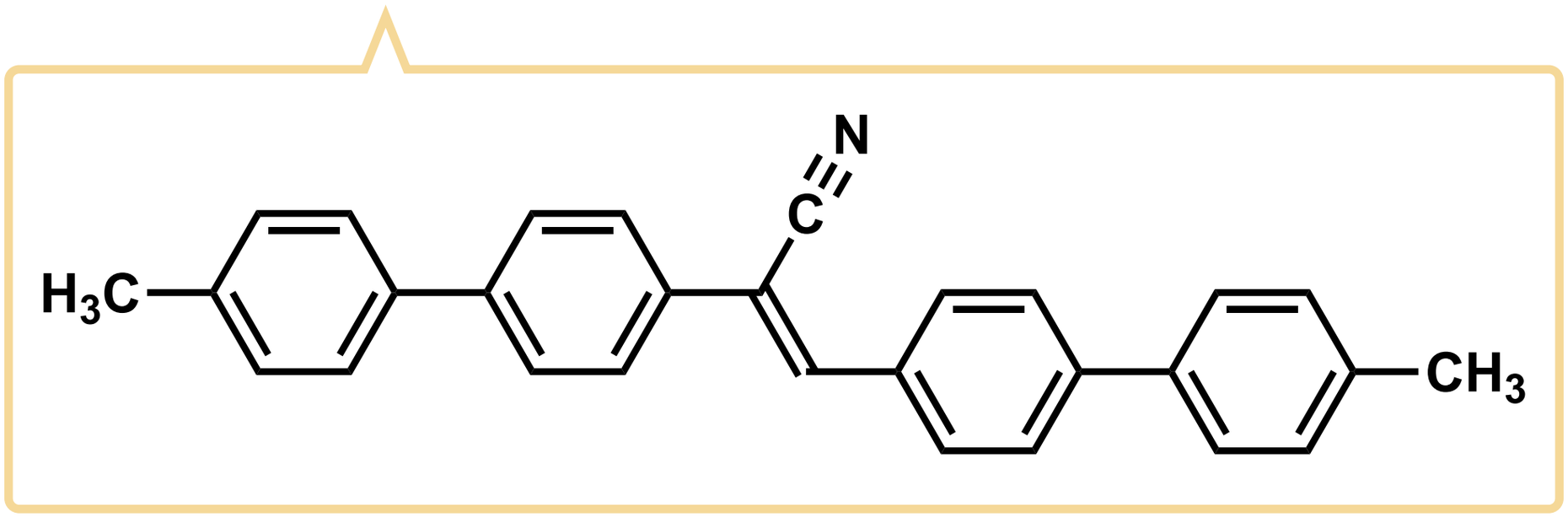
Free energy profile analysis of aggregation-induced emission (AIE) for a cyanostilbene derivative

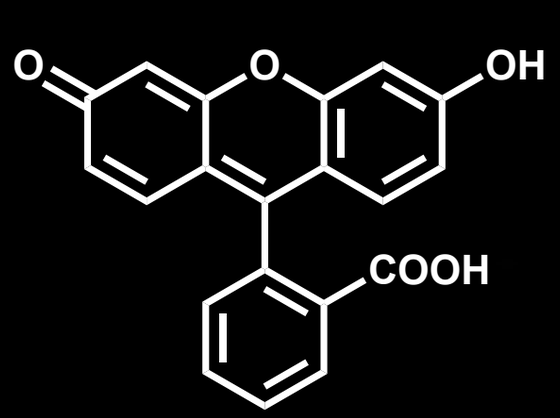


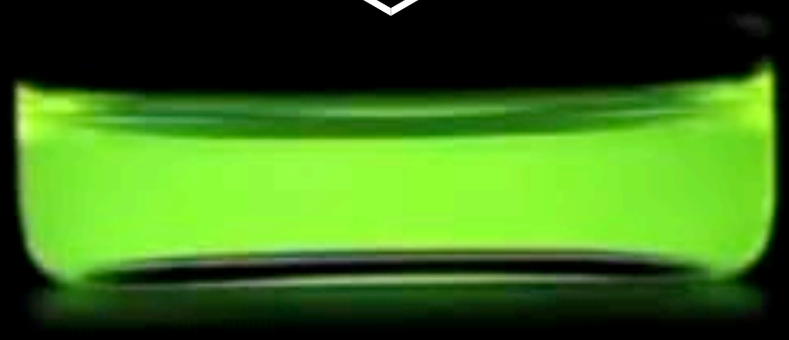
CN-MBE

Norifumi Yamamoto | **Chiba Institute of Technology, Japan**

ACQ

Aggregation Caused Quenching

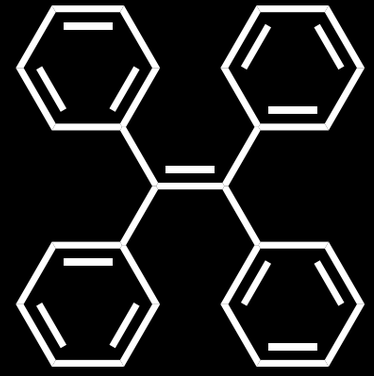




conventional **luminogen**

AIE

Aggregation Induced Emission

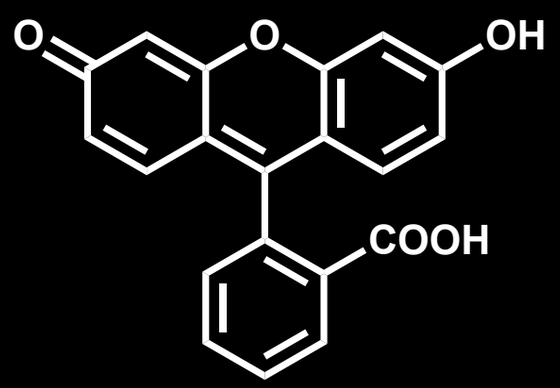


AIE **luminogen**

Tang, et al, *J. Phys. Chem. Lett.*, 6, pp 3429–3436 (2015)

ACQ

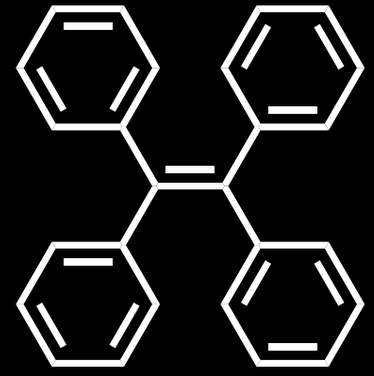
Aggregation Caused Quenching



***conventional* luminogen**

AIE

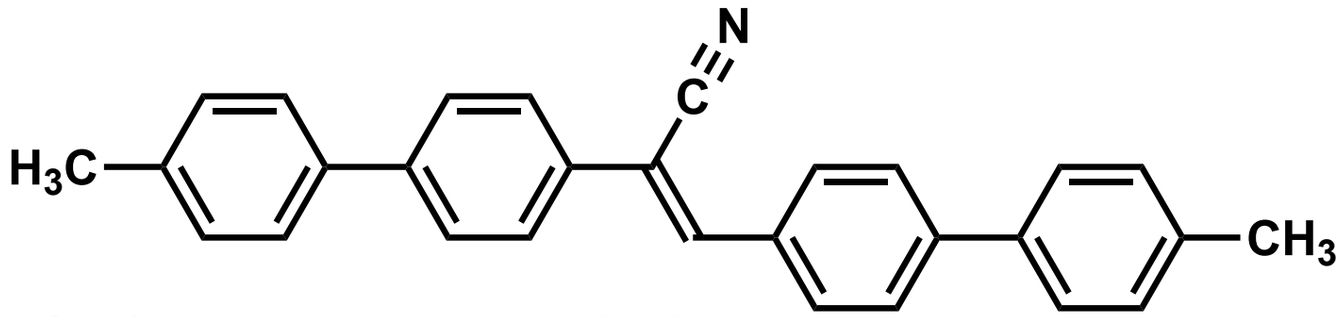
Aggregation Induced Emission



***AIE* luminogen**

Tang, et al, *J. Phys. Chem. Lett.*, 6, pp 3429–3436 (2015)

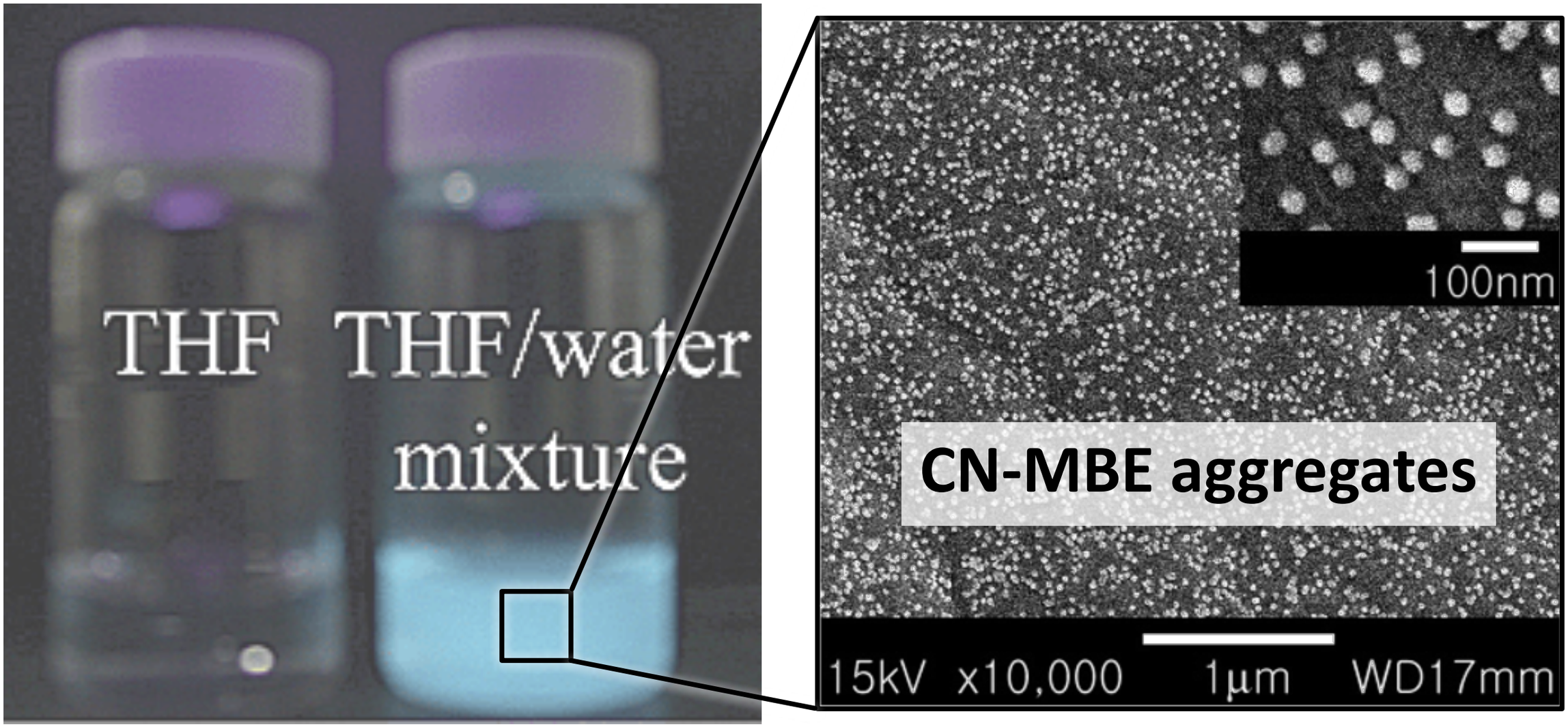
CN-MBE



- **CN-MBE** shows **AIE**:

