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Communication

Spectroscopic Quantification of the Inverted Singlet−Triplet Gap in Pentaazaphenalene

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ABSTRACT: We report the direct and accurate spectroscopic quantification of the inverted singlet−triplet gap in 1,3,4,6,9b-pentaazaphenalene. This measurement is achieved by directly probing the lowest singlet and triplet states via high-resolution cryogenic anion photoelectron spectroscopy. The assignment of the first excited singlet state is confirmed by visible absorption spectroscopy in an argon matrix at 20 K. Our measurements yield an inverted singlet−triplet gap with ΔE_{ST}= −0.047(7) eV. The accurate quantification of the singlet−triplet gap presented here allows for direct evaluation of various computational electronic structure methods and highlights the critical importance of the proper description of the double excitation character of these electronic states. Overall, this study validates the idea that despite Hund's multiplicity rule, useful organic chromophores can have inherently inverted singlet−triplet gaps.

The need to increase fluorescence efficiency in organic light-emitting diodes has led to recent development of chromophores with very small energy difference between the lowest-energy singlet (S_1) and triplet (T_1) excited states (commonly termed the singlet−triplet gap, ΔE_{ST}).[1−3] In a typical closed-shell organic molecule, T_1 is lower in energy than S_1, as stated by Hund's multiplicity rule.[4] Reducing the energy gap between them thus minimizes the loss of excitation energy via the triplet channel by allowing for additional thermally activated delayed fluorescence (TADF) via reverse intersystem crossing, i.e., from T_1 to S_1. For a simplified two-electron, two-orbital system, ΔE_{ST} is proportional to the exchange integral between the two orbitals composing the system.[5] Hund's multiplicity rule applies in this case because the exchange integral can only be positive. A small ΔE_{ST} can be achieved by minimizing the spatial overlap between the HOMO and LUMO, which minimizes the exchange integral.[6] For traditional TADF emitters, this condition is achieved by having spatially separated electron donor and acceptor groups resulting in excitation with significant charge transfer-character.[2,3] While the simplified picture is useful for the design of emitters, a more accurate model of ΔE_{ST}, which can account for efficient fluorescence and reverse intersystem crossing, must also include contributions from states with local excitation character.[7]

More recently, a different type of chromophore design is being explored in which a minimal exchange integral is achieved by localizing the HOMO and LUMO electron densities on alternating atoms in the molecule.[8−13] The azaphenalenes, shown in Figure 1, are the most widely studied prototypical molecules exhibiting this characteristic. Intriguingly, many recent computational studies[8,14−22] on azaphenalenes predict a *negative* ΔE_{ST}, i.e., where S_1 is slightly lower in energy than T_1. The potential for a molecule to break Hund's multiplicity rule has been known for a long time.[5] Spin

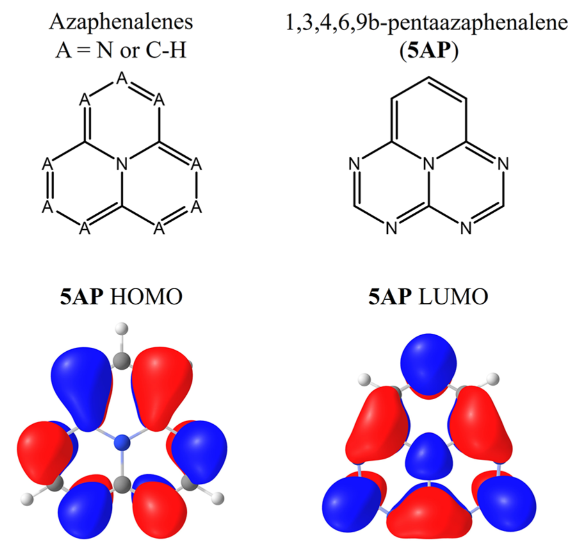

Figure 1. Chemical structures of the azaphenalene family and **5AP**. HOMO and LUMO depictions of **5AP**.

polarization effects[23,24] can overcome a small exchange integral and cause inversion of the two states. In terms of modern electronic structure theory, a negative ΔE_{ST} can result from the contribution of doubly excited electronic configurations preferentially stabilizing the S_1 state over the T_1 state.[25]

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Indeed, many theoretical studies have shown that the inclusion of doubly excited configurations is crucial in predicting a negative ΔE_{ST} in azaphenalenes.[8,18−20] However, the calculated ΔE_{ST} values are small and well within the typical uncertainties[26] expected for most excited-state computational methods accessible for molecules of the size of azaphenalenes. Accurate predictions of the magnitude and possible inversion of ΔE_{ST} in azaphenalenes are still at the forefront of the electronic structure theory. It remains uncertain whether singlet−triplet inversion is generally possible in azaphenalenes or if it is simply an artifact of the approximate electronic structure theory used.[27]

