Modelling Aggregation Induced Emission In Molecular Crystals

Rachel Crespo Otero
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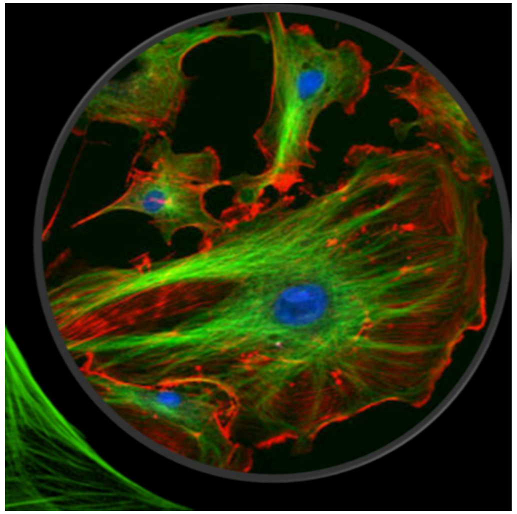
Queen Mary
University of London

Miguel Rachel Michael

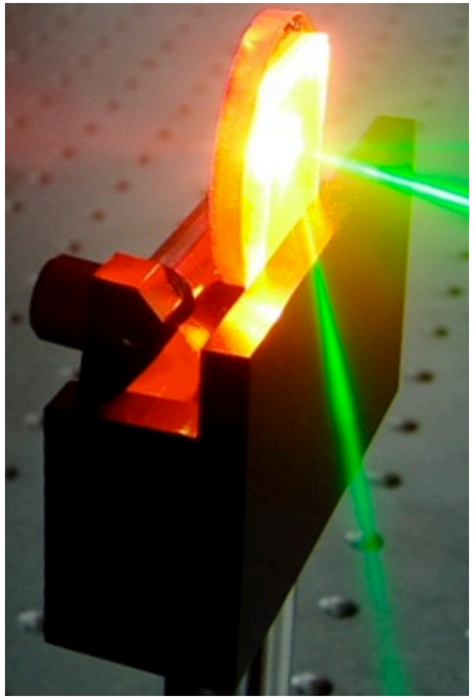
HIGHLY EMISSIVE ORGANIC MATERIALS

ORGANIC LIGHT - EMITTING DIODES (OLEDs)

