Computational Design of Efficient Thermally Activated Delayed Fluorescence Emitters Based on Carbazole and Phenoxazine Donor Groups

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Abstract

- Thermally activated delayed fluorescence (TADF) emitters, which generate light by utilizing both singlet and triplet excitons without the use of noble metals, are becoming the next generation of organic electroluminescent materials.
- Our research focuses on compounds derived from Carbazole and Phenoxazine-based donor groups, and Anthraquinone and Xanthone-based acceptor groups, bonded to different carbon atoms at various dihedral angles.
- The goal was to create a molecule where the HOMO (Highest Occupied Molecular Orbital) and the LUMO (Lowest Unoccupied Molecular Orbital) are on donor and acceptor units, respectively, and to optimize the molecule to a point where the repulsive force is minimized.

Introduction

- OLEDs are critical in display and lighting technologies due to their efficiency and flexibility, but conventional types are limited by low quantum efficiency or reliance on rare metals. To overcome these issues, TADF OLEDs, which do not use noble metals, are emerging as a promising next-generation solution with applications in displays, lighting, microscopy, and sensing.

- The TADF mechanism involves generating singlet and triplet states by combining holes and electrons, with singlet excitons decaying radiatively through prompt fluorescence or converting into triplet excitons via intersystem crossing (ISC). Triplet excitons can either decay nonradiatively or up-convert to the singlet level through an endothermic reverse ISC process, resulting in delayed fluorescence. Optimizing these energy transitions can lead to an internal quantum efficiency (IQE) close to 100%. Key factors include minimizing the singlet–triplet energy splitting (ΔE_{ST}) to enhance reverse ISC efficiency, as described by the Arrhenius equation and Fermi's golden rule. A ΔE_{ST} of less than 0.2 eV is crucial for high TADF efficiency.

- Most TADF molecules have a twisted equilibrium shape that results in a small overlap between the double-bonded π orbitals of the donor and acceptor units. TADF molecules with perpendicular donor and acceptor orientations have low emission intensities, but this angle can be adjusted through specific intramolecular interactions, such as hydrogen bonds.

- Fortunately, TADF molecules based on separated donor and acceptor units connected by a single chemical bond can easily activate soft twisted states, producing a wide range of shapes at room temperature. These states exhibit slightly different absorption and emission energies, and naturally, different ΔE_{ST} values. The thermal excitation of these soft vibrational states also leads to broad and structureless absorption and emission spectra. Thermal motion around twisted equilibrium structures positively affects luminescence because it allows molecular geometries with larger oscillator strengths to be populated.

Computational Details

- Quantum chemical calculations were performed using ORCA 4.2.1 software. Molecular geometries for the S_0 ground state were optimized using density functional theory with the PBE0 functional and the def2-SVP basis set. Time-dependent density functional theory (TDDFT) calculations were also carried out using several density functionals, including PBE0, to minimize repulsive forces and determine the optimum dihedral angle between the donor and acceptor groups. Spin-Orbit Coupling (SOC) calculations were later performed using different halogen atoms, such as chlorine, bromine, and iodine, with an additional calculation using hydrogen only.