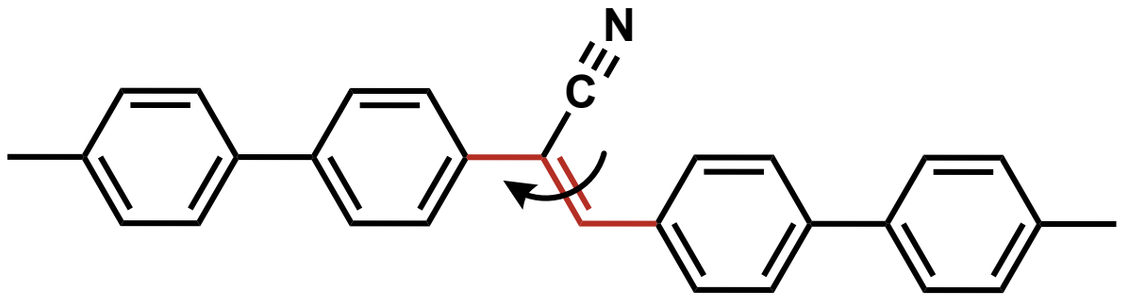
  → **When dispersed in THF solution**, it is **non-emissive**.

  → **When water is added**, it becomes **emissive** by forming aggregates.

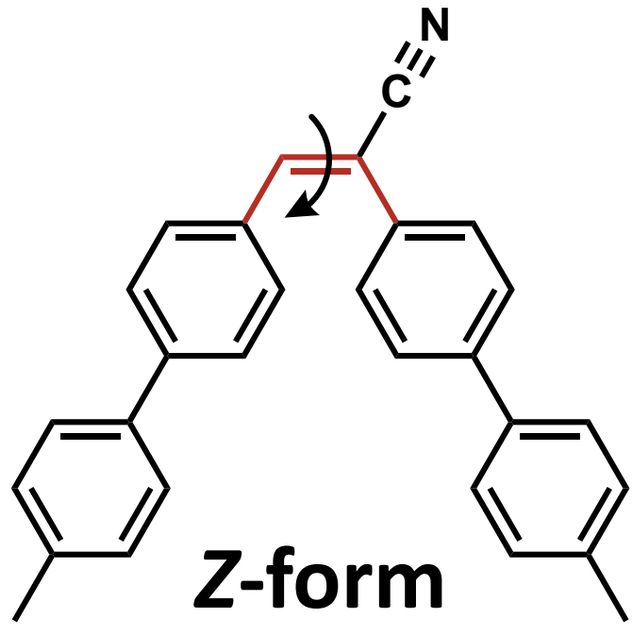


An, B-. K., et al, *J. Am. Chem. Soc.*, 124, 14410−14415 (2002)

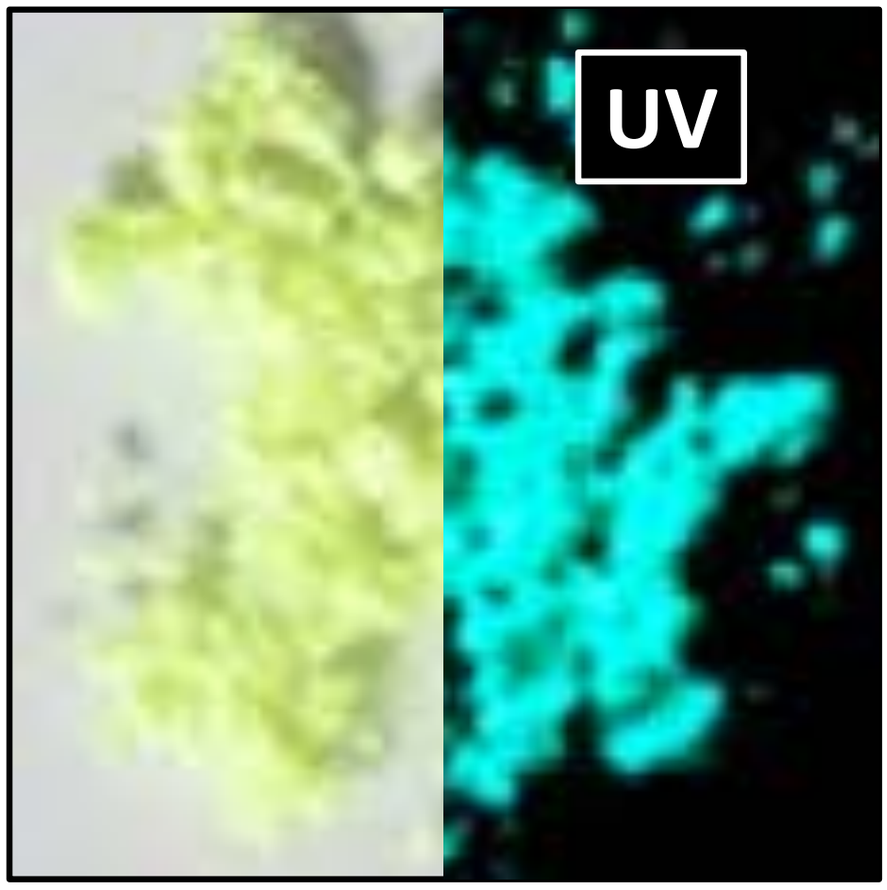
CN-MBE has two isomers



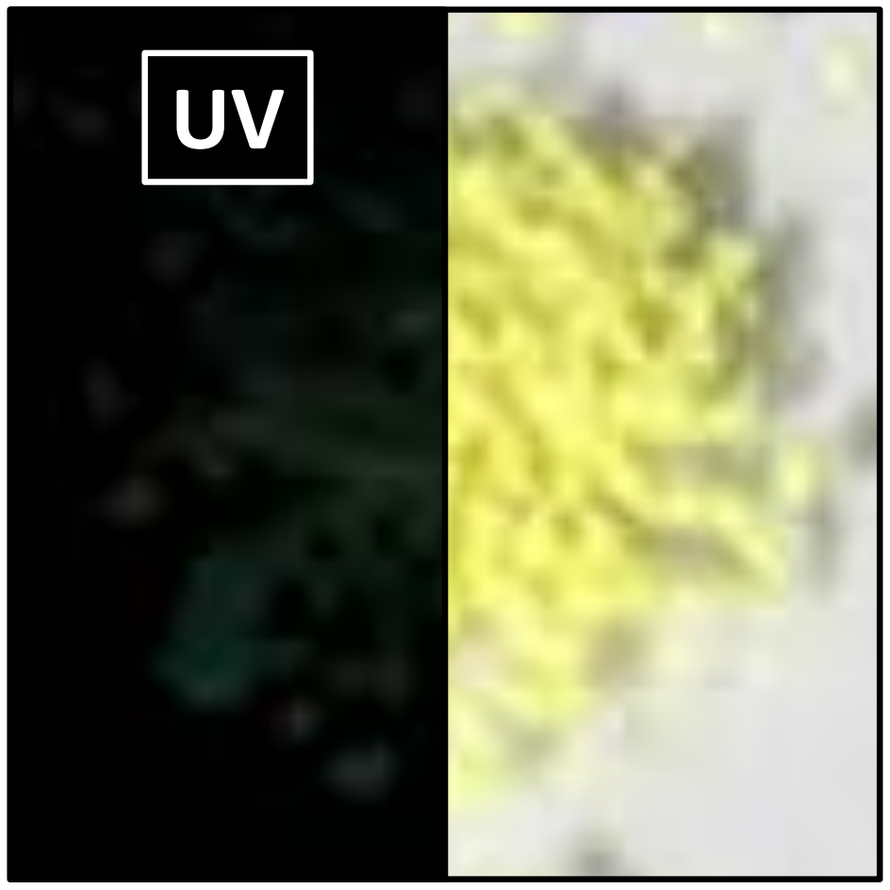
***E*-form**



***Z*-form**



Aggregation induces emission.



Aggregation doesn't induce emission.

Chung, et al, *J. Phys. Chem. C*, 117, 11285−11291 (2013)

How does fluorescence quench?

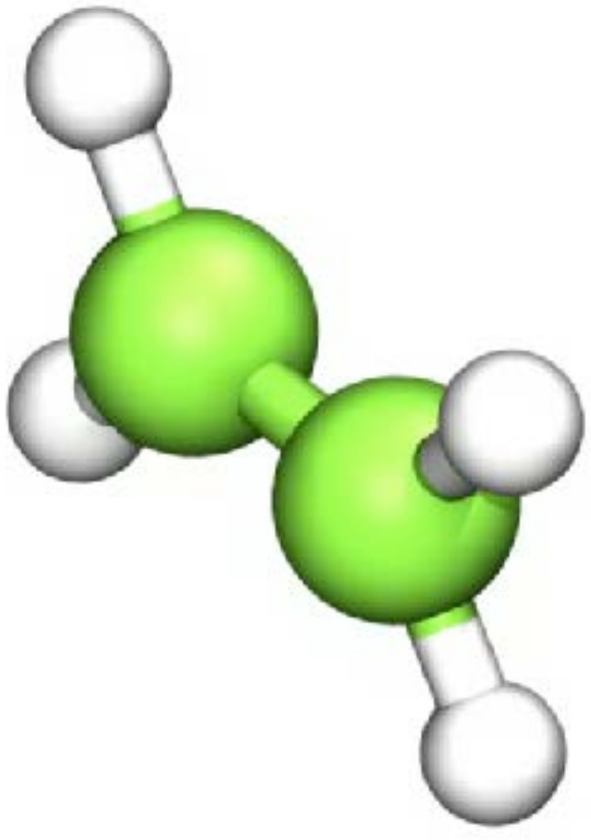
→ **Conical intersection (CI)** can play an important role.

