



TOKYO METROPOLITAN UNIVERSITY

首都大学東京

新技術説明会  
New Technology Presentation Meetings!

# ナノシートとの複合化による 強発光性材料の開発

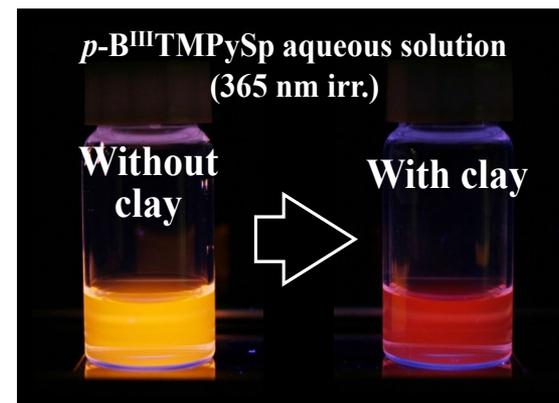
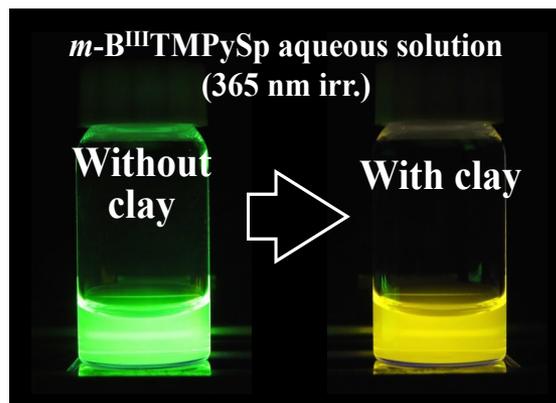
首都大学東京 大学院  
都市環境科学研究科 環境応用化学域  
教授 高木 慎介

2019年7月30日



# 本研究で提案する新技術

無機ナノシートと混ぜるだけで、  
有機系色素の発光効率の増強技術  
分子の種類によっては100倍以上の増強  
色調の変化も可能  
環境応答性を利用したセンサー機能を有する  
耐久性の向上も期待できる





# 従来技術とその問題点

従来は、発光性色素を開発するために、分子設計を行い、新規色素を合成する必要があった。

本技術では、単に混ぜるだけで、発光増強が期待できる＝少ない開発コスト

色素の構造が分かれば発光増強の成否予測が可能

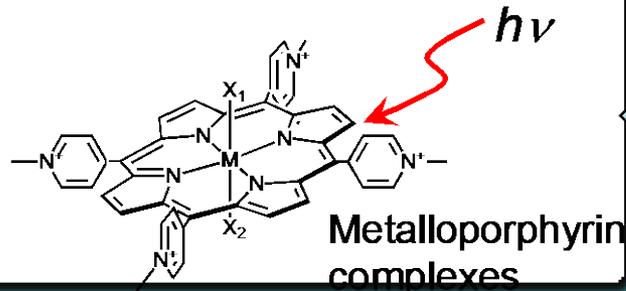


## 想定される用途

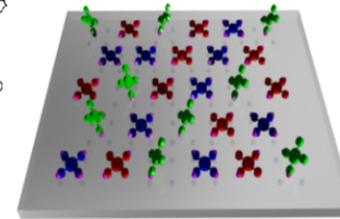
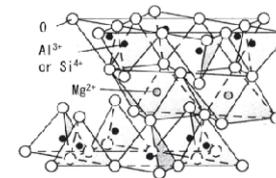
- 本技術の特徴を生かすためには、発光材料、表示材料に適用することで、簡便な性能向上が期待できる。
- 環境応答性を利用したセンサー機能が期待できる。
- 上記以外に、色調変化、耐久性向上の効果も期待できる。

