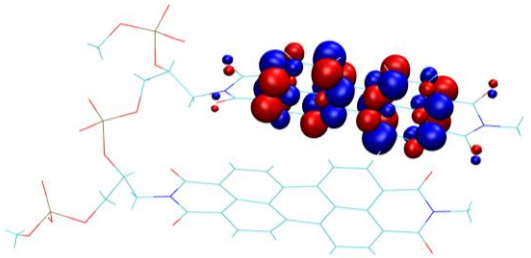
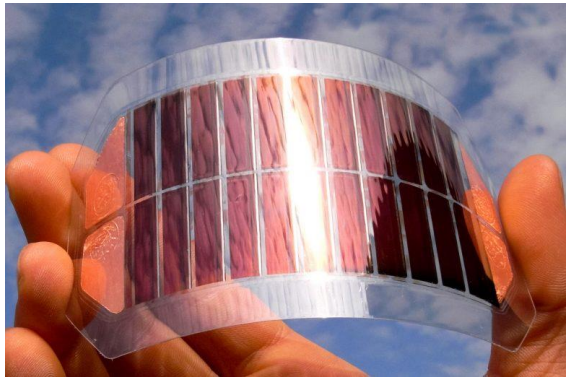
# Photoexcitation Dynamics in Perylene Diimides



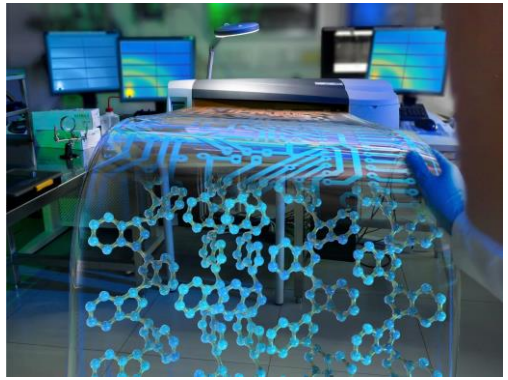
Aliya Mukazhanova

DMR-1847774

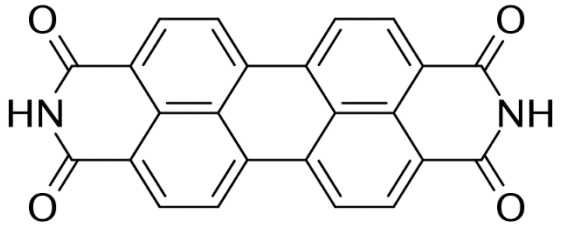
# Perylene Diimide



https://scitechdaily.com/new-flexible-ultrathin-organic-solar-cell-is-both-highly-efficient-and-durable/



https://phys.org/news/2015-06-optimized-enables-custom-electronics.html




Perylene-3,4,9,10-tetracarboxylic diimide
(PTCDI)

- Promising for organic optoelectronics and light harvesting
- Controllable electronic characteristics
- Outstanding chemical, thermal and photostability
- High electron conductivity, strong light absorption
- Affinity to self-assemble

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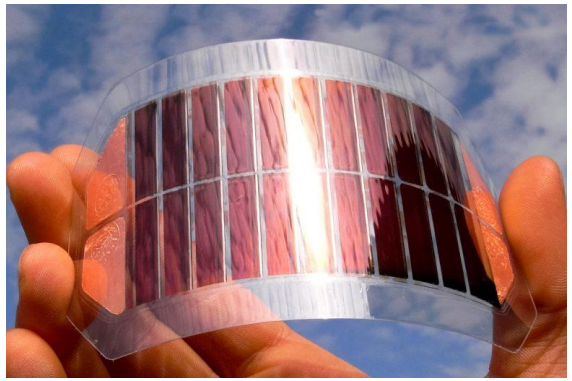
# Perylene Diimide



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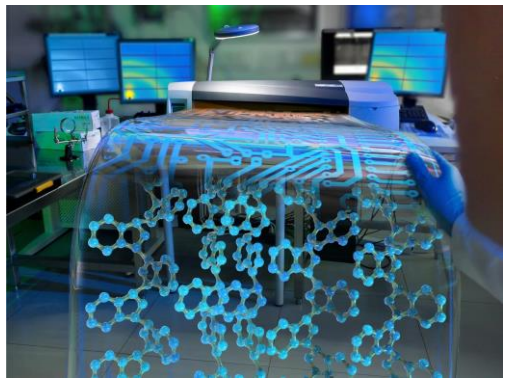
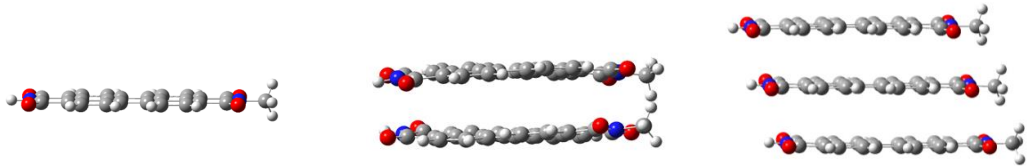


https://phys.org/news/2015-06-optimized-enables-custom-electronics.html

- Transport optical excitation energy efficiently[1-3]
- The excited-state lifetime and decay pathway are highly dependent on inter-molecular orientation[4-7]
- **This work**: How inter-molecular interactions influence energy transfer and exciton localization dynamics? What vibrational modes assist the electronic relaxation?



monomer dimer trimer


1. Mazaheripour, A. et al. *Mater. Horizons* **2017**, *4* (3), 437–441
2. Schubert, A. Et al. *J. Phys. Chem. A* **2014**, *118* (8), 1403–1412
3. Ma, L. et al. *J. Phys. Chem. A* **2014**, *118* (5), 838–843 (11)
4. Brown, K. E. et al. *J. Phys. Chem. Lett.* **2014**, *5* (15), 2588–2593.
5. Farag, M. H. et al. *J. Phys. Chem. C* **2018**, *122* (45), 25753–25763.
6. Le, A. et al. *J. Am. Chem. Soc.* **2018**, *140* (2), 814–826.
7. Wirsing, S. et al.*J. Phys. Chem. C* **2019**.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# Non-adiabatic Excited State Dynamics