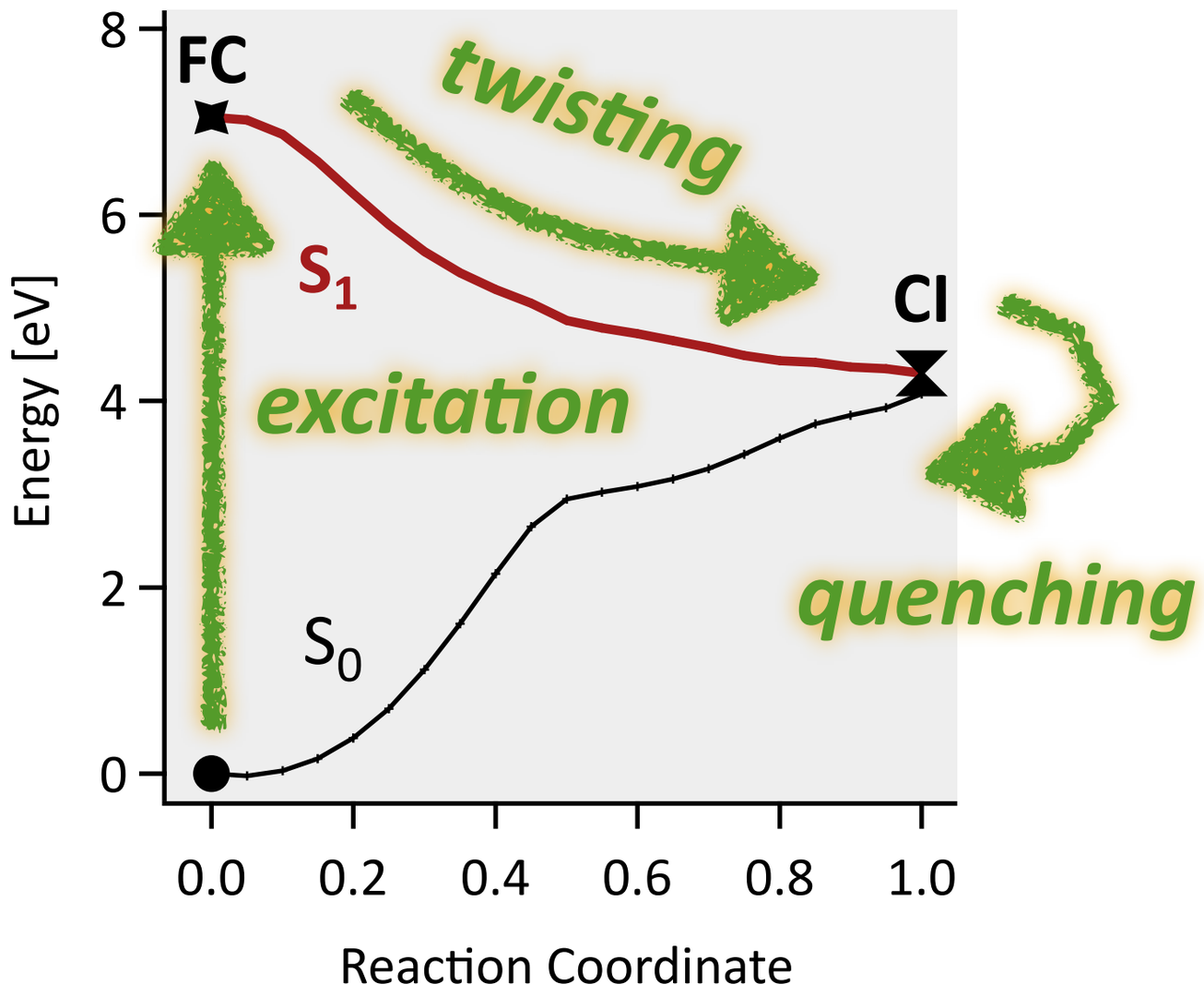
e.g., **ethylene**

→ After photo-excitation, along the relaxation pathway on S_1,

the C=C bond twisting occurs to reach **the CI between S_0/S_1**.

→ At the **CI**, **it returns to S_0 without fluorescence (FL)**. → **FL quenches.**





Relaxation pathway of CN-MBE after photo-excitation

- **For monomer,**

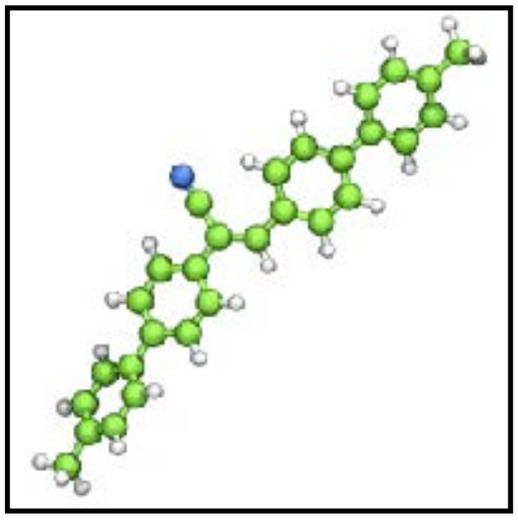
  → (1) **conical intersections (CIs)** of CN-MBE were investigated,

  → (2) **minimum energy paths (MEPs)** that lead to CIs were determined,

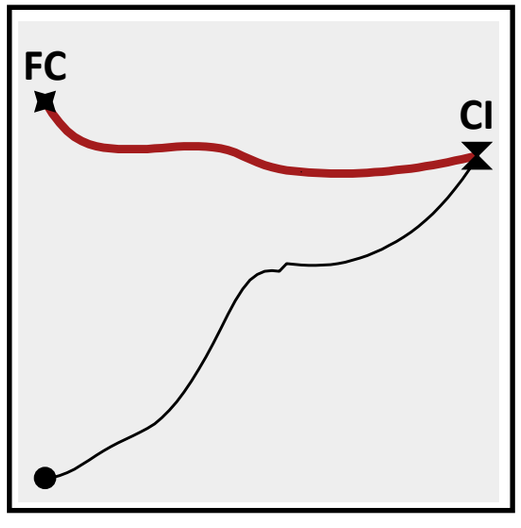
- **In aggregates, along the MEPs** (determined for the monomer)

  → (3) **MD simulations** were performed,

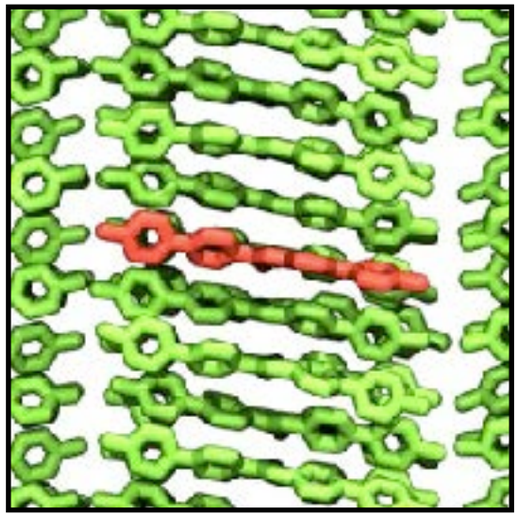
  → (4) **free-energy profiles (FEPs)** were analyzed.



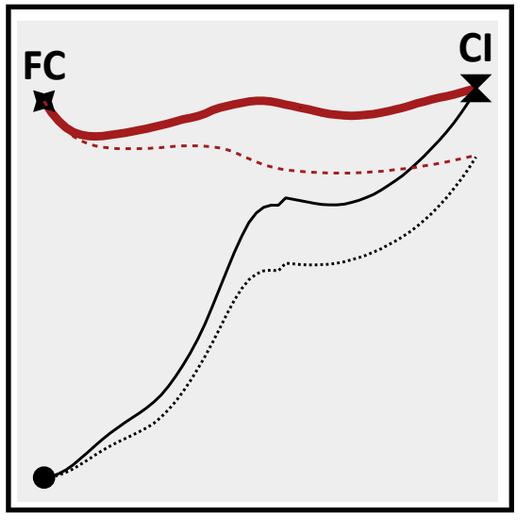
(1) CI



(2) MEP



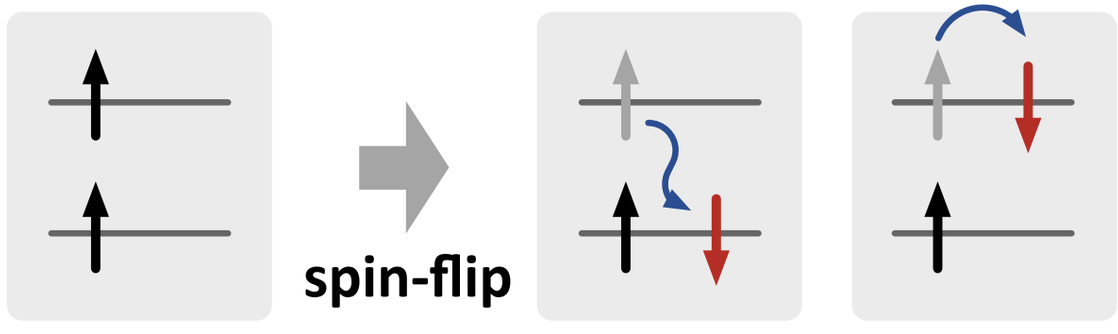
(3) MD



(4) FEP

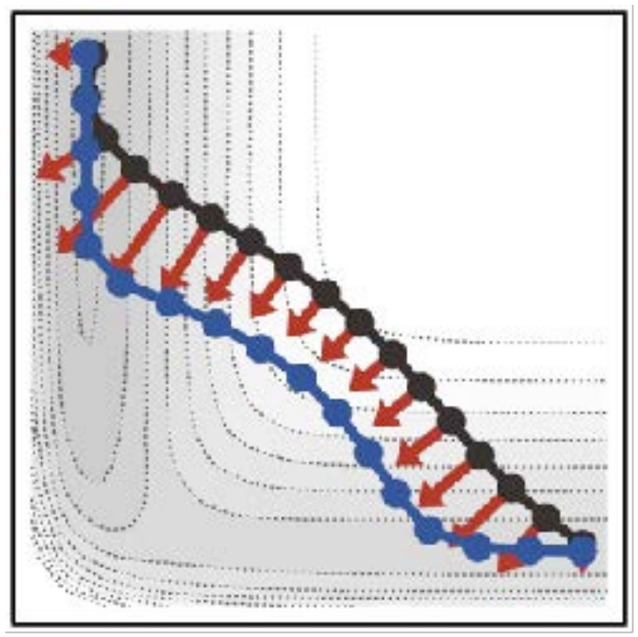
Computational methods for CN-MBE monomer

