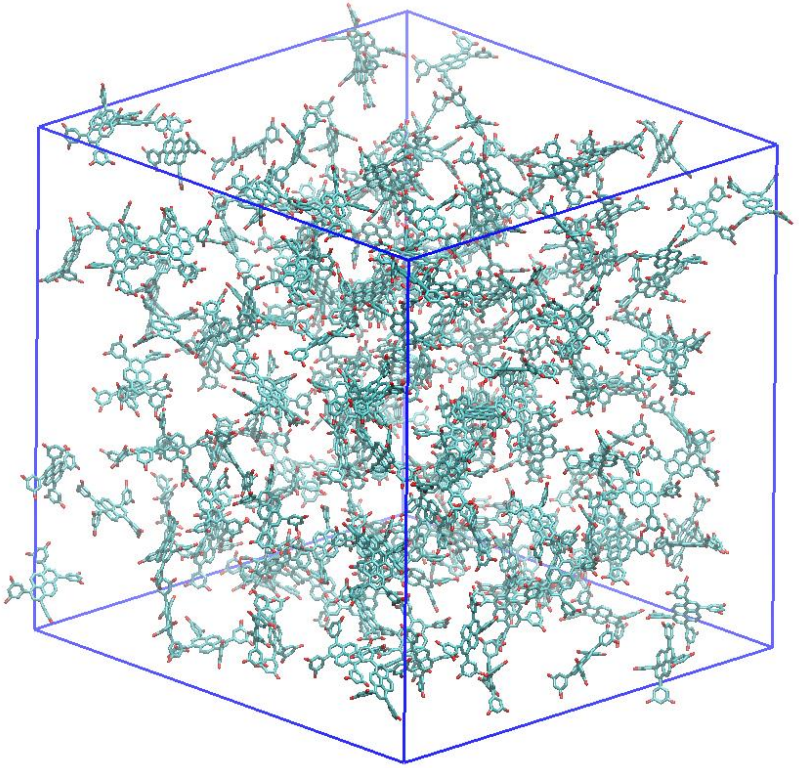
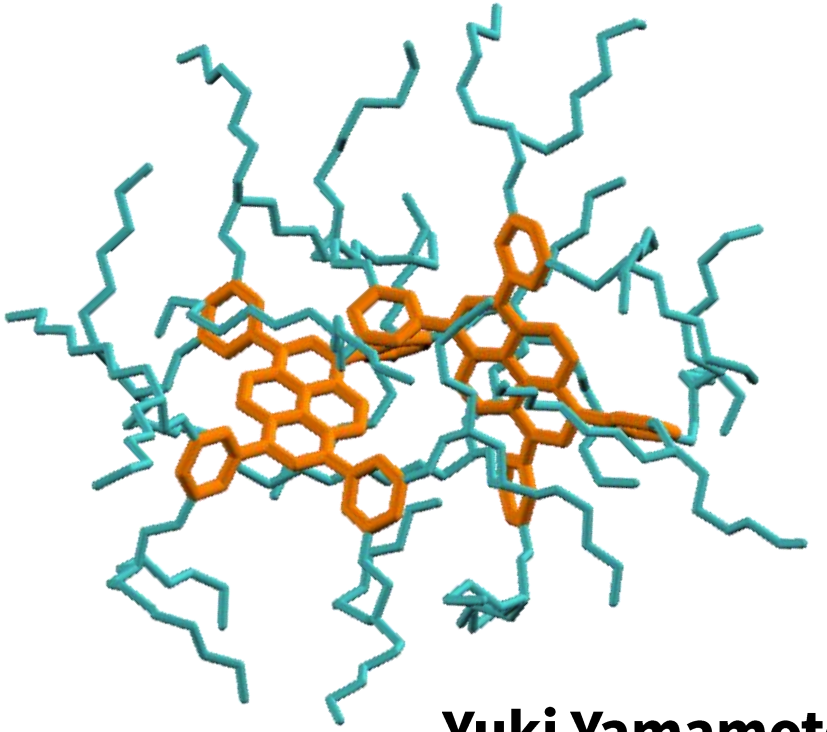
Molecular dynamics simulation and theoretical analysis of liquid pyrenes

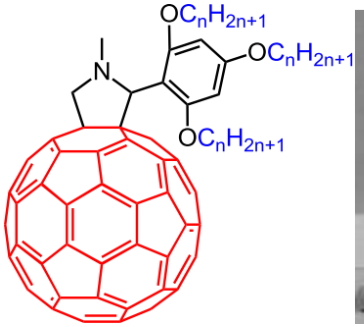


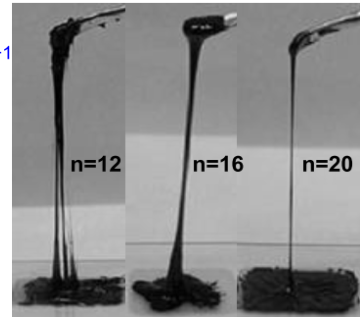


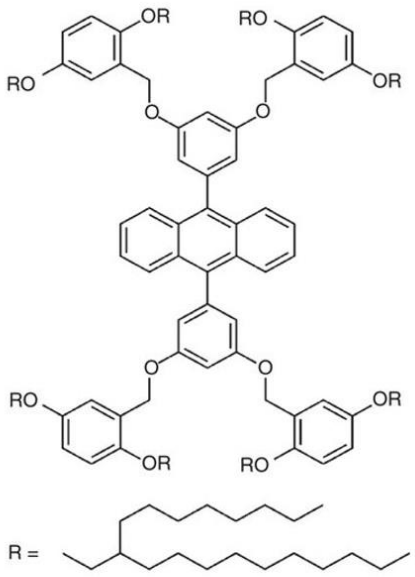
Yuki Yamamoto

Kyoto Univ.

Alkyl-π engineered molecular liquid





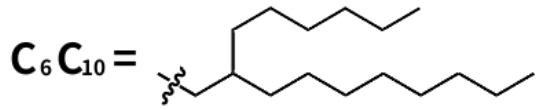


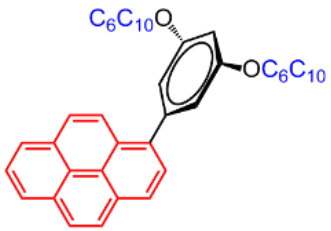
Liquid Anthracene

Nakanishi, T. et al. *J. Am. Chem. Soc.*, **2006**, *128*, 10384. / *Nat. Commun.* **2013**, *4*, 1969

- **Newtonian-type liquid at room temperature in solvent-free condition.**
- **the physical properties were extensively tunable by the number, length, substituent position, and motif of alkyl chains attached to the π conjugated moieties.**

Liquid pyrenes (targets of this study)





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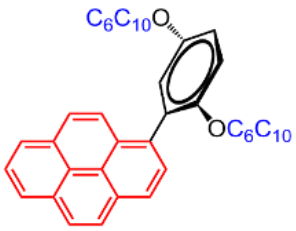

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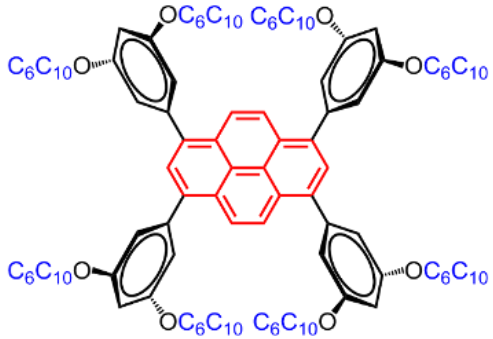

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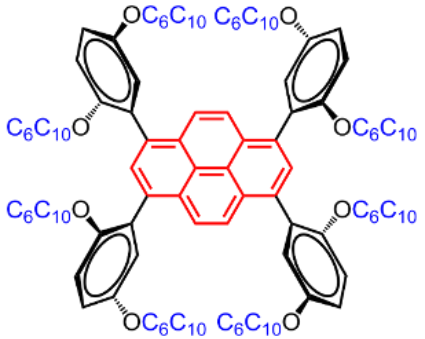
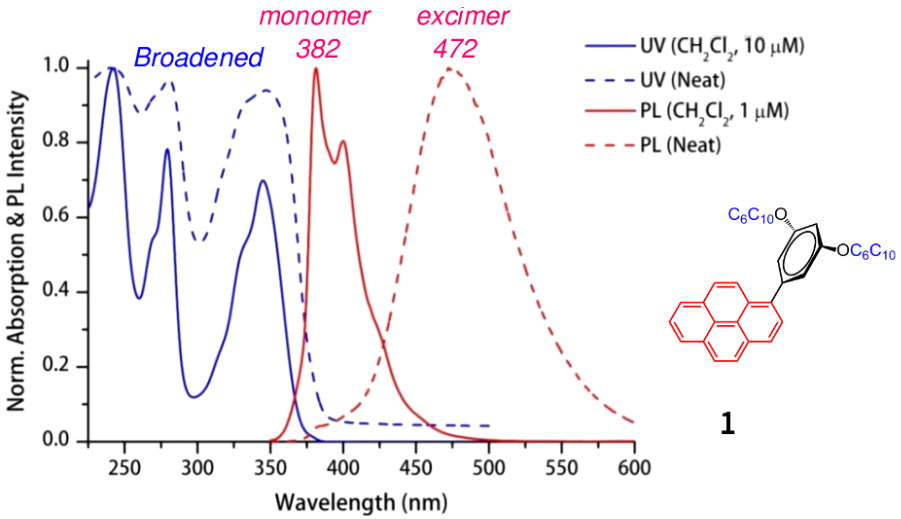