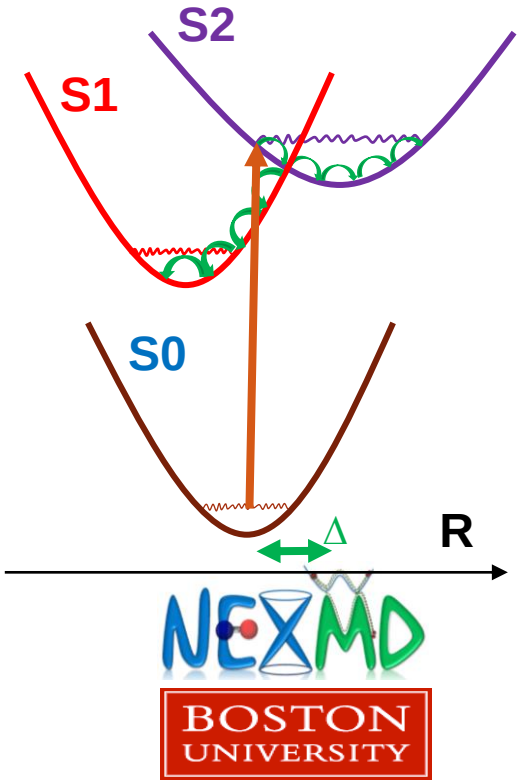

With Sergei Tretiak (LANL)
Sebastian Fernandez-Alberti (The National University of Quilmes)

**Ground state geometry** → Optimized with wB97-XD functional in Gaussian16 code

**Ground state wavepacket** → Classical molecular dynamics run for 300 ps

**Excited-State Spectrum** → AM1 Hamiltonian 700 trajectories

**Non-adiabatic excited state dynamics** → Tully's fewest switches surface hopping 1 ps trajectory




$$Mi\ddot{R}i(t) = -\nabla E\alpha\big(R(t)\big) - \varsigma M\dot{R}\, i(\mathrm{t}) + \mathrm{A(t)}$$

Langevin equation of motion for nuclei

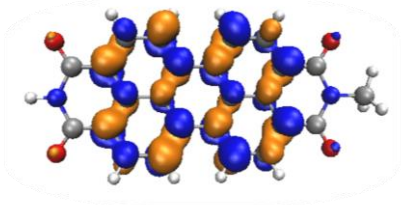
$$i\hbar\frac{\partial c_\alpha(t)}{\partial t} = c_\alpha(t)E\alpha - i\hbar\sum_\beta c_\beta(t)\dot{R}d_{\alpha\beta}$$

Time-dependent expansion coefficients

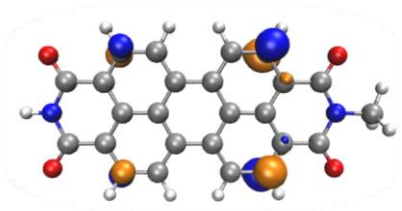

T. Nelson, S. Fernandez-alberti, V. Chernyak, A. E. Roitberg and S. Tretiak *J. Phys. Chem. B*, 2011, **115**, 5402; T. Nelson, S. Fernandez-Alberti, A. E. Roitberg and S. Tretiak *Acc. Chem. Res.*, 2014, **47**, 1155; J. C. Tully *J. Chem Phys.*, 1990, **93**, 1061.

# Monomer Internal Conversion Dynamics

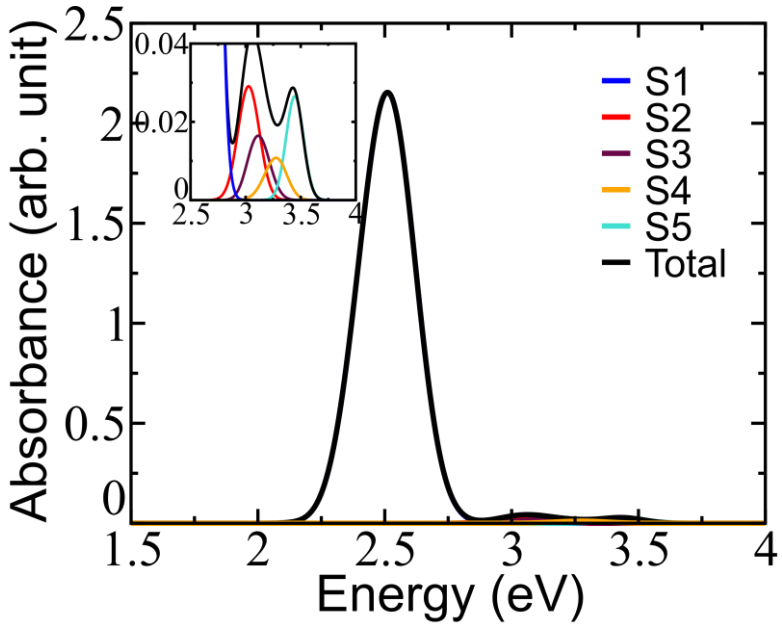
- Excite S2, non-radiative decay to S1 over ~ 1 ps