One crucial, but still missing, piece of information is the accurate spectroscopic quantification of ΔE_{ST} in these chromophores, which is difficult to obtain because of the spin-forbidden nature of the S_0−T_1 transition and the difficulties arising from the near degeneracy of S_1 and T_1. Instead, chromophores with a small ΔE_{ST} are usually characterized via the temperature dependence of the delayed fluorescence rate and quenching of the delayed fluorescence signal by O_2. Such experimental approaches have shown the presence of an inverted singlet−triplet gap in a handful of functionalized azaphenalenes.[9,11,12,28,29]

Here we use cryogenic high-resolution anion photoelectron (PE) spectroscopy[30,31] to provide a direct spectroscopic quantification of the inverted singlet−triplet gap in 1,3,4,6,9b-pentaazaphenalene (**5AP**), whose structure is shown in Figure 1. **5AP** is easily accessible via a single-step synthesis from commercially available reagents[32] and has been predicted to offer a good trade-off between having a negative ΔE_{ST} and maximizing the fluorescence rate for potential light emission applications.[14] In anion PE spectroscopy, electrons are photodetached from a molecular anion such as the **5AP**$^-$ radical anion, and their kinetic energies (eKE) are measured to map the vibronic energy levels of the corresponding neutral molecule. Starting from the radical anion ground-state (D_0), the photodetachment selection rules permit the spectroscopic observation of both neutral singlet and triplet states and therefore provide direct spectroscopic quantification of ΔE_{ST}. Moreover, the chromophores are probed at low temperature and without solvent perturbation, yielding experimental excitation energies that can be directly compared with the results of electronic structure computations. This experimental approach has been successfully used to quantify ΔE_{ST} in a variety of organic chromophores, such as the very small singlet−triplet gap in azulene.[33]

The anion PE spectra shown in the bottom panel of Figure 2 were acquired using our high-resolution cryogenic anion photoelectron spectrometer, described previously,[34] and in the Supporting Information. These spectra are plotted as a function of electron binding energy (eBE), which is defined as the difference between the photodetachment photon energy and measured eKE.

The first group of peaks, located in the 1.20−1.45 eV eBE range, is assigned to transitions to the neutral **5AP** ground electronic state (S_0). Peak A is assigned to the 0−0 origin transition, and its position yields an adiabatic electron affinity of 1.235(2) eV for **5AP**. This assignment is in good agreement with the calculated value of 1.20 eV at the B3LYP-D3/ma-def2-TZVPP level of theory. The weaker features in this group are assigned to D_0−S_0 vibronic transitions, in agreement with the Franck−Condon simulations shown in the Supporting Information. The second group of peaks appears in the 3.15−

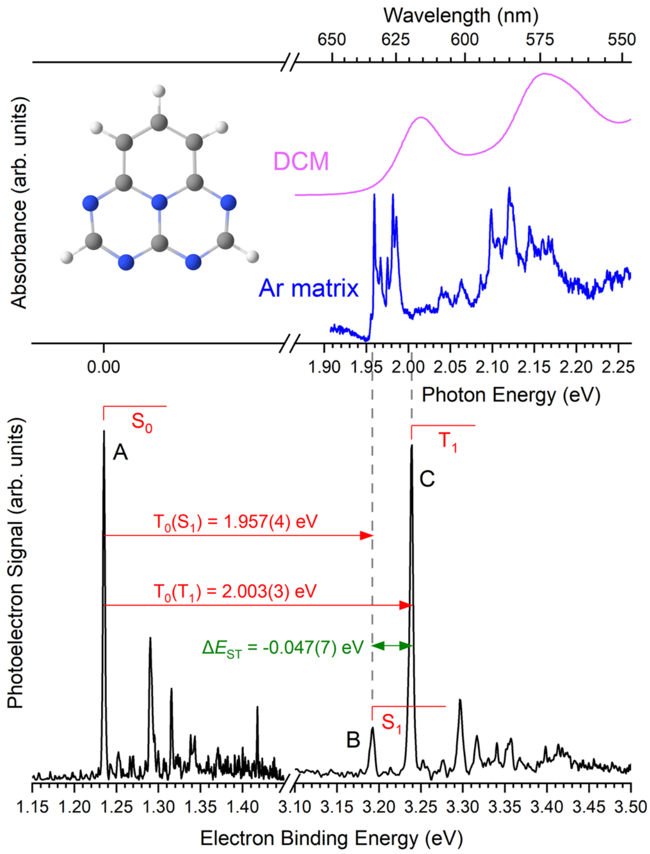

Figure 2. (top panel) Absorption spectra of **5AP** in DCM and in annealed 20 K argon matrix. (bottom panel) Anion photoelectron spectra of **5AP**$^-$ in the energy ranges corresponding to the neutral S_0, S_1, and T_1 states. The horizontal scales of both panels are aligned to allow for a direct comparison of the position of the S_1 state in the absorption and photoelectron spectra.

