NANYANG TECHNOLOGICAL UNIVERSITY SINGAPORE

School of Physical and Mathematical Sciences
College of Science

# CBC SEMINAR ANNOUNCEMENT


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## Ultrafast Excited State Dynamics of Twisted Aromatics

Self-assembling of organic chromophoric systems into elegant supramolecular architectures with emergent properties has received prodigious attention in recent years.[1] The notion of 'emergence upon assembly' is evidenced in the unusual photoexcited state dynamics exhibited by chromophoric assemblies. In the first example, a naphthalene-naphthalimide donor-acceptor (D-A) dyad assembled into segregated D-A stacks in the crystalline state. The photo-induced charge separated state in the aggregate state lasts 10,000 times longer than the monomeric dyad. The femtosecond transient absorption spectra depicted the spectroscopic signature for naphthalene dimer radical cation indicating the migration of charges through the stacks.[2] In the second example, we report the crystalline evidence for Greek cross-dipole (α=90°) stacking of 1,7-dibromoperylene-3,4,9,10-tetracarboxylic tetrabutylester (PTE-$Br_2$) displaying null excitonic coupling and thereby monomeric optical behavior. Additionally, the semi-classical Marcus theory of charge-transfer rates predicted a selective hole transport phenomenon in the orthogonally stacked PTE-$Br_2$.[3] In the third example, we showcase a radial assembly of 1,8-dibromonaphthalene(2,6-diisopropylphenyl)imide ($NIBr_2$) in crystalline phase driven by hexabromine synthon.[4] $NIBr_2$ exhibits ultrafast intersystem crossing[5] and solid-state room temperature phosphorescence. We believe the fundamental understanding of noncovalent interactions dictating the unorthodox assembly of chromophores[6] and probing of emergent properties are paramount for the rational design and construction of robust functional materials.

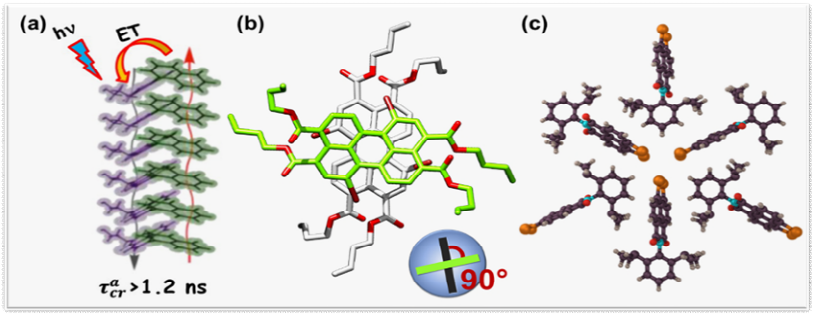


**Figure**. Representative strategies adopted in our group to spatially organize organic chromophores for emergent properties.

**References:**


1. Cheriya, R. T.; Mallia, A. R.; Hariharan, M. *Energy Environ. Sci.* **2014**, *7*, 1661.
2. Mallia, A. R.; Salini, P. S.; Hariharan, M. *J. Am. Chem. Soc.* **2015**, 137, *50*, 15604.
3. Sebastian, E.; Philip, A. M.; Benny, A.; Hariharan, M. *Angew. Chem., Int. Ed.* **2018**, *57*, 15696.
4. Niyas, M. A.; Ramakrishnan, R.; Vijay, V.; Sebastian, E.; Hariharan, M. *J. Am. Chem. Soc.* **2019**, *141*, 4536.
5. Nagarajan, K.; Mallia, A. R.; Muraleedharan, K.; Hariharan, M. *Chem. Sci.* **2017**, *8*, 1776.
6. Ramakrishnan, R.; Niyas, M. A.; Lijina, M. P.; Hariharan, M. *Acc. Chem. Res.* **2019**, 52, ASAP


**Date:** 20th Friday 2019 (Friday)
**Time:** 2.30pm to 4.00pm
**Venue:** SPMS Graduate and Research Conference Room
**Host:** Associate Professor Edwin Yeow