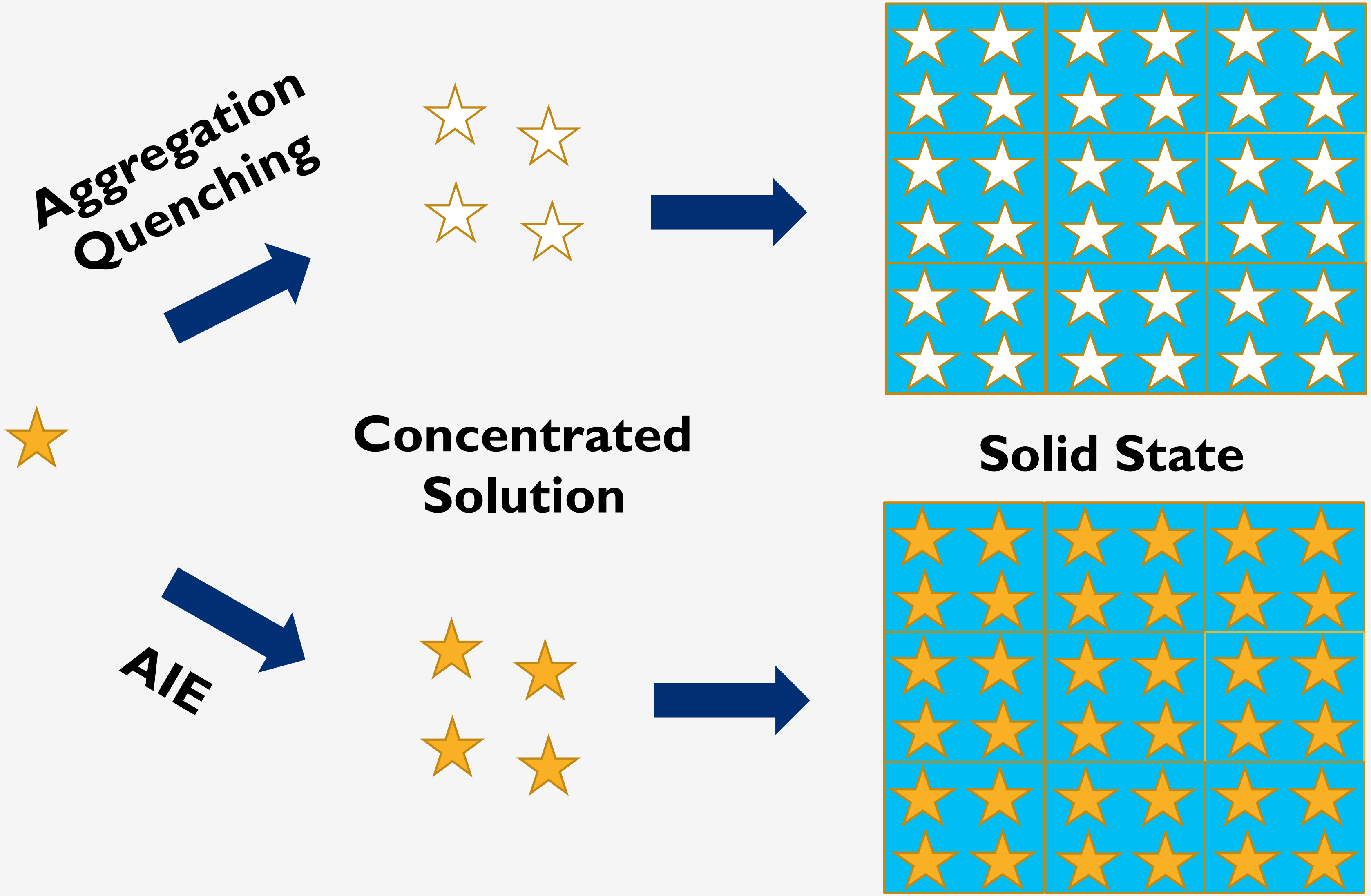
FLUORESCENSE BIOPROBES



ORGANIC LASERS

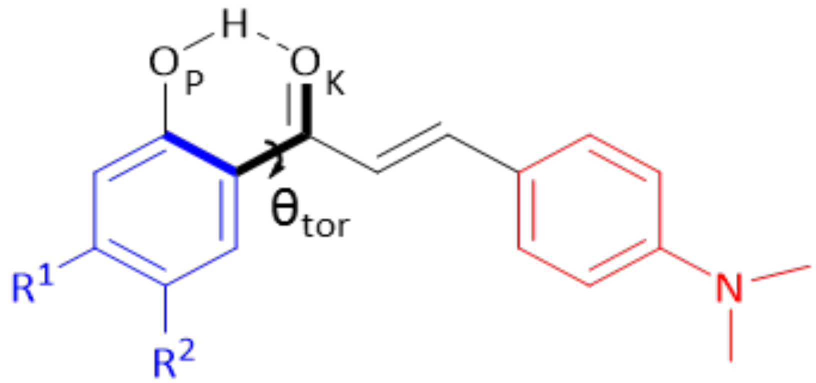


AGGREGATION INDUCED EMISSION (AIE)

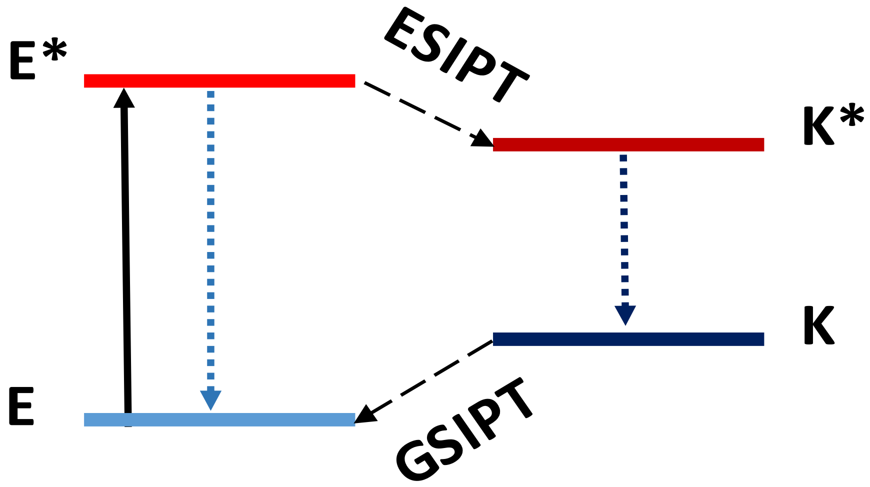


There is a lack of a fundamental understanding of structure–property relationships.