# 光化学とナノ構造化学

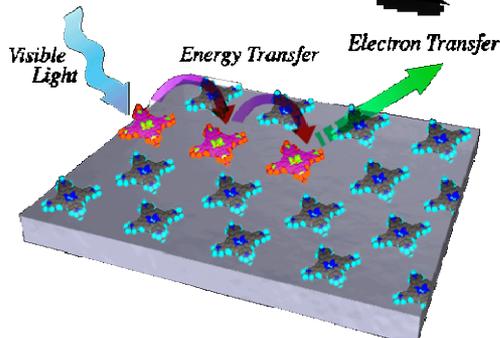
Photochemistry



Nanoscience



Organic/inorganic Hybrid



Artificial Photosynthesis

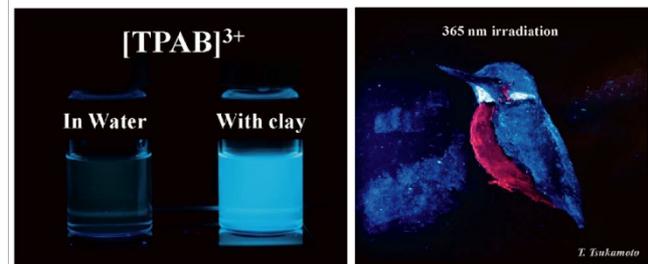
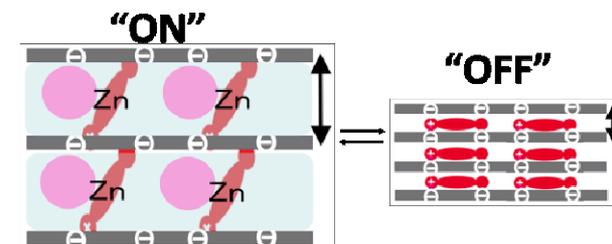


Photo-functional Materials

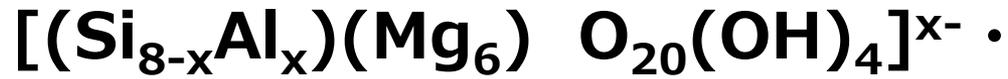
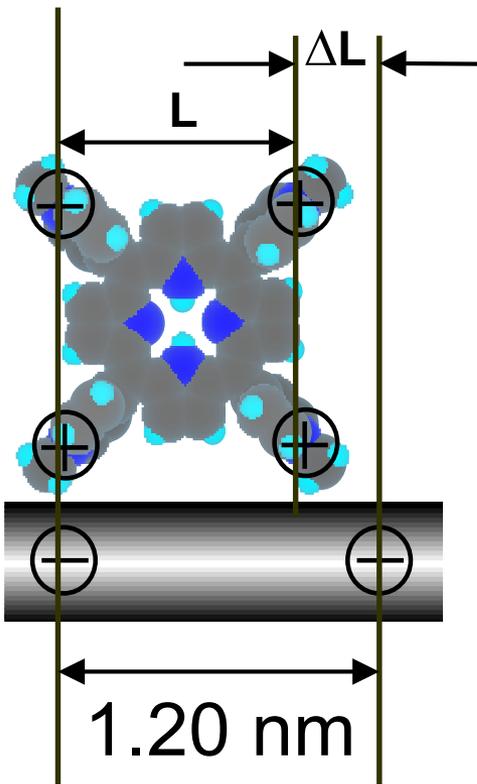


