect, which has been reported to be even stronger than the internal effect. [16]

The second proposed requirement for optical spin injection is to excite the triplet with circularly polarized light. There are several point groups that can support circularly polarized transitions: C_n, C_{nh}, S_m (n = 3,4,5,6; m = 4,6,8,10). Each of these groups has a doubly degenerate irreducible representation (irrep) that transforms as (x + iy, x - iy). Circularly polarized transitions can be identified using group theory, however, information on the left or right polarization is obtained only from double group theory.

II.1. SYMMETRY OF AN EXCITED STATE

The excited state consists of an occupied orbital above Fermi level and an unoccupied orbital below Fermi level. Assuming that both orbitals are on the same molecule, according to group theory, the symmetry of an excited state ($\Gamma_{excited\ state}$) can be predicted based on the symmetries of the hole and the electron. The orbital symmetry of an unoccupied orbital is given by the conjugate of the symmetry of the same orbital occupied. The excited state

symmetry is a cross product of symmetries of initial ($\Gamma_{\text{initial orbital}}$ conjugated), final orbitals ($\Gamma_{\text{final orbital}}$) and the symmetry of the spin part ($\Gamma_{\text{spin part}}$):

$$\Gamma_{excited\ state} = \Gamma_{initial\ orbital}{}^* \otimes \Gamma_{final\ orbital} \otimes \Gamma_{spin\ part} = \Gamma_{orbital\ part} \otimes \Gamma_{spin\ part} \quad (1)$$

The symmetry of the spin part of the wavefunction depends on the excited state spin quantum number. A singlet transforms as an irreducible representation (irrep) corresponding to the function: $x^2 + y^2 + z^2$, a triplet with $m_S = 0$ transforms as an irrep corresponding to orbital angular momentum operator l_Z (R_Z) and finally triplets with $m_S = \pm 1$ transform as an irrep corresponding to l_X, l_Y (R_X, R_Y). [17] The same holds true for double group theory. The ground state in most cases has a symmetry of the fully symmetric irrep (ie. A', A_1, A_g, A_{1g} or Γ_1 in double group notation).

We note that SOC is required in order for triplet excitations to be allowed. In what follows, we assume that SOC is present and is sufficiently strong to allow triplet excitations, and hereafter focus on the question of which singlet or triplet state excitations are optically allowed based on the symmetry. For a transition to be symmetry allowed the transition dipole moment ($d_{i\to f}$) between the initial ($\Psi_{initial\ state}$) and the final initial ($\Psi_{final\ state}$) state must transform as a fully symmetric irrep (ie. A', A_1, A_g, A_{1g} or Γ_1 in double group notation).[18]

$$d_{i\to f(\sigma\pm)} = \langle \Psi_{final\ state} | (x \pm iy) | \Psi_{initial\ state} \rangle \neq 0 \text{ only if}$$

$$\Gamma_{final\ state}{}^* \otimes \Gamma_{x\pm iy} \otimes \Gamma_{initial\ state} \in \Gamma_1 \quad (2)$$

Introducing double group theory is necessary when SOC is considered.

DOUBLE GROUP THEORY

In group theory the spin of an electron does not have its own representation, thus to represent spin in double groups new symmetry elements must be introduced. The standard symmetry elements are redefined. Therefore, the identity element E is redefined as a rotation over 4π which conserves the spin and the new element $\overline{E}$ is a rotation over 2π, which can flip the spin. Similarly, the C_3 rotation is defined as a spatial rotation over $\pi/3$ without spin flip, while $\overline{C_3}$ is a spatial rotation over $\pi/3$ with spin flip. In the same way other symmetry elements are treated, increasing the number of symmetry elements and at the same time the number and character of irreps. For example, in C_{3h} point group there are four irreps, out of which two are doubly degenerate. These become the first six irreps in the C_{3h} double group (Γ_1 to Γ_6). Additionally, in the C_{3h} double group there are six irreps corresponding to half-integer spin, allowing for the possibility of changing the spin (Γ_7 to Γ_{12}). Character and cross product tables for C_{3h} double group are presented in the Supporting Information.

II.2. C_{3h} POINT GROUP – CIRCULARLY POLARIZED TRIPLET

From now on we focus on one, relatively simple, point group, C_{3h}. Table 1 shows all symmetries of possible singlet states and corresponding triplets in point group and double group notations for a system having C_{3h} symmetry. In C_{3h}, there are four irreps, among them E' that transforms as (x - iy, x + iy). From Table 1 we see that a spin-polarized triplet with E' symmetry can be obtained only from A'' or E'' orbital part symmetry. Unfortunately, A'' transforms as z, that means that neighbouring triplet with $m_S = 0$ is allowed as are singlet transitions. As we expect triplet excitation to be very weak, having strong excitations at

similar energy won't allow us to resolve spin-polarized triplet excitations. Thus we will narrow our study to triplets that originate from states with E'' symmetry for the orbital part, which make singlet and $m_S = 0$ triplet transitions forbidden.