- **Electronic Structure Calculations**
  - → **Method:** Spin-flip TD-DFT [Krylov 2001, Shao 2003]
    - Even at CIs, SF-TD-DFT can treat S_0 & S_1 states on an equal footing.
  - → **Functional:** BHHLYP
  - → **Basis Set:** 6-31G(d)
  - → **Program:** Q-Chem 5.1



- **Minimum Energy Conical Intersection (CI) Search**
  - → **Method:** Direct Method [Bearpark 1994]
  - → **Program:** Q-Chem 5.1

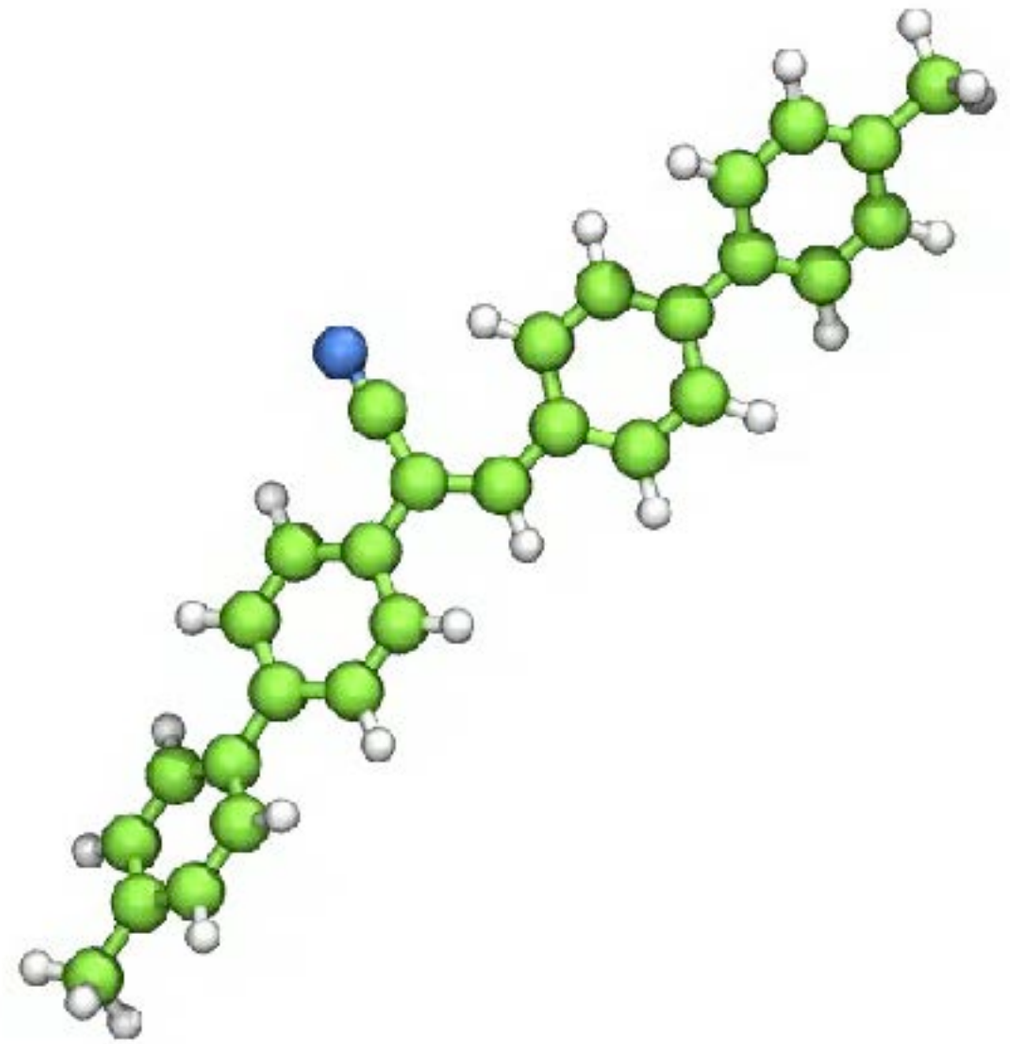
- **Minimum Potential Energy Path (MEP) Search**
  - → **Method:** String Method [E 2002, E 2007]
    - MEPs reaching to the MECI were searched.
  - → **Program:** an in-house script



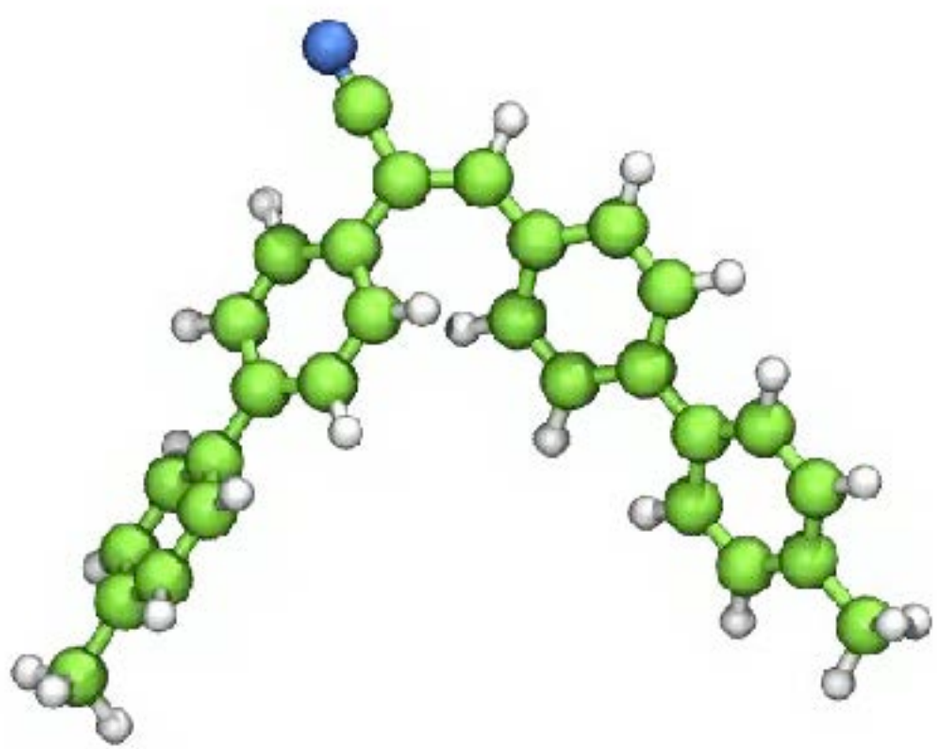
string method

MEPs between FC and CI

- Optimized geometries at the S_0 state were determined,
  which corresponds to **the Frank-Condon (FC) geometries at the S_1 state**.
- **Minimum energy point of S_0/S_1 conical intersections (CIs)** was determined.
- **Minimum energy paths (MEPs) between FC and CI** were determined.