Environment-responsive Materials

# 分子集合構造の制御

Size Matching

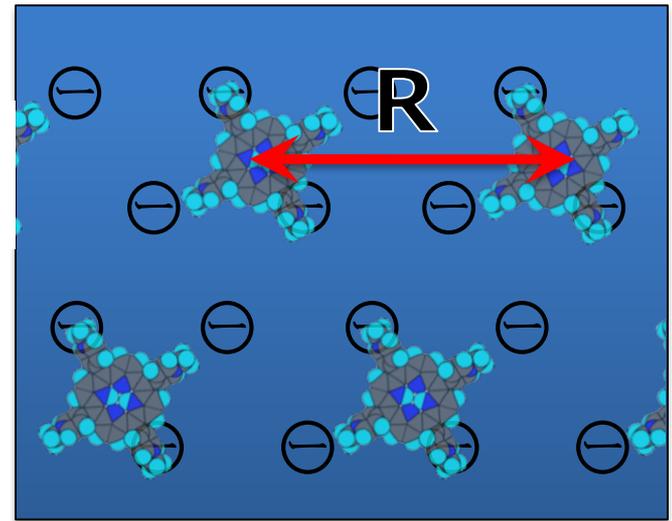
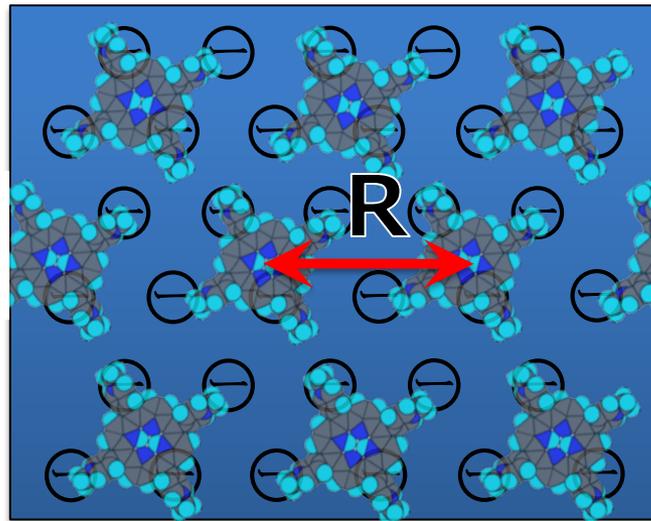
$$|\Delta L| < 0.2 \text{ nm}$$



Charge density High Charge density Low

**R: short**

**R: Long**

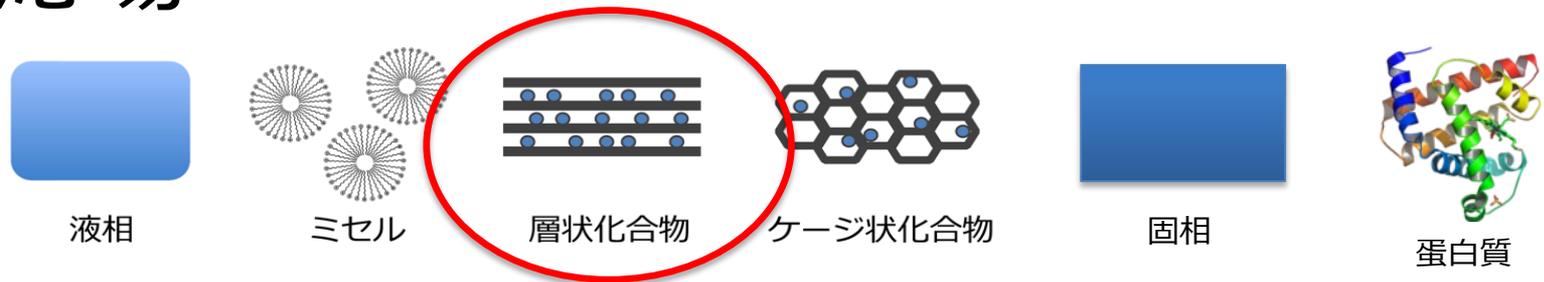


**2.3~3.0 nm**

*Langmuir*, 2011, 27, 10722.