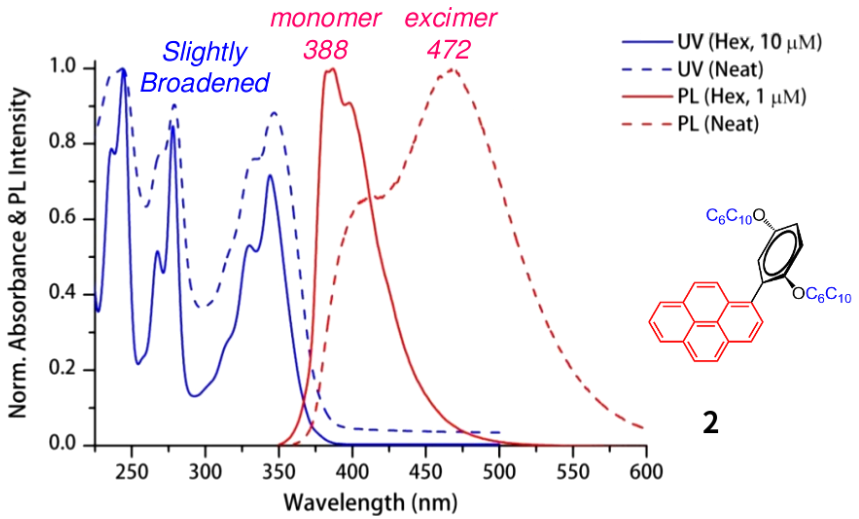
4

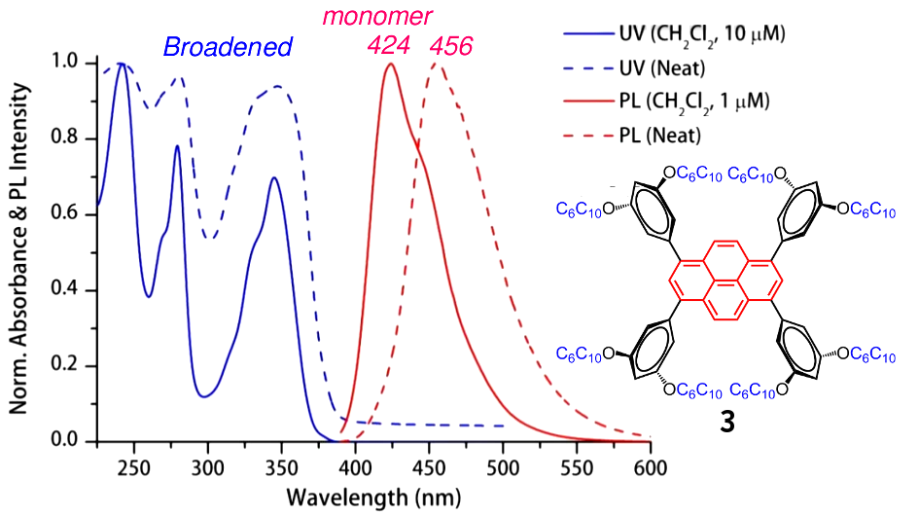
Nakanishi, T. et al. *Sci. Rep.* **2017**, 7, *3416*.

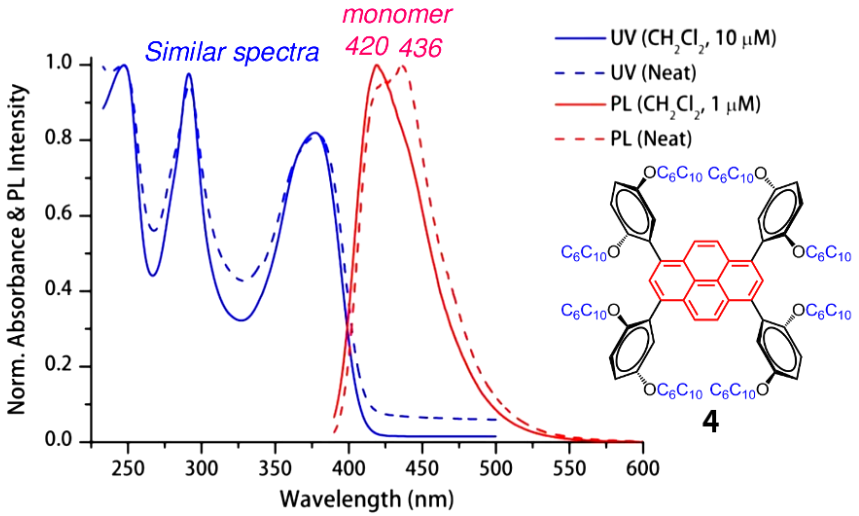
- **Newtonian-type liquids at room temperature in solvent-free condition**
- **Rheological and luminescence properties change by differences in position or number of substituted alkyl chains.**

Absorption and fluorescence spectra of liquid pyrenes



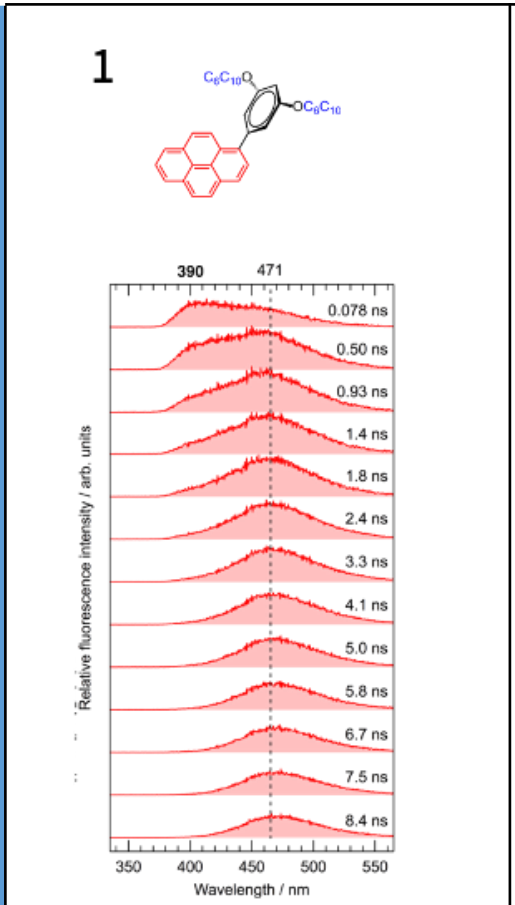
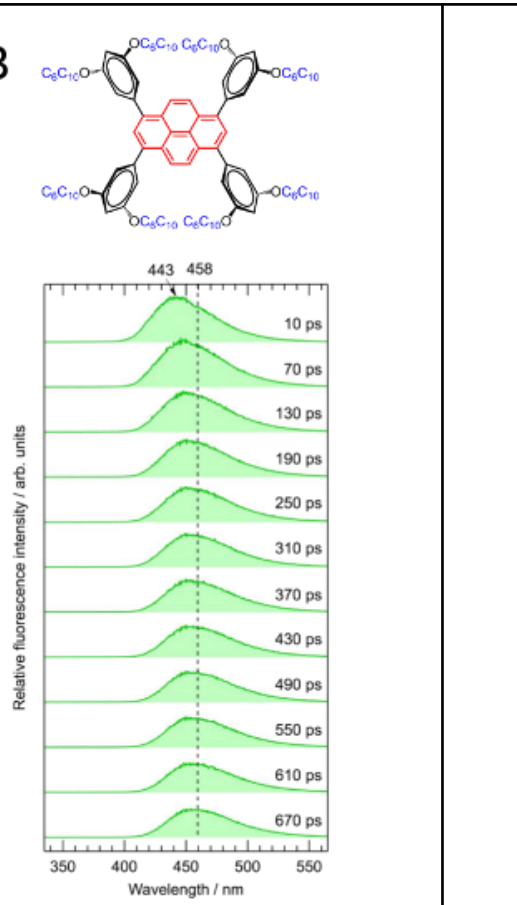
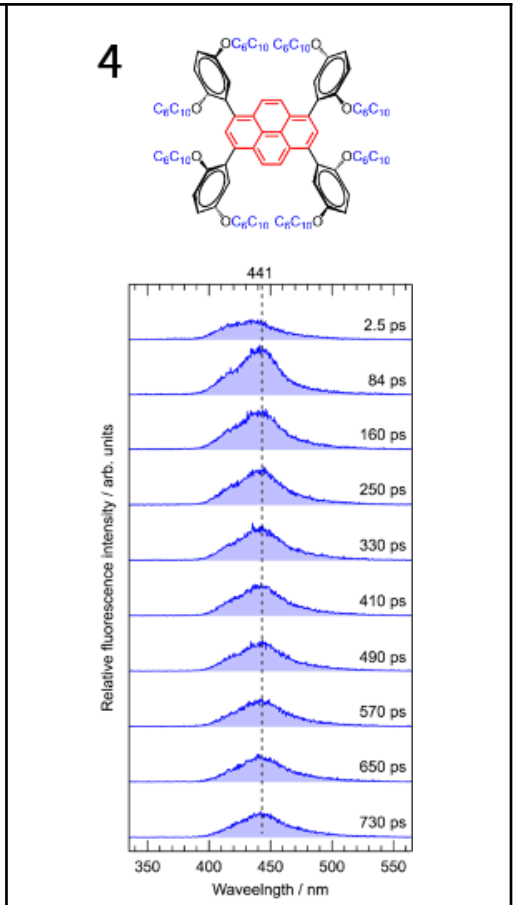




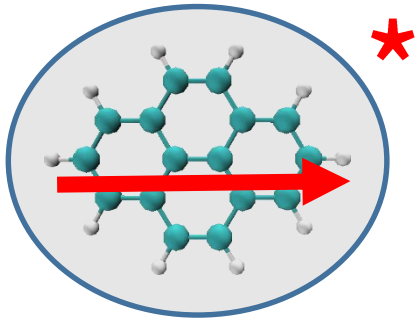


Nakanishi, T. et al. *Sci. Rep.* **2017**, 7, *3416*.