Symmetry of the orbital part $\Gamma_{orbital\ part}$	$\Gamma_{orbital\ part} \otimes \Gamma_{spin\ part}$			
	SINGLET	TRIPLET $m_S = 0$	TRIPLET $m_S = \pm 1$	TRIPLET $m_S = \pm 1$ in double group notation
A'	A'	A'	E''	$\Gamma_5 + \Gamma_6$
E'	E'	E'	E'' + 2A''	$\Gamma_5 + \Gamma_6 + 2\Gamma_4$
A''	A''	A''	**E'**	$\mathbf{\Gamma_2 + \Gamma_3}$
E''	E''	E''	**E'** + 2A'	$\mathbf{\Gamma_2 + \Gamma_3} + 2\Gamma_1$

Table 1 Possible symmetries of excited states in a system having C$_{3h}$ symmetry.

E'' orbital symmetry combined with spin symmetry for triplets with $m_S = \pm 1$ gives E'+2A' symmetric states. In C$_{3h}$ point group, the E' representation splits into two representations, Γ_2 and Γ_3, in double group notation. Γ_2 and Γ_3 are conjugations of each other. The former one transforms like (x - iy) and latter one as (x + iy).

In a molecule having C$_{3h}$ symmetry it is possible to selectively excite states of symmetry Γ_2 or Γ_3 with right or left circularly polarized light, respectively, as shown below in eq. 3. Transitions between Γ_1 ground state ($\Psi_{\Gamma 1}$) and Γ_2 excited state ($\Psi_{\Gamma 2}$) are only allowed with σ- CPL and transitions between Γ_1 ground state ($\Psi_{\Gamma 1}$) and Γ_3 excited state ($\Psi_{\Gamma 3}$) are only allowed with σ+ CPL. Accordingly, transitions between Γ_1 ground state ($\Psi_{\Gamma 1}$) and Γ_2 excited state ($\Psi_{\Gamma 2}$) are forbidden with σ+ CPL and transitions between Γ_1 ground state ($\Psi_{\Gamma 1}$) and Γ_3 excited state ($\Psi_{\Gamma 3}$) are forbidden with σ- CPL.

$$d_{1\to2(\sigma-)} = \langle\Psi_{\Gamma_2}|(x-iy)|\Psi_{\Gamma_1}\rangle \neq 0 \text{ because } \Gamma_2^*\otimes(\Gamma_2\otimes\Gamma_1) = \Gamma_3\otimes\Gamma_2 = \mathbf{\Gamma_1}$$

$$d_{1\to2(\sigma+)} = \langle\Psi_{\Gamma_2}|(x+iy)|\Psi_{\Gamma_1}\rangle = 0 \text{ because } \Gamma_2^*\otimes(\Gamma_3\otimes\Gamma_1) = \Gamma_3\otimes\Gamma_3 = \Gamma_2$$

$$d_{1\to3(\sigma-)} = \langle\Psi_{\Gamma_3}|(x-iy)|\Psi_{\Gamma_1}\rangle = 0 \text{ because } \Gamma_3^*\otimes(\Gamma_2\otimes\Gamma_1) = \Gamma_2\otimes\Gamma_2 = \Gamma_3$$

$$d_{1\to3(\sigma+)} = \langle\Psi_{\Gamma_3}|(x+iy)|\Psi_{\Gamma_1}\rangle \neq 0 \text{ because } \Gamma_3^*\otimes(\Gamma_3\otimes\Gamma_1) = \Gamma_2\otimes\Gamma_3 = \mathbf{\Gamma_1}$$

(3)