Results

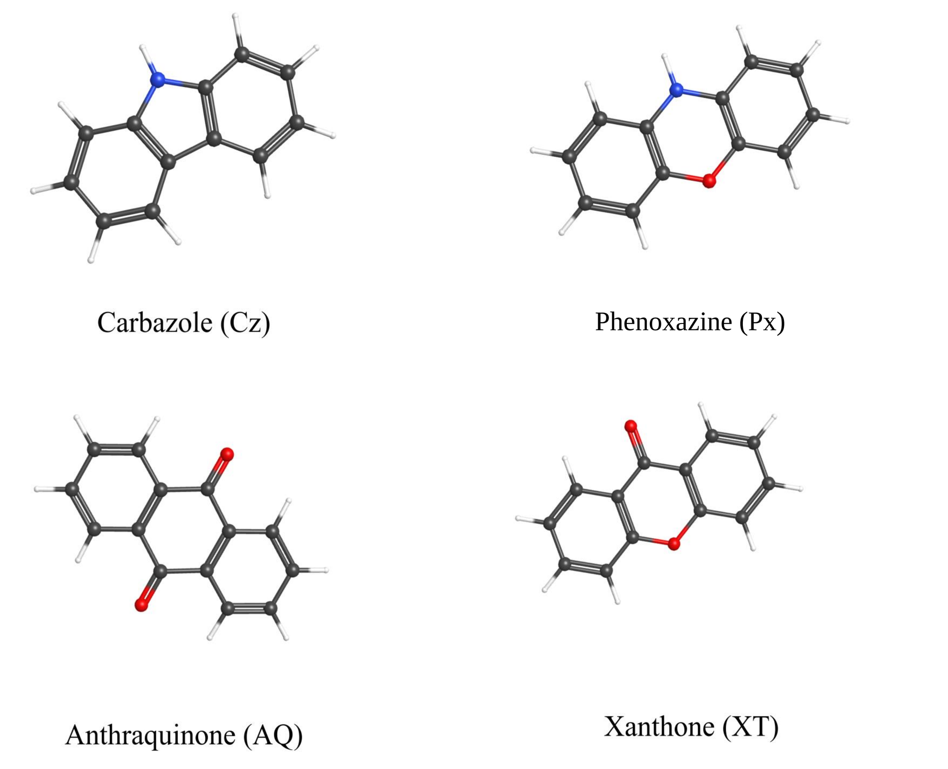
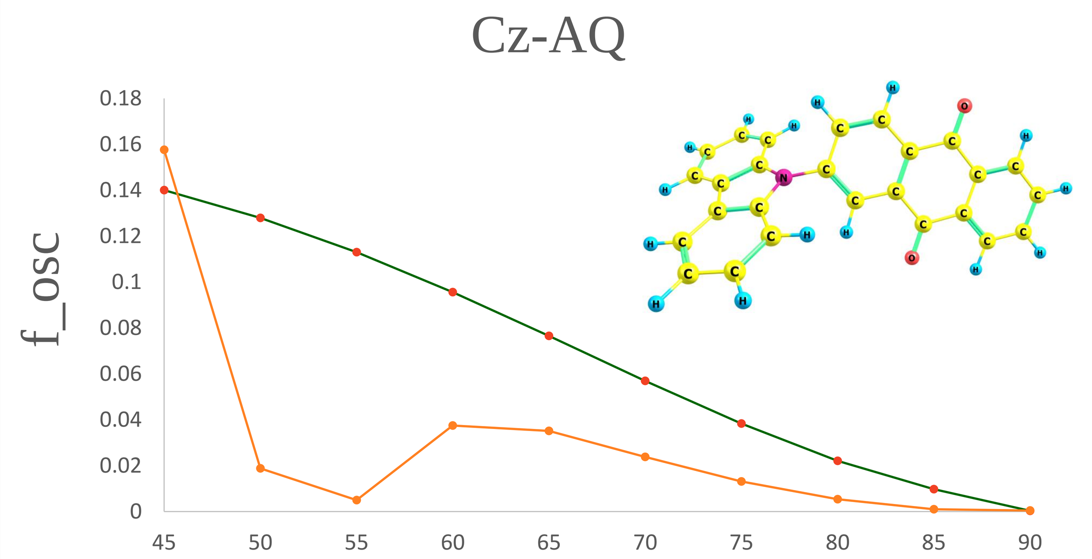