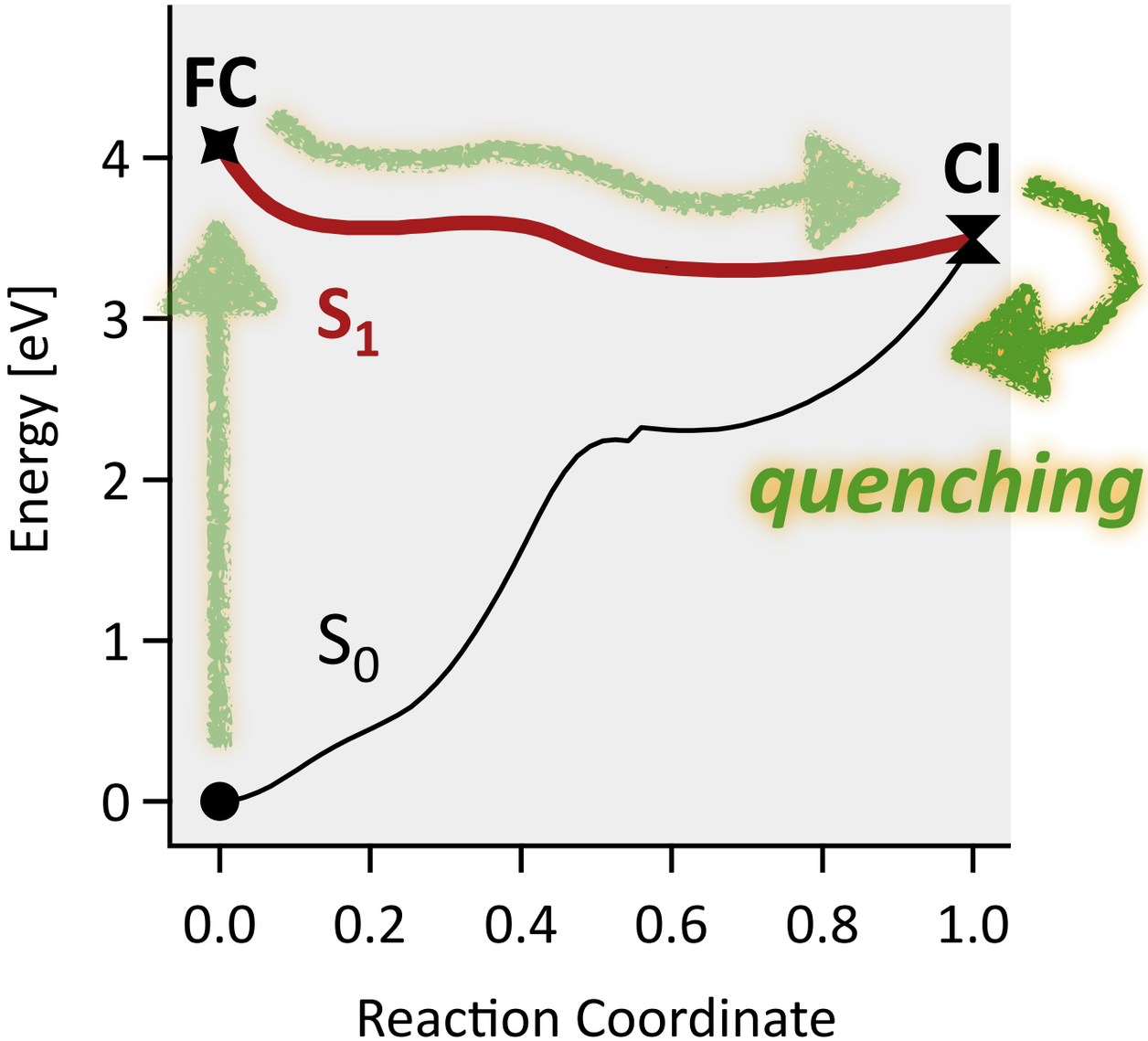
FC *E*-form → CI

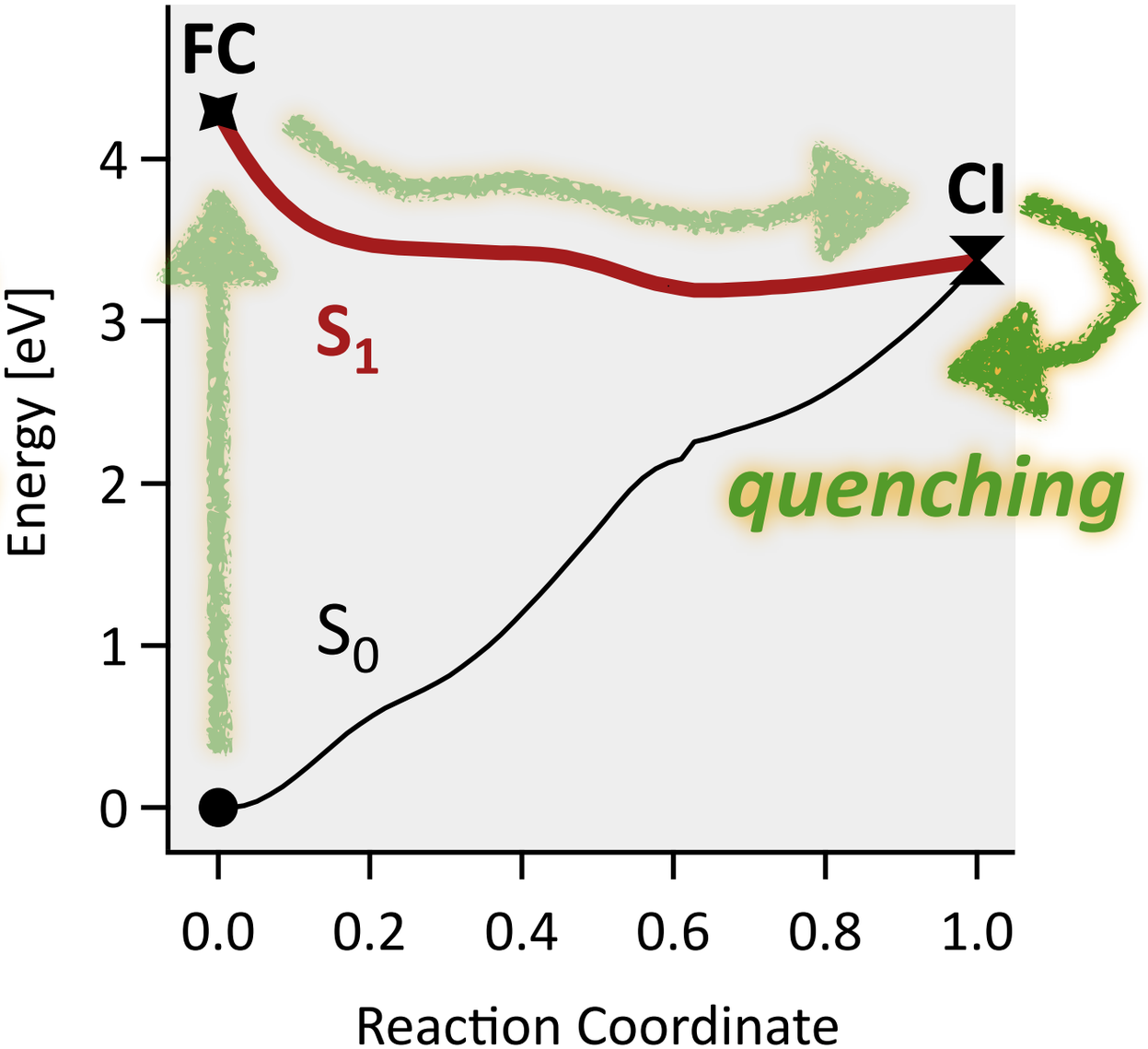


FC *Z*-form → CI

Potential energy changes along the MEPs

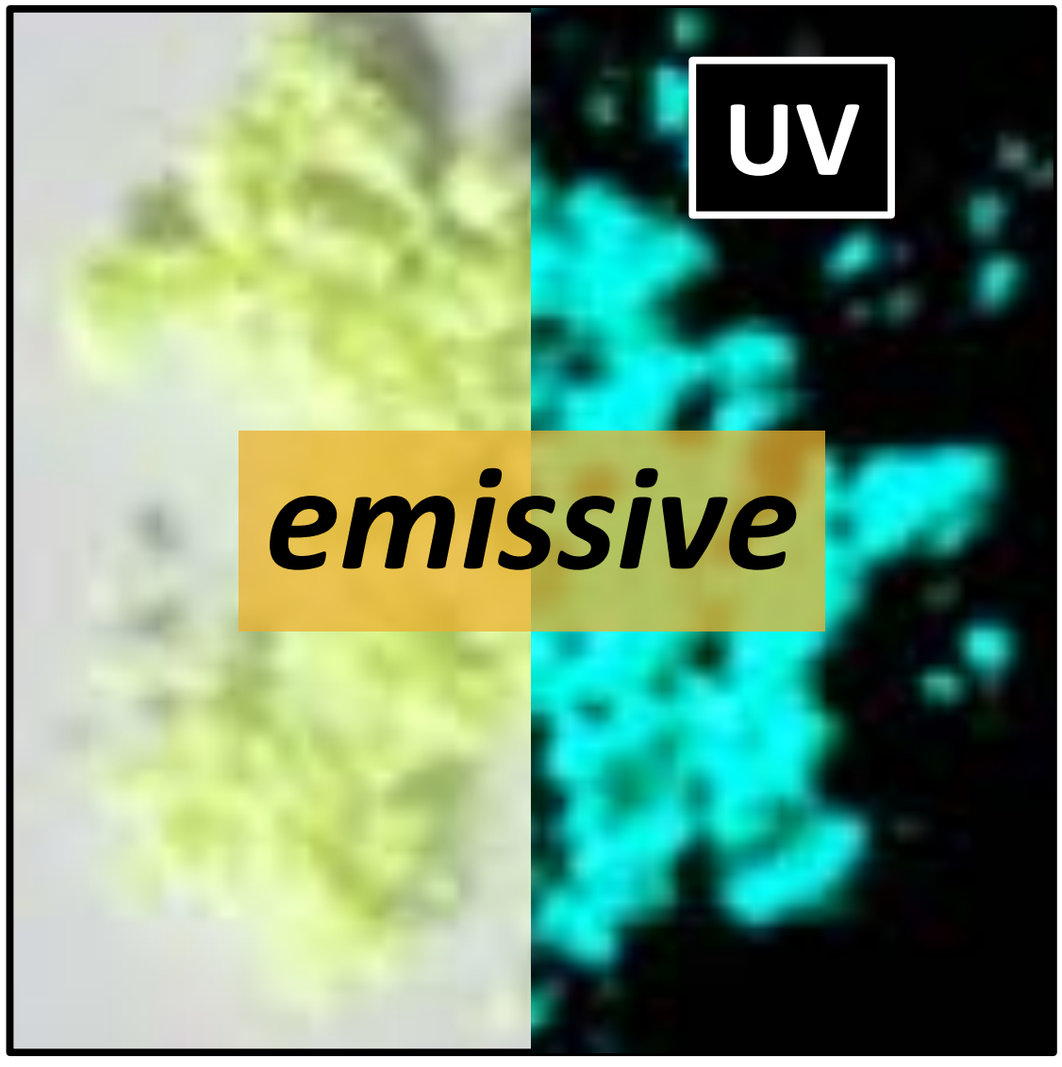
- There is **no energy barrier** along the MEPs on the S_1 surface.
- After photo-excitation, **it arrives at the CI** spontaneously,
  returns to S_0 **without fluorescence emission**.
- CN-MBE is non-emissive when isolated. → ***What happens after aggregation?***