Figure 1 depicts the same transitions in a C_{3h} symmetric systems, when considered using point group or double group notation.
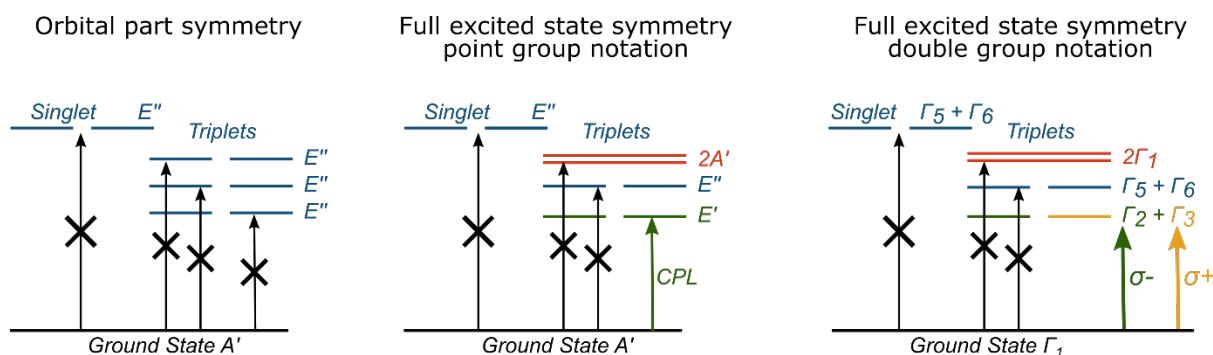

Figure 1 Schematic of singlet and triplet excited states with E'' orbital part symmetry showing how the total symmetry and excited states' polarization changes with including the spin part and double group theory. We assume that SOC is strong enough for excitations of triplet excited states.

II.3. C_{3h} POINT GROUP – DOUBLE GROUP THEORY APPLIED TO ORBITALS

Given that Γ_2 and Γ_3 triplet states correspond to m_S equal +1 or -1, information regarding which state has $m_S = 1$ and which one $m_S = -1$ can be obtained from the symmetries of participating orbitals.

An E' triplet with $m_S = \pm1$ is a result of an electron transition between orbitals of symmetry a' and e'', a'' and e' or e' and e'' (According to standard notation, symmetries of orbitals are denoted with small letters).

The double group theory allows us to include the electron and the hole spins at the orbital level instead of in the spin part of the state wavefunction. 'Spin up' transforms as Γ_7, 'spin down' transforms as Γ_8 (Supplementary Information Table S2). The cross product of the

spatial orbital symmetries with spin symmetries defines the symmetries of electrons occupying those orbitals. The symmetry of a hole is the conjugate of the symmetry of an electron if the orbital is occupied. Also the spin of the hole is opposite to the electron's spin.

Figure 2 presents an example of electronic structure with e' ($\Gamma_2+\Gamma_3$) as HOMO and a'' (Γ_4) as LUMO. By taking the cross product of these irreps with the Γ_7 and Γ_8 double group irreps for spins we obtain a full orbital picture. From this picture we can determine possible transition symmetries by taking the cross product of the symmetry of that of the potential hole and the potential excited electron. Out of eight possible transitions only two are symmetry allowed.

The excitation of an electron from $\Gamma_{11}\uparrow$ orbital to $\Gamma_{10}\downarrow$ results in Γ_2 excited state ($\Gamma_{11}{}^*\otimes\Gamma_{10} = \mathbf{\Gamma_2}$) and the excitation of an electron from $\Gamma_{12}\downarrow$ orbital to $\Gamma_9\uparrow$ results in Γ_3 excited state ($\Gamma_{12}{}^*\otimes\Gamma_9 = \mathbf{\Gamma_3}$). These states are also shown in Figure 2 and Table 2.

Symmetry and spin of the hole	Symmetry and spin of the excited electron	Symmetry of the excited state	Polarization of the excited state
$\Gamma_{11}{}^*\downarrow$	$\Gamma_{10}\downarrow$	Γ_2	(x-iy)
$\Gamma_{12}{}^*\uparrow$	$\Gamma_9\uparrow$	Γ_3	(x+iy)

Table 2 Symmetry and spin of holes and excited electrons for two optically accessible triplets Γ_2 and Γ_3.

The excitation of the triplet Γ_2 with left circularly polarized light (x - iy, σ-) leads to a spin flip from 'up' to 'down' and a state with m_S = -1. Exciting the triplet Γ_3 with right circularly polarized light (x + iy, σ+) leads to spin flip from 'down' to 'up' and an excited state with m_S = +1.