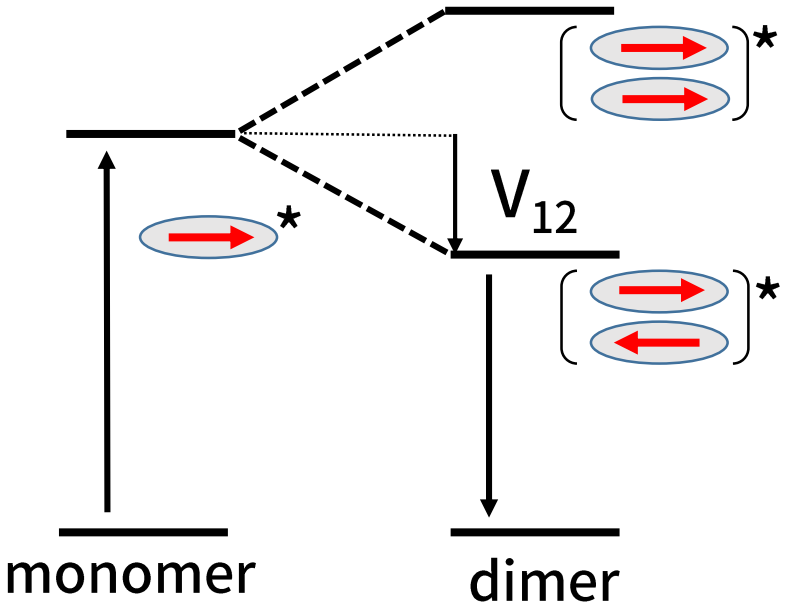
Time-resolved fluorescence spectra of liquid pyrenes

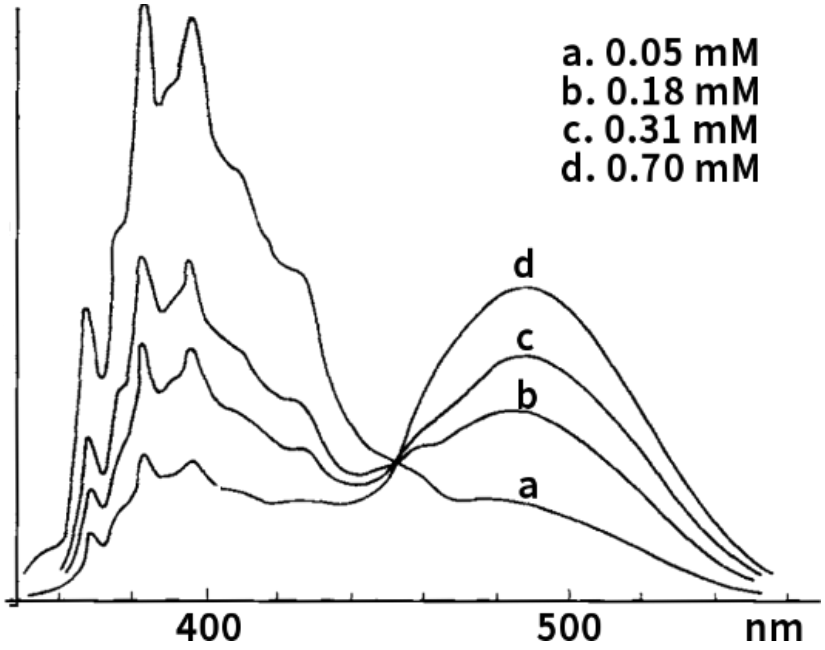
	1	3	4
			
Dynamic Stokes shifts	**Large**	**A little**	**None**
Fluorescence lifetime	**Long**	**Fast**	**Fast**

Excimer emissions of pyrene



Transition dipole



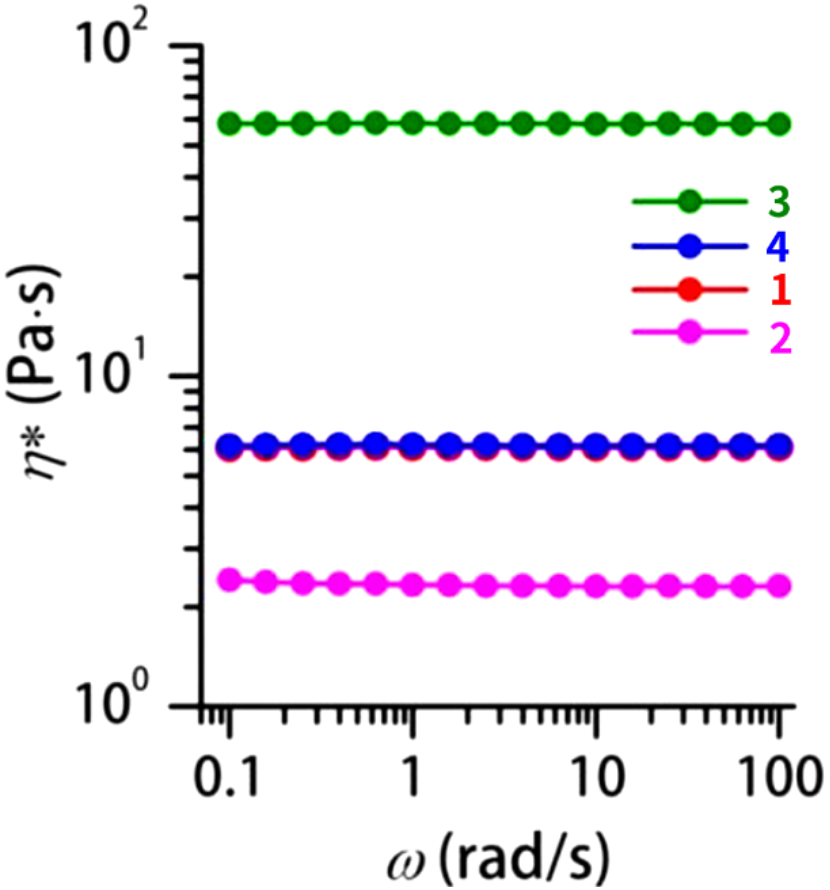


Emission wavelength spectrum of pyrene in n-heptane

Förster, T. *Angew. Chem.* **1969**, *8(5)*, 333

- **The emission characteristic of pyrene depends on the fluorescence lifetime of the exciton and the collision frequency**

Rheological properties of liquid pyrenes



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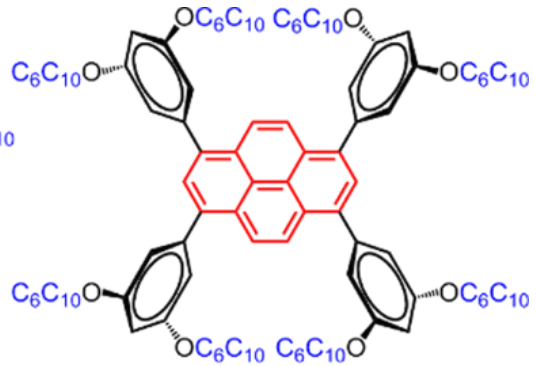

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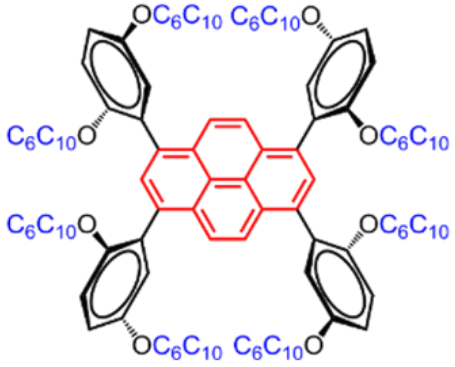
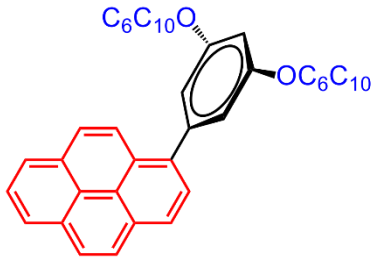