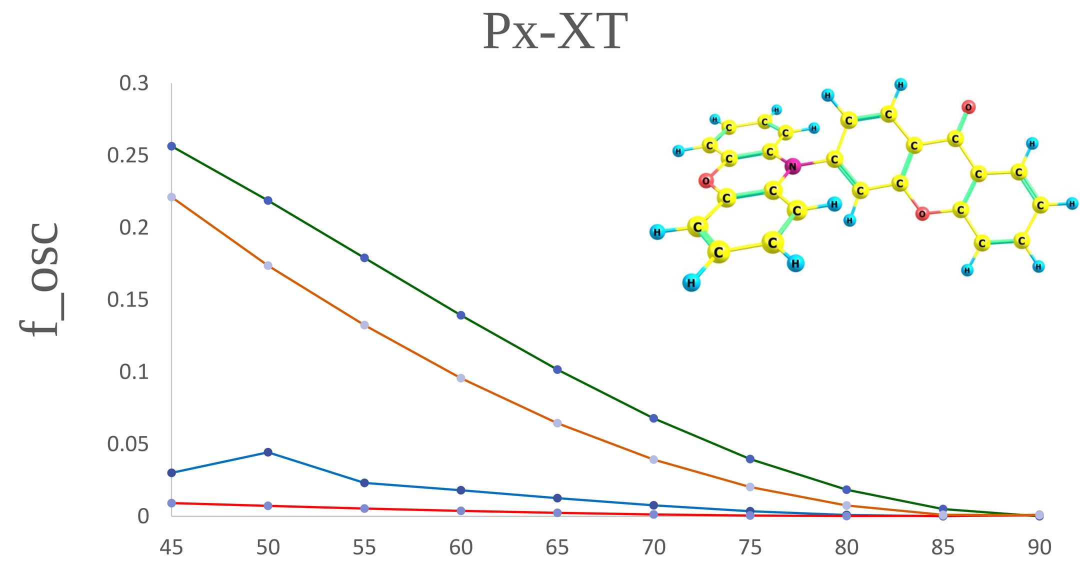
Figure 1- Donors And Acceptors

Isomers	T1 (eV)	S1 (eV)	S1 f_{osc}	Triplet No.	Triplet Energy (eV)	Triplet f_{osc}
Cz-AQ-I (2)	2.382	2.675	6.56E-02	T2	2.674	2.33E-04
Cz-AQ-I (3)	2.372	2.682	6.87E-02	T2	2.680	9.03E-03
I-Cz-AQ (2)	2.533	2.917	5.97E-02	T4	2.898	5.23E-06
I-Cz-AQ (3)	2.491	2.804	6.32E-02	T3	2.765	1.85E-05
Cz-XT-I (2)	2.983	3.501	1.77E-01	T6	3.437	1.31E-06
Cz-XT-I (3)	2.982	3.526	1.96E-01	T6	3.445	2.91E-07
I-Cz-XT (2)	2.928	3.761	1.99E-01	T6	3.420	2.45E-06
I-Cz-XT (3)	2.967	3.631	1.19E-01	T6	3.386	2.78E-06
Px-AQ-I (2)	1.801	1.955	4.67E-02	T1	1.800	8.67E-07
Px-AQ-I (3)	1.807	1.987	5.59E-02	T1	1.807	2.95E-07
I-Px-AQ (2)	2.023	2.180	3.97E-02	T1	2.023	2.53E-07
I-Px-AQ (3)	1.969	2.153	5.53E-02	T1	1.969	1.82E-06
Px-XT-I (2)	2.541	2.804	1.01E-01	T2	2.804	3.05E-02
Px-XT-I (3)	2.520	2.835	1.62E-01	T2	2.757	1.56E-07
I-Px-XT (2)	2.656	2.992	1.19E-01	T3	3.215	3.53E-07
I-Px-XT (3)	2.623	2.970	1.59E-01	T3	3.216	1.17E-07

Figure 2- Data Table



The graph highlighted by the green line represents the molecule exhibiting the highest oscillator strength (f_osc) at a dihedral angle of 60 degrees



The graph highlighted by the green line represents the molecule exhibiting the highest oscillator strength (f_osc) at a dihedral angle of 60 degrees