In C_{3h} point group molecule the same result (that some orbital transitions become allowed in CPL when double group symmetry is considered) holds true for transitions between a' and e'' orbitals. The transition between e'' and e' orbitals is more complicated, due to 12 possible triplet states, but the spin flip via CPL excitation still can be obtained. However, for the

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efficient spin injection, a triplet with $m_S = \pm 1$ should not have other optically active states that lead to different outcome. The summary for other circularly polarized point groups is presented in the Supplementary Information.
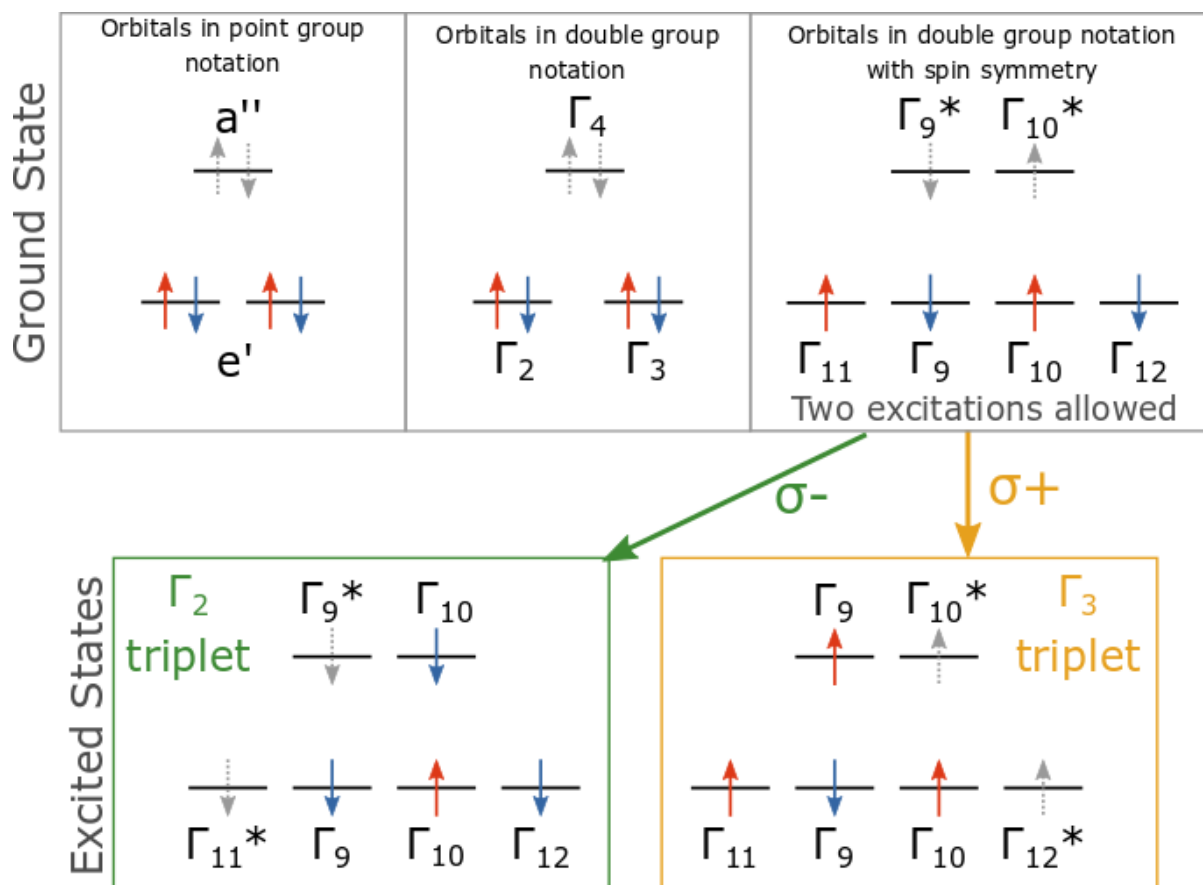

Figure 2 Spin symmetry applied to molecular orbitals. Comparison between different notations of orbitals: point group, double point group and double group with spin included. When spin is included at the orbital level it can be shown that triplet Γ_2 with $m_S = -1$ is allowed with σ- CPL and triplet Γ_3 with $m_S = +1$ is allowed with σ+ CPL. The irrep of a hole is a conjugation of irrep of the electron and spin of a hole is opposite to the one of the electron.

II.4. SPIN-ORBIT COUPLING ENERGY SPLITTING

Here, we want to calculate how doubly-degenerate triplets split in energy due to spin-orbit coupling and resulting coupling with corresponding singlet. In order to do this, we express the orbital part of the triplet and singlet states using spherical harmonics. The E'' orbital part of the triplet or singlet transforms as spherical harmonics: Y_2^{-1} and Y_2^{+1}. Together with the spin (s,m_s) parts, $(1,1)$, $(1,0)$, $(1,-1)$ for the triplet and $(0,0)$ for the singlet, we express our

basis set as eight states: [2,1](1,1), [2,1](1,0), [2,1](1,-1), [2,-1](1,1), [2,-1](1,0), [2,-1](1,-1), [2,1](0,0) and [2,-1](0,0). For conciseness in writing the Hamiltonian, we denote each state using only the m_l and m_s quantum numbers, indicating triplets and singlets by 'T' and 'S' subscripts, e.g. $[2,1](1,0) \equiv (1,0)_T$, $[2,1](0,0) \equiv (0,0)_S$.