MODEL MATERIALS



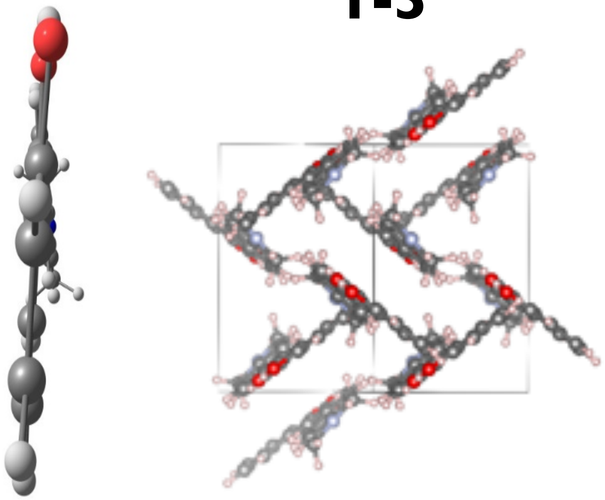
1: R^1=H, R^2= H;
2: R^1=CH_3, R^2= H,
3: R^1= OCH_3, R^2= H,
4: R^1=H, R^2= CH_3,
5: R^1=H, R^2= OCH_3



THE FOUR-LEVEL LASSER PHOTO-CYCLE

AGGREGATION INDUCED EMISSION: 2-HYDROXYLCHALCONE

1-3

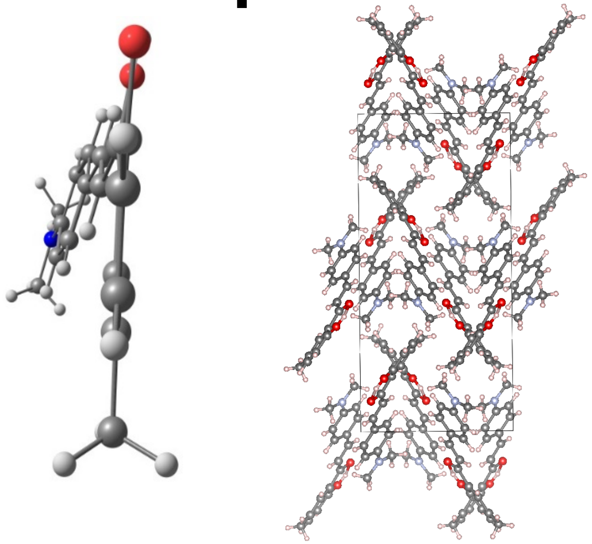


Planar ✓

Edge – Face Packing ✓

Emissive

4

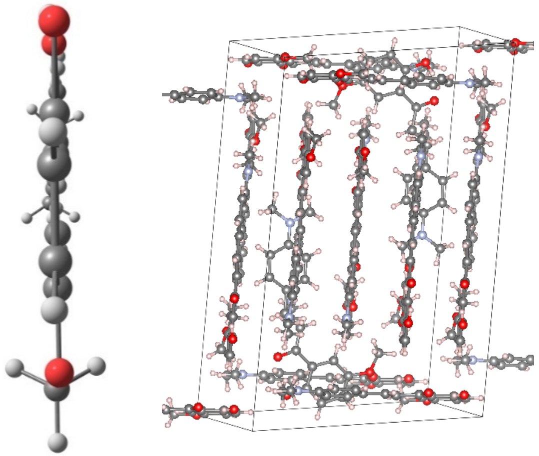


Distorted

Edge – Face Packing ✓

Non-emissive

5



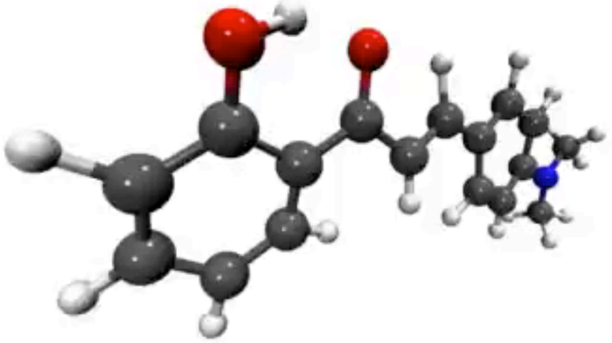
Planar ✓

Edge – Face Packing

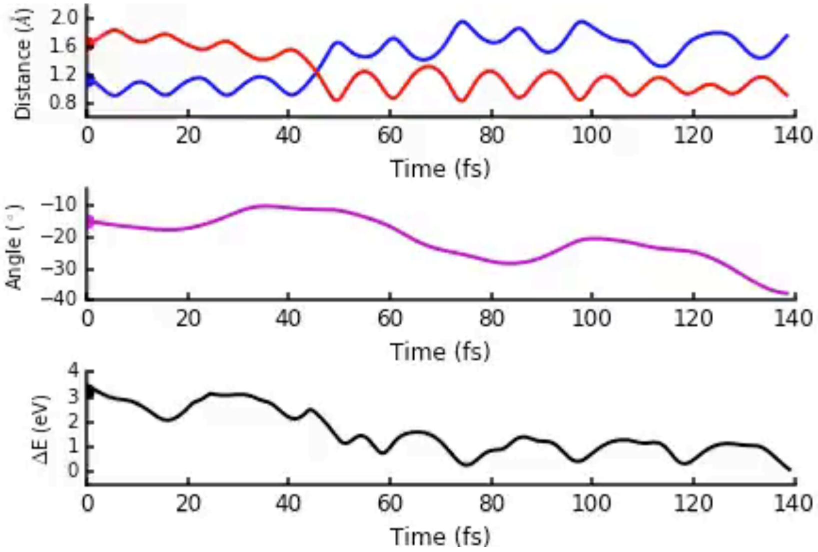
Non-emissive

S. Wang, X. Yan, Z. Cheng, H. Zhang, Y. Liu and Y. Wang, *Angew. Chemie - Int. Ed.*, 2015, 54, 13068.

NON-ADIABATIC DYNAMICS



ADC(2)/SV(P)



