

CPP 25: Molecular Electronics and Excited State Properties II

Time: Wednesday 9:30–11:00

Location: H 0111

CPP 25.1 Wed 9:30 H 0111

Solvent-Induced Isomerization in Stilbene. Possible Solution to a Longstanding Problem. — ●J. LUIS PEREZ LUSTRES¹, ALEXANDER L. DOBRYAKOV², DARIA SCHRIEVER¹, MARTIN QUICK³, ILYA IOFFE⁴, and SERGEY A. KOVALENKO³ — ¹Fachbereich Physik, Freie Universität Berlin — ²Moscow — ³Institut für Chemie, Humboldt Universität zu Berlin — ⁴Moscow

Stilbene isomerization reaction was studied in the gas phase at collisionless conditions and analysed by RRKM theory [1], which however fails to explain acceleration by buffer gas pressure [2]. In solution, RRKM provides no explanation for, a much faster rate and the small effect of excess excitation energy [3]. We revisited the problem with fs transient absorption in solution at λ_{exc} of 325 and 267 nm. The latter results in a molecular temperature of 600 K at time zero. Consistent with gas phase, an average barrier of 1236 cm⁻¹ is deduced in nonpolar solvents. λ_{exc} -dependence is explained by complete IVR and vibrational cooling with a rate constant of 10 ps [4]. This is reconciled with RRKM theory by postulating an additional activation by the solvent, which would be dominant in solution.

References

[1] J. S. Baskin *et al.*, *J. Phys. Chem.* **1996**, *100*, 11920-11933. [2] A. Meyer *et al.*, *J. Phys. Chem. A* **1999**, *103*, 10528- 10539. [3] S. A. Kovalenko, A. L. Dobryakov, *Chem. Phys. Lett.* **2013**, *570*, 56-60. [4] S. A. Kovalenko *et al.*, *J. Chem. Phys.* **2001**, *115*, 3256-3273.

CPP 25.2 Wed 9:45 H 0111

Spatial Anisotropy of the Excitonic Coupling in β -Phase Zinc-Phthalocyanine Single Crystals — ●LISA SCHRAUT-MAY¹, KILIAN STRAUSS¹, GABRIELE TAUSCHER², HEINRICH SCHWOERER², and JENS PFLAUM^{1,3} — ¹Experimental Physics VI, University of Würzburg, 97074 Würzburg — ²Max Planck Institute for the Structure and Dynamics of Matter, 22761 Hamburg — ³CAE Bayern, 97074 Würzburg

Since the anisotropic molecular packing in crystalline solids significantly influences their optical properties and their spatial dependence, the microscopic interplay between crystallographic structure, excitonic coupling and resulting optical characteristics defines an important research topic in organic opto-electronics [1]. In this context, metal-phthalocyanines (M-Pc) represent model systems, as they show different polymorphs and can be functionalized e.g. by gradual fluorination of their periphery [2]. In the case of ZnPc, the fluorination leads to changes in the unit cell parameters without strongly affecting the optical properties of the individual molecules. Here, we investigate single crystals of β -phase ZnPc by means of temperature dependent micro-photoluminescence (μ -PL). Besides discussing the microscopic coupling mechanisms associated with the temperature dependent structural changes and leading to superradiant PL enhancement in β -phase ZnPc at cryogenic temperatures, polarization dependent emission studies on various crystallographic facets prepared by microtomy of the crystals complete the picture of excitonic coupling along different crystallographic directions. [1] Hestand *et al.*, *Chem. Rev.* (2018) [2] Rödel *et al.*, *J. Phys. Chem. C* (2022)

CPP 25.3 Wed 10:00 H 0111

Large Two-Photon Absorption in Open-Shell N-Heteropolycycles — ●GABRIEL SAUTER¹, AUDREY POLLIN², KATHLEEN FUCHS³, ANTONIA PAPAPOSTOULOU⁴, ANDREAS DREUW⁴, UWE BUNZ³, and PETRA TEGEDER¹ — ¹Physikalisch-Chemisches Institut, University Heidelberg — ²ENS Paris-Saclay, Paris-Saclay University, France — ³Organisch-Chemisches Institut, University Heidelberg — ⁴Interdisciplinary Center for Scientific Computing, University Heidelberg, Germany

We present a study on the third-order nonlinear optical (NLO) properties of organic open-shell compounds, focusing on two-photon absorption (TPA).

TPA provides distinct advantages over single-photon absorption, such as high spatial resolution and penetration depth, while minimizing photodamage. Effective design is crucial for achieving molecules with significant TPA properties. Molecules with a push-pull system, large extended π -system, and rigid planar structure have shown potential for high TPA.