The SOC Hamiltonian is given by the products of angular and spin momentum (Eq. 4).[19]

$$H_{SO} = \lambda(r)\boldsymbol{l} \cdot \boldsymbol{s}. \tag{4}$$

In the basis set as defined above, spin-orbit coupling gives rise to diagonal elements for triplets with $m_S = \pm 1$ and terms related to the interaction between triplet and singlet states.[20,21] Eq. 5 presents the full Hamiltonian, where E_T and E_S represent the energies of triplet and singlet, respectively, without SOC induced splitting.

$$
H_0 + H_{SO} =
\begin{matrix}
 & (-1,1)_T & (-1,-1)_T & (1,1)_T & (1,-1)_T & (-1,0)_T & (1,0)_T & (1,0)_S & (-1,0)_S \\
\end{matrix}
$$

$$
H_0 + H_{SO} =
\begin{pmatrix}
E_T - \frac{Z}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & E_T + \frac{Z}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & E_T + \frac{Z}{2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & E_T - \frac{Z}{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & E_T & 0 & \frac{Z}{2} & 0 \\
0 & 0 & 0 & 0 & 0 & E_T & 0 & -\frac{Z}{2} \\
0 & 0 & 0 & 0 & -\frac{Z}{2} & 0 & E_S & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{Z}{2} & 0 & E_S \\
\end{pmatrix}
\tag{5}
$$

Z is defined as a H_{SO} matrix element:

$$Z = 2\langle(-1,-1)_T|H_{SO}|(-1,-1)_T\rangle = 2\langle(-1,0)_T|H_{SO}|(1,0)_S\rangle$$

and can be interpreted as the strength of the SOC. Diagonalization of (H_0+H_{SO}) yields triplet and singlet excited states energies with SOC included. The energy of $(-1,1)_T$ and $(1,-1)_T$ triplets decreases by $\frac{Z}{2}$ to $E_T - \frac{Z}{2}$, while the energy of $(-1,-1)_T$ and $(1,1)_T$ triplets increases by

$\frac{Z}{2}$ to $E_T + \frac{Z}{2}$. The two triplets with $m_S = 0$, $(-1,0)_T$ and $(1,0)_T$, mix with corresponding singlets and thus are stabilized by an energy equal to $Z^2/4\Delta E_{ST}$ (to second order in Z). The energy splitting between triplet excited state components is shown in Figure 4(b). It is important to note that triplets with opposite spin are degenerate, as predicted from double group theory in the previous section.

III. RESULTS OF CALCULATIONS ON TEST STRUCTURES

In order to support the presented theory, we performed calculations of a set of simple example molecules that possess the required symmetry and contain heavy atoms. Calculations of molecular orbitals, excited states energies, symmetries and oscillator strengths were performed using density functional theory (DFT) implemented in Gaussian and time-dependent density functional theory (TDDFT) implemented in two pieces of software: Gaussian[22] and Dirac[23]. Dirac was used due to its function to include spin interactions: spin-other spin, spin-same orbit, spin-other orbit. Unfortunately, the spin polarization of excited states is not computationally implemented, thus we can only verify our symmetry-based theoretical predictions by comparing symmetries and transition dipole moments for triplet states. The presented calculations were performed with the B3LYP functional and aug-cc-pvdz basis set (except InEt3, more in Supporting Information).

III.1 MOLECULAR ORBITALS

We selected simple examples of molecules having C_{3h} symmetry, namely the triethyl family with different central atoms (B, Al, Ga, In) to study the effect of SOC strength. Although the molecules are too small to be relevant to applications in organic spintronics, they serve as useful model systems to demonstrate our approach. The molecular structure of $GaEt_3$ is presented in Figure 3(a).