1:
$t_{ESIPT=}$ 47 fs

(E* 52%, K* 48%)

5:
$t_{ESIPT=}$ 27 fs

(E* 20%, K* 80%)

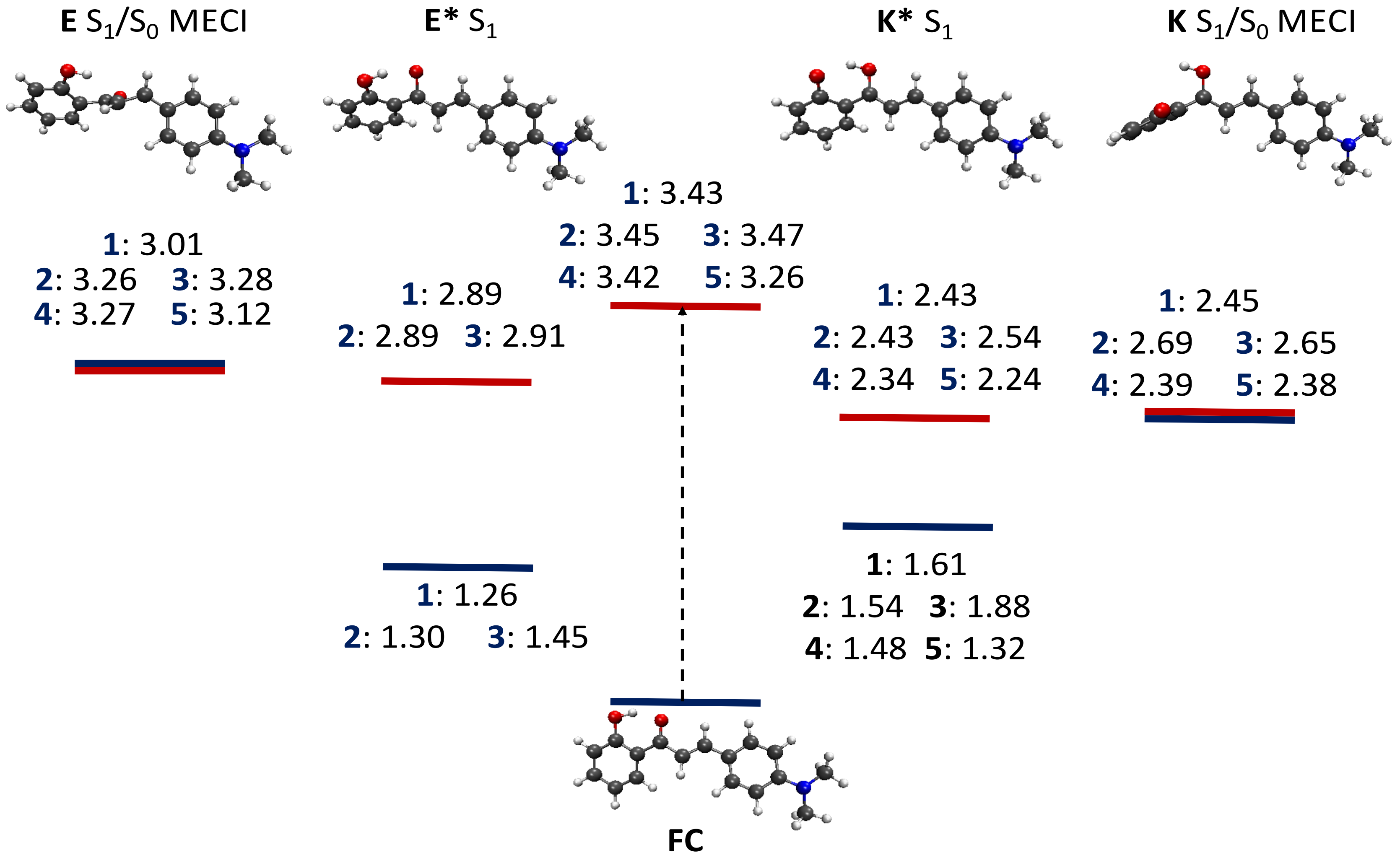
Trajectories (100 trajectories)

Dommett, M.; Crespo-Otero, R. *PCCP*. **2017**, 19, 2409.