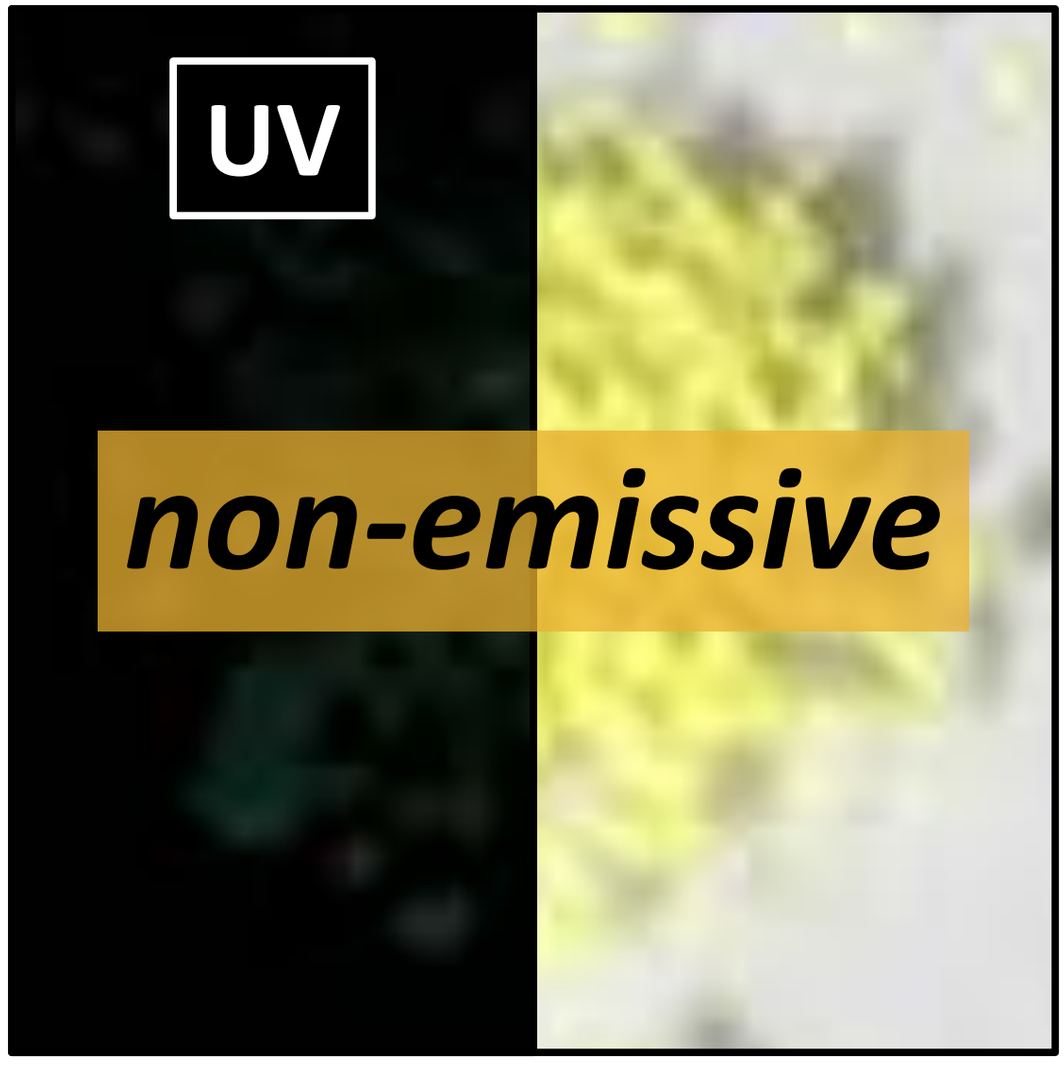


AIE of CN-MBE depends on isomeric forms

- **E-form** becomes **emissive** after aggregation formation.
- **Z-form**, however, is **non-emissive** even in aggregated state.



***E*-form**



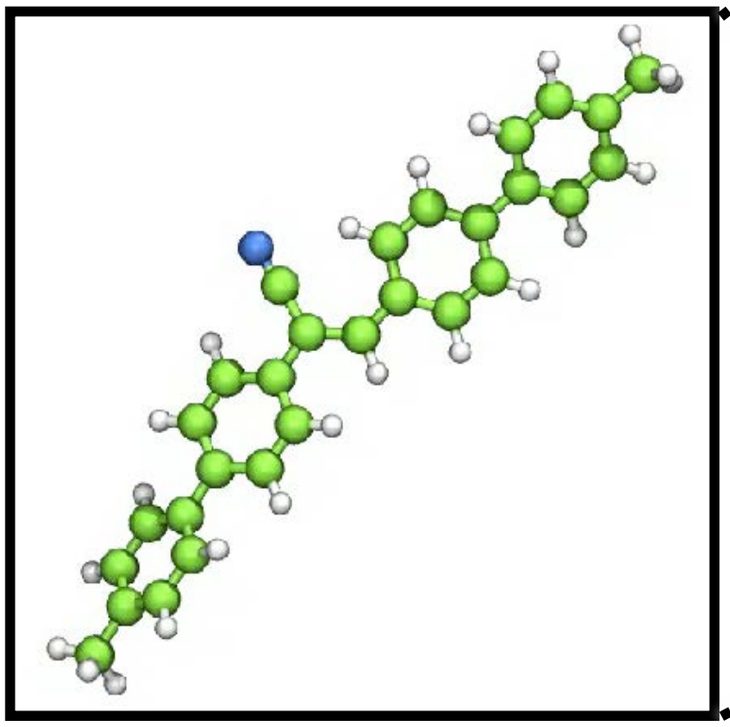
***Z*-form**

Chung, et al, *J. Phys. Chem. C*, 117, 11285–11291 (2013)

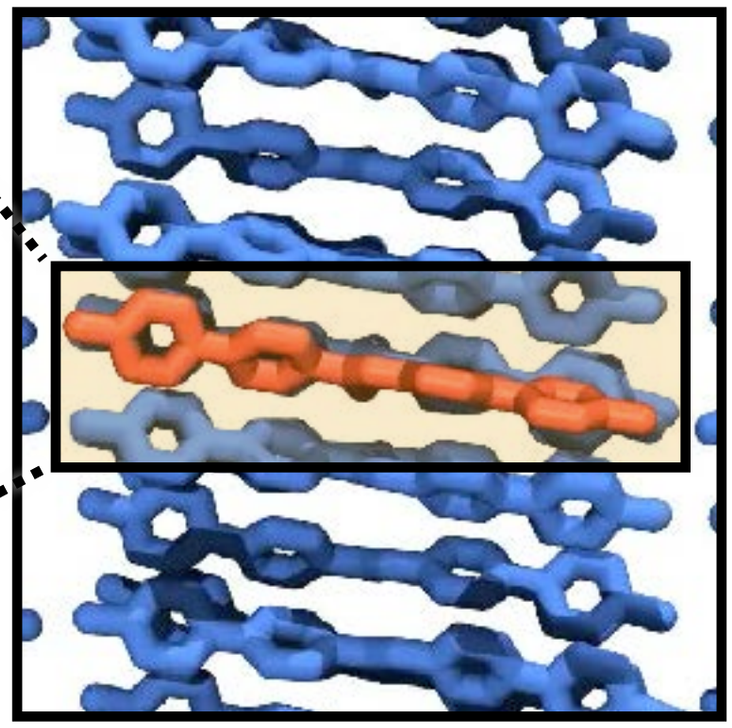
AIE mechanism? → **Free energy profiles** in the aggregated state were analyzed.

Free energy analysis of CN-MBE aggregates

- **Free energy changes along the MEPs** were analyzed using **the QM/MM Free Energy Perturbation [Zhang 2000].**
    - **One geometry was took from the MEP**, and embed into an aggregate as a **Quantum Mechanics (QM) part**.
    - **The other molecules** were set as **Molecular Mechanics (MM) parts.**



conformations along the MEP

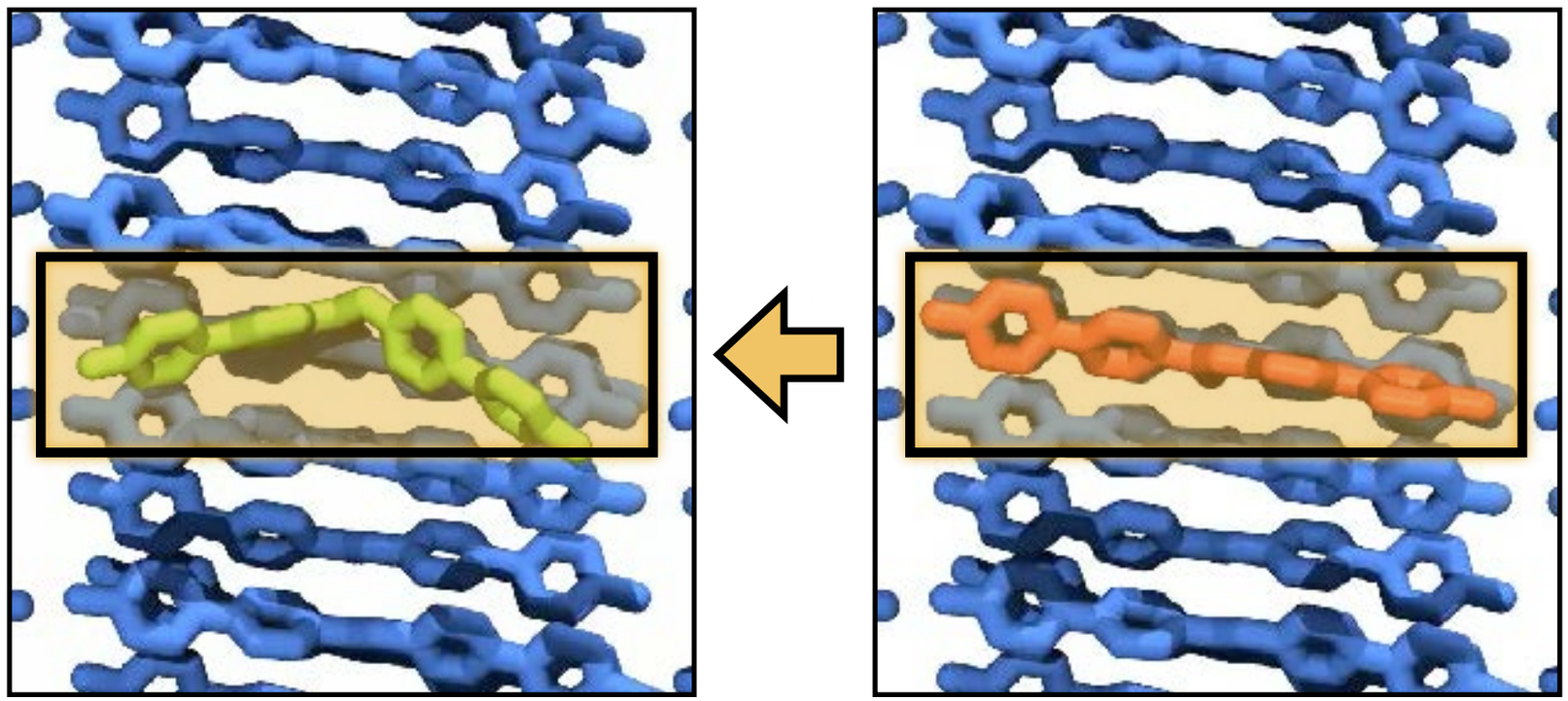


Free energy analysis of CN-MBE aggregates

- **Free energy changes along the MEPs** were analyzed using **the QM/MM Free Energy Perturbation [Zhang 2000].**

$$\Delta F = \Delta E_{\mathrm{QM}} - k_{\mathrm{B}}T \ln \left\langle \exp\left(-\beta \boxed{\Delta E_{\mathrm{QM/MM}}^{(A\to B)}}\right)\right\rangle_{\mathbf{R}_{\mathrm{MM}}}$$

$$\boxed{\Delta E_{\mathrm{QM/MM}}^{(A\to B)}} = \underbrace{E_{\mathrm{QM/MM}}\left(\mathbf{r}_{\mathrm{QM}}^{(B)}, \mathbf{R}_{\mathrm{MM}}^{(A)}\right)}_{\text{perturbed}} - \underbrace{E_{\mathrm{QM/MM}}\left(\mathbf{r}_{\mathrm{QM}}^{(A)}, \mathbf{R}_{\mathrm{MM}}^{(A)}\right)}_{\text{unperturbed}}$$