# 層状化合物 (ナノシート)

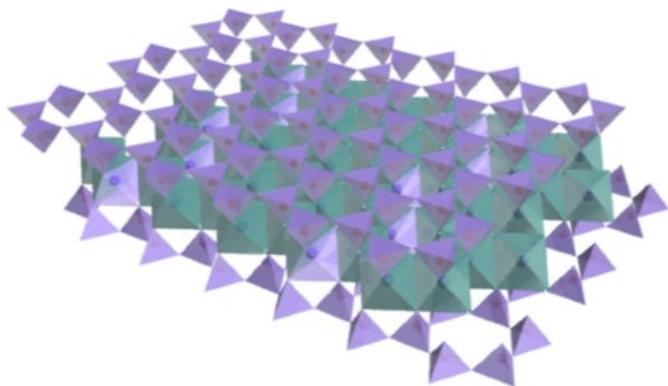
## 化学反応場



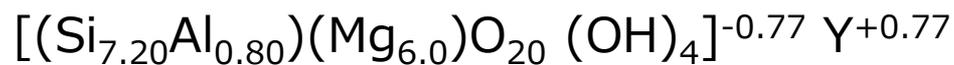
- 原子レベルで平滑な二次元平面
- 広い表面積
- 積層する能力 (層間空間)
- 環境応答性

# ナノシート

## 層状シリケート（粘土鉱物）



サポナイト



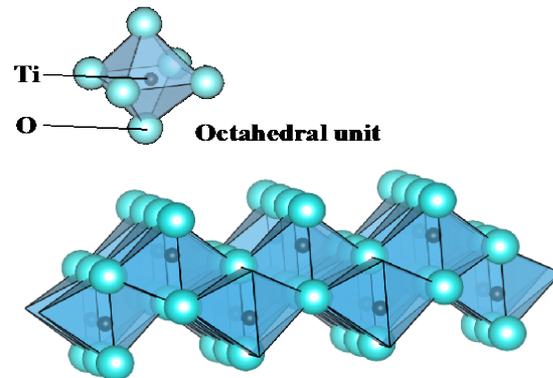
表面積：  $7.5 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$

カチオン交換容量(CEC)：  $0.997 \text{ meq g}^{-1}$

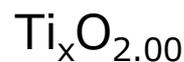
無色透明溶液

固体膜の状態においても透明

## 層状半導体



レピドクロサイト型



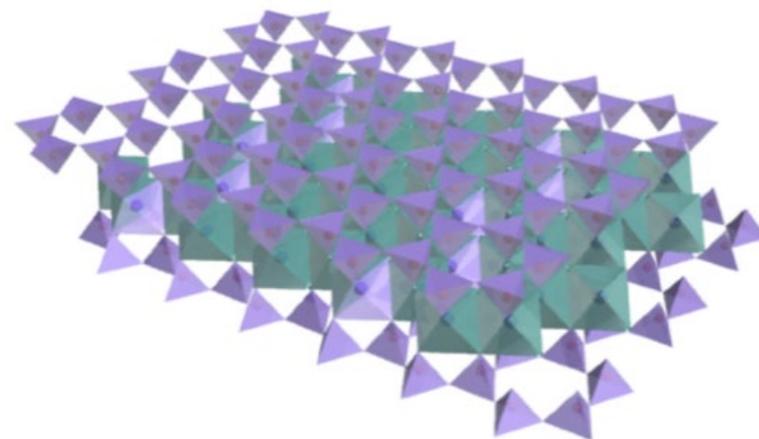
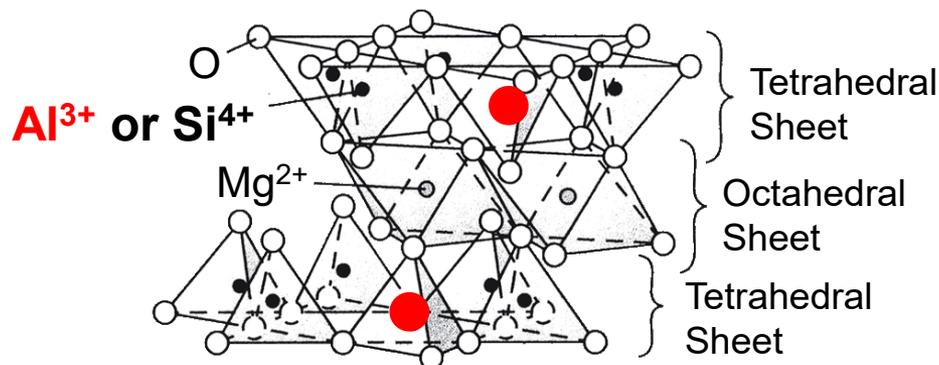
表面積：  $4.5 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$

