Assemble perfluoroalkylated aromatic molecules into donor-acceptor co-crystals for organic semiconductor materials

Background. The specific aims of this project are to: 1) assemble perfluoroalkylated aromatic molecules together with non-fluorinated aromatic molecules into organic semiconducting materials with specific solid state structures and function through co-crystallization processes; 2) advance our fundamental understanding of the correlation among molecular structure, intermolecular interactions, solid-state structures, and bulk material function; and 3) train students to solve complex problems in materials chemistry.

One of the significant challenges in developing high performance organic semiconductor materials is how to controllably transform molecular structures into desired solid-state structures with specific solid state packing motif, for example, lamellar stacked molecular packing motif.[1-14] Our previous work on rational design of perfluoroalkylated aromatics and heteroaromatics resulted in a library of over fifty new perfluoroalkylated aromatic molecules in which majority of them forms lamellar p-p stacked molecular packing motif in the solid state.[15-19] These results also provide insight on how one can modulate the solid-state structures for this type of perfluoroalkylated polyaromatic hydrocarbon (R_f-PAH) molecules through fine tuning the stereo-electronic properties at the molecular level. These findings promote us to hypothesize that a new type of donor-acceptor materials between R_f-PAHs (acceptor) and PAHs (donor) with well-organized and semi-predictable solid state packing motif can be achieved through co-crystallization approaches.

Research Approach. We plan to 1) utilize our existing R_f-PAHs and available PAHs to grow co-crystals of R_f-PAH:PAH under various conditions including using different pairs of R_f-PAH and PAH compounds, different solvents, at different temperatures, and with various crystal growth methods; 2) determine the crystal structures with single crystal x-ray diffraction method; 3) analyze intermolecular interactions through computational chemistry approaches (e.g. dispersion-corrected DFT method). We expect to *1)* identify Rf-PAH and PAH pairs that form p-p stacked lamellar structures in solid-state; *2)* gain insight into tuning weak non-covalent intermolecular interactions to design new donor-acceptor semiconductor materials with p-p stacked lamellar structures; and *3)* train students the skills for solving complex problems in materials science.

References

1. Boterashvili, M.; Lahav, M.; Shankar, S.; Facchetti, A.; van der Boom, M. E., On-Surface Solvent-Free Crystal-to-Co-crystal Conversion by Non-Covalent Interactions. *J. Am. Chem. Soc.* **2014,** *136* (34), 11926-11929.
2. Guerrini, M.; Valencia, A. M.; Cocchi, C., Long-range order enhances charge transfer in donor/acceptor co-crystals. *arXiv.org, e-Print Archive, Condensed Matter* **2021**, 1-31.
3. Hu, P.; Du, K.; Wei, F.; Jiang, H.; Kloc, C., Crystal Growth, HOMO-LUMO Engineering, and Charge Transfer Degree in Perylene-FxTCNQ (x = 1, 2, 4) Organic Charge Transfer Binary Compounds. *Crystal Growth & Design* **2016,** *16* (5), 3019-3027.
4. Hutchins, K. M.; Unruh, D. K.; Verdu, F. A.; Groeneman, R. H., Molecular Pedal Motion Influences Thermal Expansion Properties within Isostructural Hydrogen-Bonded Co-crystals. *Crystal Growth & Design* **2018,** *18* (2), 566-570.