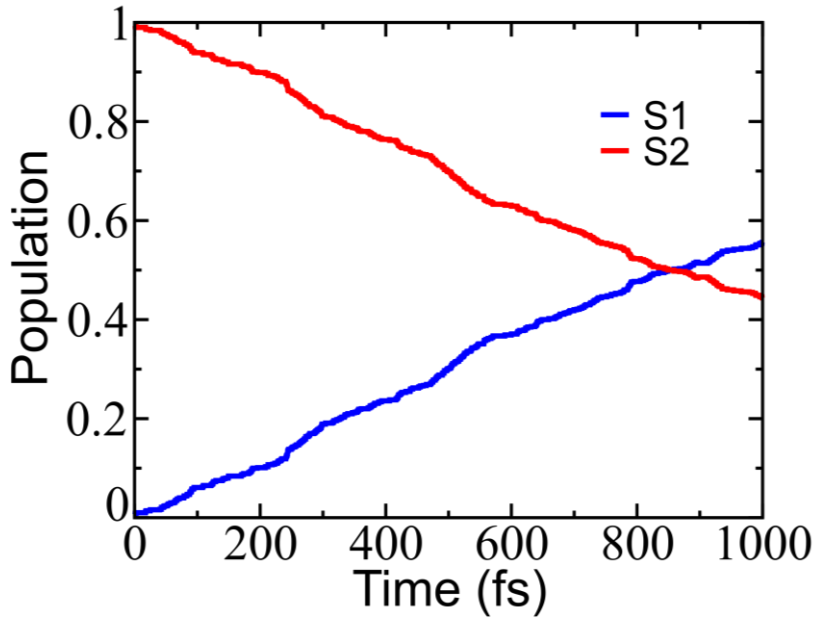


**S1 (2.55 eV, f=0.57)**



**S2 (3.10 eV, f=0.01)**




- 50% decay to S1 at 860 fs

A. Mukazhanova, W. Malone, H. Negrin-Yuvero, S. Fernandez-Alberti, S. Tretiak, S. Sharifzadeh, JCP (2020)

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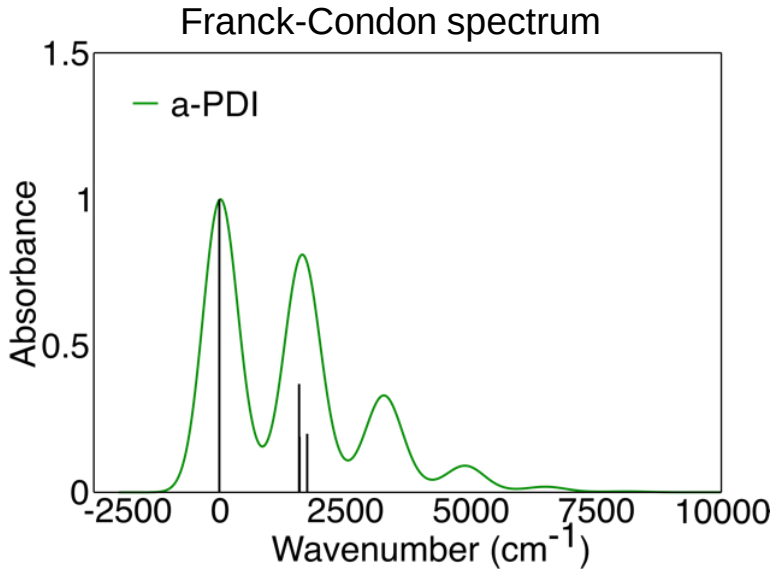
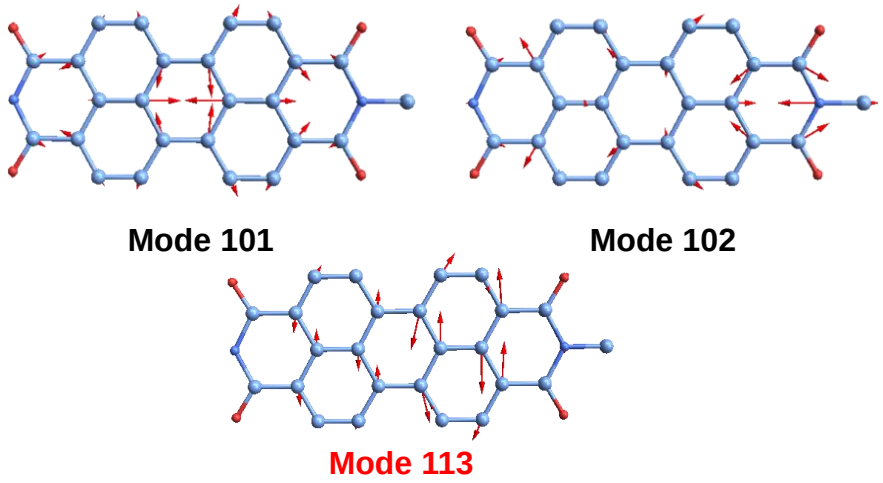
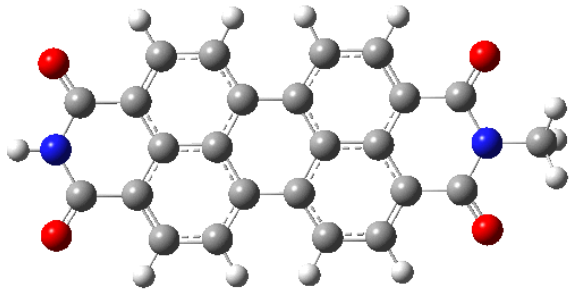
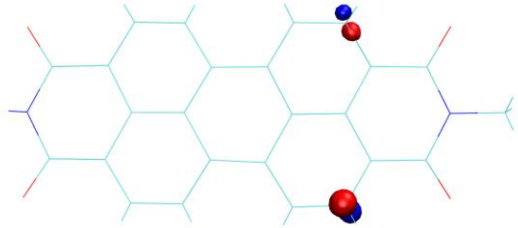
# Vibrational Excitations from Franck-Condon analysis : monomer




Atomic motion suggests Franck-Condon active C-C breathing modes important for dynamics





H. Negrin Yuvero, A. Mukazhanova, V. Freixas, S. Tretiak, S. Sharifzadeh, S. Fernandez-Alberti, *J. Phys. Chem. A* (2022)

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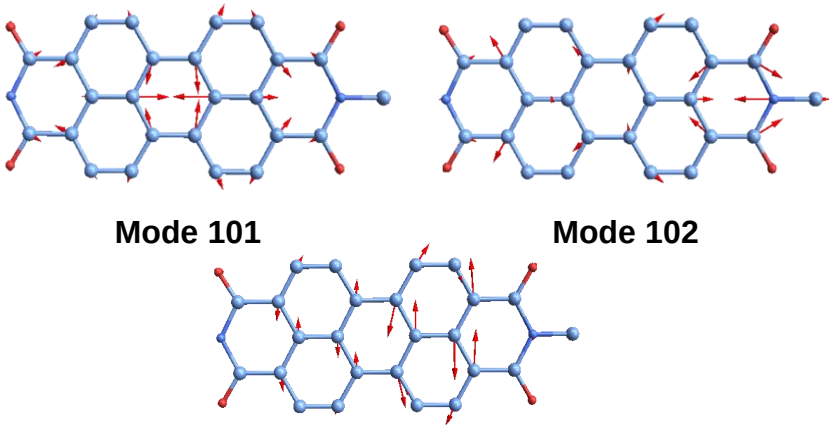
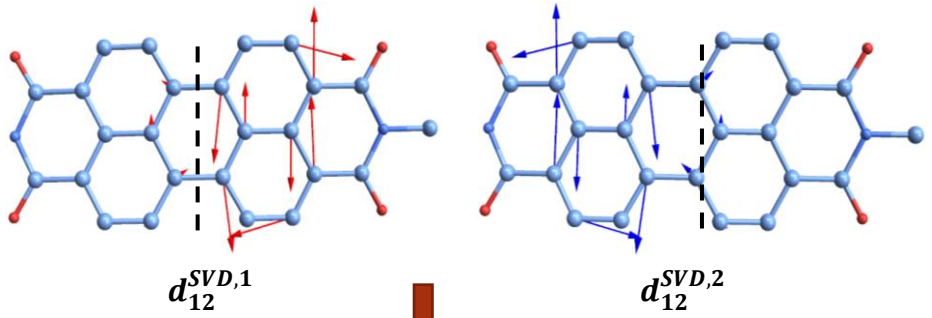
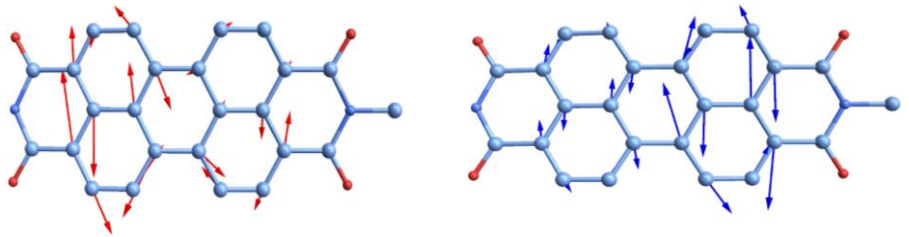
# Vibrational Excitations During Dynamics: monomer