3.45 eV eBE range, where T_1 and S_1 are expected. Based on computed Franck−Condon spectra, we expect the 0−0 origin transition to be the most intense feature for both the S_1 and T_1 state. Therefore, we assign the predominant feature, peak C at eBE = 3.239(3) eV, to be one of the origin transitions. The weaker peak B, at eBE = 3.192(4) eV, is the only feature located at lower eBE than peak C. In the absence of hot bands, which is reasonably expected for anions thermalized to ∼10 K, peak B can only be assigned as the origin transition of the other electronic state. Subtracting the electron affinity determined above thus yields adiabatic term energies of 1.957(4) and 2.003(3) eV for these two states relative to the S_0 state. Unfortunately, the PE spectra themselves do not allow us to unambiguously distinguish which transition corresponds to S_1 vs T_1.

To achieve an unambiguous assignment, we turn to electronic absorption spectroscopy where only the S_0−S_1 transition is spin-allowed. The absorption spectrum of **5AP** in dichloromethane (DCM) solution is shown in the top panel of Figure 2 (purple trace). To facilitate a direct comparison with the anion PE spectra, the absorption spectrum is plotted in terms of photon energy (eV) with the origin of the energy axis aligned with the S_0 origin transition (peak A). The more familiar wavelength (nm) units are shown on the top axis. The S_0−S_1 transition is a broad feature centered at around 2.02 eV, which is slightly blue-shifted with respect to both peaks B and C. Solvents with higher polarity induce a larger solvatochromic

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Table 1. Summary of Computed Transitions Energies and ΔE_{ST} for 5AP

computational method	$E(S_0-S_1)$ (eV)	$E(S_0-T_1)$ (eV)	ΔE_{ST} (eV)	ref
vertical transition energies				
ADC(2)/def2-TZVP	2.154	2.296	−0.142	18
ADC(2)/aug-cc-pVTZ	2.159	2.298	−0.139	21
CC2/def2-TZVP	2.231	2.365	−0.134	18
CC2/aug-cc-pVTZ	2.235	2.366	−0.131	21
CC3/aug-cc-pVDZ	2.164	2.284	−0.120	21
EOM-CCSD/cc-pVDZ	2.251	2.329	−0.078	14
EOM-CCSD/cc-pVTZ	2.343	2.372	−0.030	this work
EOM-CCSD/aug-cc-pVTZ	2.374	2.394	−0.020	21
EOM-CCSDt/cc-pVTZ	2.223	2.315	−0.092	this work
(0−0) transition energies				
ADC(2)/def2-TZVP	1.901	1.995	−0.094	18
CC2/def2-TZVP	1.971	2.056	−0.085	18
EOM-CCSD/cc-pVTZ//B3LYP	2.192	2.168	+0.024	this work
EOM-CCSDt/cc-pVTZ//B3LYP	1.942	1.964	−0.022	this work
experimental	**1.957(4)**	**2.003(3)**	**−0.047(7)**	this work

blue-shift in 5AP (see Figure S4). This result is consistent with predictions from DFT computations with a polarizable continuum model (Table S2). However, because the magnitude of the solvatochromic blue-shift is difficult to compute accurately, the solution phase absorption spectrum alone is still insufficient. Hence, we acquired the absorption spectrum of **5AP** in an annealed 20 K argon matrix, as shown also in Figure 2A (blue trace). Similar to other solvents, argon is expected to produce a solvatochromic blue-shift, but with a much smaller magnitude than DCM. The S_0−S_1 origin transition in the Ar matrix appears as several peaks in the 1.95−2.00 eV range which we attribute to a distribution of unique matrix sites based on comparison of annealed and unannealed matrix spectra (see the Supporting Information). Nonetheless, these features are all located above peak B and below peak C. Therefore, we can now conclusively assign peak B in the PE spectrum to the 0−0 origin transition of the S_1 state, which leaves peak C as the 0−0 origin transition of the T_1 state. This combination of anion PE spectroscopy and electronic absorption spectroscopy thus provides direct evidence of an inverted singlet−triplet gap in **5AP**. The eBE difference between peaks B and C yields a value of −0.047(7) eV for the singlet−triplet gap.

