

MODELLING EXCITED STATES IN MOLECULAR CRYSTALS

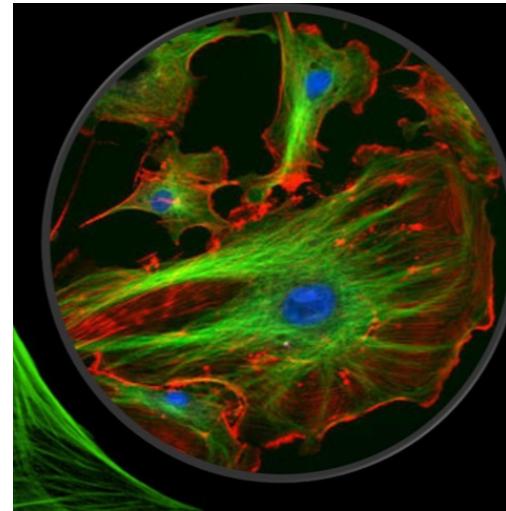
Rachel Crespo Otero

HIGHLY EMISSIVE ORGANIC MATERIALS

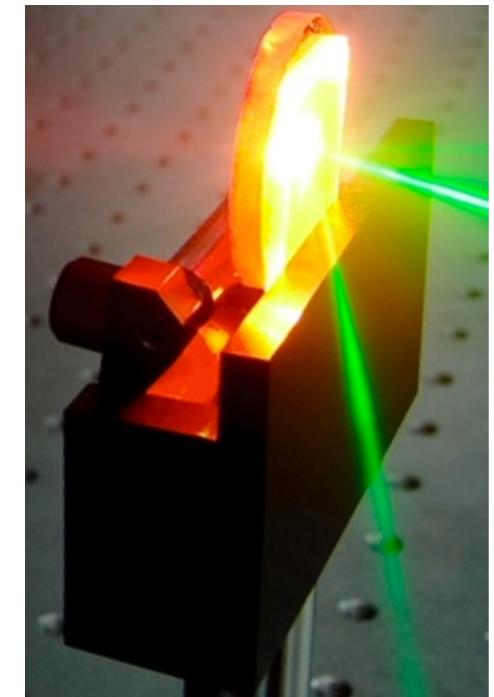
ORGANIC LIGHT - EMITTING DIODES (OLEDs)



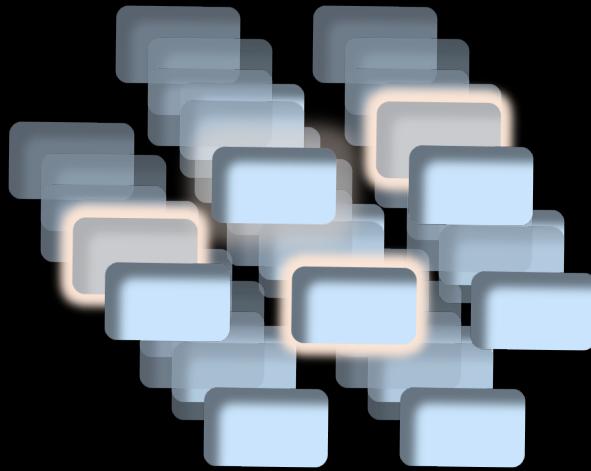
FLUORESCENCE BIOPROBES



ORGANIC LASERS



AGGREGATION INDUCED EMISSION (AIE)

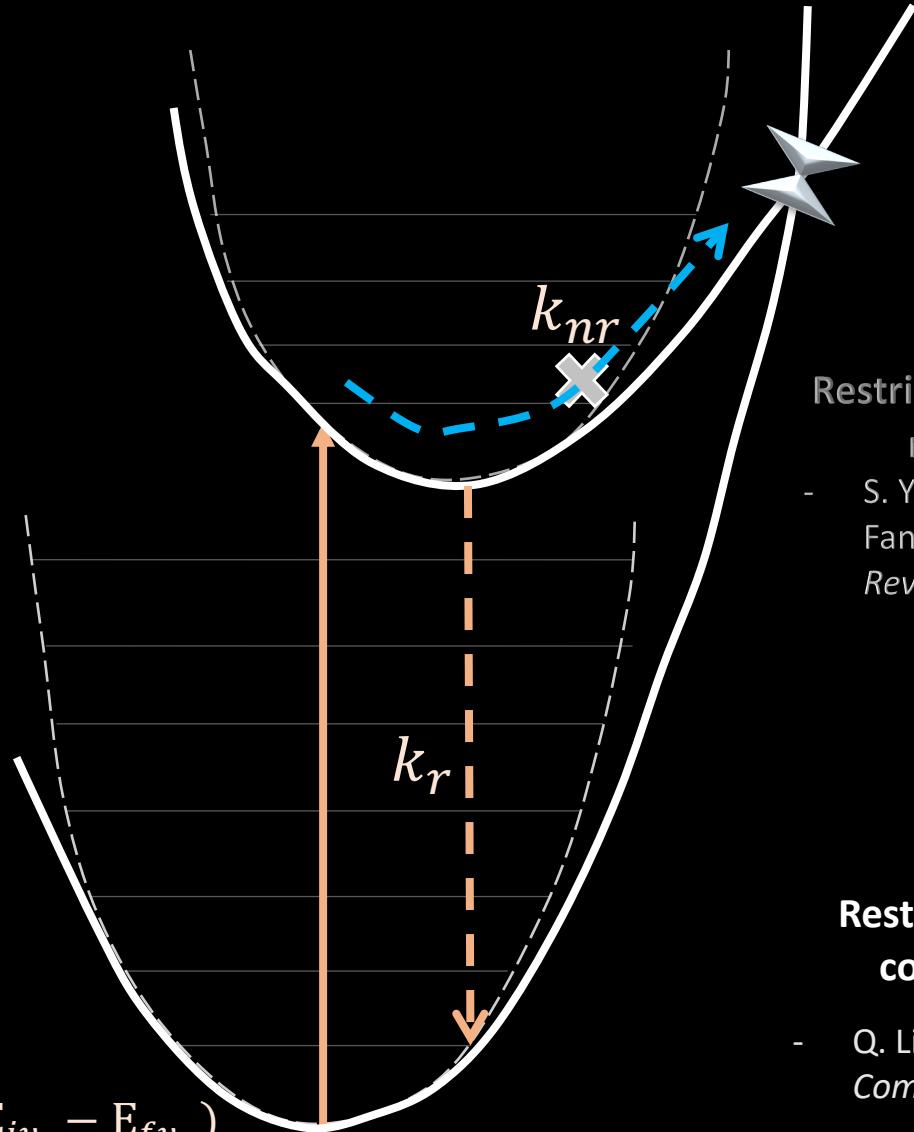


$$\Phi = \frac{k_r}{k_r + k_{nr}} \uparrow$$

**CONCENTRATED SOLUTION
SOLID STATE**

Fermi-Golden Rule

$$k_{nr} = \frac{2\pi}{\hbar} \sum_{v_i, v_f} P_{iv_i}(T) \left| \sum_k \langle \psi_f | \hat{\mathbf{P}}_k | \psi_i \rangle \langle \Theta_{fv_f} | \hat{\mathbf{P}}_k | \Theta_{iv_i} \rangle \right|^2 \delta(E_{iv_i} - E_{fv_f})$$



RIM/RIR

Restriction of intramolecular motions/rotations

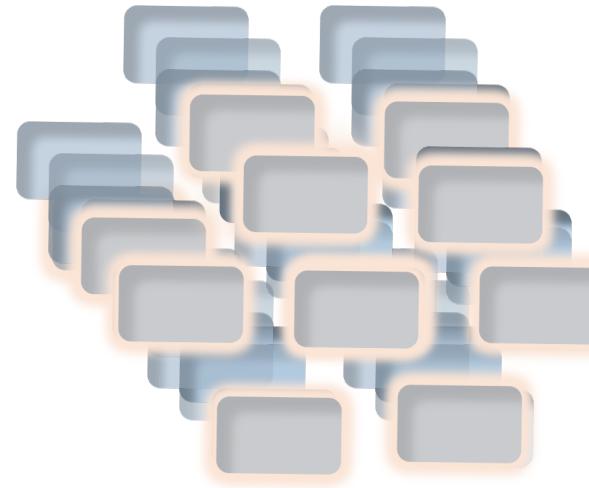
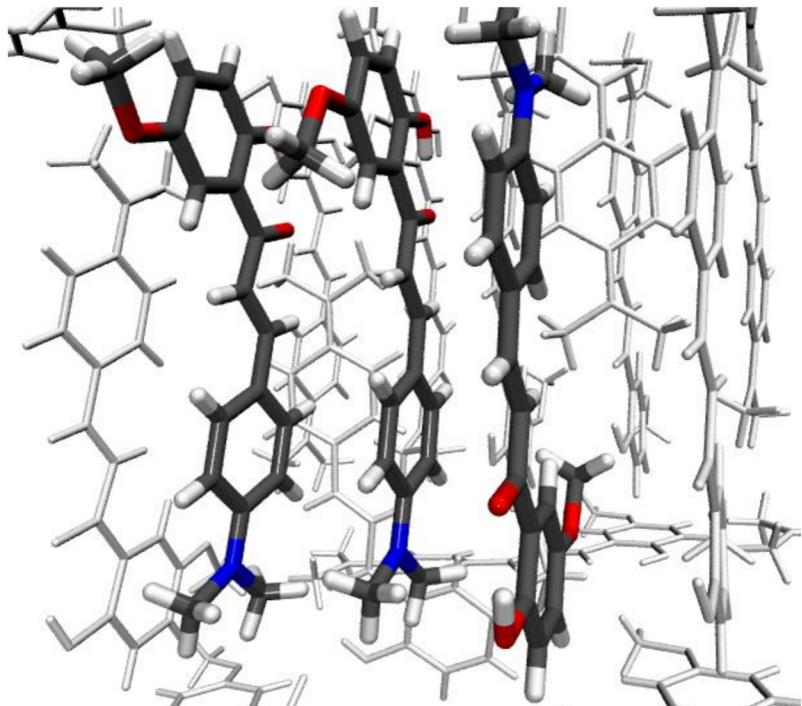
- S. Yin, Q. Peng, Z. Shuai, W. Fang, Y. H. Wang, Y. Luo, *Phys. Rev. B*. 2006, 73, 1