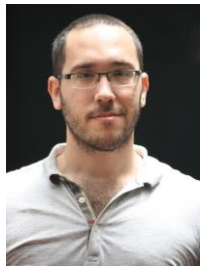

Franck-Condon active modes

Two different vectors of non-adiabatic derivative couplings $d_{12}$ are identified using the singular value decomposition (SVD)




Modes #112 and #113 provide dominant contributions to $\boldsymbol{d_{12}^{SVD,1}}$ and $\boldsymbol{d_{12}^{SVD,2}}$



Victor Frexias

Hassiel Negrin-Yuvero

H. Negrin Yuvero, A. Mukazhanova, V. Freixas, S. Tretiak, S. Sharifzadeh, S. Fernandez-Alberti, *J. Phys. Chem. A* (2022)

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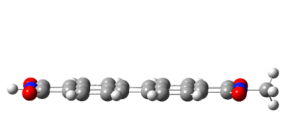
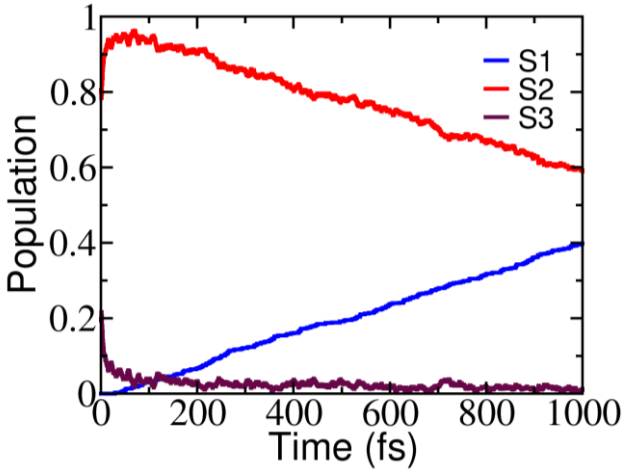
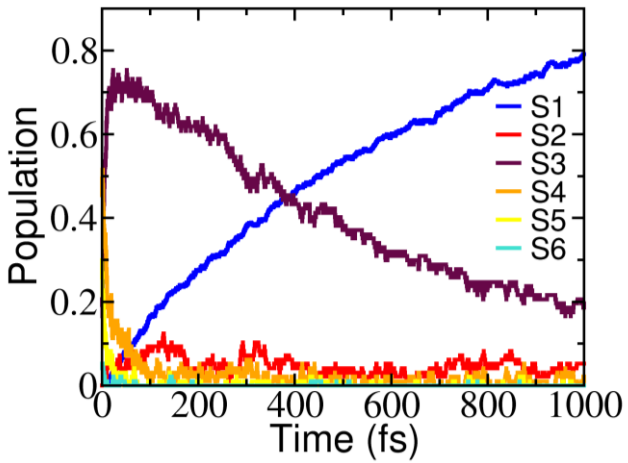
# Stacking Leads to Faster Dynamics