Our quantitative experimental measurement of ΔE_{ST} for an unsubstituted azaphenalene provides an important benchmark for various electronic structure methods. Table 1 shows a summary of some of the most important computational results for **5AP**. We note that most computations in Table 1 use the difference between the vertical excitation energies of S_1 and T_1 to calculate ΔE_{ST}. This approximation avoids performing expensive computations by assuming that the molecular geometry and vibrational frequencies of the S_1 and T_1 states are very similar to each other. With this approach and using the ADC(2), CC2, and CC3 wave function methods, Tuckova et al.[18] and Loos et al.[21] reported ΔE_{ST} which are ∼0.07−0.09 eV more negative than the experimental value. The closest values are obtained with the EOM-CCSD method. In particular, the use of EOM-CCSD with larger triple-ζ basis sets yields ΔE_{ST} values in excellent agreement with the experimental value (−0.047eV).

While most of these computational methods yield reasonable ΔE_{ST} values, they notably exhibit sharper differences in the computed vertical transition energies (see Table 1). Unfortunately, the accuracy of these values cannot be directly verified because they do not correspond to any spectroscopic observables in polyatomic molecules due to the geometry relaxation being distributed over a large number of normal modes. Fortunately, Tuckova et al.[18] did report the adiabatic and zero-point energy (ZPE) corrections to the transition energies at the ADC(2) and CC2 level of theory. These corrections result in ΔE_{ST} values that are slightly less negative compared to those obtained with vertical transition energies and in better agreement with the experimental values. Very importantly, the computed S_1 and T_1 (0−0) transitions are within ∼0.05 eV of the experimental measurements. This indicates that the good ΔE_{ST} agreement for these methods is not a fortuitous cancellation of errors involved in subtracting the vertical S_1 and T_1 transition energies.

However, the application of adiabatic and ZPE corrections to the EOM-CCSD vertical transitions leads to a slightly positive ΔE_{ST}. For example, our computations using the B3LYP geometries and frequencies with EOM-CCSD/cc-pVTZ excitation energies yield a ΔE_{ST} of +0.024 eV, in disagreement with the experimental observation of an inverted singlet−triplet in **5AP**. Moreover, the EOM-CCSD computed 0−0 transitions energies are ∼0.17−0.25 eV higher than the experimental values. This is a very important result because this method is generally considered to be very accurate and often used as the benchmark for more approximate approaches. The observed discrepancy probably originates from the known issues of EOM-CCSD in accurately describing states with significant double excitation character.[35−38] To verify this hypothesis, we performed equation of motion coupled cluster with single, double, and active triples (EOM-CCSDt/cc-pVTZ) calculations, in which the triply excited clusters are computed in a small active space comprising 3 occupied and 3 virtual orbitals.[39] This approach yields an inverted singlet−triplet gap with an ΔE_{ST} of −0.022 eV, in much better agreement with the experimental value. The computed 0−0 transitions energies are also within ∼0.02−0.04 eV of the experimental values. This agreement highlights the critical importance of properly describing the double excitation character of these states to accurately predict singlet−triplet gap inversion.

In conclusion, by mapping both S_1 and T_1 states via anion PE spectroscopy and confirming the position of the S_1 state by

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electronic absorption spectroscopy, we obtained a direct and accurate spectroscopic measurement of the inverted singlet–triplet gap in **5AP**. Our results validate the idea that despite Hund's multiplicity rule, certain useful organic chromophores can have an inherently inverted singlet–triplet gap. The accurate experimental quantification of ΔE_{ST} in **5AP** presented here also allows for the validation of computational electronic structure methods that may be useful in aiding the search and design of such chromophores. In terms of useful applications in the field of light-emitting diodes, the main disadvantage of the azaphenalene cores lies in having a generally weak S_0–S_1 oscillator strength, which can limit the fluorescence yield. However, Pollice et al.[14] have shown that the oscillator strength can be significantly improved by selecting proper ring substituents. Such functionalization of the azaphenalene core is expected to influence the chromophore's HOMO and LUMO via electron delocalization and electron donating/withdrawing effects. Therefore, experimental quantification and validation of the theoretical modeling of the substituent effects on ΔE_{ST} are certainly warranted.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c05043.

Details of the **5AP** synthesis, experimental and computational methods, solvatochromic shift computations, Franck–Condon simulations, and matrix annealing experiments (PDF)

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Notes

The authors declare no competing financial interest.

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