First, every molecule was optimized using Gaussian. Subsequently, symmetries of molecular orbitals were considered to check whether the spin-polarized transition lies close to the first optical transition. Luckily, in most triethyls the HOMO has e' symmetry and the LUMO has a'' symmetry (Figure 3(b)). In the previous section, it was shown that a transition between e' and a'' orbitals leads to spin polarized triplets allowed with circularly polarized light, which is the condition for an optically induced spin-flip (Figure 1).
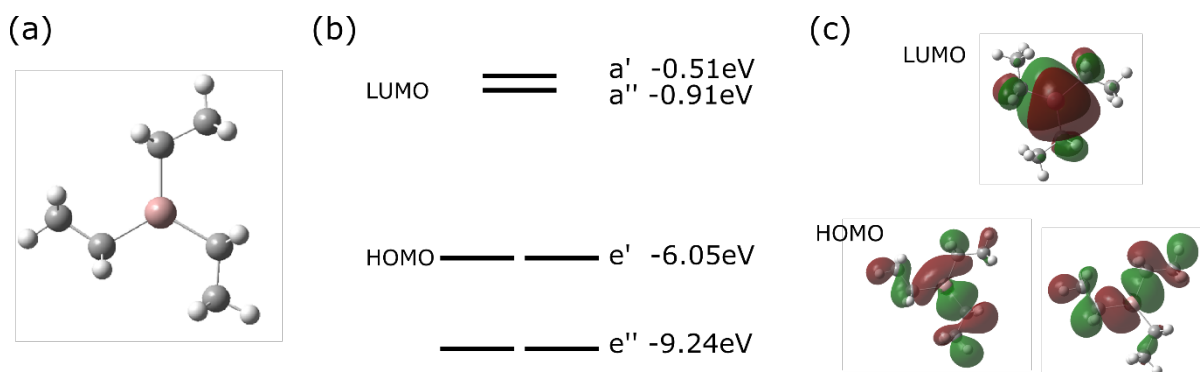

Figure 3 (a) Molecular structure of triethylgallium (GaEt3) in particular C_{3h} conformation. The exact coordinates are included in Supplementary Information. (b) Molecular orbitals of $GaEt_3$ with energies and symmetries. (c) Visualisations of the doubly degenerat e' HOMO and a'' LUMO.

At this level of theory, that is knowing the orbitals' symmetry, we can say whether a molecule is a good candidate for optical spin injection. This saves us time and computational power, because excited state symmetries do not have to be calculated in order to eliminate poor candidates. Since in triethyls we expect the CPL-excited spin polarized triplet to occur as the lowest excited state, we proceed to perform TDDFT calculations on the set of triethyl molecules.

III.2 EXCITED STATES CALCULATIONS

For each molecule we calculated excited states using Gaussian and Dirac without and with spin interactions included. Calculations of molecular excited states that include spin interactions are seldom reported. However, comparison between excited states calculated with and without spin interactions included gives us additional information on the origin of

the calculated properties. The list of the lowest excited states for them is presented in the Supporting Information. Here, we only present details of triethylgallium (GaEt$_3$). Both in Gaussian and in Dirac without spin interaction the lowest lying triplet and singlet are doubly degenerate and have E'' symmetry, which is the orbital part of the transition associated with HOMO(e') to LUMO(a'') transition. In the case of calculations with spin interactions, doubly degenerate triplet is split into six states. The symmetries of those states are given in C$_{3h}$ subgroup - C$_s$ point group, because the C$_{3h}$ point group is not implemented in Dirac. Details of how to interpret those symmetries are shown in SI. From E'' orbital part combined with spin part symmetry we get E'' triplet m$_S$ = 0 and E'+2A' triplet m$_S$ = ±1, as predicted based on symmetries of triplet states in Table 1 and Figure 1. The exact energies are presented in Figure 4(c). Furthermore, as predicted from the theory, the calculated doubly degenerate E' triplet state has non-zero oscillator strength. Oscillator strength for each of E' triplet equals 3x10^{-5}. The next bright state has energy of 0.8eV higher, which indicates how well triplet excitations can be distinct from other absorbing states.

(a)   (b)   (c)

Triplet splitting based   Triplet splitting derived   Triplets' energies
on group theory   from SOC Hamiltonian   calculated in Dirac