4

η* : complex viscosity

2 ≪ 1　　4 ≪ 3

Summary of liquid pyrene properties



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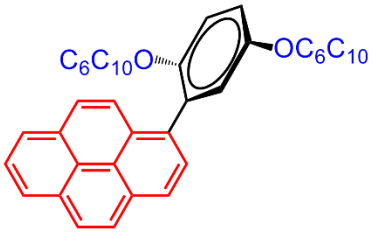

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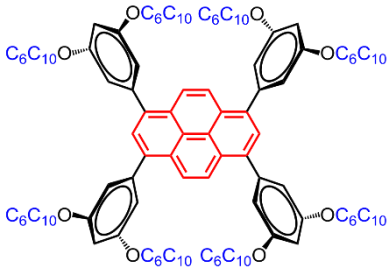

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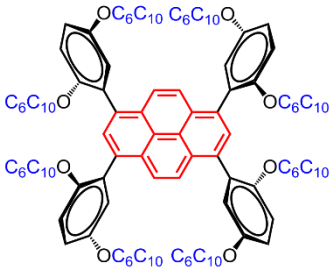


4

	1	2	3	4
Stokes shift	Large (excimer)	Large (excimer + monomer)	Little (weak excimer)	None (monomer)
viscosity	Large	Little	Very large	Large

- Luminescence and rheology are caused by structural factors of the differences of alkyl chain.
- In order to systematically understand these mechanism, it is necessary to clarify the detailed molecular structure

→ Molecular structure analysis by MD simulation is effective

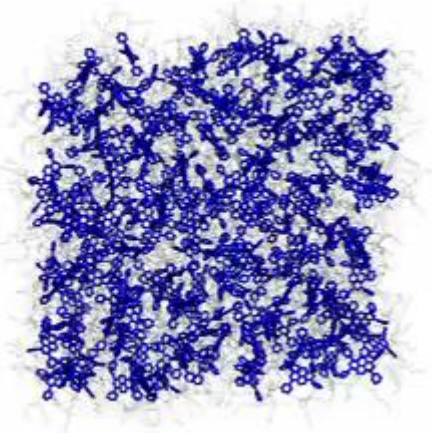
Contents

Molecular dynamics (MD) simulations

- **Development of MM force field for liquid pyrene**
- **Structural sampling of liquid pyrenes in solvent free conditions**
- **Structural analysis**

Calclation of fluorescent spectra

- **Determinant the excitonic interactions**
- **And calculation of fluorescent spectra of the balk systems**



3, NPT,300K

Molecular mechanics force field

- **force field (AMBER)**

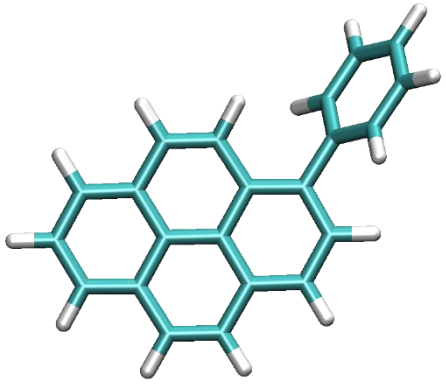
$$E_{MM} = \sum_k \alpha_{bond,k}(r_k - r_{eq,k})^2 + \sum_l \alpha_{angle,l}(\theta_l - \theta_{eq,l})^2 + \sum_m \sum_n \frac{\alpha_{dihedral,m}}{2}(1 + \cos(n\omega_m - \gamma_m)) + \sum_i \sum_{j>i} \left\{ \epsilon_{ij} \left(\left(\frac{r_{0,ij}}{r_{ij}}\right)^6 - 2\left(\frac{r_{0,ij}}{r_{ij}}\right)^{12} \right) + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\}$$

(Bond length)

(Bond angles)

(Dihedral angles)

(VDW + electro static interactions)



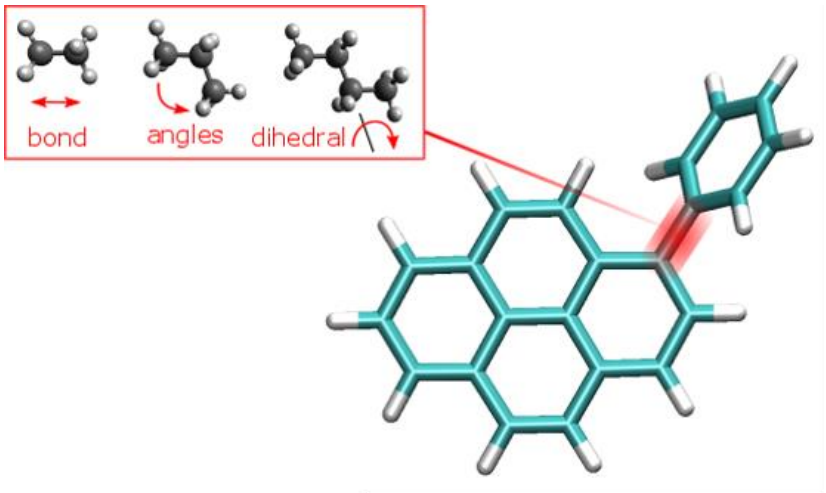
The rotational barrier of the phenyl group changes with a delicate balance of the electronic state

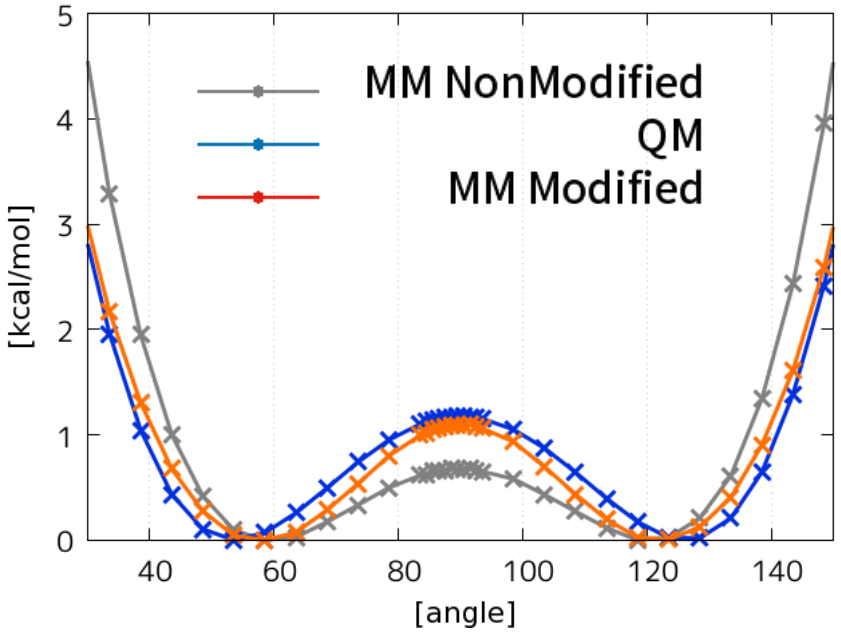
→It can not be described in general force field.

Modification of MM force field

Procedure

- Calculate the potential curve by QM calculations
- Sampling structure was created by M06-2 X/6-31G(d) structure optimization
- Fitting by least squares method to the functional form of MM force field



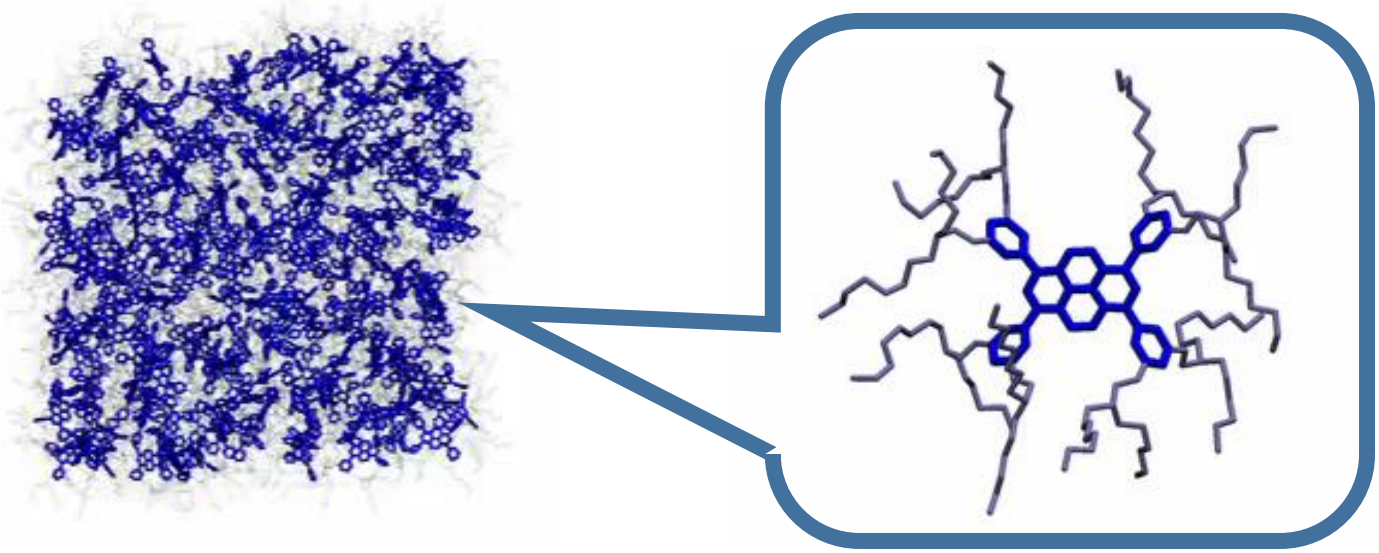


The rotation barrier and equilibrium points are reproduced

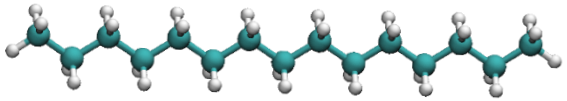
Computational details

Classical molecular dynamics (MD) simulation

- **Calculation package : AMBER14, 16**
- **200 molecules of liquid pyrenes in solvent-free conditions**
- **Periodic boundary condition**
- **Number of molecules in the unit cell : 200 for each 1~4**
- **Number of atoms in the unit cell : 26800(1,2), 91600(3,4)**