M. Barbatti, G. Granucci, M. Ruckenbauer, F. Plasser, R. Crespo-Otero, J. Pittner, M. Persico and H. Lischka, *NEWTON-X: A package for Newtonian dynamics close to the crossing seam*, http://www.newtonx.org

EFFECT OF THE SUBSTITUENT

CC2/def2-TZVP



Dommett, M.; Crespo-Otero, R. *PCCP*. **2017**, 19, 2409.

DIMERS: EXCITONIC COUPLING

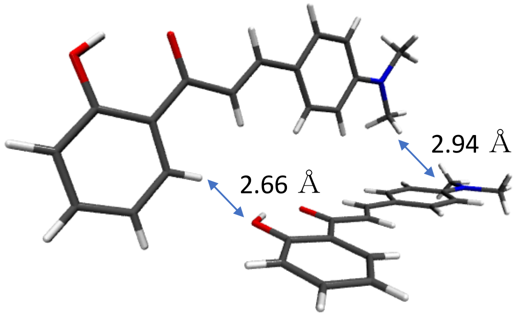
$$\mathbf{H}^D = \mathbf{C}\mathbf{H}^A\mathbf{C}^*$$

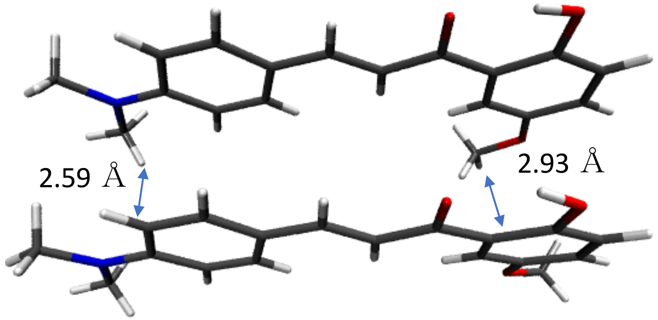
1

5

Head to Head
HH_1

J = 0.003 eV



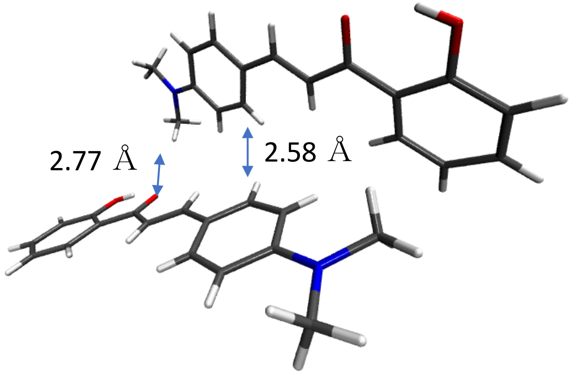


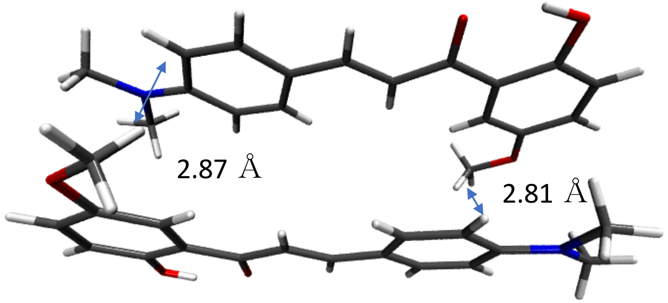
Head to Head
HH_5

J = 0.109 eV

Head to Tail
HT_1

J = 0.105 eV



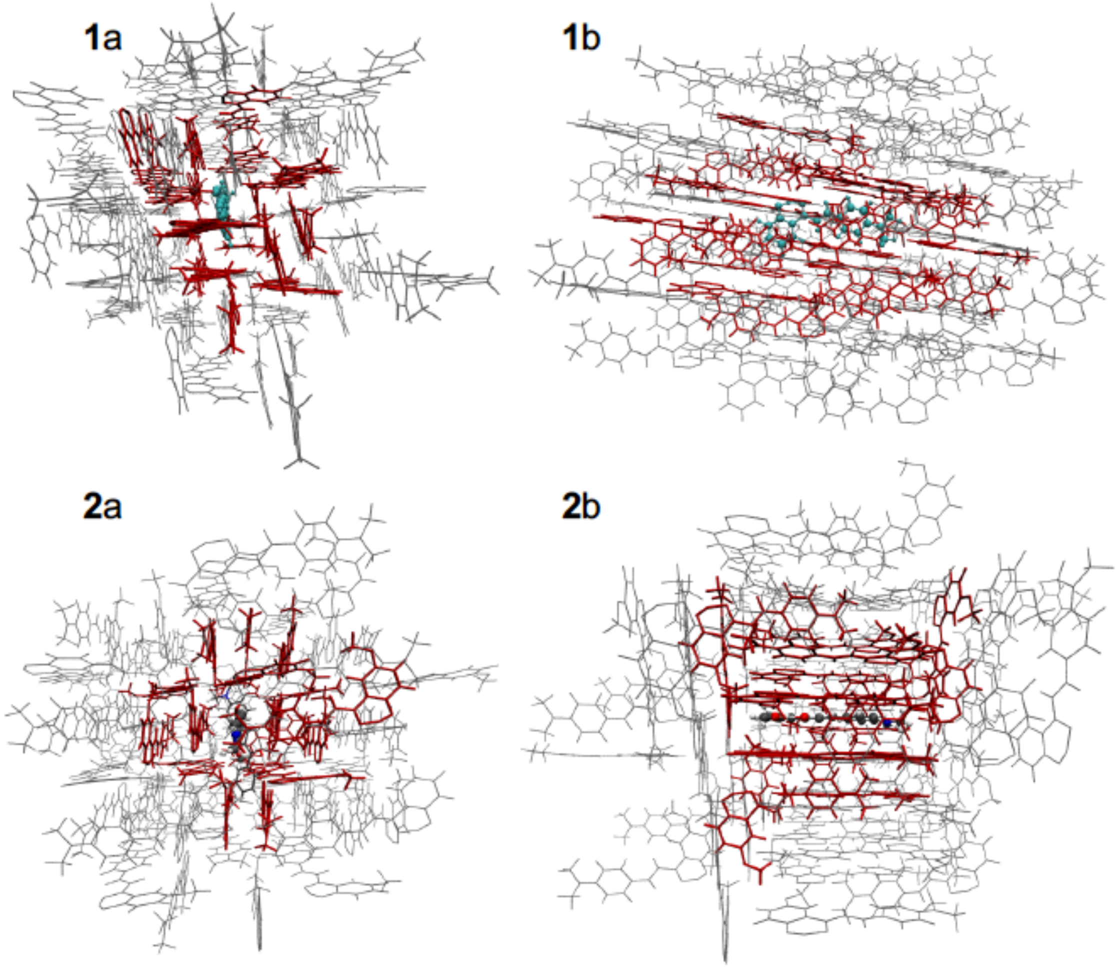


Head to Tail
HT_5

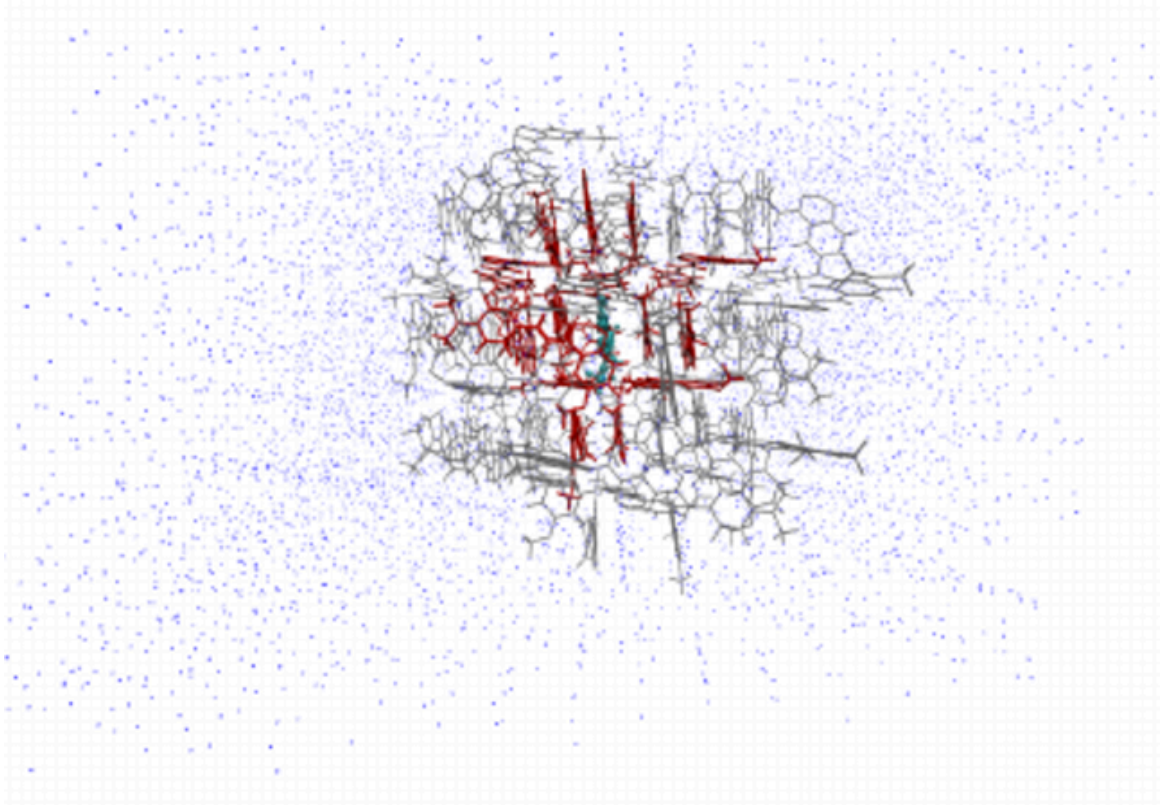
J = 0.150 eV

Method for the calculation of *J* proposed by Arago and Troisi (PRL 2015, 114, 1)