2A' ms =+1 or -1 |2,1>(1,1) |2,-1>(1,-1)   2A' 4.395eV

                                                          Z/2   0.020eV
E'' ms =0   -----------------------------   E'' 4.375eV
                         |2,1>(1,0) |2,-1>(1,0)   Z/2
E' m$_S$ =+1 or -1   E' 4.358eV   0.016eV
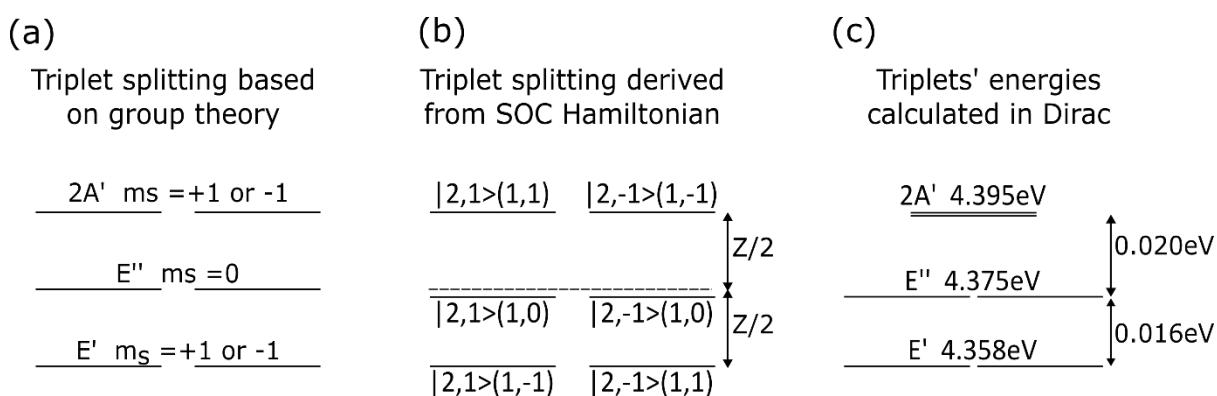 |2,1>(1,-1) |2,-1>(1,1)

Figure 4 Comparison between triplets splitting obtained using different methods: (a) based on group theory (Sec II.2), (b) derived from SOC Hamiltonian (Sec II.4), and (c) calculated for GaEt$_3$ in Dirac with spin interactions included.

Figure 4 shows comparison between triplet splitting obtained using spin-orbit Hamiltonian, group theory (energy splitting is not determined) and finally Dirac calculations. Using calculated energy splitting, we can get Z = 0.036eV. Moreover, from Dirac TDDFT

calculations with spin interactions, we obtain the transition dipole moments for the doubly degenerate triplet. The transition dipole moments of doubly degenerate triplet transitions E' at the energy equal 4.358eV are perpendicular to each other (given in au): μ_1 = (0.0025, 0.0162, 0.0) and μ_2 = (-0.0162, 0.0025, 0.0). That implies that the transitions are circularly polarized.

III.3 <u>EFFECT OF SPIN ORBIT COUPLING ON TRIPLET EXCITATIONS</u>

Having at least one heavy atom in a molecule is important for the strength of SOC, which is critical for spin injection. In Table 3 we show the comparison between analogues of $GaEt_3$ with Ga replaced with different atoms from the same group. Together with mass change, the transition energy and oscillator strength of the CPL responsive spin polarized triplet E' change. The energy of the triplet decreases with molecular mass and the oscillator strength increases as a result of increased spin orbit coupling. Here, we define the energy splitting Z as the difference between the highest and lowest triplets out of the six in the set in analogy to the matrix elements for SOC Hamiltonian. This splitting also increases with molecular mass. These relations are shown in Figure 5.

	Molecular mass [au]	Triplet E' transition energy [eV]	Triplet E' transition oscillator strength	Energy splitting between triplets, Z [eV]
BEt_3	56	5.527	0.00000002	0.0022
$AlEt_3$	64	4.653	0.00000069	0.0061
$GaEt_3$	82	4.358	0.00002861	0.0372
$InEt_3$	100	3.830	0.00021963	0.1015