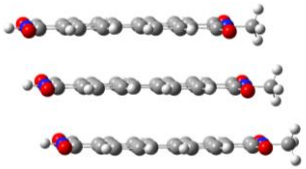


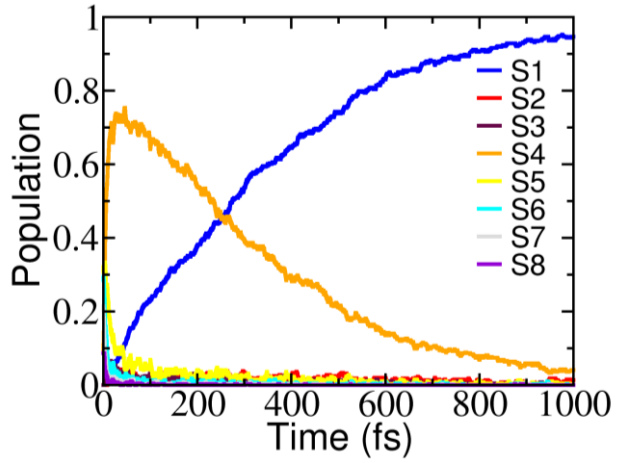



Excited at S2
50% decay at > 1 ps

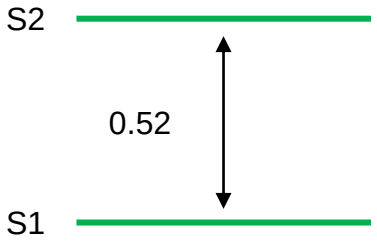


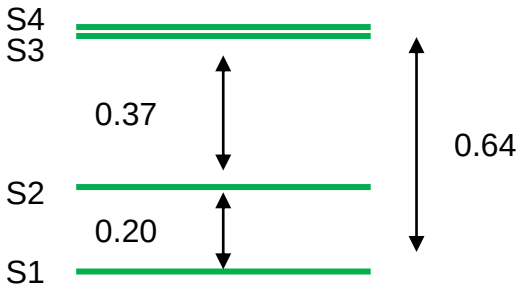

Excited at S4
50% decay to S1 at 400 fs

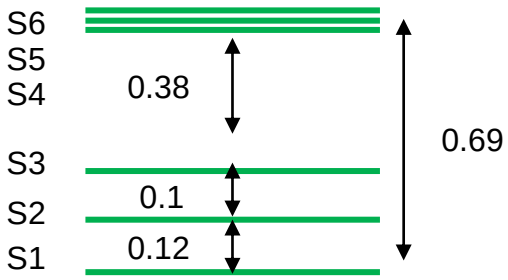





Excited at S6
50% decay to S1 at 240 fs




**Reduced energy splitting results in more efficient funneling of energy**

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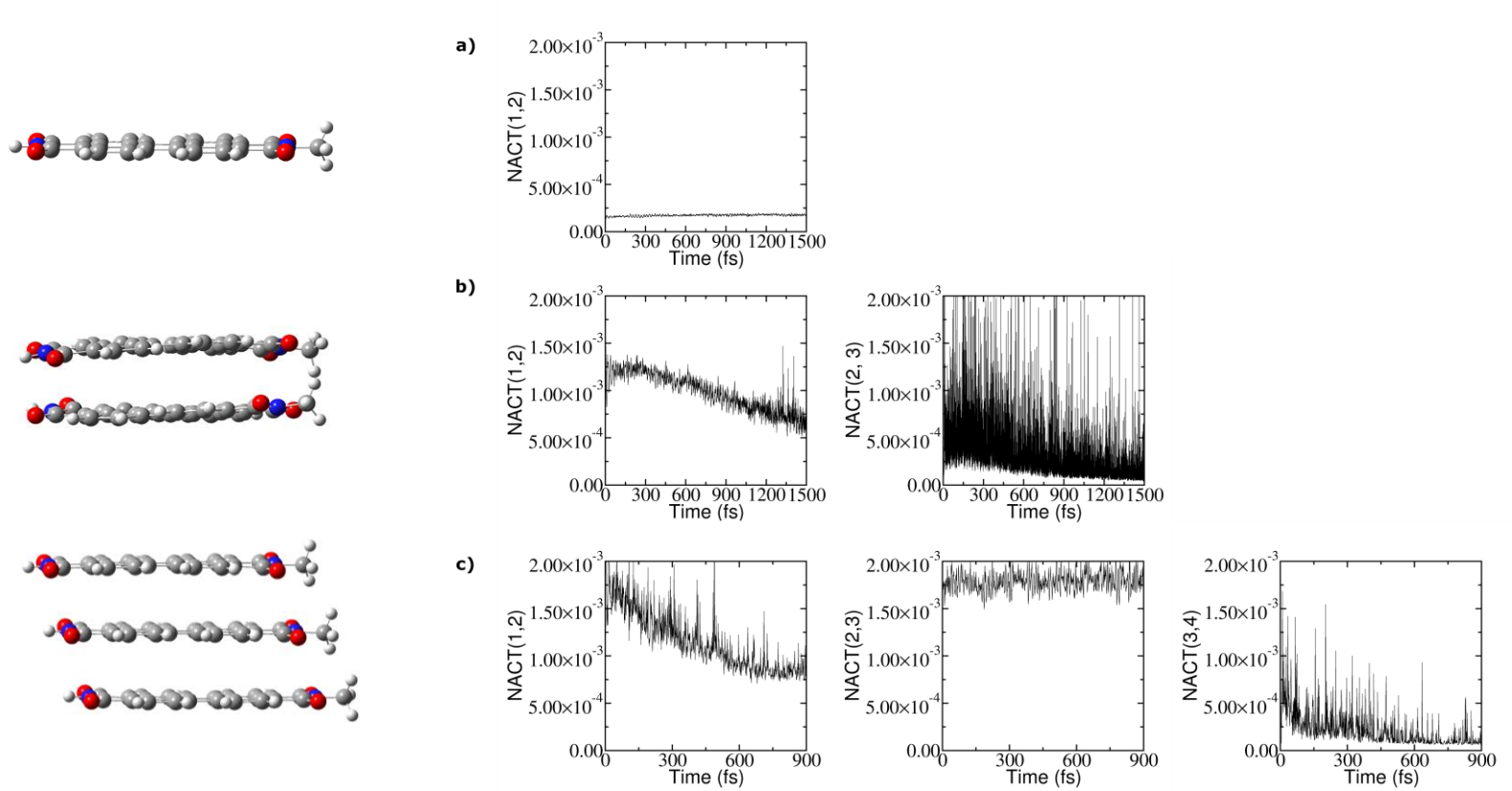
A. Mukazhanova, H. Negrin-Yuvero, V. Frexias, S. Fernandez-Alberti, S. Tretiak, S. Sharifzadeh, *J. Mater. Chem. C* (2023)

# Stacking Leads to Faster Dynamics




- The analysis of non-adiabatic coupling terms (NACT) explains increase of energy decay in stacked molecules
- The internal energy conversion has a sequential character from highest to lower excited state

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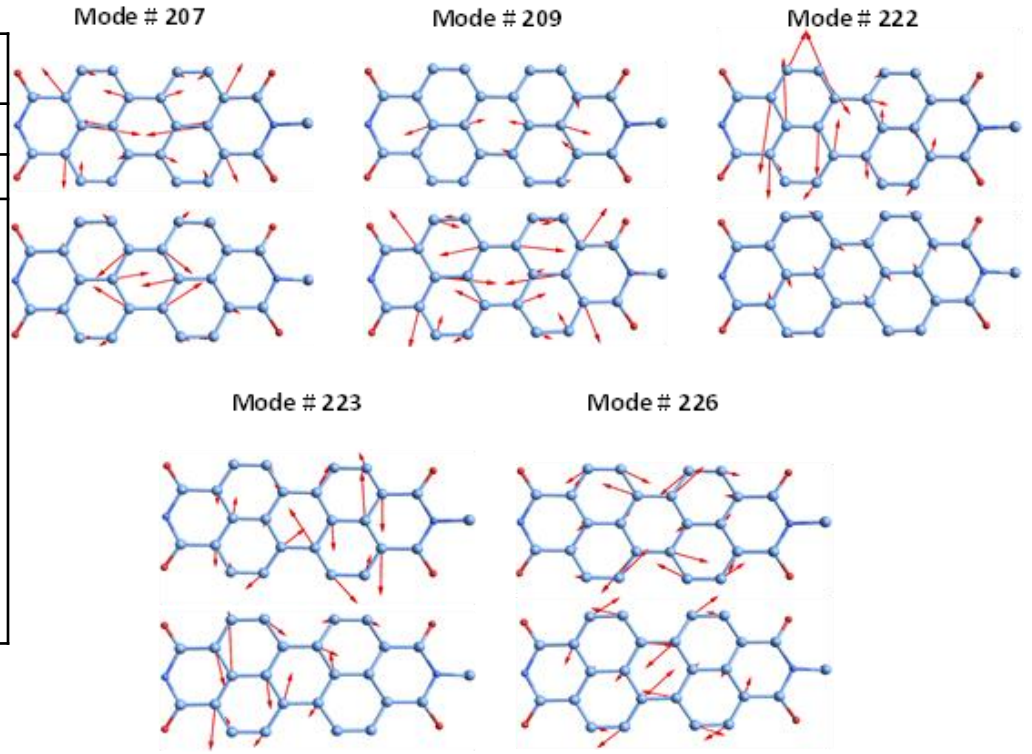
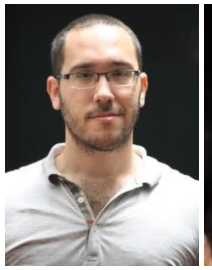
# Vibrational Excitations During Dynamics: dimer