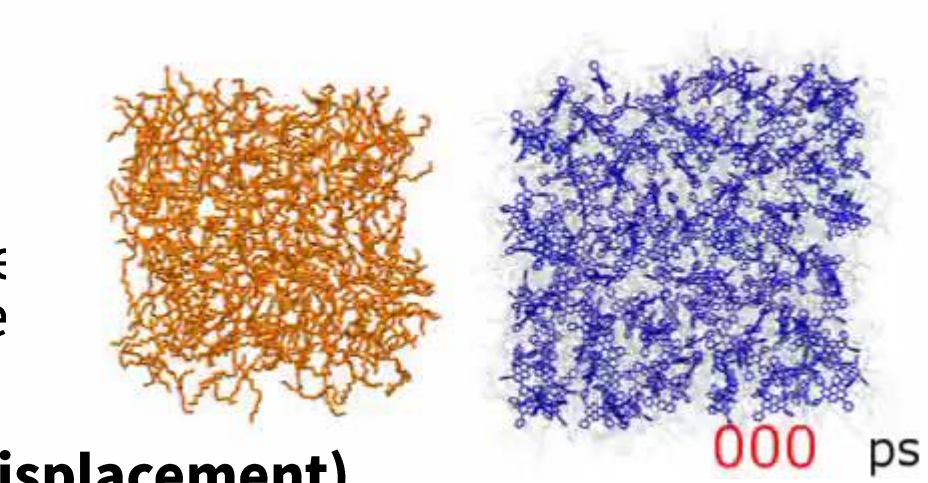


Comparison of diffusion process

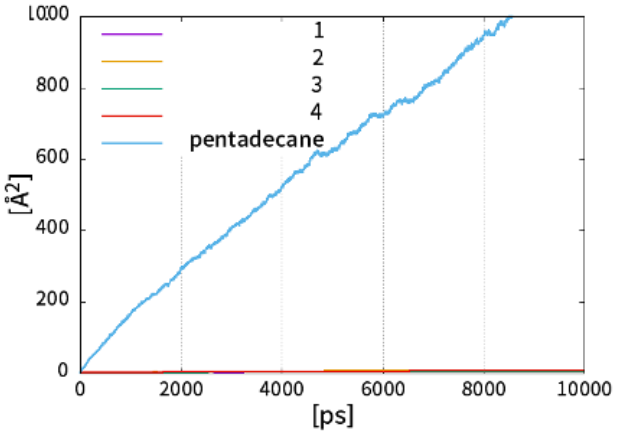


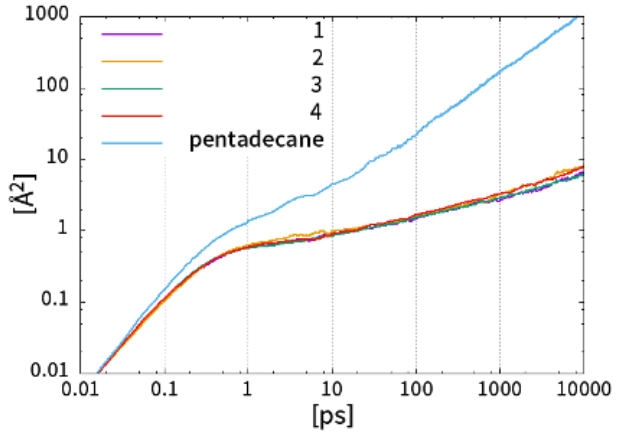
Reference : n-pentadecane

A linear alkane having the same number of carbon atoms as the alkyl chain of liquid pyrene



MSD (Mean squared displacement)



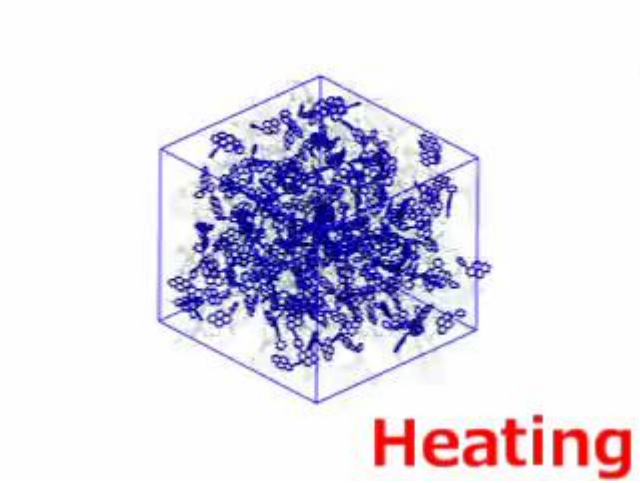


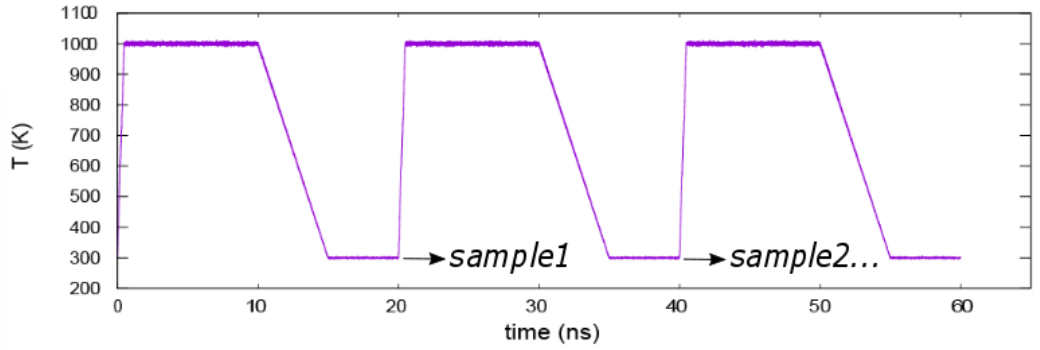
The liquid pyrene system does not reach the diffusion process during the simulation time scale

Structural sampling

Efficient sampling method

- **1000 K for 10 ns for randomization**
- **5 ns for cooling**
- **300 K for 5ns for equilibration**



