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

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**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**

Hans Lischka

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A colorful molecule model

Description automatically generated with medium confidenceA person in a suit and tie

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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(TT) by means of intramolecular vibrational modes.1 It has been shown that charge transfer (CT) plays a crucial role in mediating the S1-1(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(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(TT) state monitored by time-resolved mid-IR absorption spectroscopy.3

**References**

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)**

Kakarlamudi Akhil Chakravarthya,b

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A diagram of a graph

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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 nanohoops” 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