Table 3 Comparison of basis parameters for triethyls with different central atoms. Data based on results from Dirac.
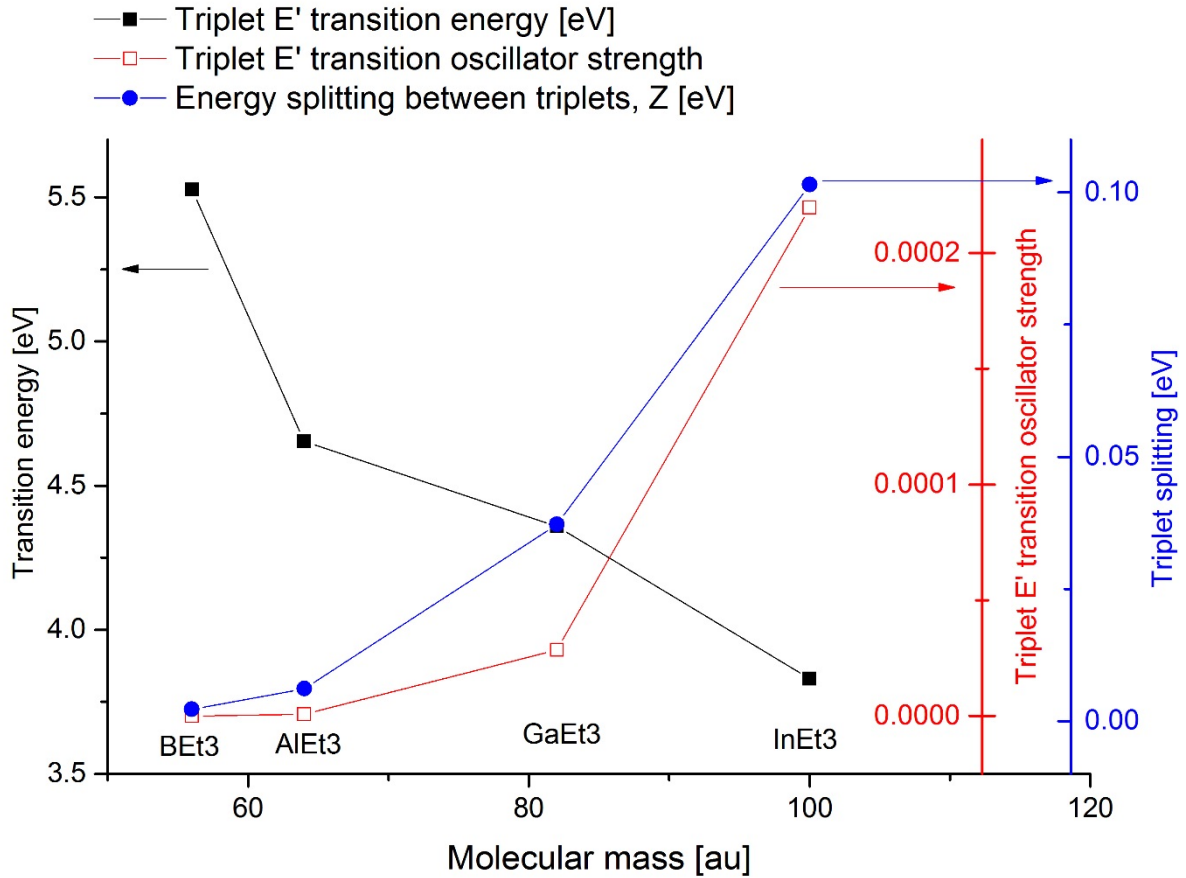
Figure 5 Dependence on the heavy atom mass of the triplet energy, its oscillator strength and energy splitting between triplets.

IV. <u>CONCLUSIONS</u>

We proposed that in order to obtain spin polarized excited state with specified polarization in molecular material, we have to directly excite the triplet state, which (a) corresponds to quantum number m_S equal +1 or -1 and (b) has a circularly polarized symmetry.

Based on this hypothesis and exploiting group and double group theories, we have proposed the list of requirements for a potential molecule for optical spin injection exploiting spin polarized triplet state, that can be excited selectively using left and right handed circularly polarized light. Here, design principles are concluded based on symmetries of molecules, molecular orbitals and excited states and are as follows:

1. The potential molecule has to have one of the following symmetries: C_n, C_{nh}, S_m (n = 3, 4, 5, 6; m = 4, 6, 8, 10).

2. The molecule has to contain heavy atoms to increase spin orbit coupling and thus the strength of spin injection.

3. The HOMO, LUMO pair should have one of the symmetries listed in Table 1 in Supporting Information. This would imply that triplet with $m_S = \pm 1$ associated with HOMO-LUMO transition is circularly polarized and σ- CPL excites triplet with $m_S = -1$ and σ+ CPL excites triplet with $m_S = +1$.

4. Additionally, for application purposes the energy of spin injection transition should lie in the visible region. To test for this property, excited states must be calculated.

The advantage of the symmetry-based molecular design is that at the very beginning it allows us to eliminate a great number of molecules based on their symmetries and thus save a lot of time and computational power. The design principles concluded from symmetries, in general and specifically reported in this publication, are simple and readily accessible in other contexts. Having molecular orbitals' symmetries for a molecule with a circularly polarized point group from DFT calculations, researchers can compare HOMO-LUMO symmetries with the table included in Supporting Information and predict whether the first triplet transition is a spin polarized triplet. Of course, for this excitation to be sufficiently strong, the spin-orbit coupling must be enhanced by either internal or external heavy-atom effect. [16, 24]

We show theoretically that spin can be injected into organic molecular compounds selectively via circularly polarized light providing that molecule has a symmetry that supports circularly polarized transitions and that the lowest energetically triplet with $m_S = \pm 1$ is circularly polarized. We also tested our design rules on simple model triethyl molecules. Whilst the triethyls serve as simple test systems for our theory, the same approach can of course be applied to more complex and application-relevant compounds of the appropriate symmetry.

SUPPORTING INFORMATION is available at xxxxxxxx (address).

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