RACI

Restricted access to the conical intersection

- Q. Li and L. Blancafort, *Chem. Commun.*, 2013, 49, 5966

ORGANIC MOLECULAR CRYSTALS: SOLID STATE LUMINESCENT ENHANCEMENT



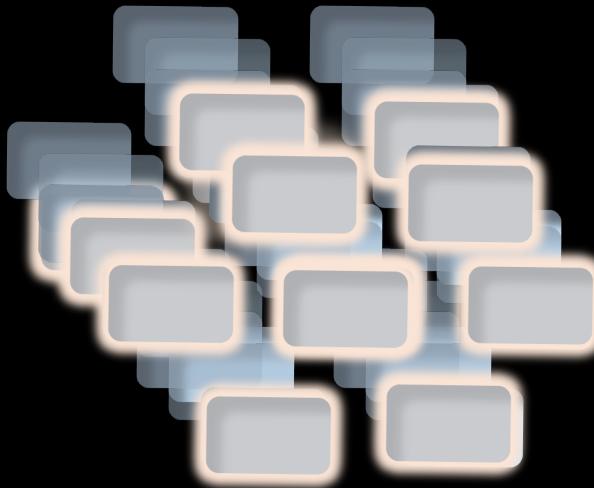
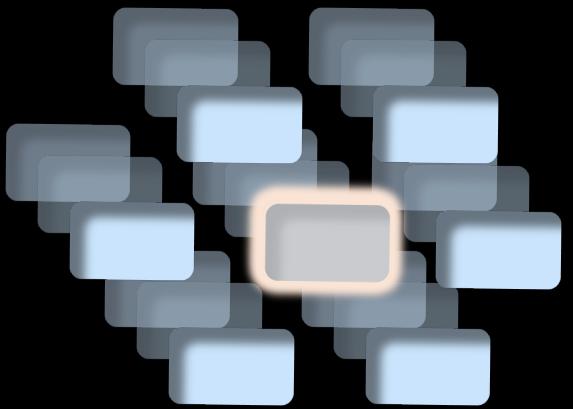
Molecules held by intermolecular forces

EXCITED STATES IN ORGANIC MOLECULAR CRYSTALS

LOCALISED

VS

DELOCALISED



EMBEDDING

PERIODIC

ELECTROSTATIC INTERACTIONS EWALD SUMMATION

$$V^{Ewald}(\mathbf{r}) = \sum_{\mathbf{L}_s} q_s \frac{\operatorname{erfc}(\gamma|\mathbf{r} - \mathbf{L} - \mathbf{R}_s|)}{|\mathbf{r} - \mathbf{L} - \mathbf{R}_s|} + \frac{4\pi}{v_c} \sum_{\mathbf{G} \neq \mathbf{0}} \frac{1}{G^2} e^{-G^2/4\gamma^2} \left[\sum_s q_s e^{i\mathbf{G}(\mathbf{r} - \mathbf{R}_s)} \right]$$

Real space

Reciprocal space

\mathbf{L} is for each lattice translation

\mathbf{s} for each site within one unit cell

\mathbf{G} is the reciprocal lattice translation

S. E. Derenzo, M. K. Klintenberg and M. J. Weber, *J. Chem. Phys.*, 2000, 112, 2074

M. Klintenberg, S. E. Derenzo and M. J. Weber, *Comput. Phys. Commun.*, 2000, 131, 120

EWALD EMBEDDING

Defects in ionic crystals,
NMR properties in molecular crystals

Array of 10^4 charges
Zone II (500 charges)

Ewald potential is
calculated
for zones I and II
(any dipole moment
is removed)

Zone III
(variable charges)

The charges in zone III are
changed to reproduce
the electrostatic potentials
in zones I and II

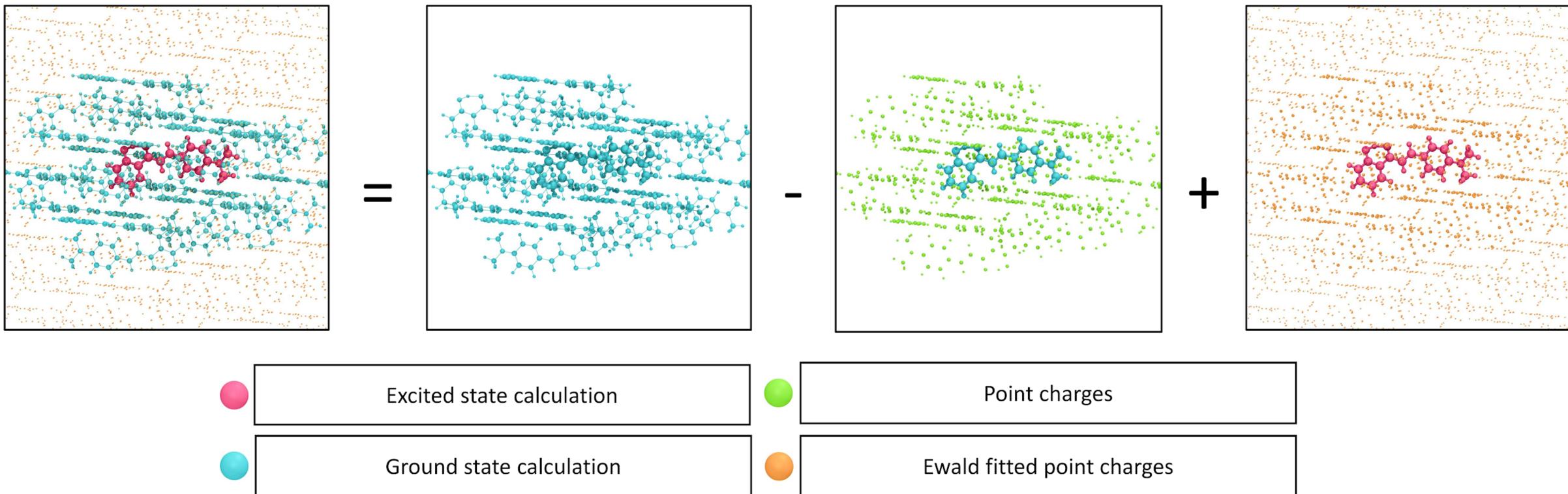
Zone II (buffer,
fixed charges)

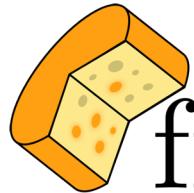
M. Klintenberg, S. E. Derenzo and M. J. Weber,
Comput. Phys. Commun., 2000, 131, 120

Zone I (QM,
fixed charges)