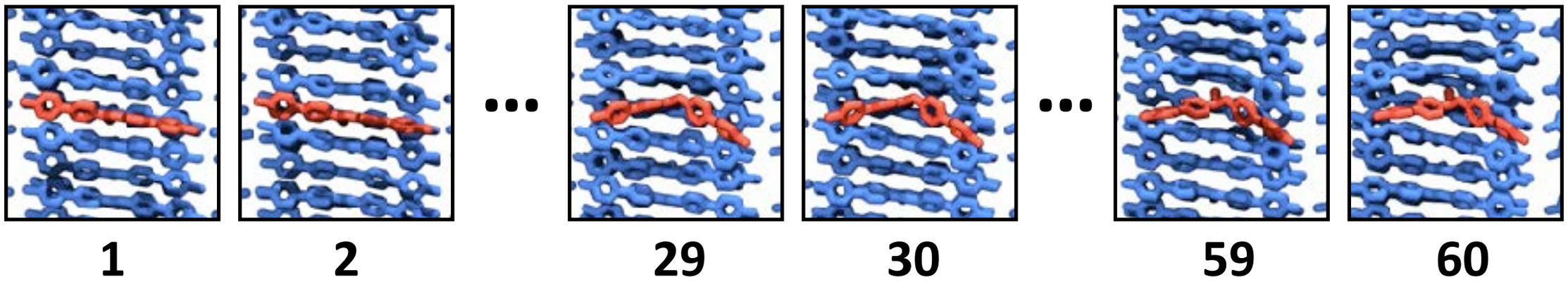
Free energy analysis of CN-MBE aggregates

- **Molecular Dynamics (MD) Simulations** were performed

  → for **60 QM/MM systems** separately, where

  QM molecules were **fixed** to optimized structures on the MEP, and

  MM molecules fluctuated under given canonical ensembles.



→ **Condition:** **NpT** (p = **1** atm; T = **300** K)

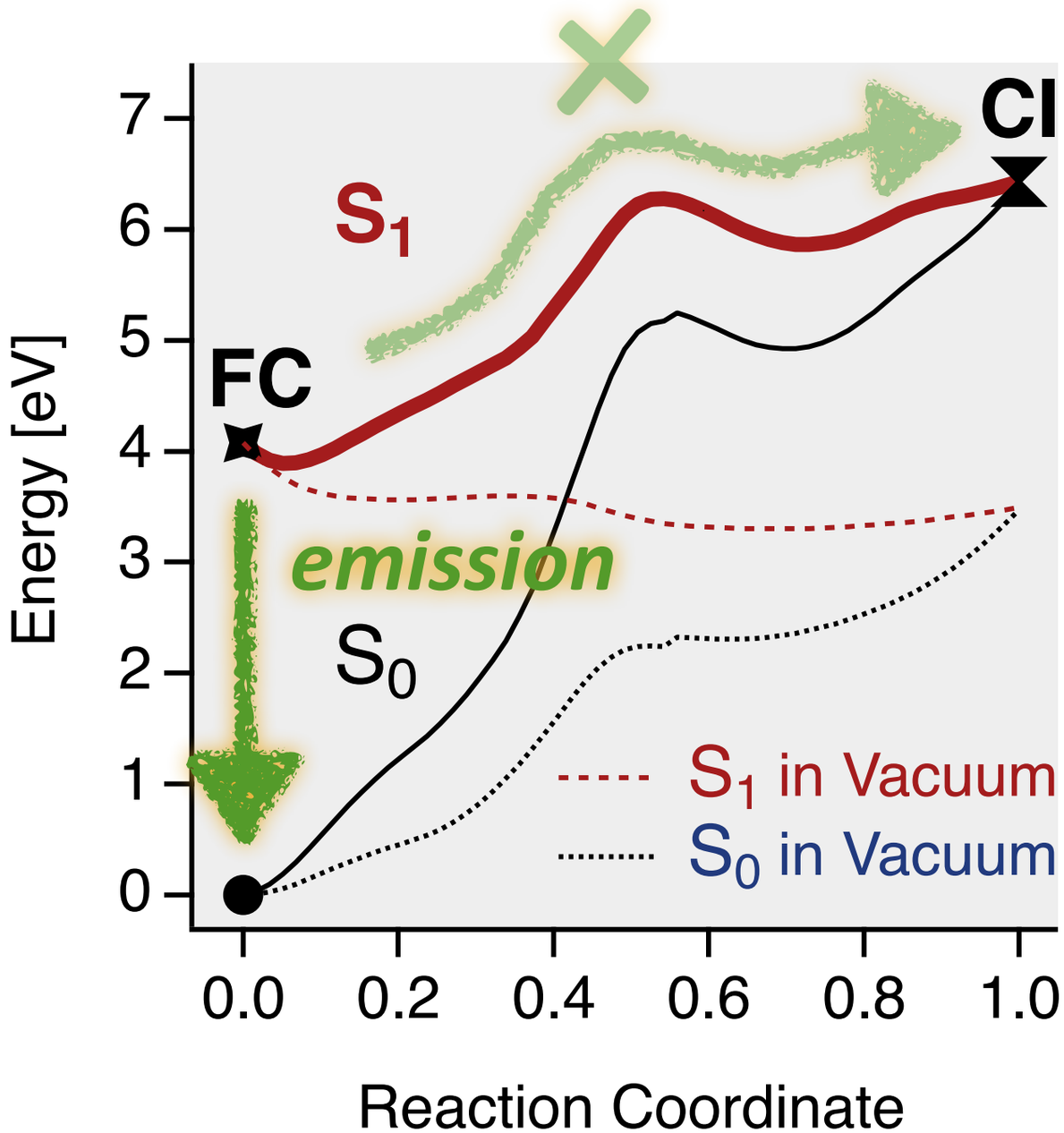
→ **Length:** **2 ns** (1,000,000 steps × 2 fs/step)

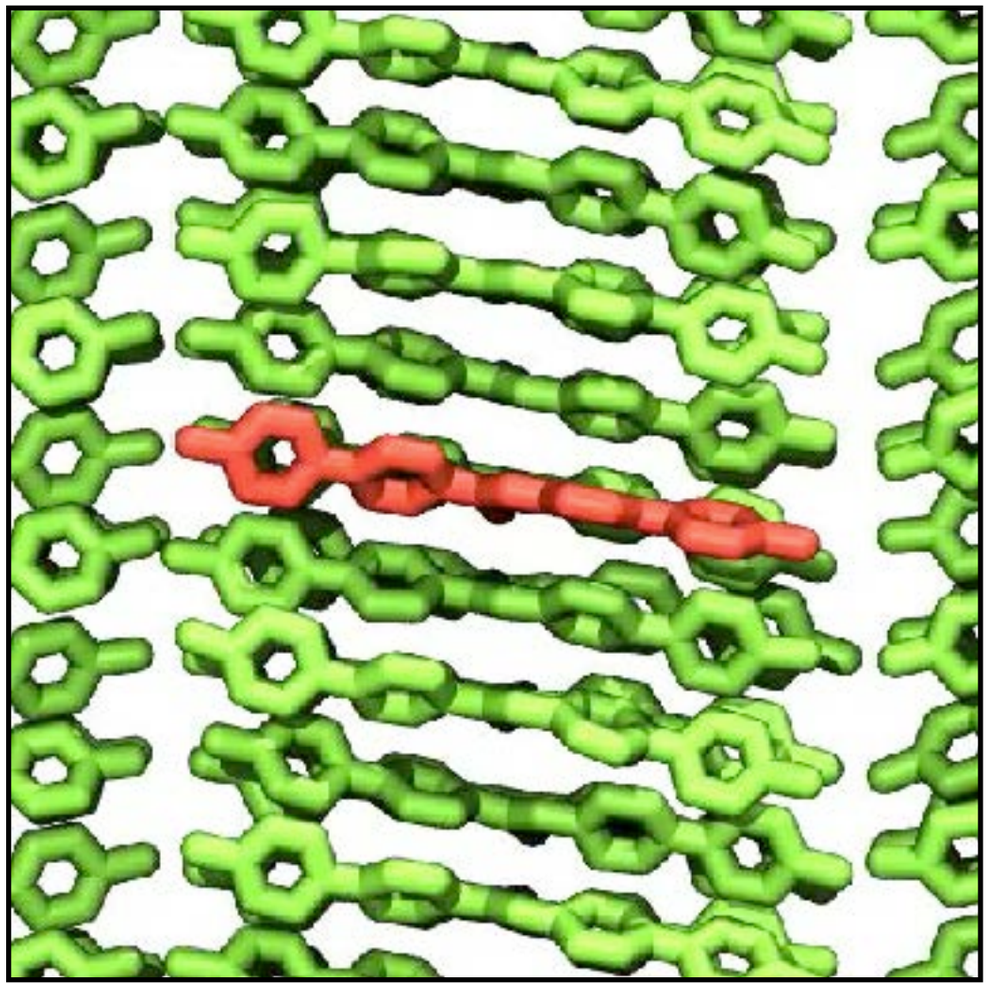
→ **Force Field:** **GAFF** (General Amber FF)