| Effective hop | | | |
|---|---|---|---|
| $S_3 \rightarrow S_2$ | | $S_2 \rightarrow S_1$ | |
| # Mode | Overlap | # Mode | Overlap |
| 226(1865) | 0.78 | 226(1865) | 0.88 |
| 209(1693) | 0.27 | 223(1795) | 0.16 |
| 207(1679) | 0.25 | 222(1792) | 0.16 |
| 222(1792) | 0.14 | 207(1679) | 0.14 |
| 199(1596) | 0.13 | 225(1797) | 0.12 |
| 223(1795) | 0.13 | 122(908) | 0.10 |
| 122(908) | 0.11 | 121(904) | 0.10 |
| 175(1416) | 0.10 | 209(1693) | 0.10 |
| 121(904) | 0.10 | 224(1795) | 0.09 |
| 234(2025) | 0.09 | 234(2025) | 0.08 |





Victor Frexias


Hassiel Negrin-Yuvero

**Similar vibrational modes assists the energy transfer making it more efficient and faster**

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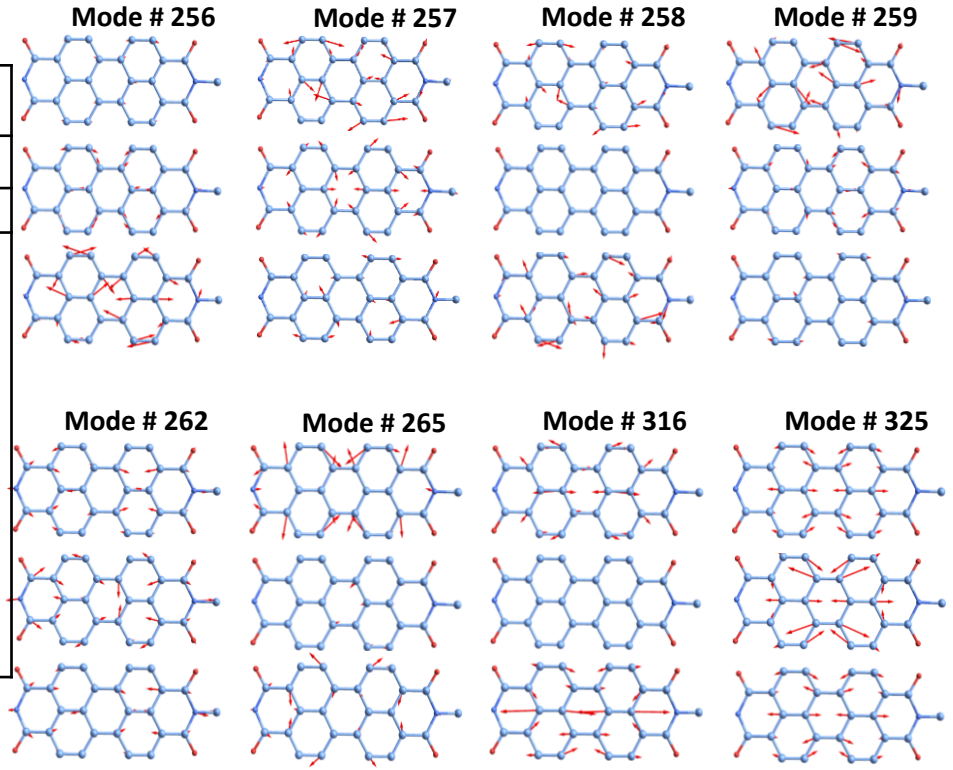
A. Mukazhanova, H. Negrin-Yuvero, V. Frexias, S. Fernandez-Alberti, S. Tretiak, S. Sharifzadeh, *J. Mater. Chem. C* (2023)

# Vibrational Excitations During Dynamics: trimer

| Effective hops | | | | | |
|---|---|---|---|---|---|
| $S_4 \rightarrow S_3$ | | $S_3 \rightarrow S_2$ | | $S_2 \rightarrow S_1$ | |
| # Mode | Overlap | # Mode | Overlap | # Mode | Overlap |
| 259 (1410) | 0.45 | 256 (1402) | 0.51 | 256 (1402) | 0.53 |
| 325 (1763) | 0.38 | 265 (1431) | 0.40 | 265 (1431) | 0.39 |
| 257 (1408) | 0.37 | 316 (1719) | 0.37 | 316 (1719) | 0.38 |
| 265 (1432) | 0.32 | 259 (1410) | 0.33 | 258 (1408) | 0.31 |
| 262 (1419) | 0.25 | 258 (1408) | 0.31 | 259 (1410) | 0.31 |
| 264 (1428) | 0.16 | 310 (1647) | 0.18 | 310 (1647) | 0.18 |
| 261 (1418) | 0.16 | 274 (1480) | 0.18 | 274 (1480) | 0.17 |
| 294 (1580) | 0.15 | 261 (1418) | 0.12 | 271 (1476) | 0.11 |
| 286 (1524) | 0.14 | 271 (1476) | 0.11 | 261 (1418) | 0.10 |
| 244 (1335) | 0.13 | 287 (1525) | 0.09 | 264 (1428) | 0.10 |