L. Wilbraham, C. Adamo, F. Labat and I. Ciofini,
J. Chem. Theory Comput., 2016, 12, 3316

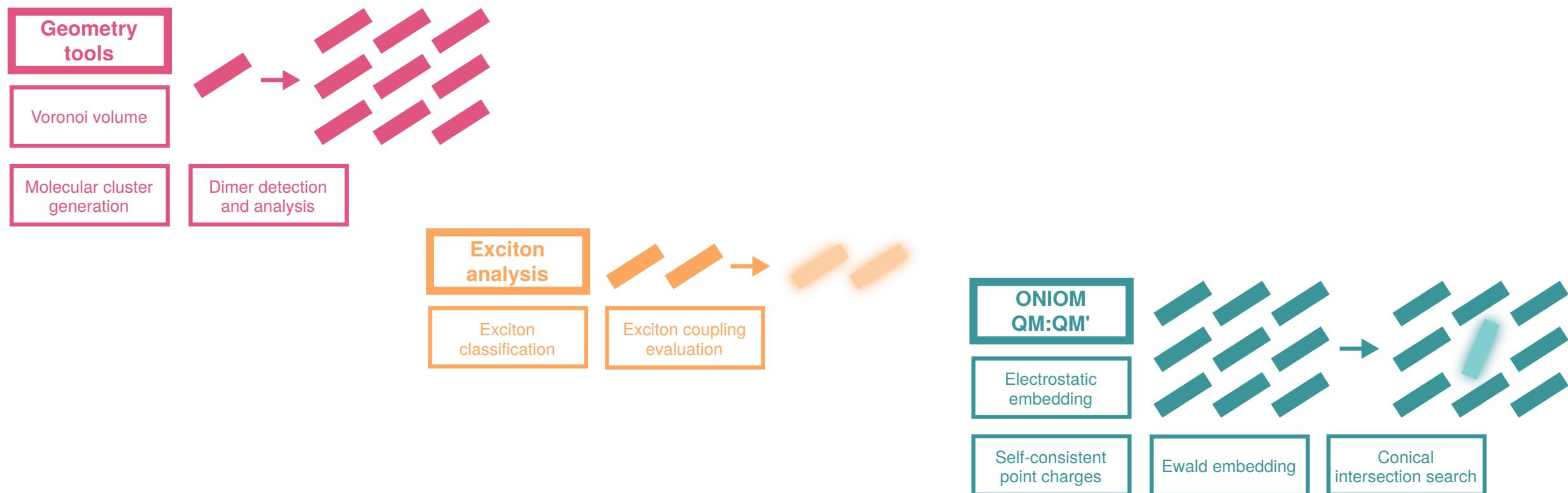
EWALD EMBEDDED CLUSTER MODEL





fromage

FRAMEWORK FOR MOLECULAR AGGREGATE EXCITATIONS

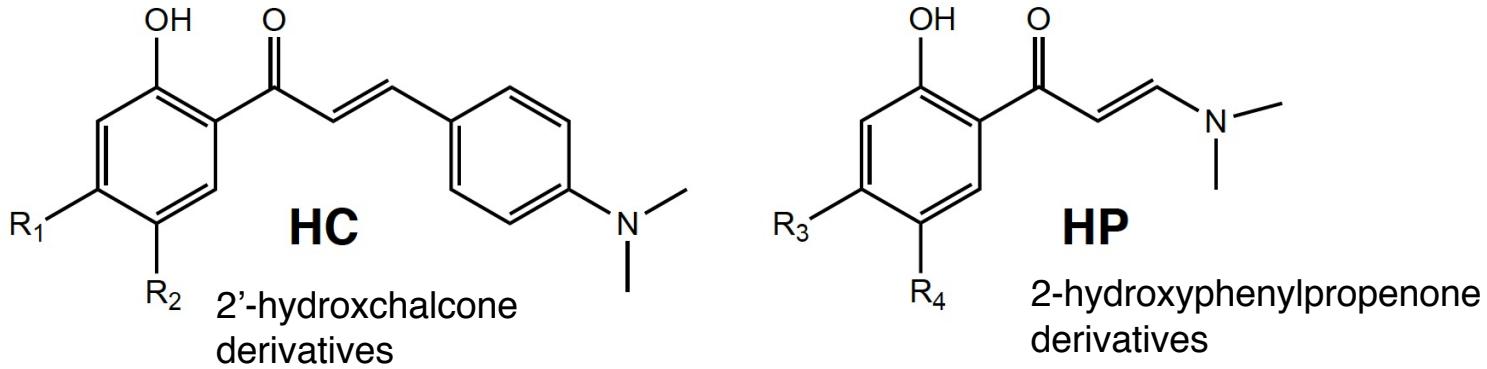


<https://github.com/Crespo-Otero-group/fromage>

Rivera, M; Dommett, M; and Crespo-Otero, R. *J. Chem. Theory Comput.* **2019**, 15, 2504

Rivera, M.; Dommet, M.; Sidat, A.; Rahim, W.; Crespo-Otero, R. *J. Comp. Chem.*, **2020**, 41, 1045

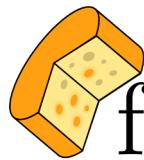
AIE IN INTRAMOLECULAR PROTON TRANSFER CHROMOPHORES



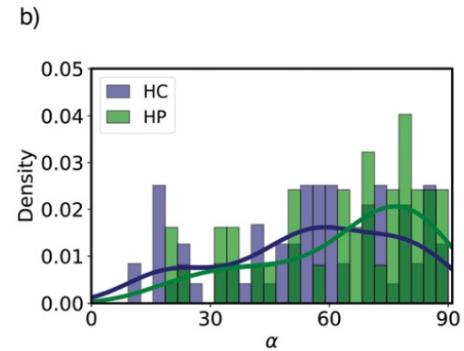
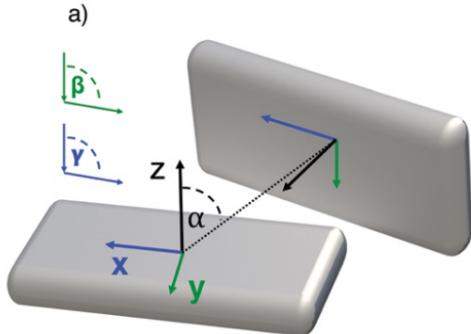
	R ₁	R ₂	Φ		R ₃	R ₄	Φ
HC1	H	H	0.32		HP1	H	0.74
HC2	CH ₃	H	0.25		HP2	F	0.84
HC3	OCH ₃	CH ₃	0.26		HP3	H	0.77
HC4	H	CH ₃	<0.01		HP4	H	0.72
HC5	H	OCH ₃	<0.01				
HC6	F	H	0.41				
HC7	H	F	0.10				

HC1: 50 % J-dimers, **HC5:** 34 % J-dimers, **HP1:** 50% J-dimers

X. Cheng, K. Wang, S. Huang, H. Zhang, H. Zhang and Y. Wang, *Angew. Chem., Int. Ed.*, **2015**, *54*, 8369. B. Tang, H. Liu, F. Li, Y. Wang and H. Zhang, *Chem. Commun.*, **2016**, *52*, 6577. X. Cheng, Y. Zhang, S. Han, F. Li, H. Zhang and Y. Wang, *Chem. Eur. J.*, **2016**, *22*, 4899