→ **Program:** Amber 18 package

E-form aggregate

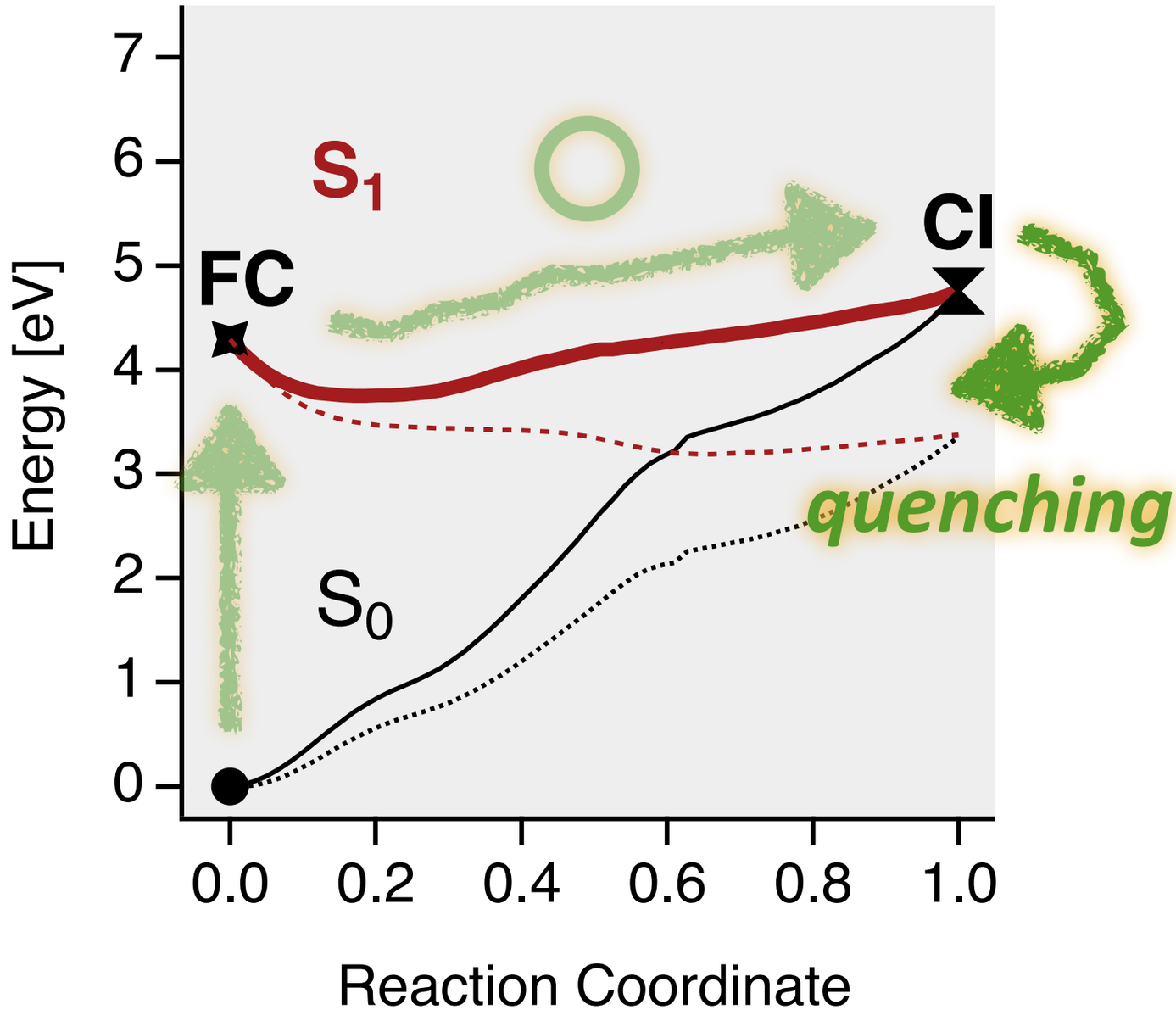
- The free-energy profile shows **the FC-to-CI *"twisting"* path** is **an uphill,** where **the CI point** is **2.3 eV higher** than the FC point.
- **The twisting is restricted.** → **The molecule can not reach CIs.**
- Excitation energy **does not vanish through CIs.** → **FL emission occurs.**

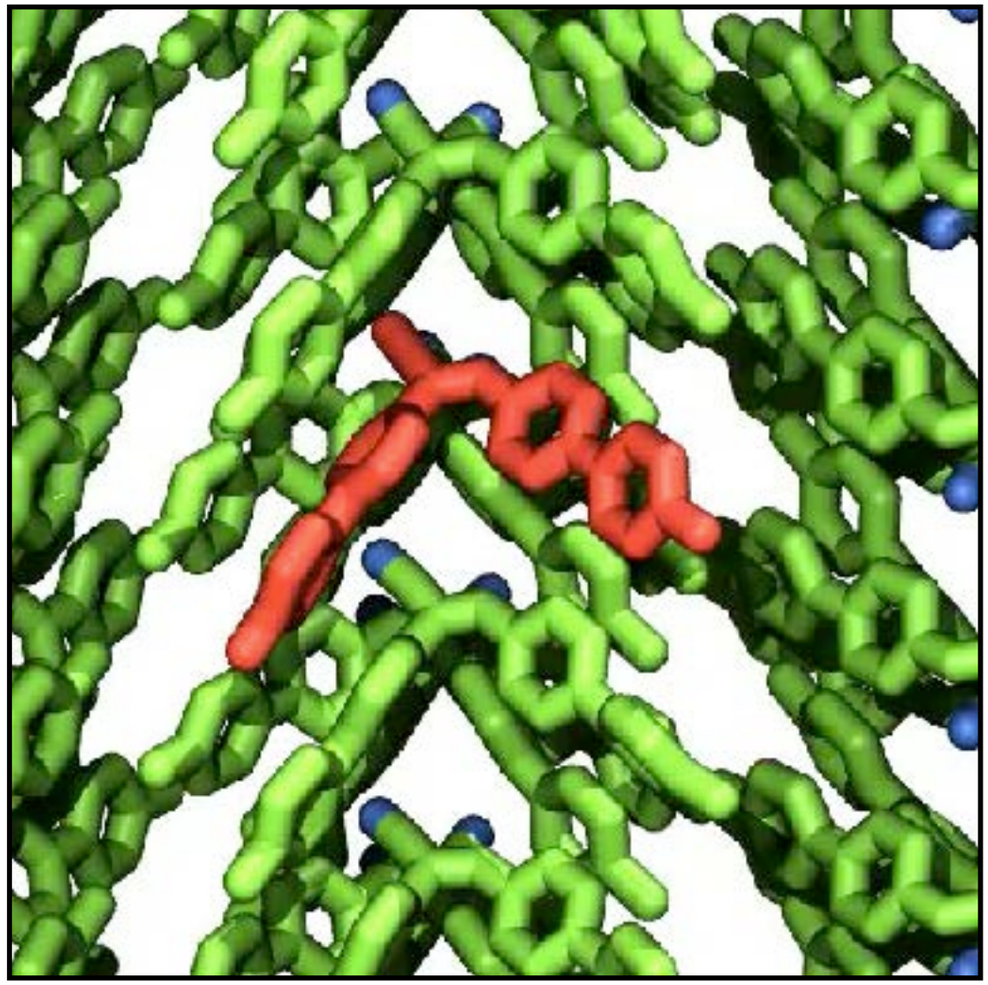




Z-form aggregate

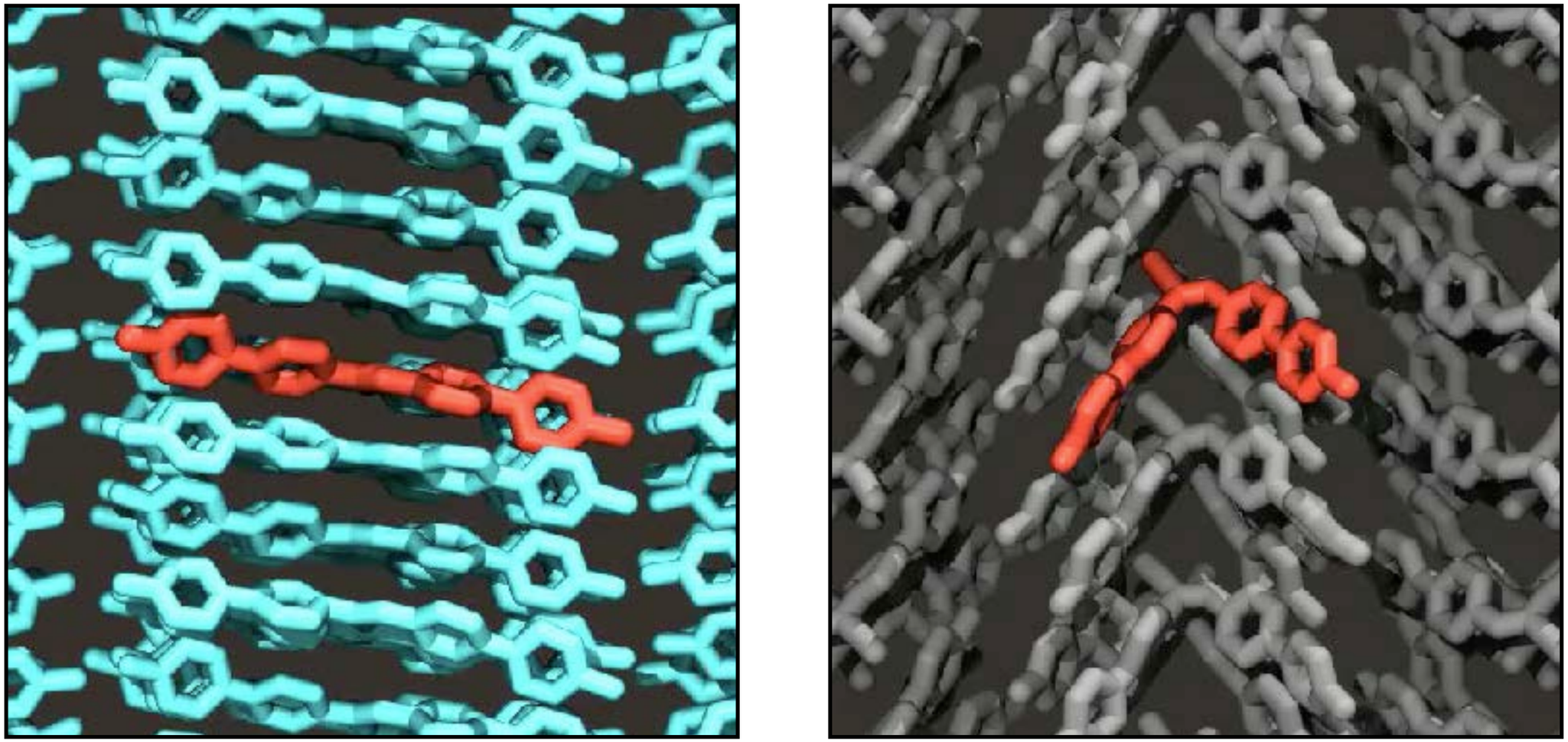
- The free-energy profile shows **the FC-to-CI *"twisting"* path** is **a slight uphill,** where **the CI point** is **0.5 eV higher** than the FC point.
- **The twisting is energetically favorable.** → **The molecule can reach CIs**.
- Excitation energy **vanishes via CIs**. → **FL quenches** even in aggregates.





Conclusion

- **Free energy profiles** along the FC-to-CI pathways successfully captured **the AIE mechanism of CN-MBE**.
- **Our approach used in this study** can be applied to **various optical materials**.



Yamamoto, *Phys. Chem. Chem. Phys.*, Vol. 23, pp. 1317–1324 (2021)