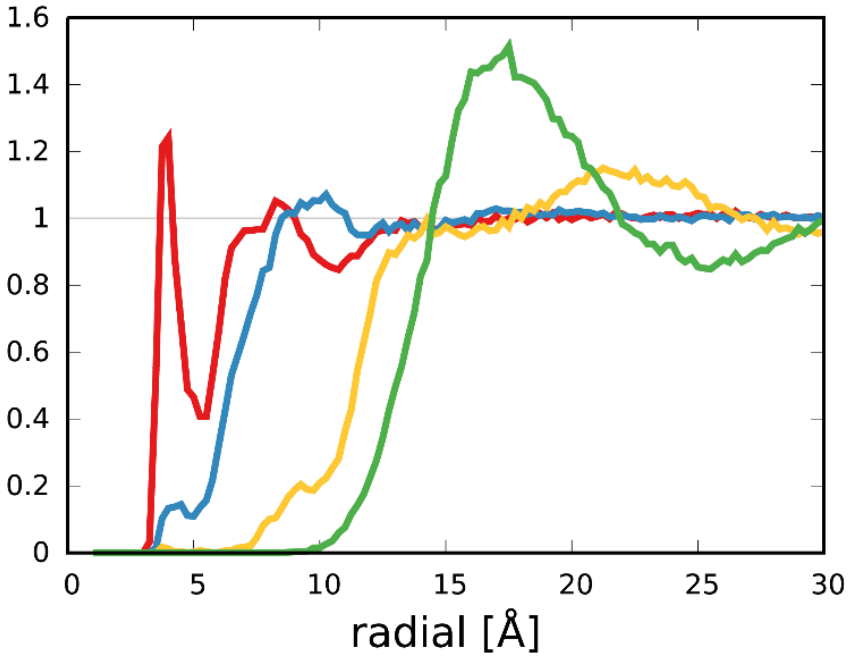


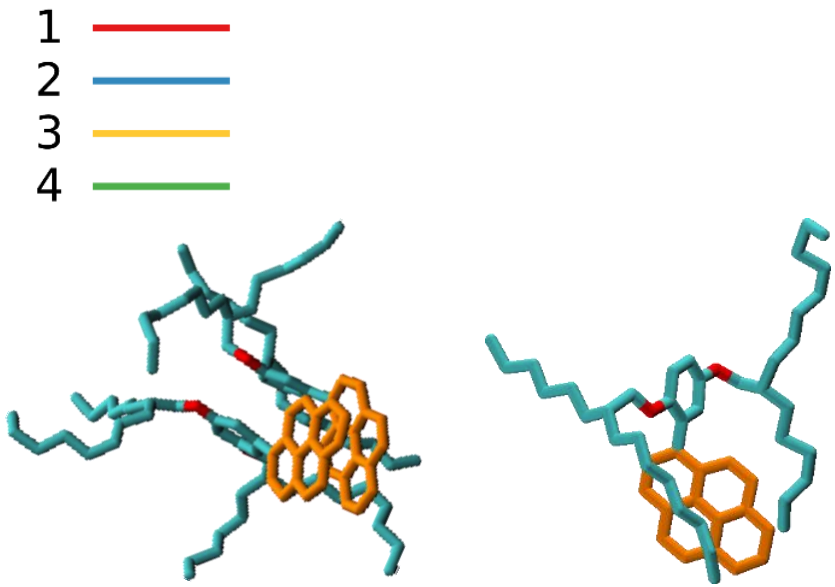
After equilibration, all samples converge to a constant volume

Structural analysis of liquid pyrene

Radial distribution function (RDF) g(r) between π conjugate parts

$$g(\boldsymbol{r}) = \frac{\langle n(\mathbf{r}) \rangle}{4\pi r^2 dr \rho}$$



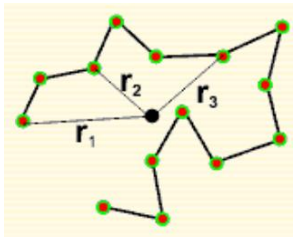


- **1,2 : form strong π-π stacking between pyrene moieties**
- **3 : pyrene moiety can enter the second solvation area around the other pyrene**
- **4 : pyrene is completely separated by alkyl chains**

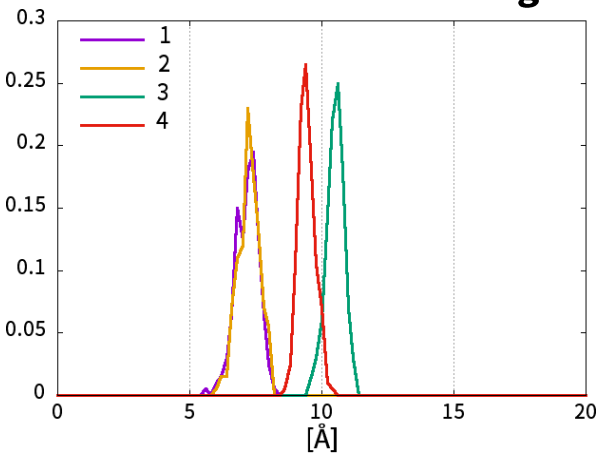
Structural analysis of liquid pyrene

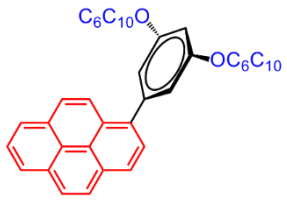
radius of gyration R_g

$$R_G = \sqrt{\frac{1}{N}\sum_i r_i^2}$$



Histograms of R_g





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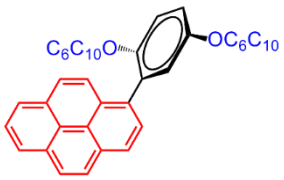

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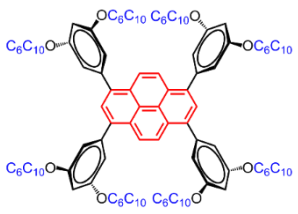

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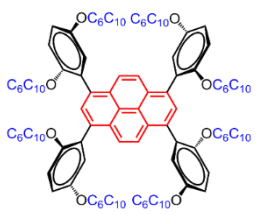


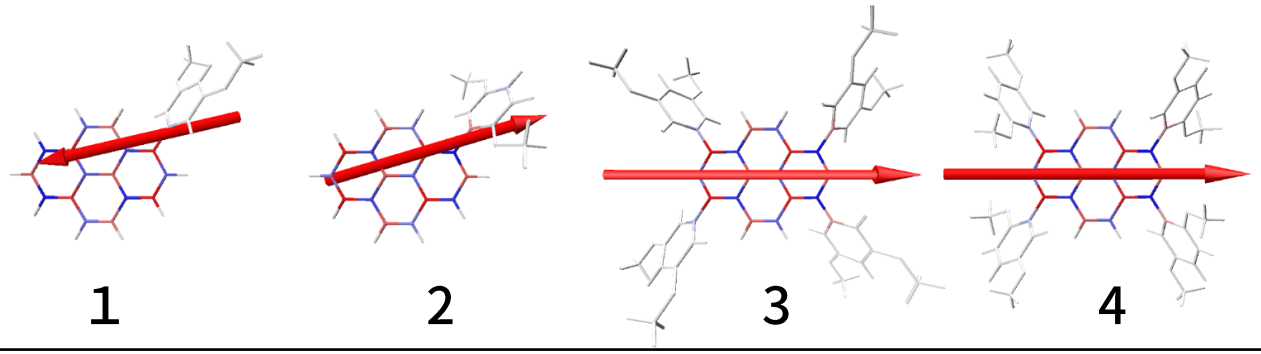
4

R_G [Å]	7.303	7.356	10.588	9.522

- There is no difference between particle size 1 and 2
- 4 is folded more compactly than 3

Excitation state calculation for liquid pyrene

TD-DFT CAMB3LYP/6-31G(d) //M06-2X/6-31G(d)
Computational package ：GAMESS（Development version）



S0→S1	1	2	3	4
Transition dipole(D)	**10.31**	**11.23**	**16.00**	**15.47**
Oscilator Strength	**0.451**	**0.525**	**0.964**	**0.964**

- **In all cases, the lowest excited state is HOMO → LUMO transition character that have shorter fluorescence lifetime**
- **In addition, the structural relaxation is slower than the relaxation of the excited state**

How do liquid pyrenes emit excimer fluorescence?

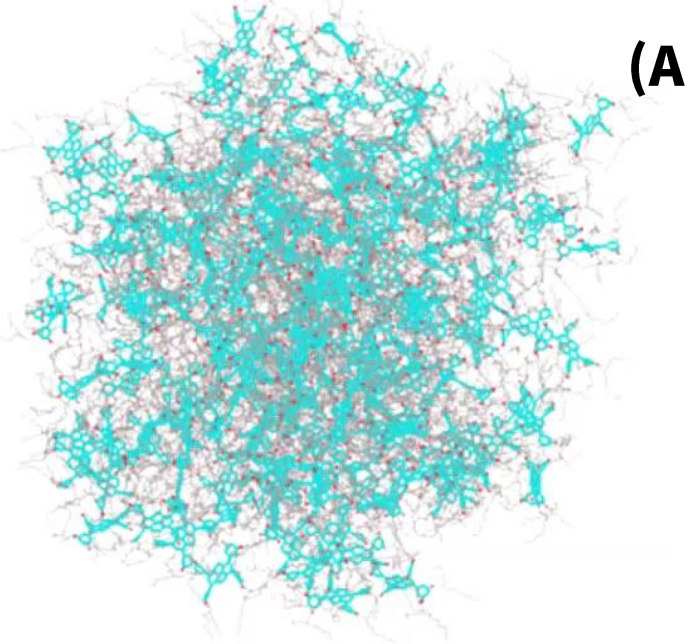
Excitation energy transfer (EET)mechanism

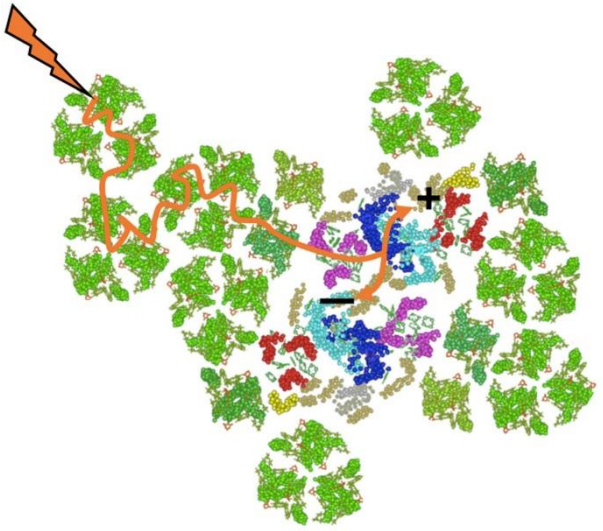
- **Structural relaxation is slow and it is difficult to form association in a short time due to structural change.**

Hypothesis

- **Excitons migrate to lower state (excimer clusters) and emit light**

(A similar system to photosystem II)





→Do the excimer clusters exist?