MODELS FOR THE CRYSTAL



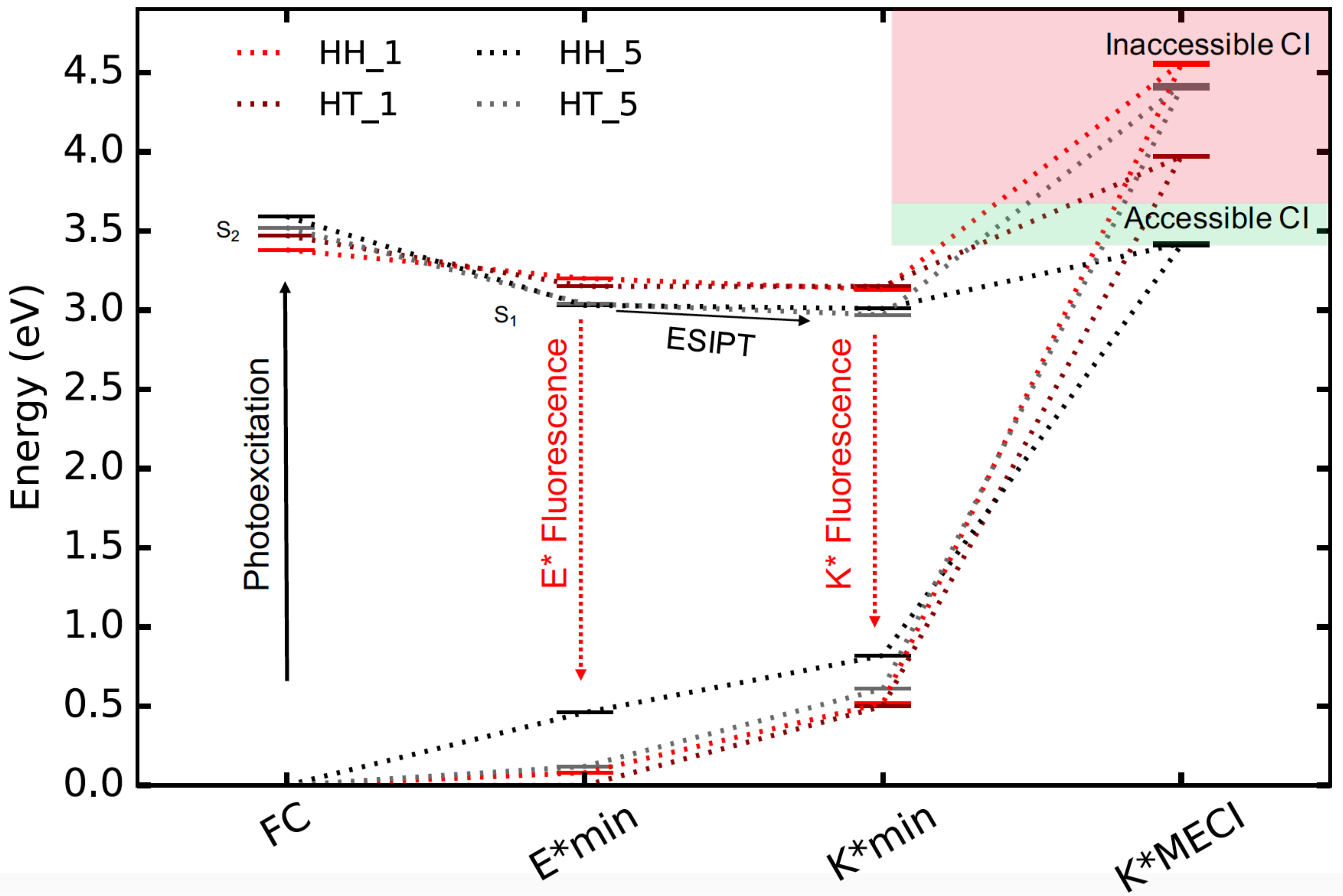
QM/MM (**ONIOM**), TDDFT-ωB97XD/6-311++G(d,p): AMBER
Conical intersections with CASSCF (12,11): AMBER



Crystal optimised with **PBE-D2** (Quantum Espresso)