Recent synthesis efforts have focused on N-heteropolycyclic derivatives incorporating this design. By employing the Z-scan technique, we

can analyze how molecular design influences NLO properties and find pronounced TPA cross sections in the near-infrared region by introducing open-shell character, revealing remarkable values (up to 8400 GM) compared to similar organic compounds.

CPP 25.4 Wed 10:15 H 0111

Third-Order Nonlinear Optical Properties of N-Heteropolycycles — ●AUDREY POLLIN^{1,2}, GABRIEL SAUTER², KATHLEEN FUCHS³, UWE BUNZ³, and PETRA TEGEDER² — ¹ENS Paris-Saclay, Paris-Saclay University, Gif-Sur-Yvette, France — ²Physikalisch-Chemisches Institut — ³Organisch-Chemisches Institut, Heidelberg University, Heidelberg, Germany

Third-order nonlinear optical (NLO) properties are observed in large π -conjugated organic molecules, characterized by the polarization of the material depending on the intensity of an applied electromagnetic field, giving rise to valuable properties such as two-photon absorption (TPA), self-focusing, or self-defocusing. Materials exhibiting third-order polarizability are essential for various photonics and optoelectronics applications, including bioimaging, three-dimensional microfabrication, optical data storage, optical limiting, and photodynamic therapy.

We show that open-shell N-heteropolycyclic compounds possess remarkable third-order NLO coefficients although they have a relatively small size and a metal-free nature compared to other molecules reported in the literature with such high properties. They are of particular interest due to their potential applications as photoinitiators and as chiral open-shell N-heteropolycycles in photonics. The third-order NLO properties of N-heteropolycyclic compounds are investigated using Z-scan techniques but also absorption, emission and fluorescence anisotropy measurements are performed for characterization.

CPP 25.5 Wed 10:30 H 0111

Uncovering the influence of OLED host properties on donor-acceptor type TADF emission by single molecule spectroscopy — ●BJÖRN EWALD¹, THEODOR KAISER¹, and JENS PFLAUM^{1,2} — ¹Experimental Physics 6, University of Würzburg, 97074 Würzburg — ²CAE Bayern, 97074 Würzburg

Molecular emitters exhibiting thermally activated delayed fluorescence (TADF) define a promising class of materials for implementation in commercial Organic Light Emitting Diodes (OLEDs). Their successful application requires an understanding and control of the microscopic TADF dynamics by the complementary host material, in particular its polarity and rigidity. However, the distinct local host emitter interactions and their consequences, e.g. on the dihedral conformation or the emerging charge transfer states, are often obscured by averaging and superimposed effects of the molecular ensemble for a given host. Hence, we introduce single molecule spectroscopy as a powerful tool for uncovering the relevant host-emitter interactions at the molecular level. Our studies on the donor-acceptor type emitter TXO-TPA embedded in amorphous PMMA, (semi-)crystalline UGH-3 and polar DPEPO reveal distinct single-photon emission properties, characteristic for the respective host and clearly discernible by antibunching, bunching and intensity histograms of the correlated photon statistics as well as by the individual spectral emission. Disclosing such fundamental relations on the single molecule level marks an important step towards understanding specific host-emitter interactions and their application in future TADF-based OLED technologies.

CPP 25.6 Wed 10:45 H 0111

Thiophene-based Polymers in Time Resolved Photoelectron Spectroscopy — ●TOBIAS REIKER¹, MAREK K. CHARYTON², KAMIL KOTWICA², ZITONG LIU³, DEQING ZHANG³, NICOLAS D. BOSCHER², and HELMUT ZACHARIAS¹ — ¹Center for Soft Nanoscience, University of Münster, Germany — ²Materials Research and Technology Department, Luxembourg Institute of Science and Technology, Esch-sur-Alzette, Luxembourg — ³Institute of Chemistry, Chinese Academy of Science, Beijing, China

Thiophene-based polymers are promising candidates for solar cell, OLED or transistor (OFET) applications. An internal donor (D) - acceptor (A) system is formed by coupling thiophene polymers with pyrrole chains. The charge transport behavior can be tuned by different alkyl side chains since they influence the electronic structure, HOMO

and LUMO level positions, and interchain interactions. With diketopyrrolopyrrole - thiophene (TDPP), diketopyrrolopyrrole - quaterthiophene (PDPP4T) and thienyl-diketopyrrolopyrrole-thieno-thiophene (PDPPTTT) we investigated the electronic dynamics of verified high hole-mobility organic semiconductors. We report results of temporally resolved photoemission studies of thiophene polymers on Silicon

substrates. Occupied electronic levels were analysed via static UPS. Dynamic 2PPE experiments were performed for the energetic position and dynamics of the unoccupied states. The systems were studied as deposited by spin coating as well as by oCVD with and without sidechains.