CEC：  $\text{Ti}_{0.89}\text{O}_{2.00} 1.5 \text{ meq g}^{-1}$

無色透明溶液

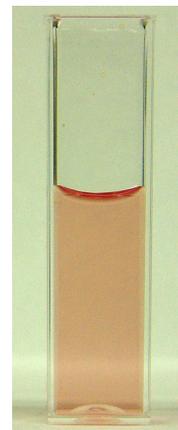
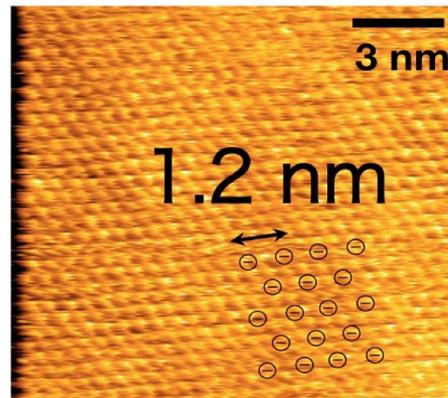
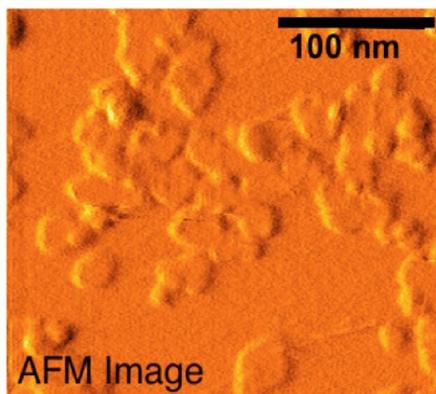
# ナノシート (粘土鉱物)

## Synthetic clay (Saponite)



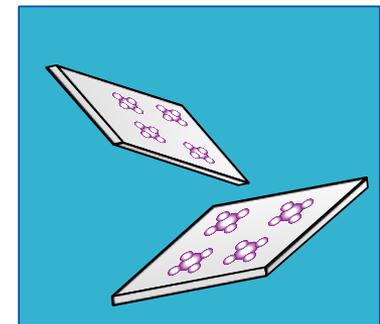
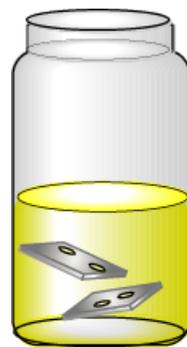
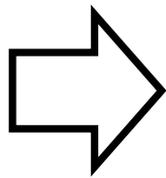
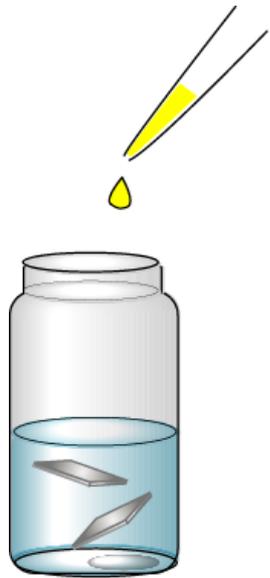
*“Flat surface at atomic level”*

*“Optically transparent”*



# 色素-ナノシート複合体

## Dye solution



transparent  
aqueous solution

$$[\text{clay}] = 4.4 \times 10^{-6} \text{ eq L}^{-1}$$
$$[\text{Dye}] = 5.0 \times 10^{-7} \text{ M}^{-1}$$

**Clay solution**

**Clay-Dye  
solution**

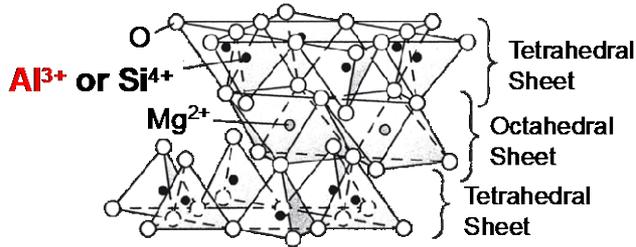
Clay sheets are exfoliated.