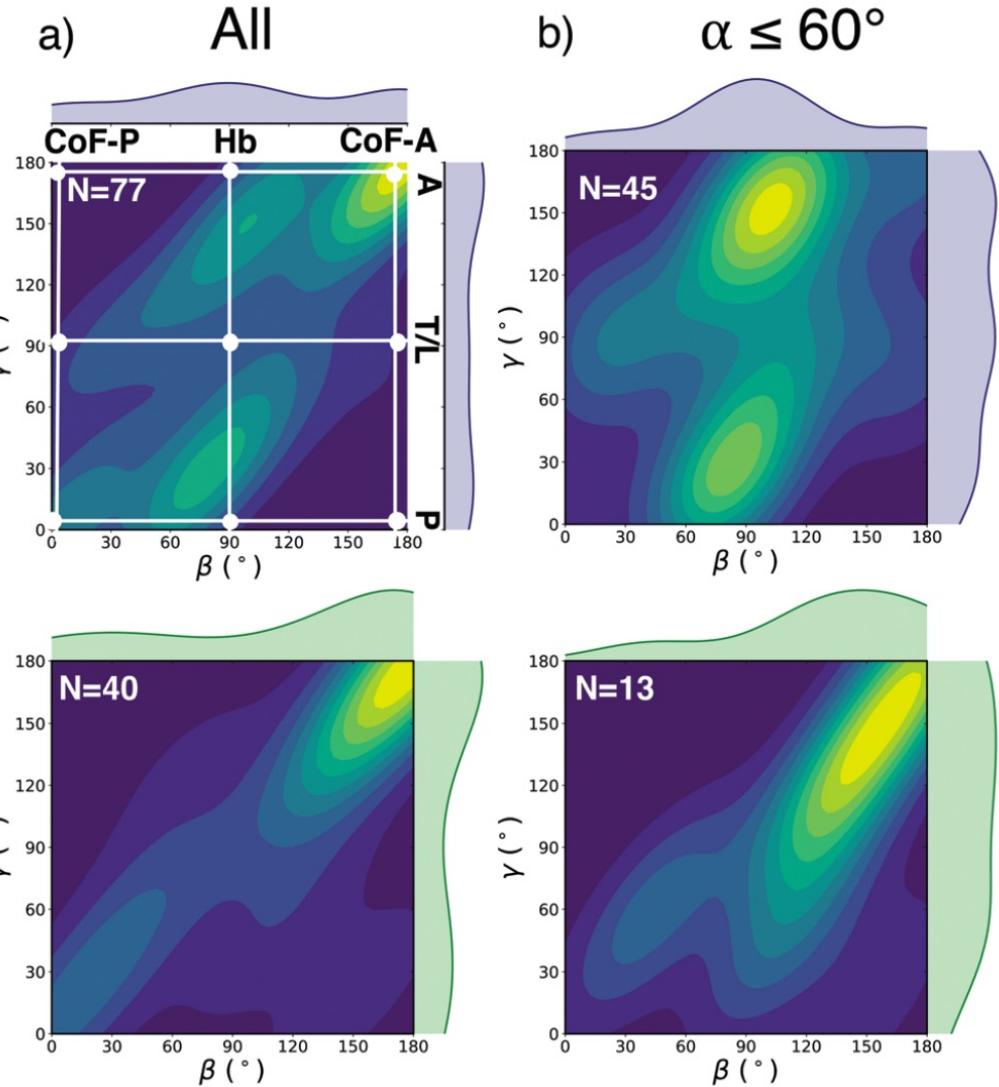


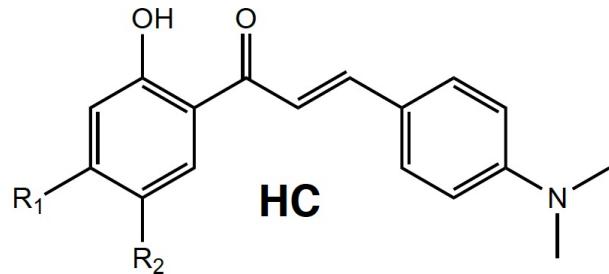
fromage



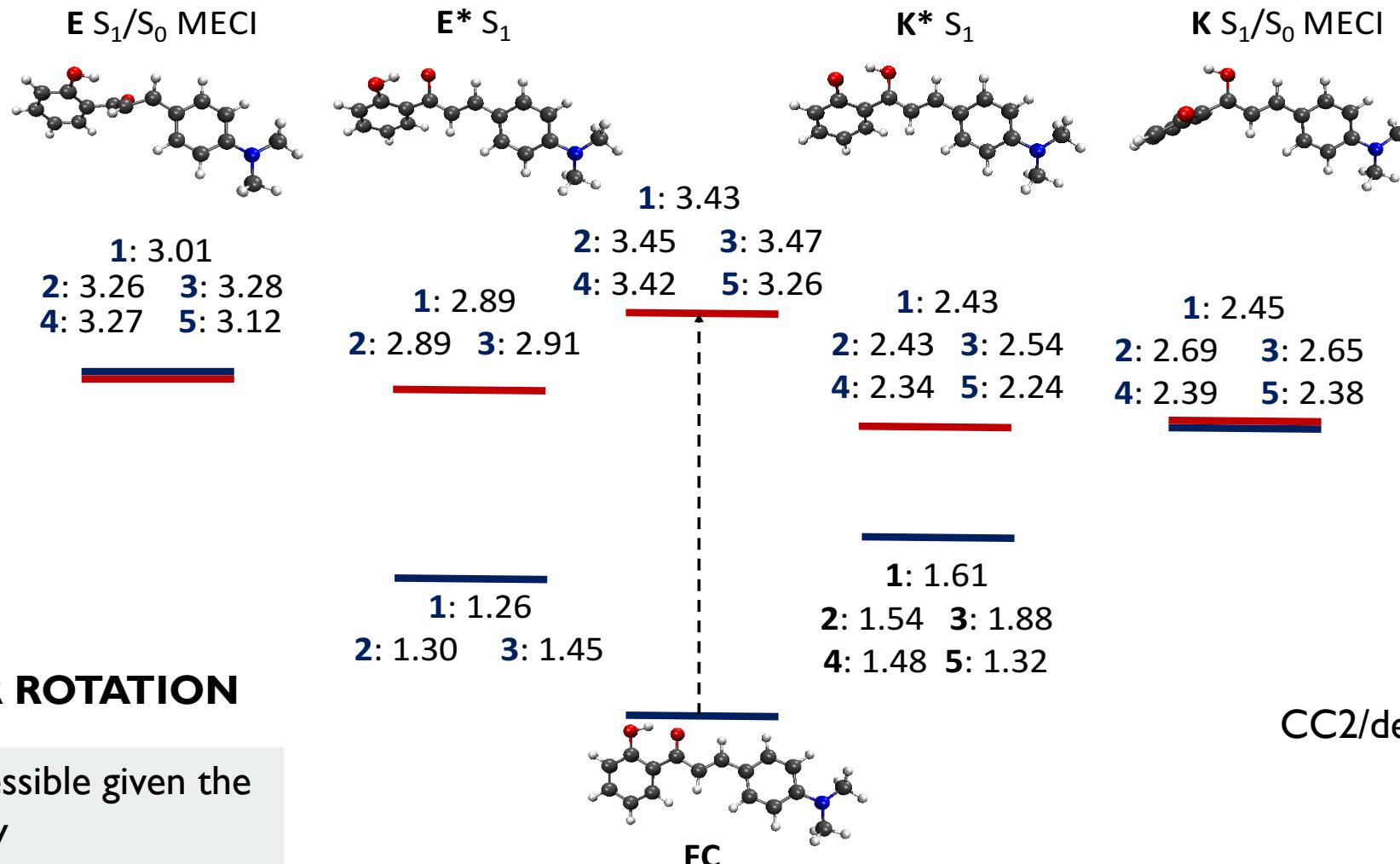
HC series → Significant population of herringbone motifs
(HC4, HC5 and HC7 have significant amount of T-shaped motifs)

HP series → T-shaped motifs are most common





THE MECHANISM: INTRAMOLECULAR ROTATION

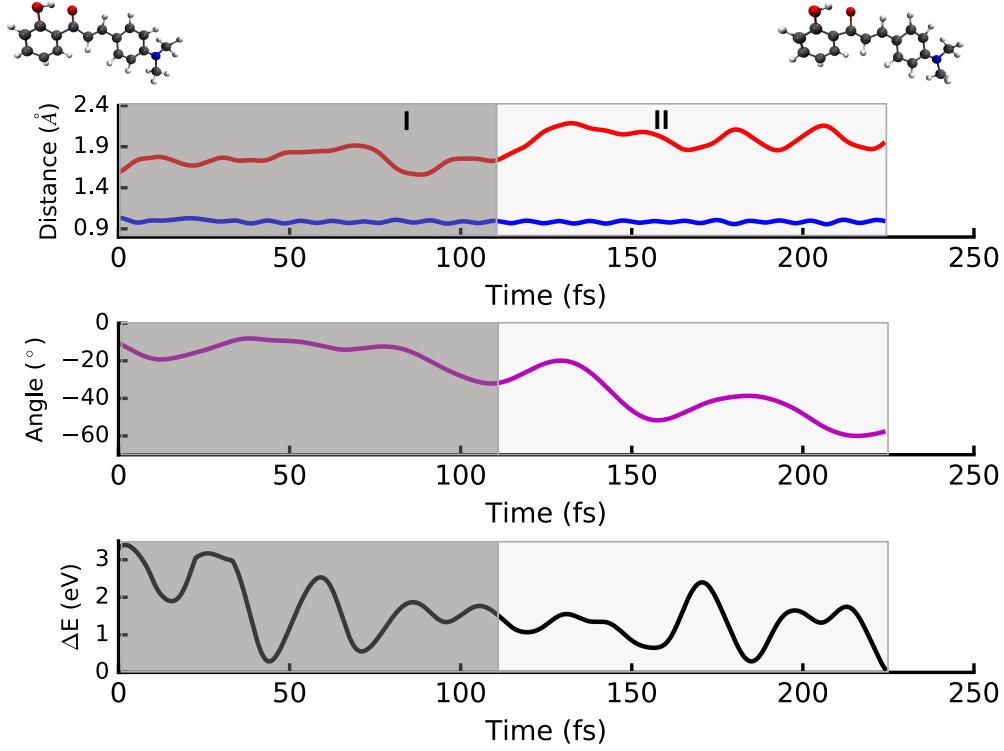


INTRAMOLECULAR ROTATION

- ✓ Both channels are accessible given the initial excitation energy
- ✓ **4** and **5** do not show stable E* minima.

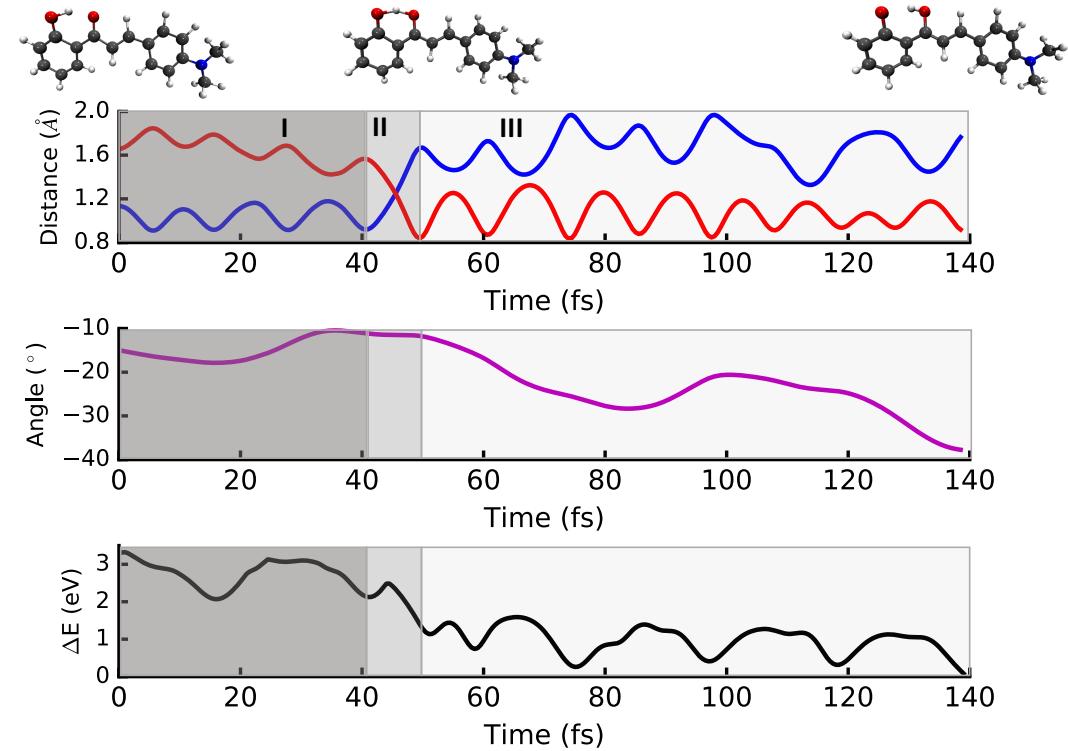
NON-ADIABATIC DYNAMICS

Enol Channel



vs.

Keto or ESIPT Channel



Relaxation

Rotation

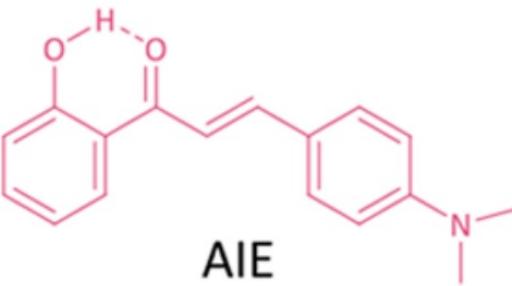
Relaxation

ESIPT

Rotation

I: E^* 52%, K^* 48% $t_{\text{ESIPT}} = 47 \text{ fs}$
 5: E^* 20%, K^* 80% $t_{\text{ESIPT}} = 27 \text{ fs}$

ADC(2)/SV(P)



Cluster model	Absorption (eV)	Emission (eV)
Vacuum	3.65	0.36
Embedded Cluster	3.27	2.40
Ewald Embedded Cluster	3.37	2.06
Experimental	3.32	1.8 – 1.9

Level of theory:

TD- ω B97X-D/6-311++G(d,p)

