

VISTA Seminar

Seminar 58

October 25, 2023

**10:00 am – 11:30 am EST / 3:00 – 4:30 pm GMT London / 4:00 pm –
5:30 pm CET Paris / 10 pm CST Beijing**

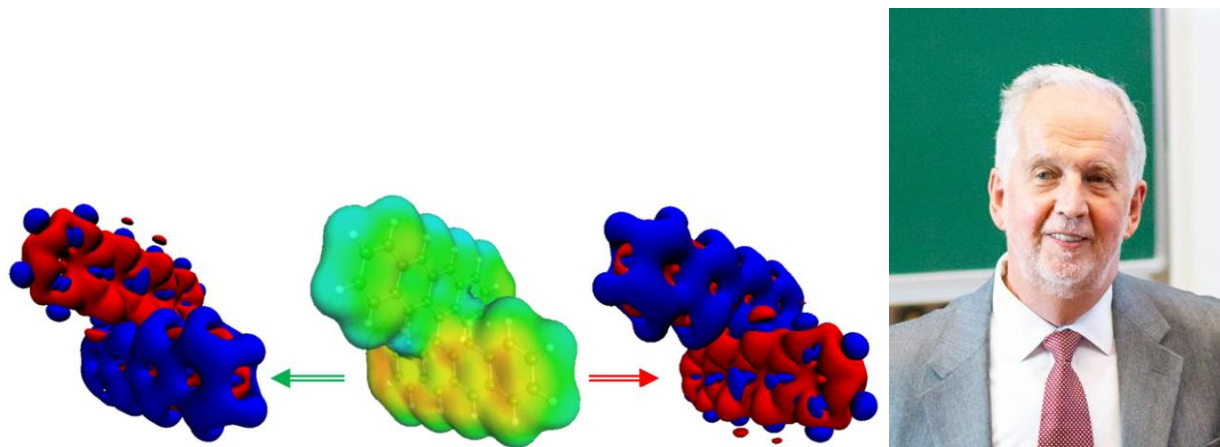
TOC:

1. Presenter 1: Prof. Hans Lischka, Texas Tech University, USA..... page 2
2. Presenter 2: Dr. Kakarlamudi Akhil Chakravarthy, Indian Institute of Science
Education and Research, Thiruvananthapuram, India.....page 3
3. How to connect..... page 4

Solvent-Enhanced Symmetry-breaking and Singlet-Fission in the Covalently-Bound Tetracene Dimer and Electronic States including the ^1TT State in Stacked TIPS-Pentacene Dimers and Trimers

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In recent years, covalently bound dimers of chromophores have attracted significant interest as singlet fission (SF) material because of better control of coupling of different electronic states to the gateway $^1(\text{TT})$ by means of intramolecular vibrational modes.¹ It has been shown that charge transfer (CT) plays a crucial role in mediating the S_1 - $^1(\text{TT})$ interaction and their influence can be conveniently tuned by solvent polarity.

Motivated by the experimental and theoretical work of Alvertis et al.,¹ we have investigated the electronic states relevant to the SF for the covalently bound tetracene dimer with the goal to provide a broader picture of the occurring photodynamical processes.² For that purpose, the second-order algebraic diagrammatic construction (ADC(2)) method in combination with the conductor-like screening model (COSMO) has been used. Vertical excitations and potential energy curves for excitonic and CT states along low-frequency symmetric and antisymmetric normal modes have been computed. These results have been combined with those obtained by density functional theory/multireference configuration interaction (DFT/MRCI) calculations for the $^1(\text{TT})$ state since its doubly-excited wavefunction is not accessible to the ADC(2) method.

In the second part of the talk, DFT/MRCI calculations on dimer and trimer TIPS-Pn will be presented with the goal of a first theoretical understanding of the photodynamics of the $^1(\text{TT})$ state monitored by time-resolved mid-IR absorption spectroscopy.³

References

¹ A. M. Alvertis, St. Lukman, T. J. H. Hele, E. G. Fuemmeler, J. Feng, J. Wu, N. C. Greenham, A. W. Chin, and Andrew J. Musser *J. Am. Chem. Soc.* 2019, **141**, 17558

² R. S. Mattos, I. Burghardt, A. J. A. Aquino, Th. M. Cardozo, H. Lischka, *J. Amer. Chem. Soc.* 2022, **144**, 23492

³ John B. Asbury et al. *J. Phys. Chem. C* 2018, 122, 2012–2022

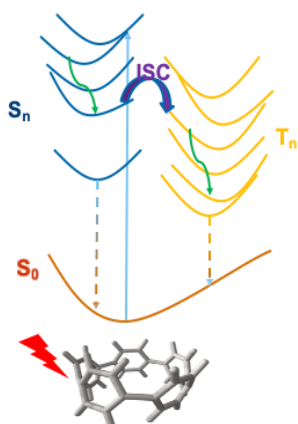
Investigating the theoretical optical properties of neutral Cycloparaphenylenes(CPPs)

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The analysis, energetics and internal conversion dynamics of singlet and triplet manifolds to identify the possible intersystem crossing pathways in odd-numbered [n]cycloparaphenylenes ([n]CPPs, n = 5, 7, and 9). Quantum wavepacket propagation calculations within the linear vibronic coupling framework suggest that both [5]- and [7]CPPs rapidly relax to S₂ upon populating “bright” higher singlet excited states. The S₂-S₁ energy decreases with the increase in CPP size, and hence, [9]CPP exhibits a faster S₂ → S₁ internal conversion decay. Higher triplet states act as receiver states for the intersystem crossing happening either via S₁ or S₂. The wavepacket evolving on the receiver triplet state would decay to lower states via multiple conical intersections and reach T₁. The estimated size-dependent fluorescence and emission energies are in good accord with the experiment.

References

1. E.R. Darzi, et al. “The dynamic, size-dependent properties of [5]–[12]cycloparaphenylenes” **Chem. Soc. Rev.** **44**, 6401-6410, 2015
2. E.J. Leonhardt, et al. “Emerging applications of carbon nano hoops” *Nat. Rev. Chem.* **3**, 672–686, 2019
3. Y.Masumoto, et al. “Near-Infrared Fluorescence from In-Plane-Aromatic Cycloparaphenylene Dications” *J. Phys. Chem. A.* **122**, 23, 5162–5167, 2018.
4. A.C. Kakarlamudi et al. “Intersystem crossing pathways in [5]-, [7]-, and [9]cycloparaphenylenes” *J. Chem. Phys.* **155**, 044301 (1-13), 2021.

How to connect

Alexey Akimov is inviting you to a scheduled Zoom meeting.

Topic: VISTA, Seminar 58

Time: Oct 25, 2023 10:00 AM Eastern Time (US and Canada)

Join Zoom Meeting

<https://buffalo.zoom.us/j/92660474949?pwd=L2JBd2pYWHPHYTdBcVI1cjZNRWk1Zz09>

Meeting ID: 926 6047 4949

Passcode: 084480