Figure 3- Determination of the Optimum Dihedral Angle

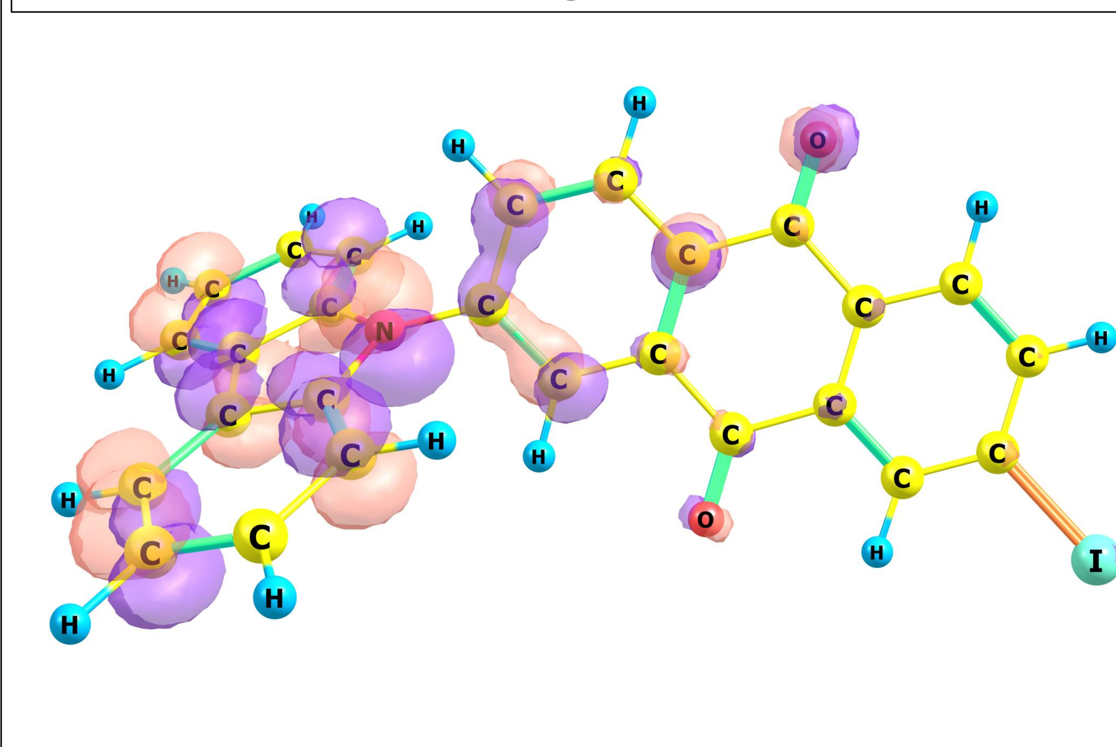


Figure 4- HOMO of Cz-AQ-I-3

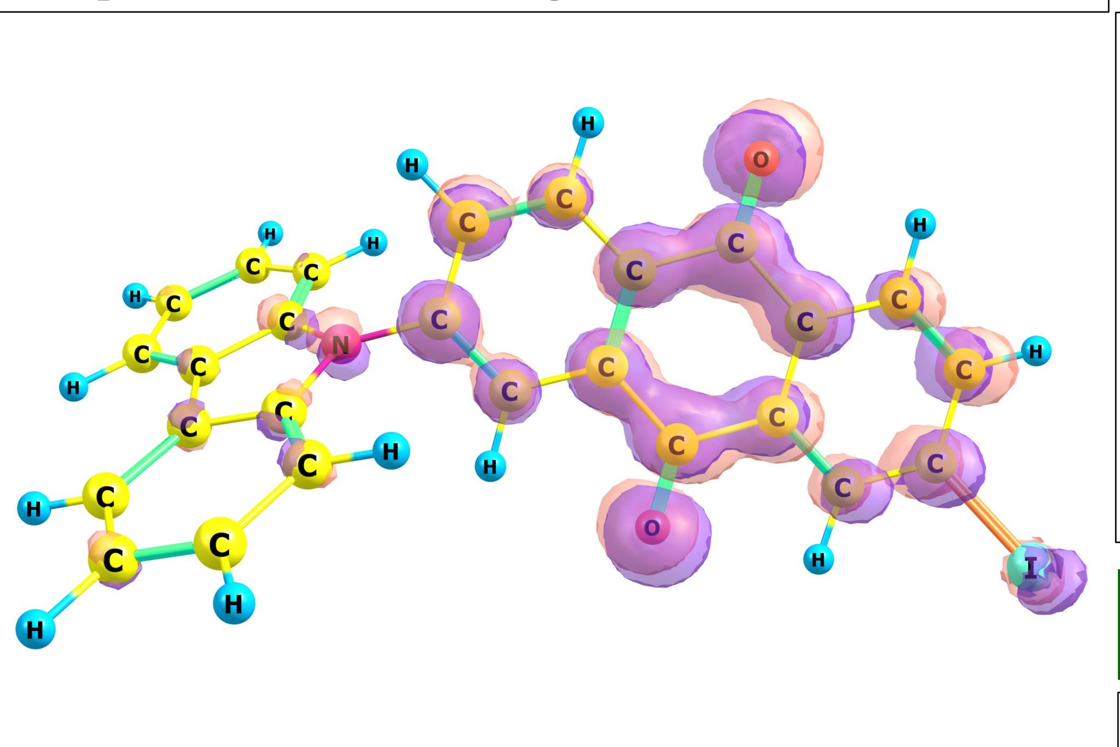


Figure 5- LUMO of Cz-AQ-I-3

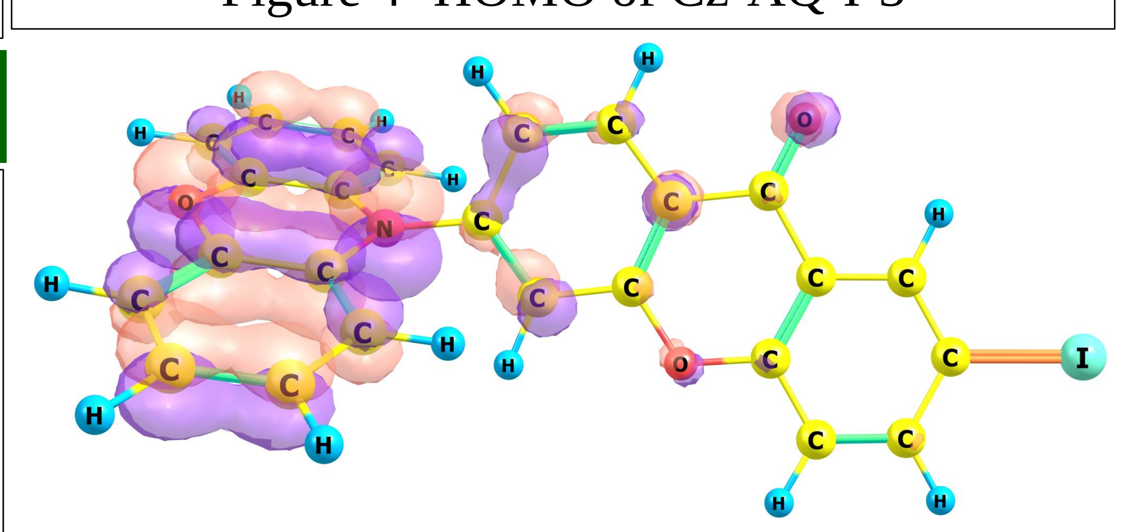


Figure 6- HOMO of Px-XT-I-2

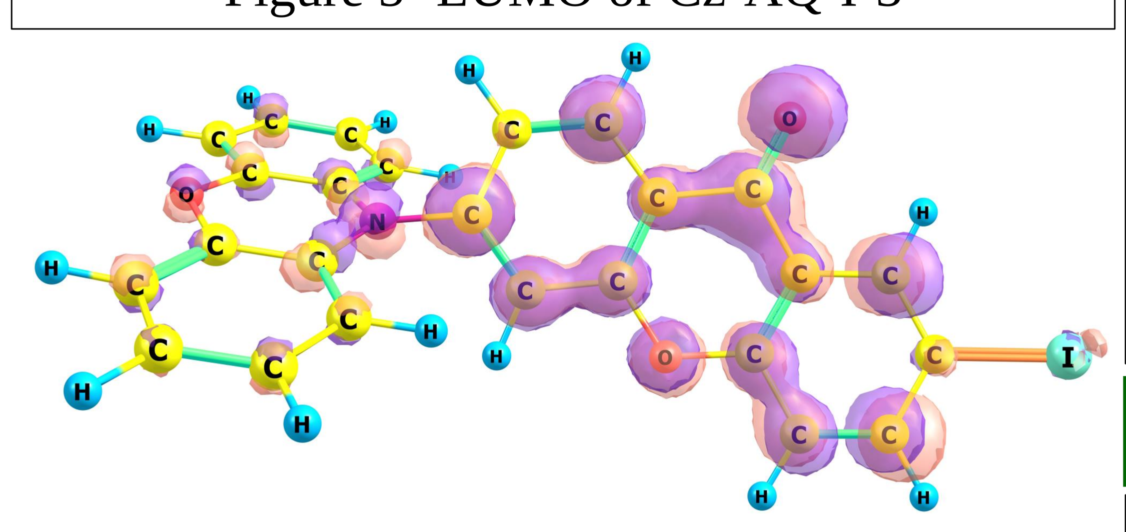


Figure 7- LUMO of Px-XT-I-2

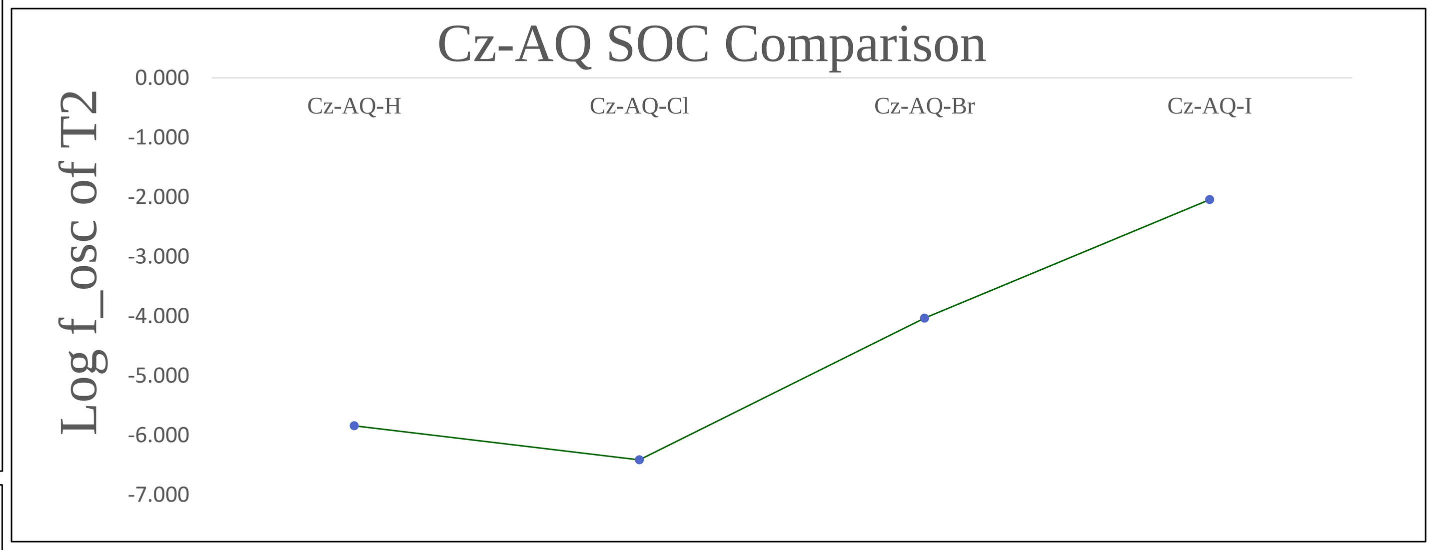
Conclusions