5. Khan, A.; Wang, M.; Usman, R.; Sun, H.; Du, M.; Xu, C., Molecular Marriage via Charge Transfer Interaction in Organic Charge Transfer Co-Crystals toward Solid-State Fluorescence Modulation. *Crystal Growth & Design* **2017,** *17* (3), 1251-1257.
6. Liu, C.-H.; Niazi, M. R.; Perepichka, D. F., Strong Enhancement of π-Electron Donor/Acceptor Ability by Complementary DD/AA Hydrogen Bonding. *Angewandte Chemie, International Edition* **2019,** *58* (48), 17312-17321.
7. Reichenbaecher, K.; Suess, H. I.; Hulliger, J., Fluorine in crystal engineering-"the little atom that could". *Chem. Soc. Rev.* **2005,** *34* (1), 22-30.
8. Salzillo, T.; Masino, M.; Kociok-Kohn, G.; Di Nuzzo, D.; Venuti, E.; Della Valle, R. G.; Vanossi, D.; Fontanesi, C.; Girlando, A.; Brillante, A.; Da Como, E., Structure, Stoichiometry, and Charge Transfer in Cocrystals of Perylene with TCNQ-Fx. *Crystal Growth & Design* **2016,** *16* (5), 3028-3036.
9. Sherman, J. B.; Moncino, K.; Baruah, T.; Wu, G.; Parkin, S. R.; Purushothaman, B.; Zope, R.; Anthony, J.; Chabinyc, M. L., Crystalline Alloys of Organic Donors and Acceptors Based on TIPS-Pentacene. *Journal of Physical Chemistry C* **2015,** *119* (36), 20823-20832.
10. Singha, S.; Jana, R.; Mondal, R.; Ray, P. P.; Bag, P. P.; Gupta, K.; Pakhira, N.; Rizzoli, C.; Mallick, A.; Kumar, S.; Saha, R., Photo-responsive Schottky diode behavior of a donor-acceptor co-crystal with violet blue light emission. *CrystEngComm* **2021,** *23* (19), 3510-3523.
11. Zhang, J.; Geng, H.; Virk, T. S.; Zhao, Y.; Tan, J.; Di, C.-a.; Xu, W.; Singh, K.; Hu, W.; Shuai, Z.; Liu, Y.; Zhu, D., Sulfur-Bridged Annulene-TCNQ Co-Crystal: A Self-Assembled Molecular Level Heterojunction" with Air Stable Ambipolar Charge Transport Behavior. *Advanced Materials (Weinheim, Germany)* **2012,** *24* (19), 2603-2607.
12. Zhang, J.; Zhao, G.; Qin, Y.; Tan, J.; Geng, H.; Xu, W.; Hu, W.; Shuai, Z.; Zhu, D., Enhancement of the p-channel performance of sulfur-bridged annulene through a donor-acceptor co-crystal approach. *Journal of Materials Chemistry C: Materials for Optical and Electronic Devices* **2014,** *2* (42), 8886-8891.
13. Zhu, W.; Yi, Y.; Zhen, Y.; Hu, W., Precisely Tailoring the Stoichiometric Stacking of Perylene-TCNQ Co-Crystals towards Different Nano and Microstructures with Varied Optoelectronic Performances. *Small* **2015,** *11* (18), 2150-2156.
14. Zhu, W.; Zheng, R.; Zhen, Y.; Yu, Z.; Dong, H.; Fu, H.; Shi, Q.; Hu, W., Rational design of charge-transfer interactions in halogen-bonded co-crystals toward versatile solid-state optoelectronics. *J. Am. Chem. Soc.* **2015,** *137* (34), 11038-11046.
15. BaniKhaled, M. O.; Becker, J. D.; Koppang, M.; Sun, H., Perfluoroalkylation of Square-Planar Transition Metal Complexes: A Strategy To Assemble Them into Solid State Materials with a π-π Stacked Lamellar Structure. *Crystal Growth & Design* **2016,** *16* (4), 1869-1878.
16. BaniKhaled, M. O.; Mottishaw, J. D.; Sun, H., Steering Power of Perfluoroalkyl Substituents in Crystal Engineering: Tuning the π-π Distance While Maintaining the Lamellar Packing Motif for Aromatics with Various Sizes of π-Conjugation. *Crystal Growth & Design* **2015,** *15* (5), 2235-2242.
17. Putta, A.; Mottishaw, J. D.; Wang, Z.; Sun, H., Rational Design of Lamellar π-π Stacked Organic Crystalline Materials with Short Interplanar Distance. *Crystal Growth & Design* **2014,** *14* (1), 350-356.
18. Sun, H.; Kramer, J. H., Perfluoroalkylated PAH n-type semiconductors: theory and experiment. **2017**, 155-176.
19. Sun, H.; Tottempudi, U. K.; Mottishaw, J. D.; Basa, P. N.; Putta, A.; Sykes, A. G., Strengthening π-π Interactions While Suppressing Csp2-H···π (T-Shaped) Interactions via Perfluoroalkylation: A

Crystallographic and Computational Study That Supports the Beneficial Formation of 1-D π-π Stacked Aromatic Materials. *Crystal Growth & Design* **2012,** *12* (11), 5655-5662.