**Activated vibrational modes are different from dimer case**

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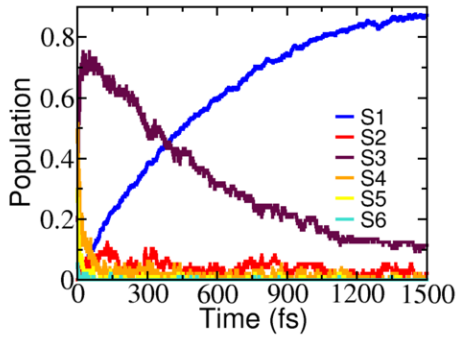
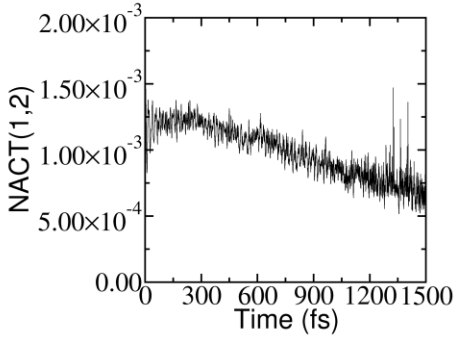
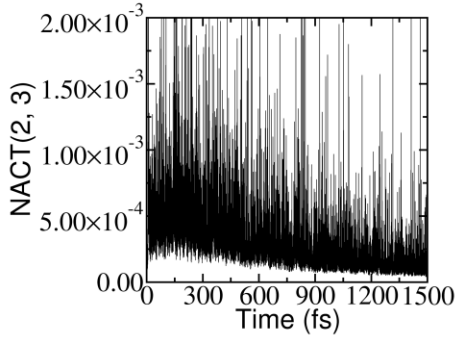
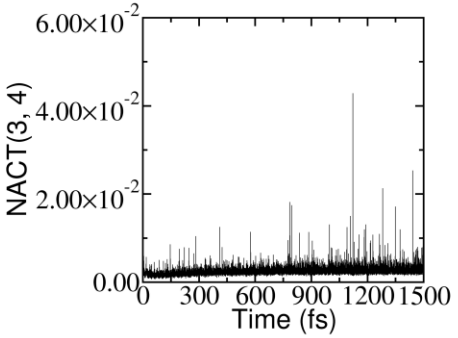
A. Mukazhanova, H. Negrin-Yuvero, V. Frexias, S. Fernandez-Alberti, S. Tretiak, S. Sharifzadeh, *J. Mater. Chem. C* (2023)

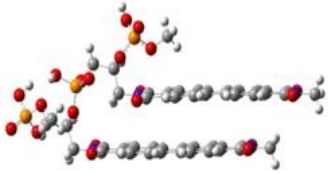
# Backbone Slows Internal Energy Conversion Dynamics

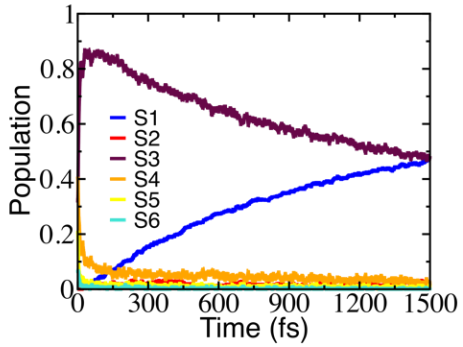


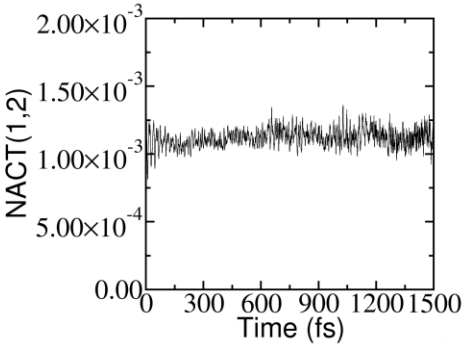



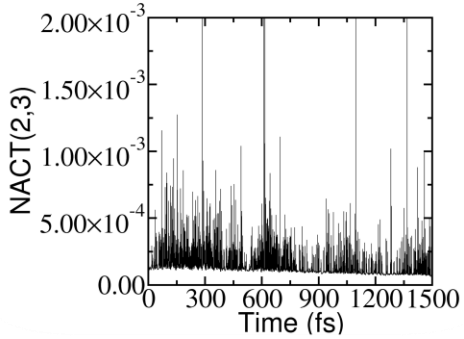



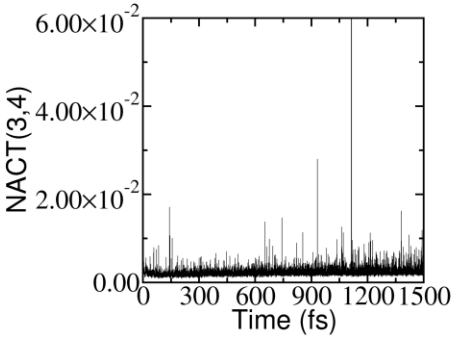






- Rapid transfers (within a few fs) from higher energy states to S3 and a slower decay from S3 to S1.
- There is 50% population transfer from S3 to S1 at 400fs for dimer and at 1500fs for dimer with backbone.
- Why backbone slows down the dynamics?

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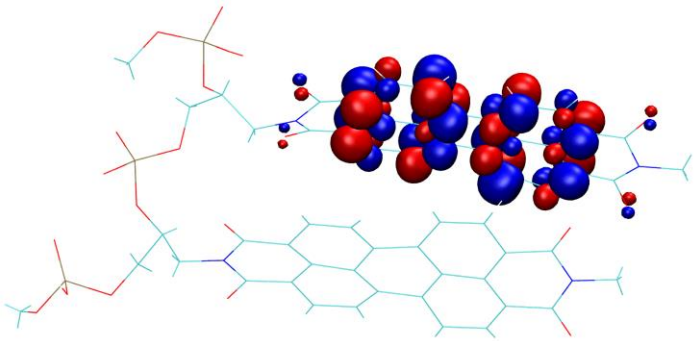
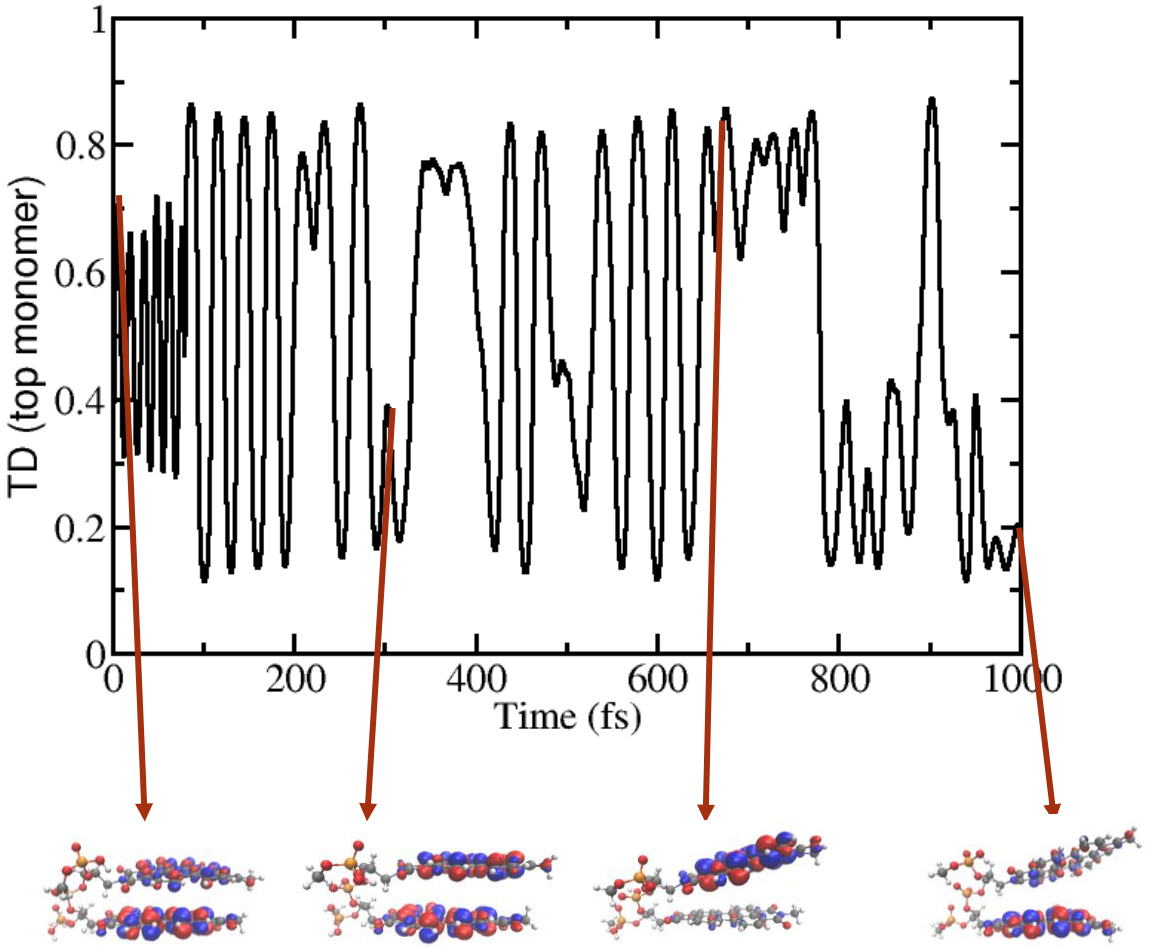
A. Mukazhanova, H. Negrin-Yuvero, V. Frexias, S. Fernandez-Alberti, S. Tretiak, S. Sharifzadeh, *J. Mater. Chem. C* (2023)