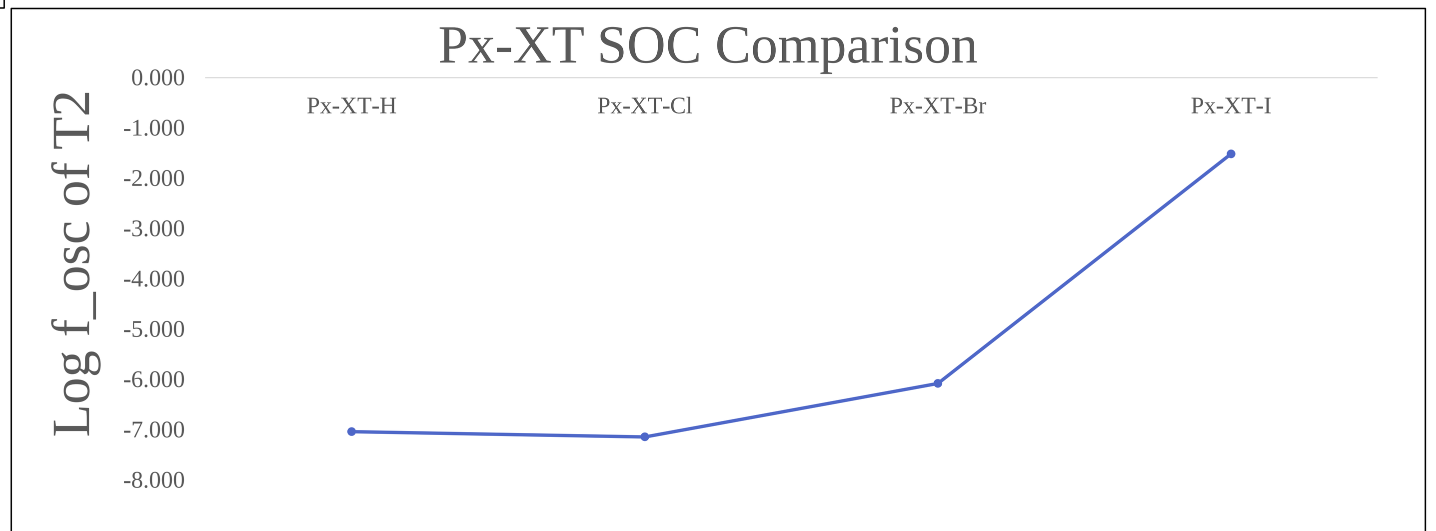
In conclusion, our data show that a dihedral angle of 60 degrees between the donor and acceptor results in a lower ΔE_{ST} (difference between the energy in the Singlet state and Triplet state) and a higher f_{osc} (oscillator strength).

The optimal carbon on the acceptor to attract the donor molecule was determined to be carbon No. 6 for the Px molecule and carbon No. 3 for the AQ molecule, which accounted for the least overlap between the electron clouds, resulting in a more stable molecule.

Adding halogens allows for relativistic effects, providing us with molecules that exhibit even more degenerate excited states with higher oscillator strengths (f_{osc}).

Spin-orbit coupling data indicates that the Cz-AQ molecule, with iodine attached to carbon 3, exhibits notable relativistic effects. In this molecule, Singlet 1 (S_1) closely aligns with Triplet 2 (T_2), showing an oscillator strength (f_{osc}) of 0.009 for T_2. Similarly, in the Px-XT molecule, where iodine is bonded to carbon 2, the Singlet 1 (S_1) aligns almost perfectly with Triplet 2 (T_2), with an oscillator strength of 0.03 for T_2, which is unexpectedly significant.





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