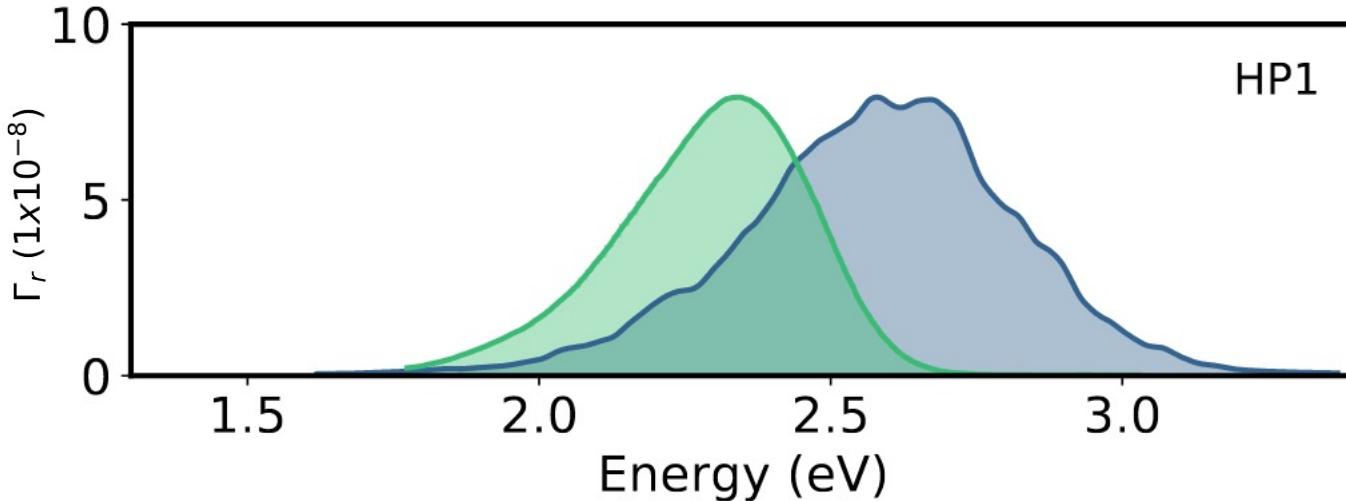
TD- ω B97X-D/6-311++G(d,p):HF/STO-3G

TD- ω B97X-D/6-311++G(d,p):HF/STO-3G:Ewald

Experimental data from: X. Cheng, K. Wang, S. Huang, H. Zhang, H. Zhang and Y. Wang, *Angew. Chemie Int. Ed.*, 2015, **54**, 8369–8373.

RADIATIVE DECAY IN THE SOLID STATE

$$k_r = \frac{1}{\hbar} \int \Gamma_r(E) dE$$



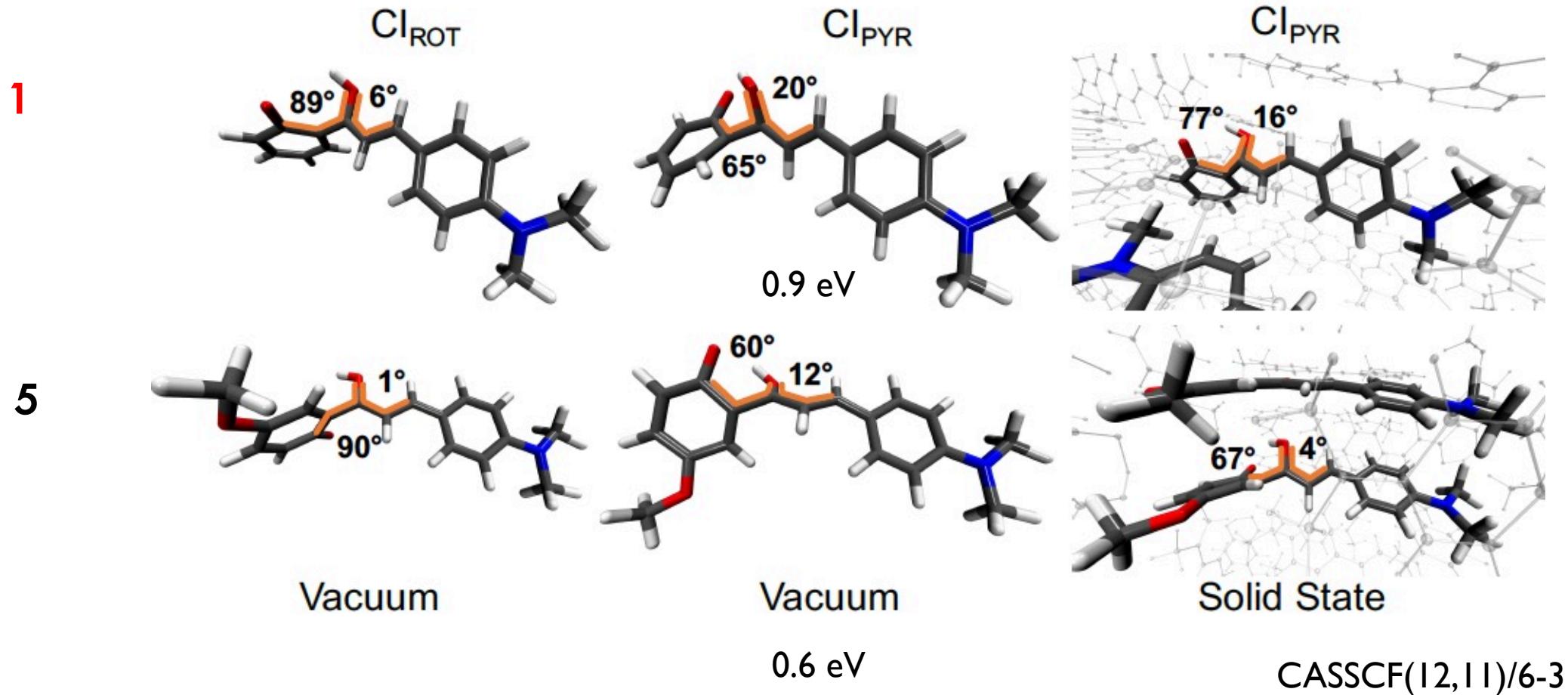
Radiative mechanisms do not explain the observed behaviour

	$k_r (s^{-1})$	$k_{nr} (s^{-1})$
HCl	6.7×10^7	1.3×10^8
HC5	7.2×10^7	7.1×10^9
HP1	6.7×10^7	7.1×10^7

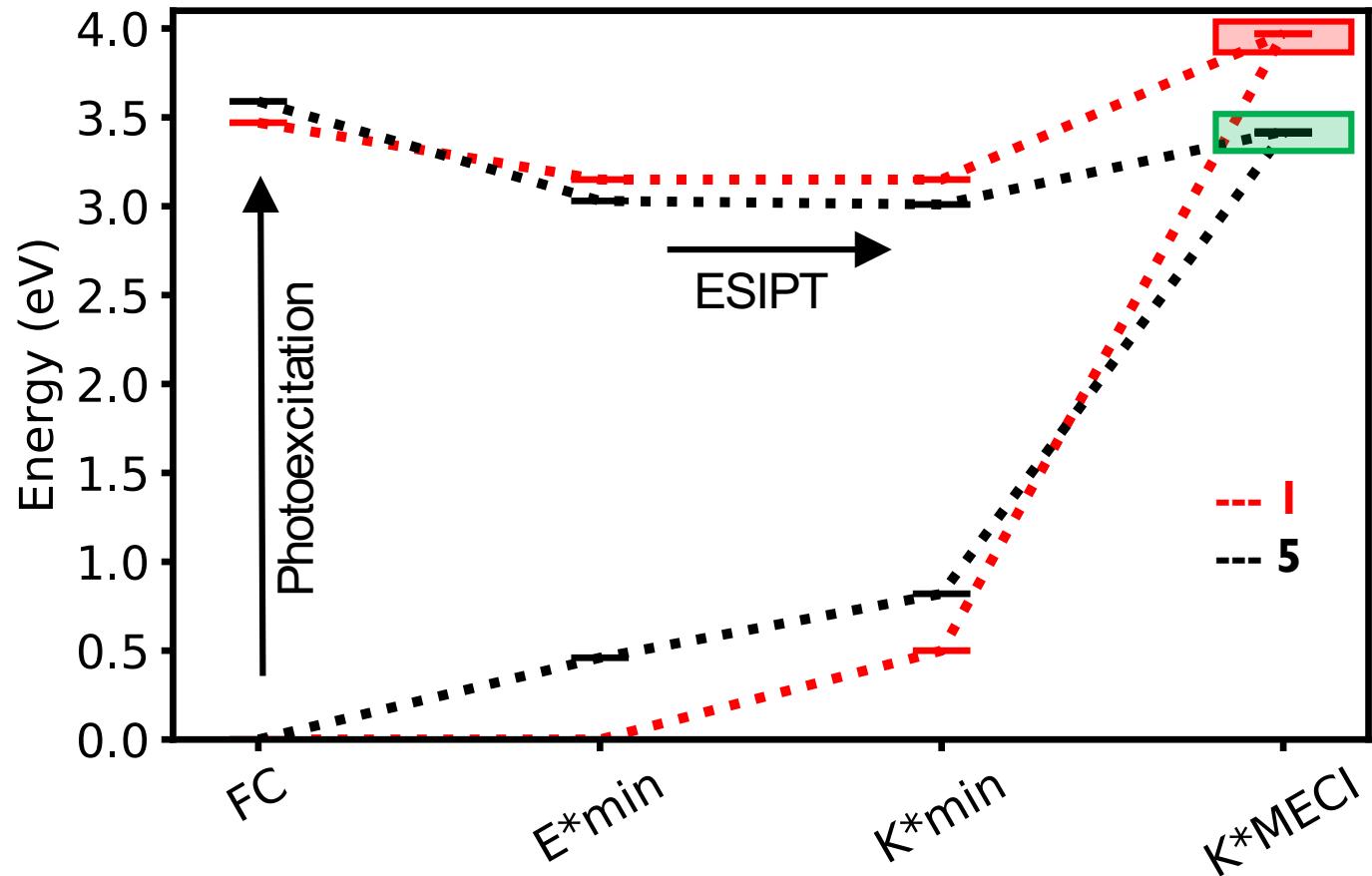
HC1:AIE
HC5: non-AIE

CONICAL INTERSECTIONS: THE EFFECT OF THE CRYSTAL

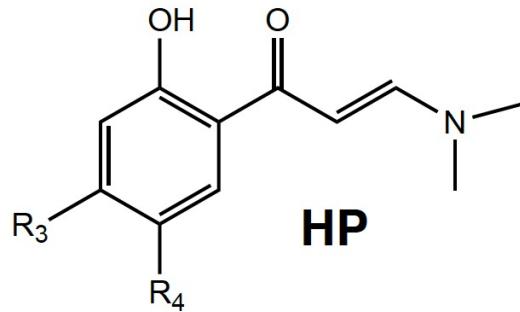
The crystalline environment determines the ordering of conical intersections and the identity of the lowest energy CI. (K^*)



