

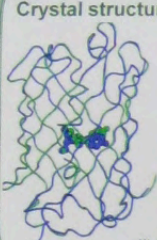
# Primary Events of Photodynamics of GFP Chromophore in Different Environments

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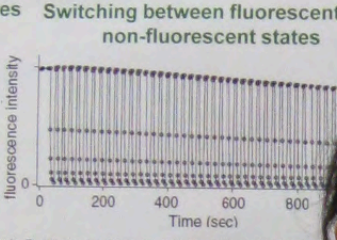
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### Crystal structures



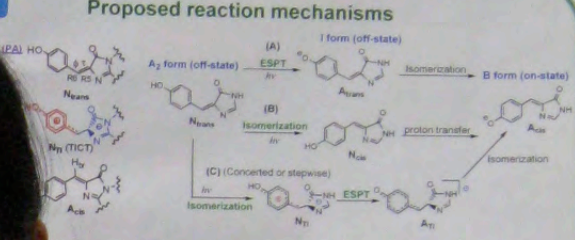
Switching between fluorescent and non-fluorescent states



(1) Ando, R.; Mizuno, H.; Miyawaki, A. *Science* 2004, 306, 1370. (2) Ando, R.; Trowitzsch, S.; Weber, G.; Egeling, C.; Wahl, M. C.; Hell, S. W. *Science* 2005, 309, 1052. (3) Ando, R.; Mizuno, H.; Miyawaki, A.; Morokuma, K. *J. Phys. Chem. B* 2010, 114, 1114.

### Background

#### Proposed reaction mechanisms

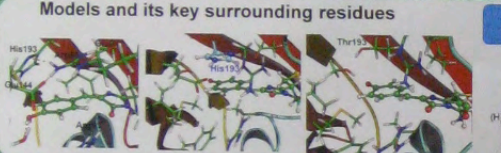


(A) A<sub>2</sub> form (off-state) → ESPT → I form (off-state) → Isomerization → B form (on-state)

(B) A<sub>2</sub> form (off-state) → Isomerization → I form (off-state) → proton transfer → B form (on-state)

(C) (Concerted or stepwise) A<sub>2</sub> form (off-state) → Isomerization → I form (off-state) → ESPT → B form (on-state)

### Models and its key surrounding residues

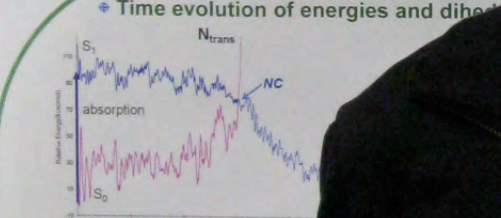


His193, His194, Thr192

### Model Systems

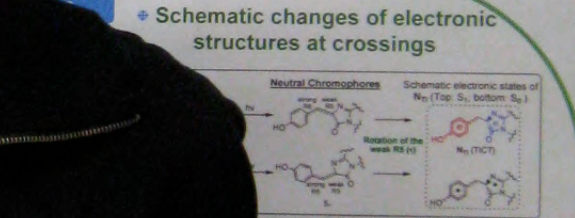
Methods:  
Non-adiabatic ONIOM(QM:MM) MD;  
QM: SA2-CASSCF; MM: Amber96  
Laudau-Zener model  
Gaussian Development Version, Molpro, Modified Tinker  
(PDB IDs: 2IOV and 2POX)

### Time evolution of energies and dihedral angles



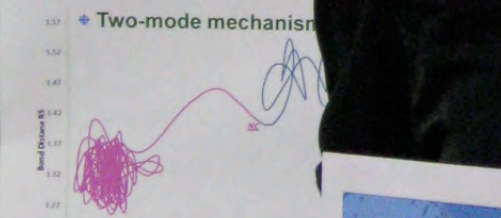
absorption, S<sub>1</sub>, N<sub>trans</sub>, N<sub>C</sub>, S<sub>0</sub>

### Schematic changes of electronic structures at crossings




Neutral Chromophores, Schematic electronic states of N<sub>1</sub> (Top: S<sub>1</sub>, bottom: S<sub>0</sub>)

### Two-mode mechanism



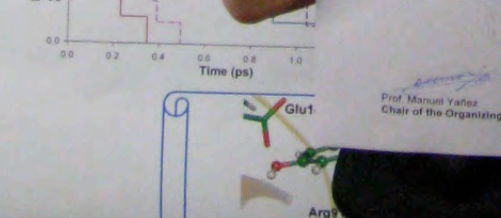
Bead Distance (Å)

### Excited-state population



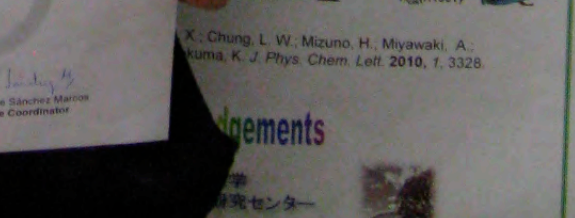
Excited-state population vs Time (ps)

### Excited-state population



Dihedral angle (194)

### Excited-state population



Excited-state population vs Time (ps)



X. Li, L. W. Chung, H. Mizuno, A. Miyawaki, K. Morokuma, *J. Phys. Chem. Lett.* 2010, 1, 3328.

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