QM/QM'
RESP charges

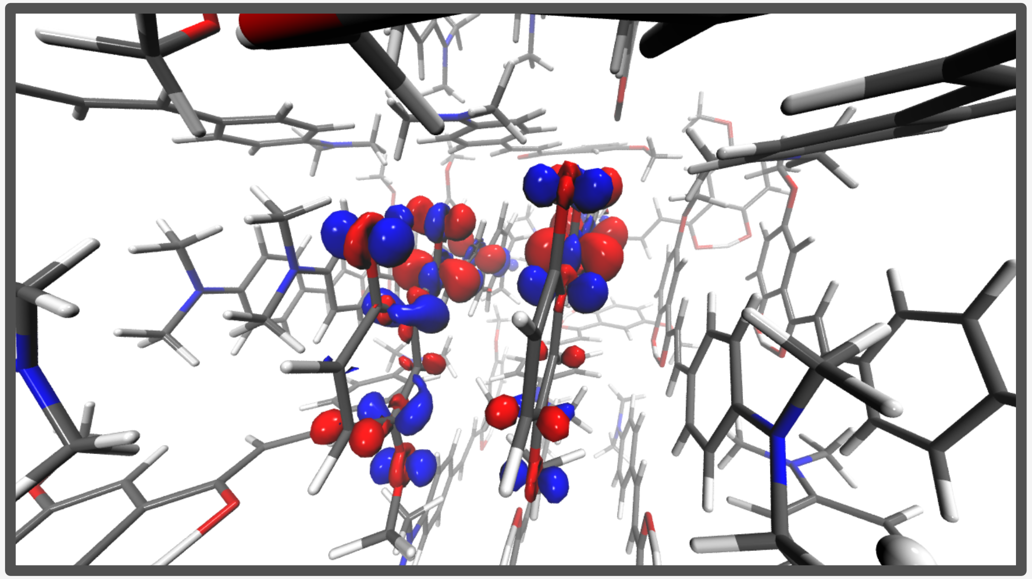
PHOTOCHEMISTRY IN THE CRYSTAL

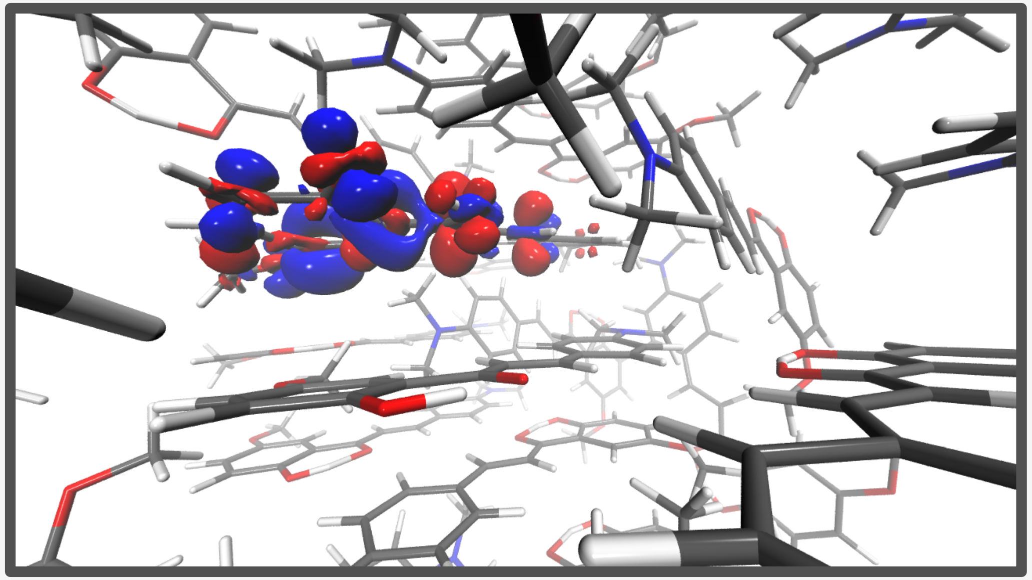


QM region:
dimers

Dommett, M.; Rivera, M.; Crespo-Otero, R. In preparation

S_1-S_0 ELECTRONIC DENSITIES





delocalised
Franck Condon
Geometry
(E E)

Red S_1
Blue S_0

localised
Franck Condon
Geometry
(K* E)

MODELLING AGGREGATION INDUCED EMISSION IN MOLECULAR CRYSTALS

- To model AIE, methods that take into account the excited states and the crystal environment are required.

- The crystal tends to increase the energy of the conical intersections (restricted access to the conical intersection model, for **HH_1**, **HT_1** and **HT_5**. For **HH_5**, the conical intersection is accessible.

- The mechanism involves localisation of the excitation followed by proton transfer, in agreement with the experimental emission data.