International Internship at the University of Arizona

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Country: United States of America (USA)
Institute: University of Arizona
Supervisor: Prof. Jean-Luc Brédas

Research

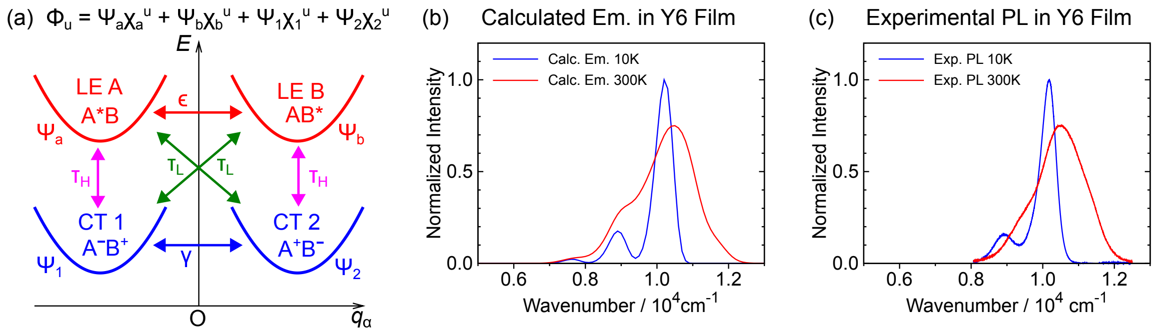
I visited the Prof. Jean-Luc Brédas' laboratory at the University of Arizona. He is famous as a professional in the theoretical/computational method for understanding and designing novel materials for organic/inorganic electronics and photonics. Recently, his research group focuses on the relation ship between molecular structure or morphology in aggregation phase and photovoltaic conversion process in organic photovoltaics (OPV). This is the reason why I chose his research group as my internship destination.

Old Chemistry Building in the University of Arizona. The Brédas' laboratory is on the third floor of this building.

I performed the conducting research with Prof. Jean-Luc Brédas, Prof. Veaceslav Coropceanu, and Dr. Saied Md Pratik during my internship. My research theme was "Four-State Model for Organic Photovoltaics." I and Prof. Coropceanu derived the theory for a vibronic model including two charge transfer (CT) states and two locally excited (LE) states as an electronic basis set, i.e., four-state model (The concept of this model is described in the following figure). This model is valuable to describe the complex vibronic structure in the aggregation phase of the OPV using non-fullerene acceptors, in which the CT states are formed between two acceptors[1,2], because the mixed vibronic states are considered exactly. Then, I made the Python program for calculating absorption and emission spectra of the materials for the OPV based on this model. This model well reproduced the spectral lineshapes and temperature dependences of the well-known acceptor materials for the efficient OPV, Y6 and ITIC (Our paper will be published soon). Here, the Y6 neat film is especially known to show the characteristic temperature dependence in the photoluminescence (PL) spectrum.

In the first month, I studied about the prior theories for the vibronic model in mixed-valence systems.[3,4] Then, in the second month, I put this into the framework of the crude adiabatic (CA) representation, constructing two-LE-state model, which is the vibronic model including two LE states. Here, I found that the CA representation was effective to describe the vibronic structures of the mixed vibronic states compared to the Born–Oppenheimer representation. The two-LE-state model could reproduce the lineshape and temperature dependence of the PL spectrum in the ITIC film, in which the Jahn–Teller distortion is caused between two ITICs.[1] However, two-LE-state model could not describe the characteristic temperature dependence in the PL spectrum of the Y6 film. This was considered to be because the PL of Y6 occurs from the CT states under the LE states.[2] Thus, I and Prof. Coropceanu introduced the electronic coupling between the LE and CT states into two-LE-state model, constructing the four-state model.

In the third to fifth months, we derived the four-state model. At first, this model could not reproduce the temperature dependence in the Y6 PL well. I found this was because certain important vibrational-modes and those vibronc couplings were ignored (Such modes could be ignored in the previous studies[3,4]). Finally, the four-state model was completed two weeks before I returned to Japan. The result of the four-state model is shown in the following figures.



(a) Concept of the four-state model. Φ_u is the vibronic wavefunction. Ψ_i $(i = a, b, 1, 2)$ is the electronic wavefunction, whereas χ_i^u is the vibrational wavefunction. (b) Calculated emission and (c) experimental PL spectra in the Y6 film. The calculated spectra reproduce both of the lineshape and temperature dependence in the experiments.

My life in Tucson

I stayed in the residential area located in the north of Tucson, which is called 'Winter Haven.' In summer, the temperature in Tucson is high, reaching to 40 °C. The humidity is quite low, giving it the feel of a true desert city. If you do not bring a lot of water, you will dry out immediately. From autumn to winter, it is warm enough (about 20 °C) to go outside in just a shirt during the day. In contrast, it is very cold at night (about 3 °C). There is almost no rain throughout the year. The fauna there is much different from that in Japan, and there are cacti growing all over the town.

My room.

My apartment was located 7 km north of the university and it took 30 minutes from home to the campus by my bicycle. Veronique Brédas, a daughter of Prof. Brédas, owned it. The residential area, i.e., the Winter Haven, holds big festivals every year on Halloween and Christmas. Especially the Christmas festival is huge and lasts for two weeks. The Winter Haven decked out in Christmas decorations was spectacular (See the following figure). On the other hand, there are very few entertainment facilities north of Tucson. For example, the nearest movie theater is 10 kilometers away from my apartment. Thus, I often spent my days off at home.

Tucson is a town surrounded by mountains on three sides, west, north, and east, like Kyoto. I enjoyed climbing Mt. Kimball in the Catalina mountains located north of Tucson. In the west of

Tucson, there is the Arizona-Sonora Desert Museum. I learned about the ecosystem of the desert in Arizona and Sonora states there (Sonora state is a state in Mexico).

Tucson is placed north of Nogales in Sonora state in Mexico. Thus, the culture in Tucson is influenced by Mexican culture a lot. In particular, tacos and other Mexican food are popular in Tucson. There are many Mexican immigrants in Tucson, and they speak Spanish everywhere.

Christmas festival in the Winter Haven.

Foot of Mt. Kimball.

Tacos made by me.

Acknowledgement

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Picture of a farewell party for me.

Reference

1. T. Zaima *et al.*, *J. Phys. Chem. Lett.* **14**, 9706 (2023).
2. S. Mahadevan *et al.*, *Nature Commun.* **15**, 2393 (2024).
3. K. Y. Wong and P. N. Schatz, *Prog. Inorg. Chem.* **28**, 369 (2009).
4. V. Coropceanu *et al.*, *J. Am. Chem. Soc.* **124**, 10519 (2002).