# Surface Fixation Induced Emission (S-FIE)

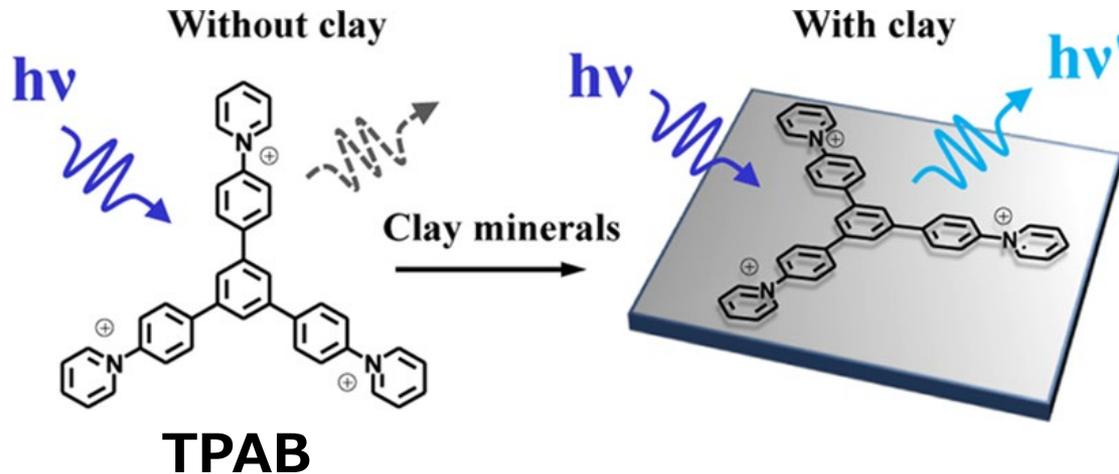
## 表面固定誘起発光増強

### 特徴

- 平滑な二次元平面
- 表面の負電荷配列
- 高い透明性



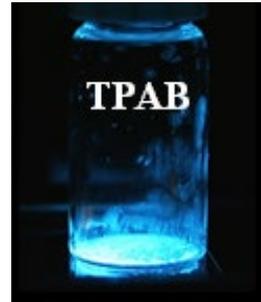
Sumecton SA (SSA)



粘土の添加による発光



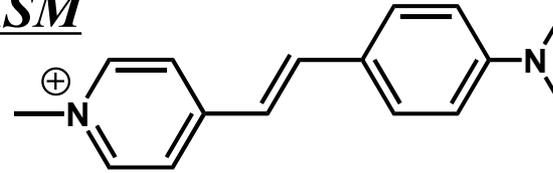
In aqueous solution



Solid state

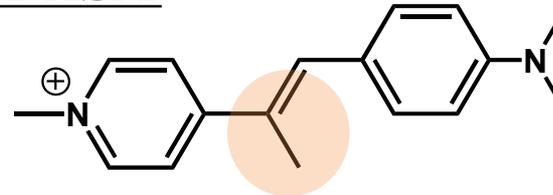
# DASM 色素

## DASM



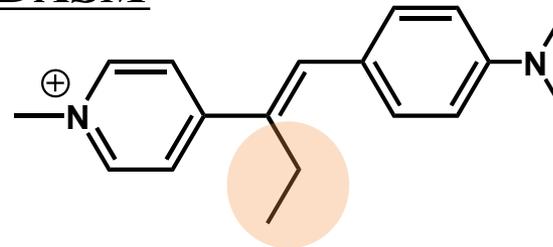
*trans*-4-[4-(dimethylamino)styryl]-  
1-methylpyridinium