RADIATIVE VS NONRADIATE DECAY

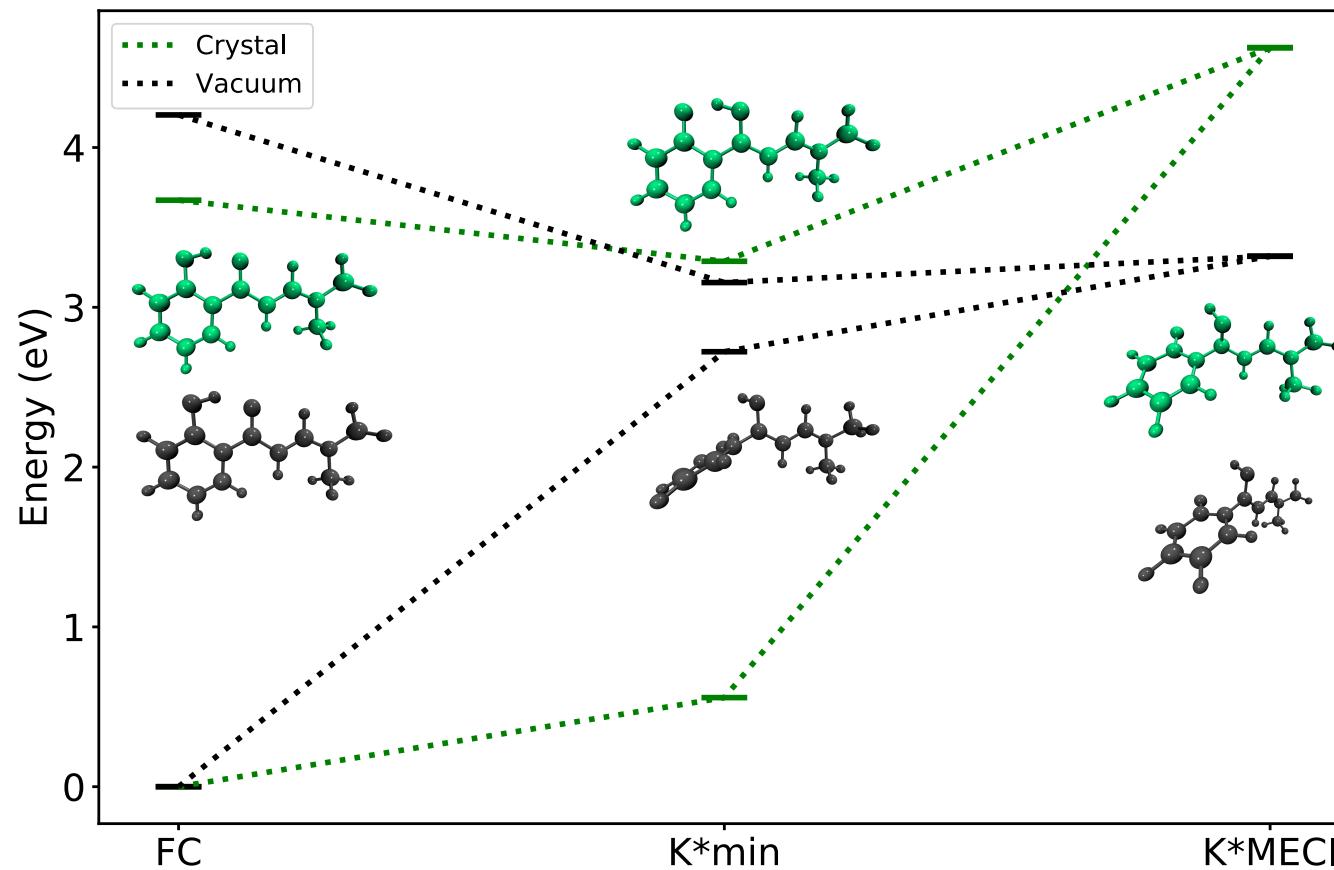


- ✓ E^{\ast} CIs are too high in energy (**I** & **5**)
- ✓ Within the mechanical embedding approach but both K^{\ast} CIs have energies lying above the photopopulated state.
- ✓ The stabilisation of the CIs is aided by the short-range electrostatic interactions with the surrounding molecules.



Highly emissive

HPI: VACUUM VS CRYSTAL



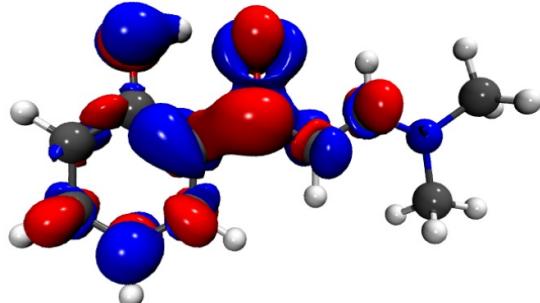
MS-3-CASPT2(12,11)/6-31G(d):AMBER

WHY HP MOLECULES ARE MORE EMISSIVE?

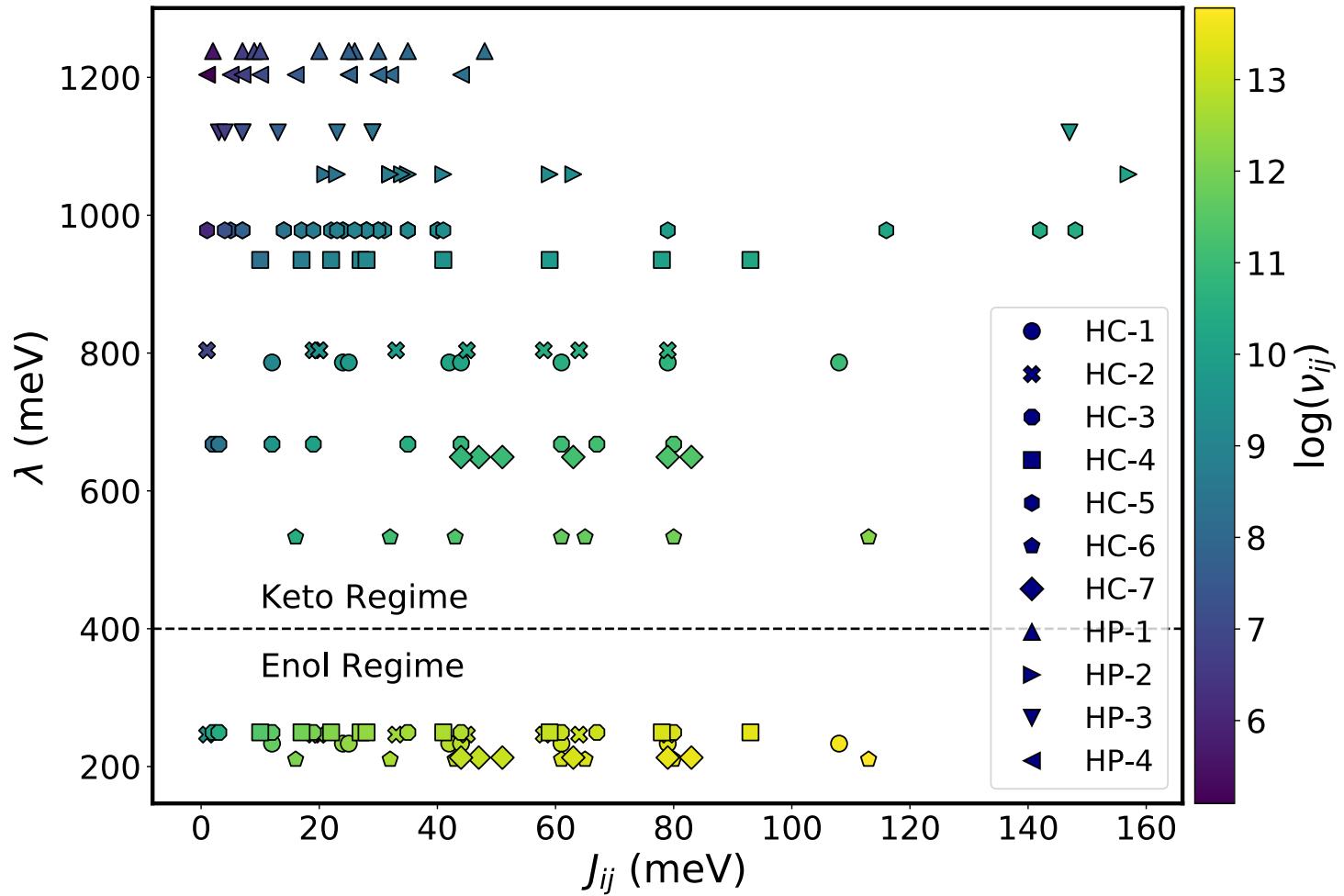
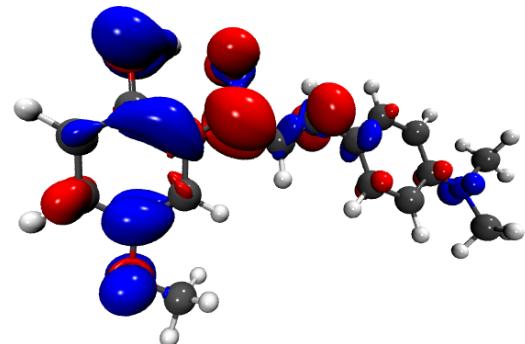
Markus model for exciton transport

$$v_{ij} = \frac{J_{ij}^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp \left[-\frac{\lambda}{4k_B T} \right]$$