Calculation method of excitonic interaction

- **It is difficult to quantum chemically solve the exciton interaction for a large systems.**
- **As a general approximation method, dipole approximation by transition dipoles is used (Dipole approximation)**

$$V_{12} \approx \frac{1}{4\pi\epsilon_0}\left\{\frac{p_1 \cdot p_2}{r_{12}^3} - \frac{3(p_1 \cdot r_{12})(p_2 \cdot r_{12})}{r_{12}^5}\right\}$$

but accuracy is poor among molecules with close distances.
→Highly accurate description of exciton couplings by effective charges determined by transition density

$$V_{12} \approx \frac{1}{4\pi\epsilon_0}\sum_i \sum_{j<i} \frac{q_i q_j}{r_{ij}}$$

Where, q are effective transition charge by ESP fitting

$$\mathrm{V_{resp}(r_i)} = \sum_j^{Natoms} \frac{q_j}{|R_j - r_j|}$$

$$\mathrm{R_{resp}} = \sum_i^{Npoints} \left(V_{qm}(r_i) - V_{resp}(r_i)\right)^2$$

Separation of energy levels by exciton interaction

Excitonic hamiltonian

$$\hat{\mathrm{H}} = \sum_{i}^{NState} |\varphi_i\rangle \epsilon \langle\varphi_i| + \sum_{i,j}^{NState} |\varphi_i\rangle V_{ij} \langle\varphi_j|$$

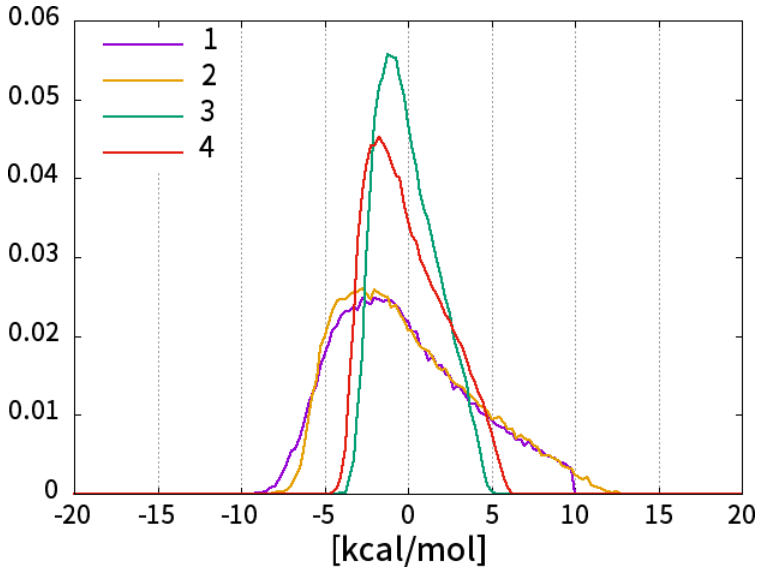
$$V_{ij} \approx \frac{1}{4\pi\epsilon_0} \sum_{m} \sum_{n<m} \frac{q_m q_n}{r_{mn}}$$

Cluster radius R_c

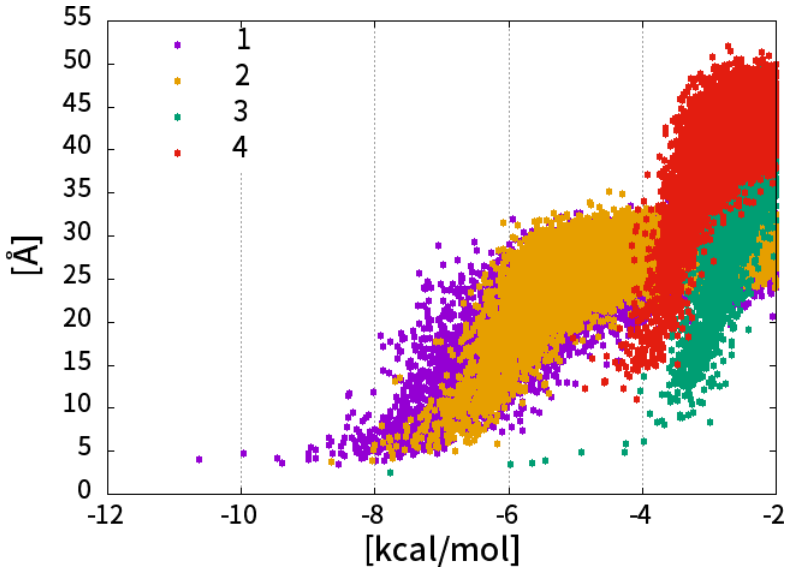
$$R_{mean} = \sum_{i} c_i^2 \boldsymbol{r}_i$$

$$R_{\mathrm{C}} = \sqrt{\frac{1}{N} \sum_{i} c_i^2 (\boldsymbol{r_i} - \boldsymbol{r}_{mean})^2}$$

Density of state

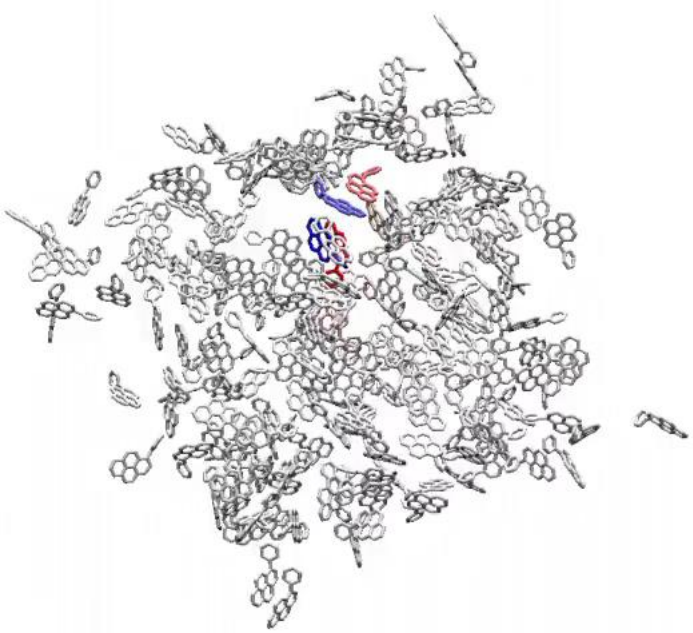


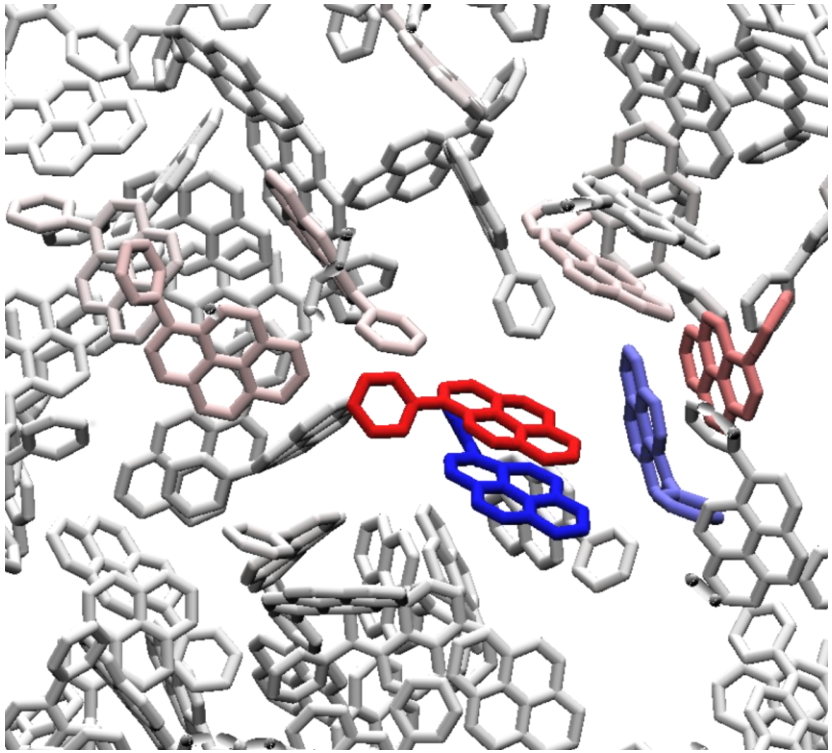
Distribution of R_c



Separation of energy levels by exciton interaction

Snap shot of an excimer claster
E = -7.396

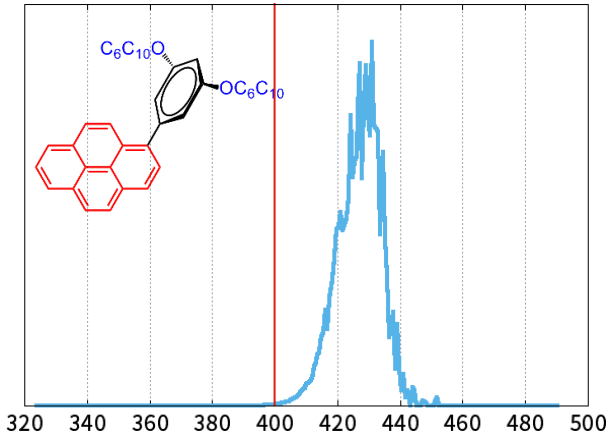




Fluorescence wavelength after exciton equilibration

$$\int \mathrm{f_i}(E)dE = \int \frac{\omega^3}{3\pi\epsilon_0^3\hbar}|\mu_i|^2\delta(\mathrm{E_i}-\mathrm{E})\mathrm{e}^{-\frac{(\mathrm{E_i}-E_0)}{\mathrm{k_b}T}}\ dE$$