# Exciton Localization in Dimer

Example trajectory:






**After decay to S1, excited-state localizes and hops between molecules**

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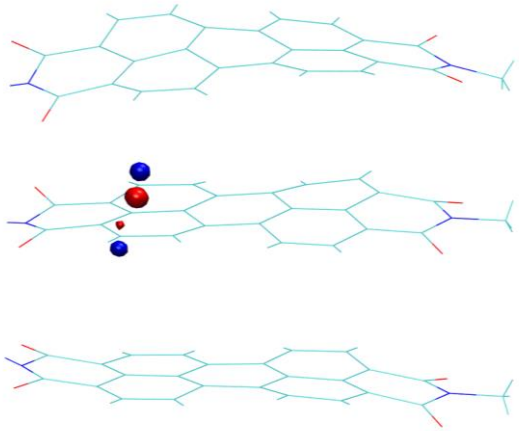
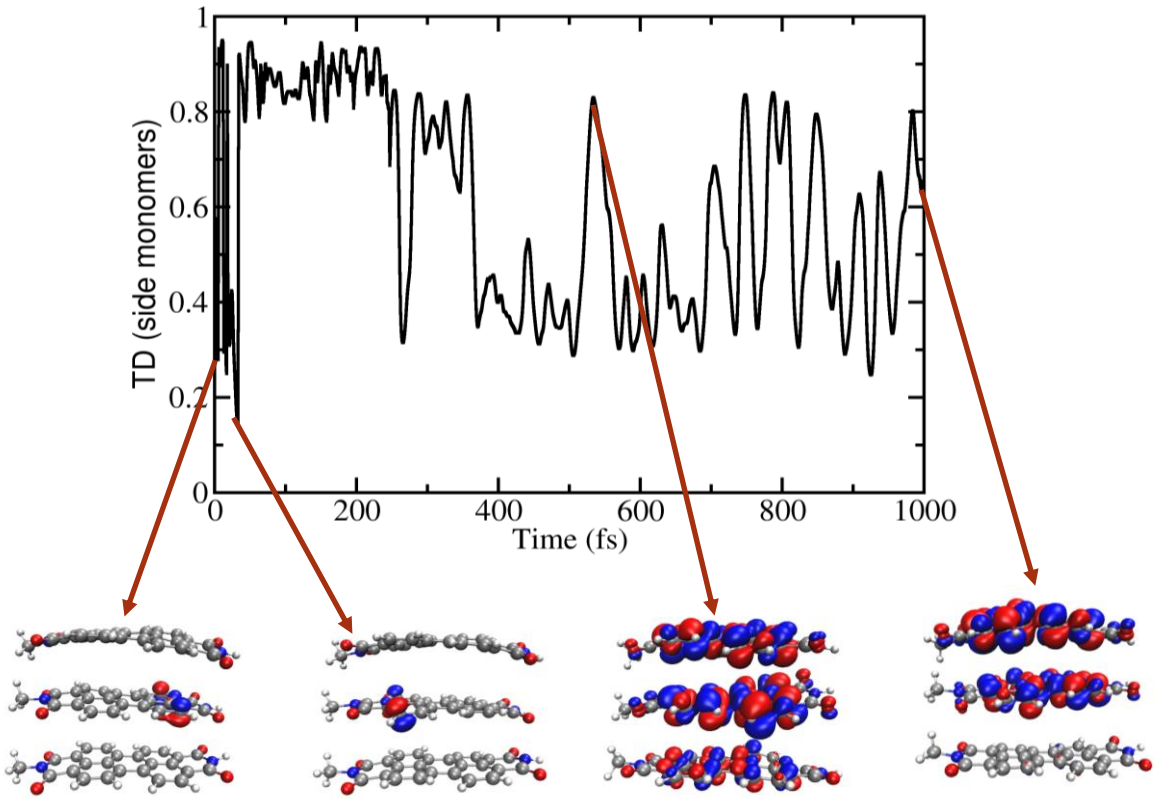
# Exciton Delocalization in Trimer






**After decay to S1 (246 fs), excited-state delocalizes**

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# Conclusions

- Photo-induced excited-state dynamics of functionalized perylene diimide monomer, dimer and trimer
- The stacking accelerates the energy transfer due to reduced effective energy gap and activation of similar vibrational modes
- The set of activated vibrational modes are different in dimer than in trimer.
- The backbone slows down the relaxation rate

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