HPI

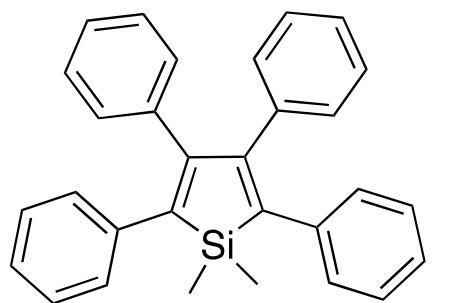


HC5

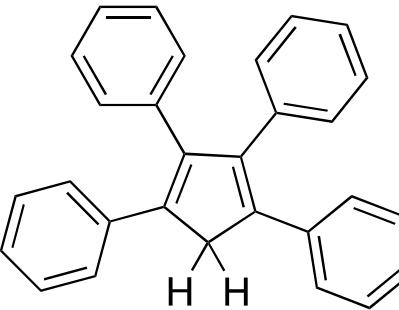


There is a bias for ESIPT in **HP** derivatives

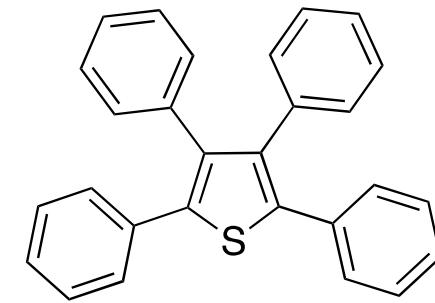
PROPELLER-SHAPED MOLECULES



DMTPS



TPC



TPT

Strong AIE

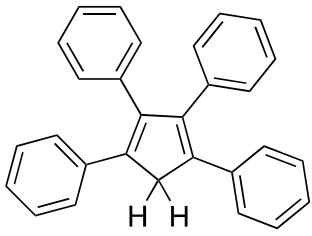
Weak AIE

Exciton Couplings: 1- 15 meV

Reorganization energies: 0.5- 0.7 eV

Stojanović, L.; Crespo-Otero, R. *ChemPhotoChem*, **2019**, 3, 907

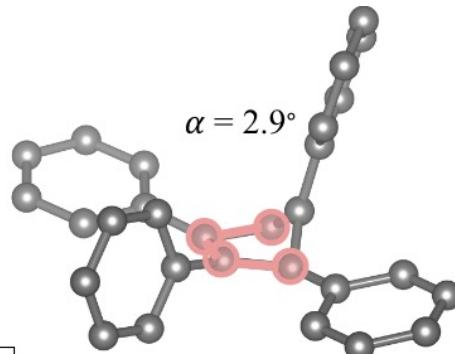
Stojanović, L.; Crespo-Otero, R. *J. Phys. Chem. C*, **2020**, 32, 17752



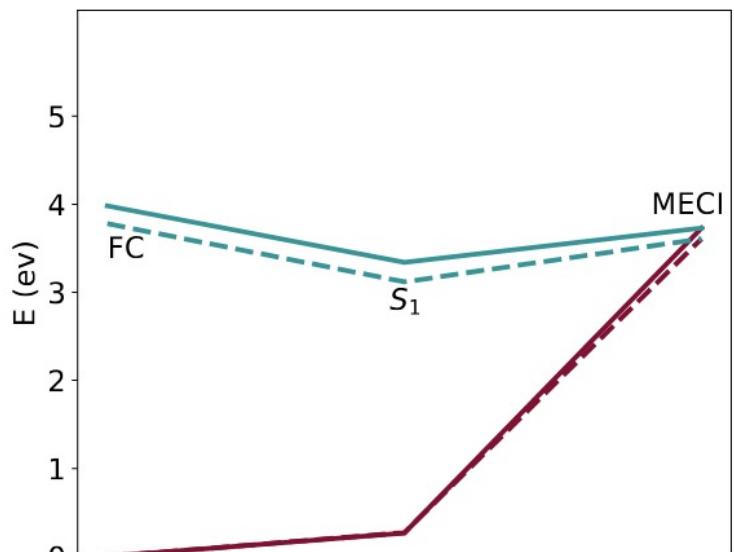
TPC: RESTRICTED ACCESS TO THE CONICAL INTERSECTION

TPC

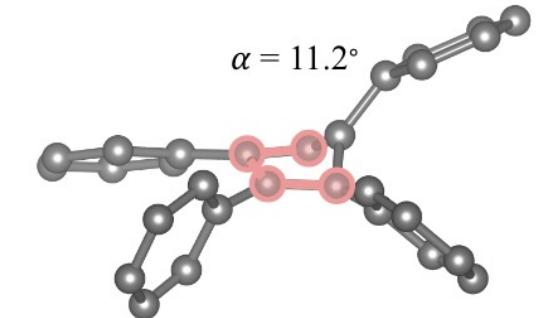
VACUUM



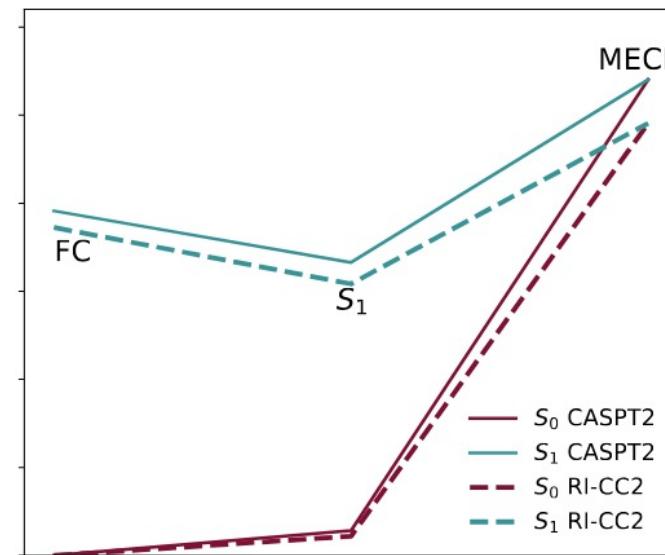
$\beta=108.1^\circ$



CRYSTAL

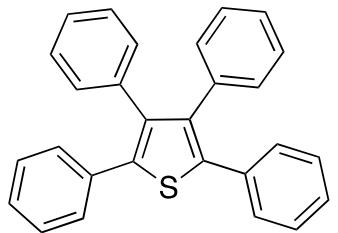


$\beta=138.7^\circ$



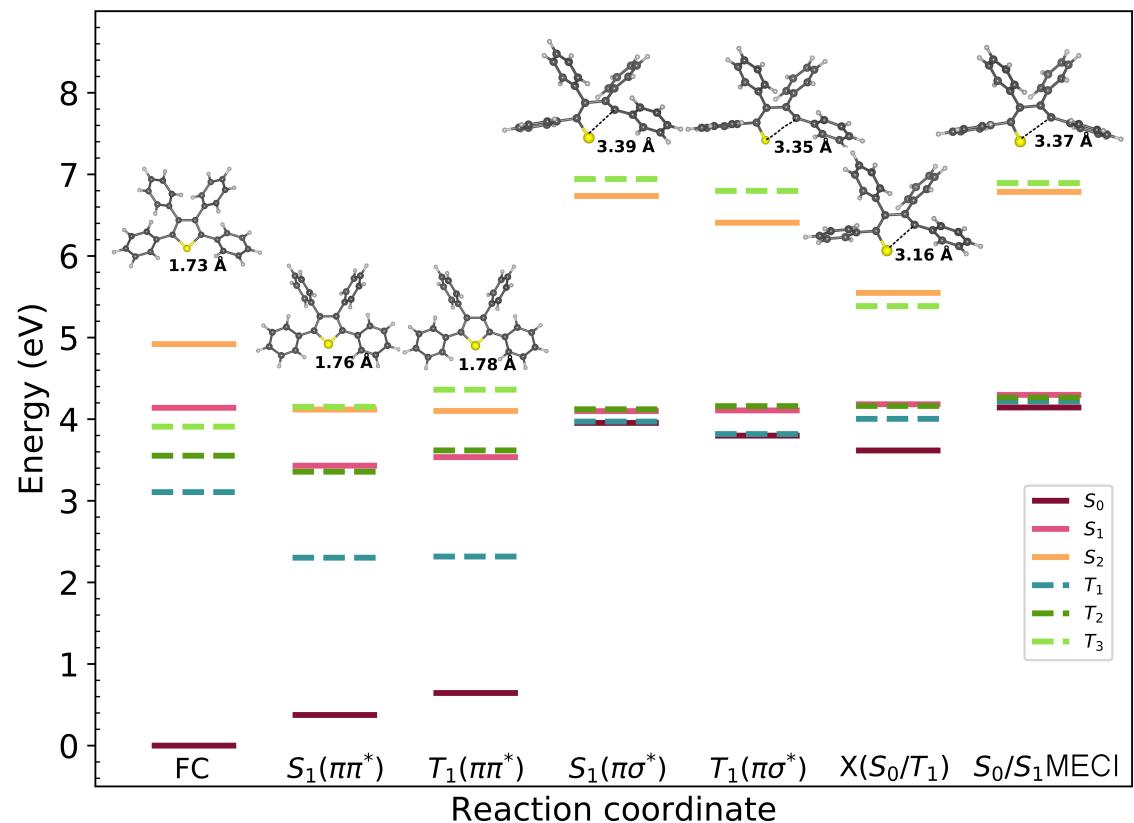
QM/MM: CASPT2/aug-cc-pVDZ//SA-2-CASSCF(10,10)/6-31G(d), MM: AMBER