1



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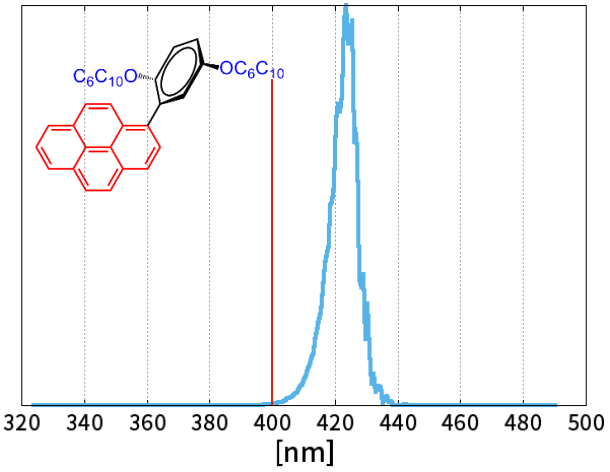

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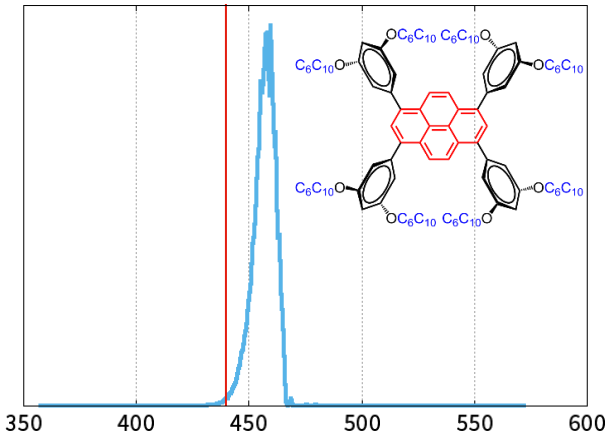

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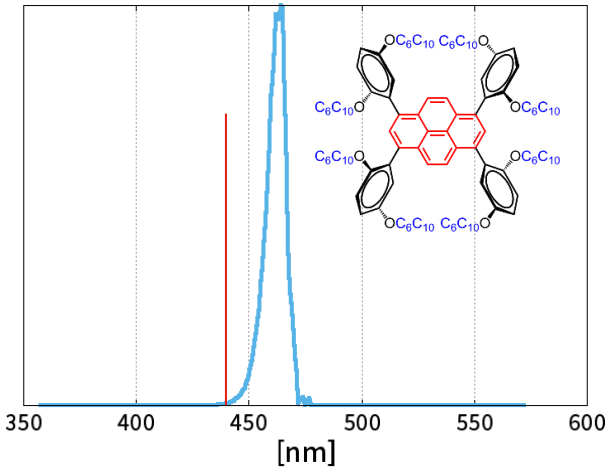

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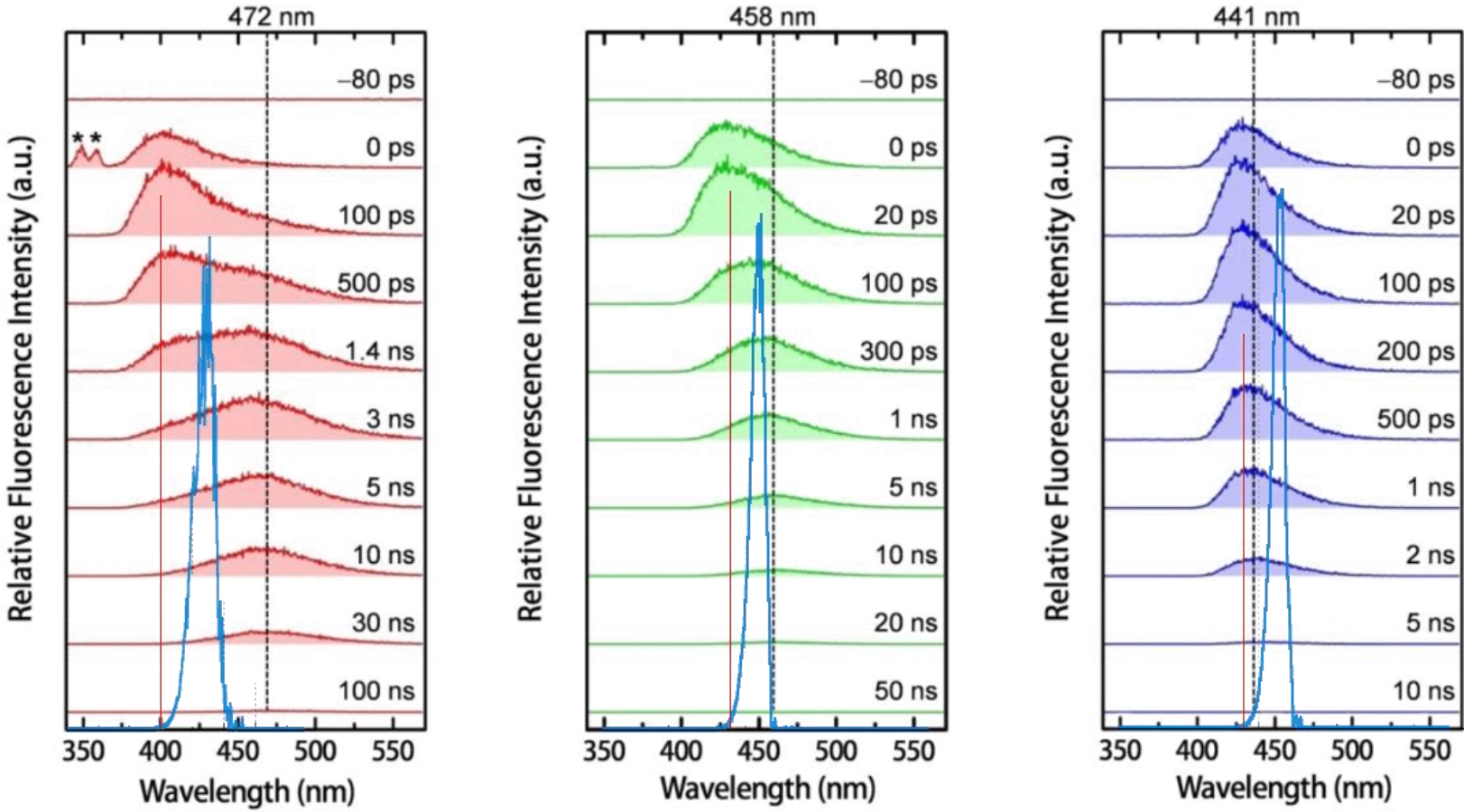


summary

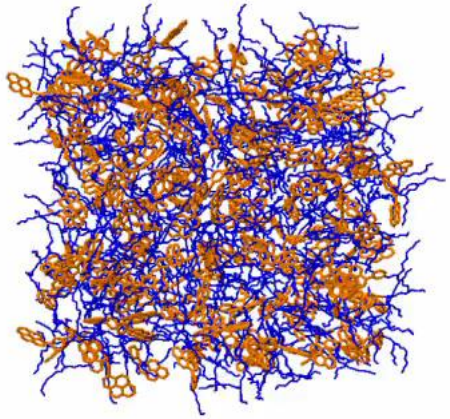
- Dynamics and fluorescence spectra of liquid pyrene were analyzed by molecular simulation.
  - ✓ MM force field was obtained by quantum chemical calculation, and MD simulation was carried out.
  - ✓ Excitonic interaction was analyzed.

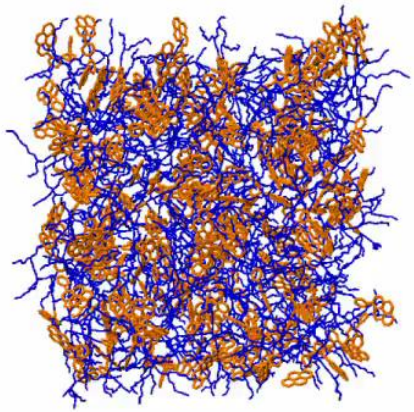
- Differences in physical properties depending on the position of the side chain were clarified at the molecular level.
  - ✓ Intermolecular interactions are regulated by changes in intramolecular alkyl-π interactions due to differences in substitution positions.

Future work

- **Analysis of excitation mobility dynamics in exciton aggregates**
  - ✓ **Overestimated wavelength shift can be corrected by considering the non-equilibrium process.**

- **Rheological analysis by long-time dynamics simulation using united-atom model**
  - ✓ **We develop a liquid pyrene force field in coarse-grained model suitable for long time simulation than All atom model, and simulate the time scale reaching diffusion process area.**





thank you for your attention