Stojanović, L.; Crespo-Otero, R. *ChemPhotoChem*, 2019, 3, 907

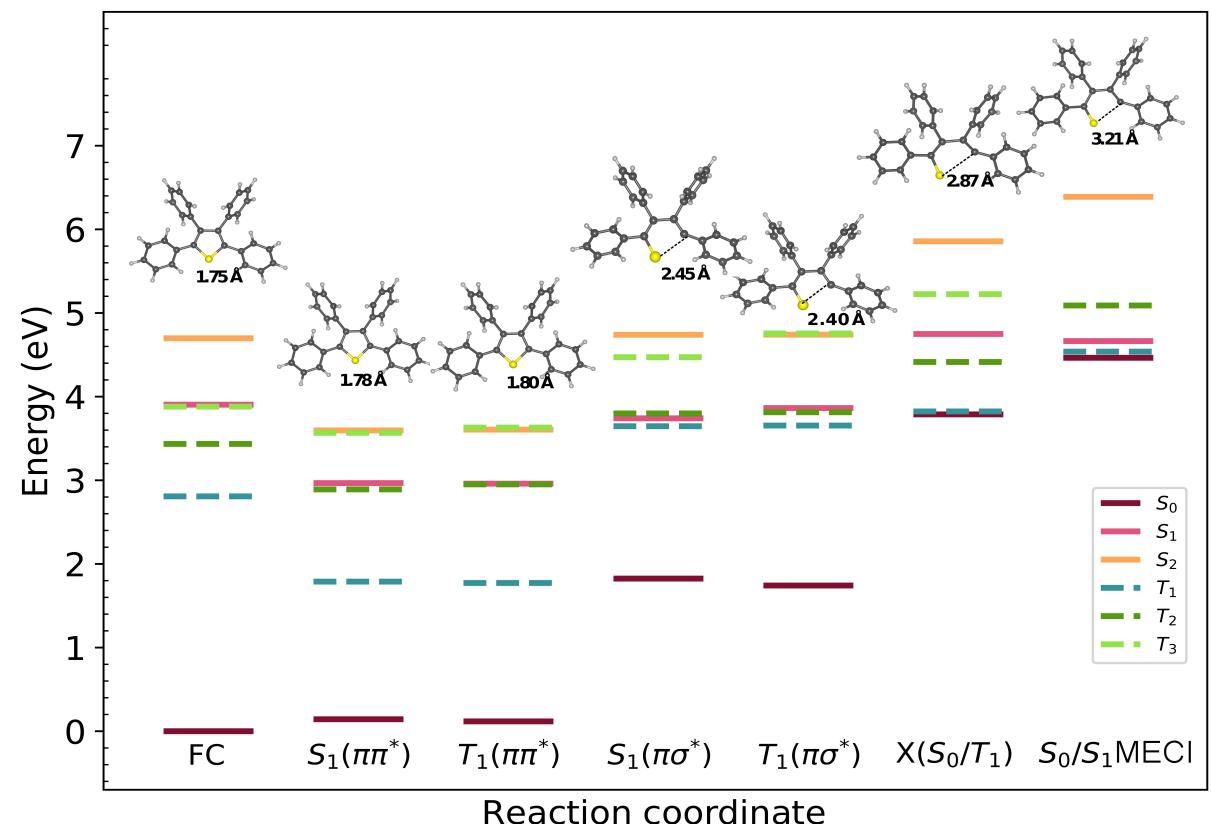


TPT: TRIPLET STATES

VACUUM

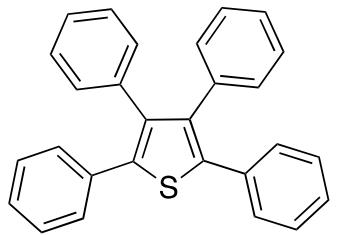


CRYSTAL



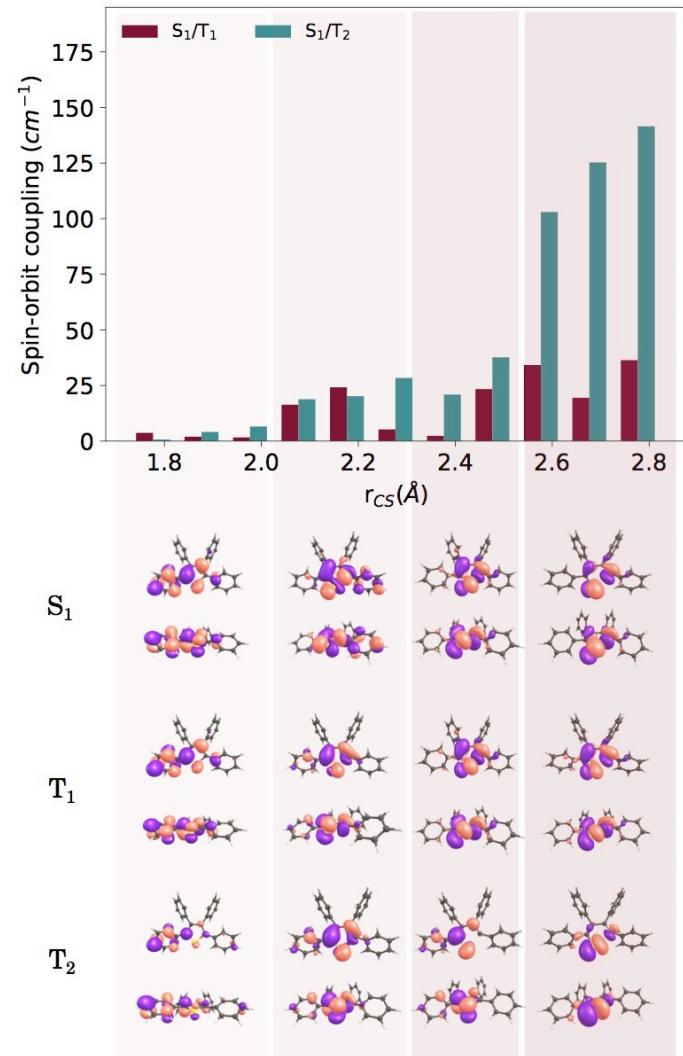
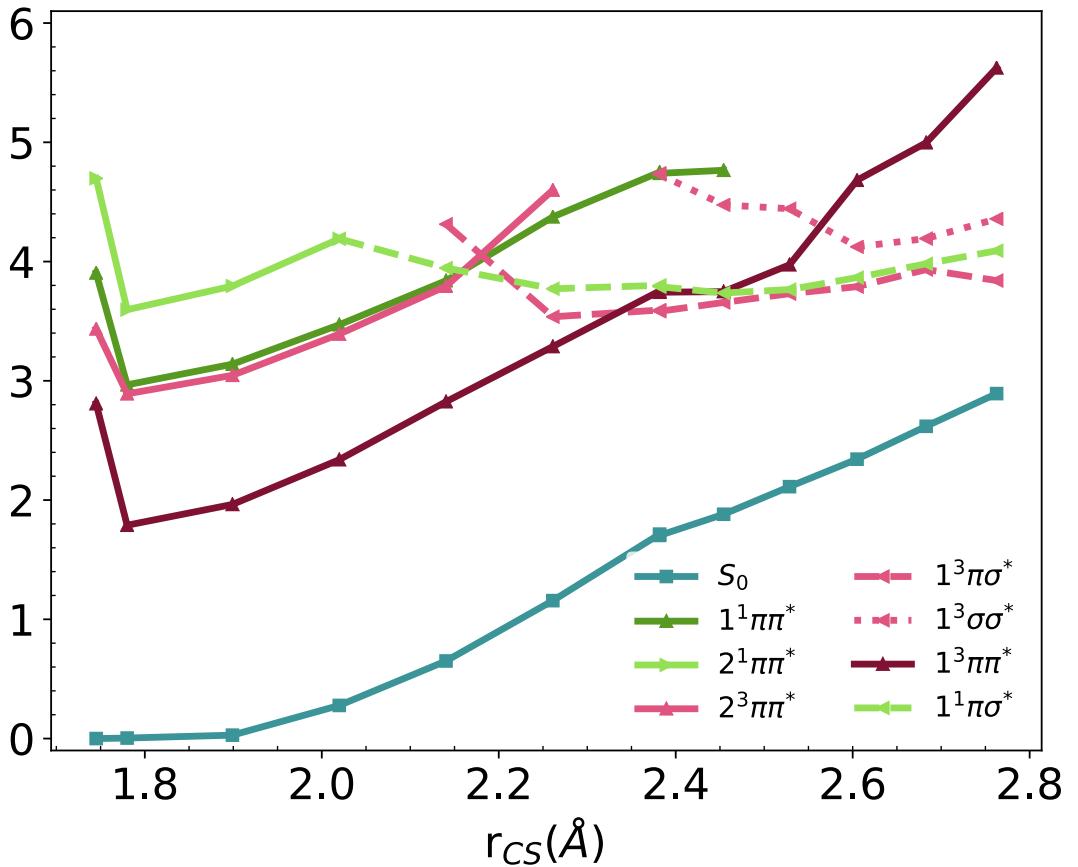
CASPT2/6-31G(d)//SA-2-CASSCF(10,10)/6-31G(d), MM: AMBER

Stojanović, L.; Crespo-Otero, R. *J. Phys. Chem. C*, 2020, 32, 17752



TPT: TRIPLET STATES

CRYSTAL



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Alston Misquitta**



**Queen Mary
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