## Me-DASM



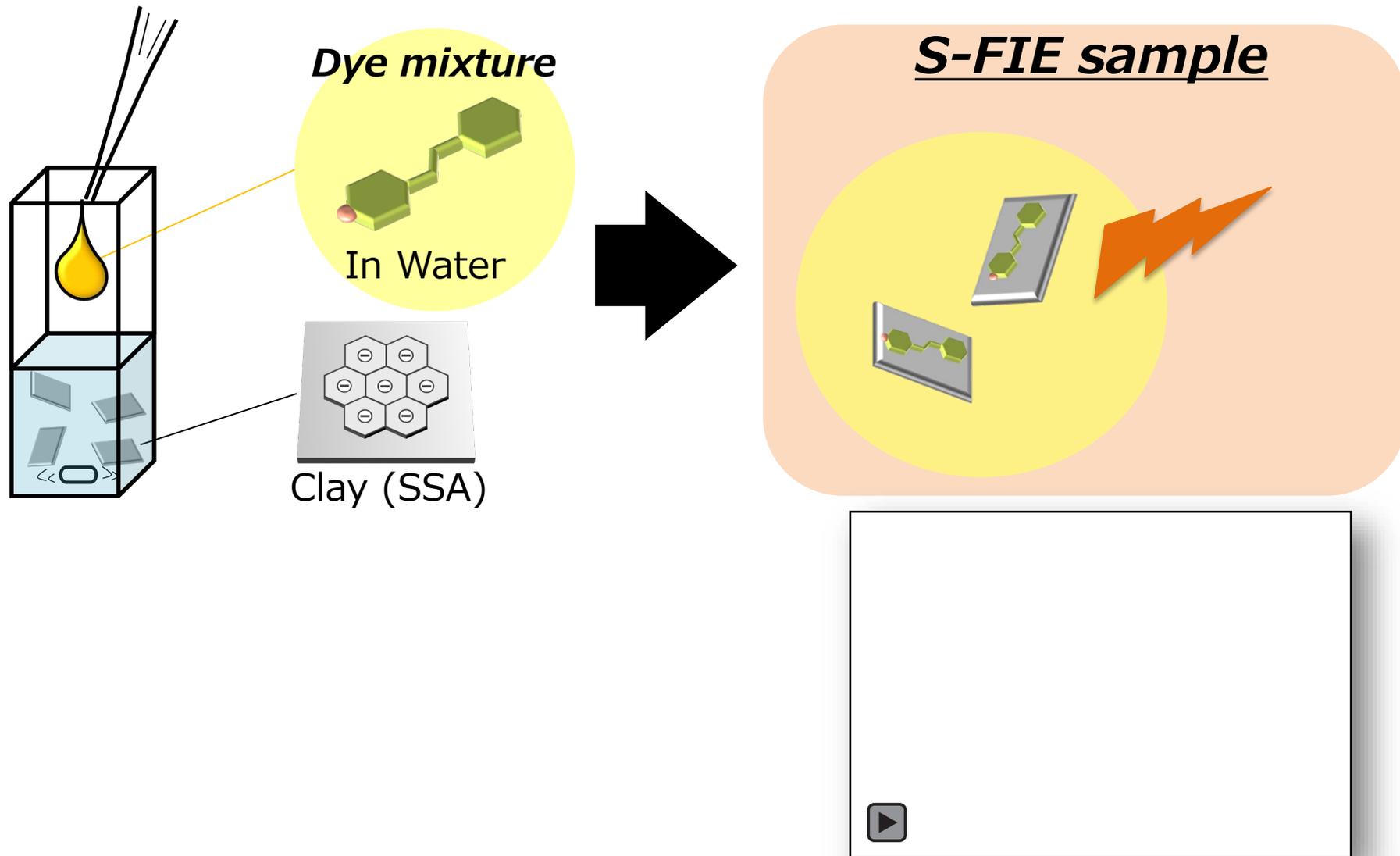
4-(4-(dimethylamino)-*trans*- $\beta$ -  
methylstyryl)-1-methylpyridinium

## Et-DASM



4-(4-(dimethylamino)-*trans*- $\beta$ -  
ethylstyryl)-1-methylpyridinium

# S-FIE 挙動

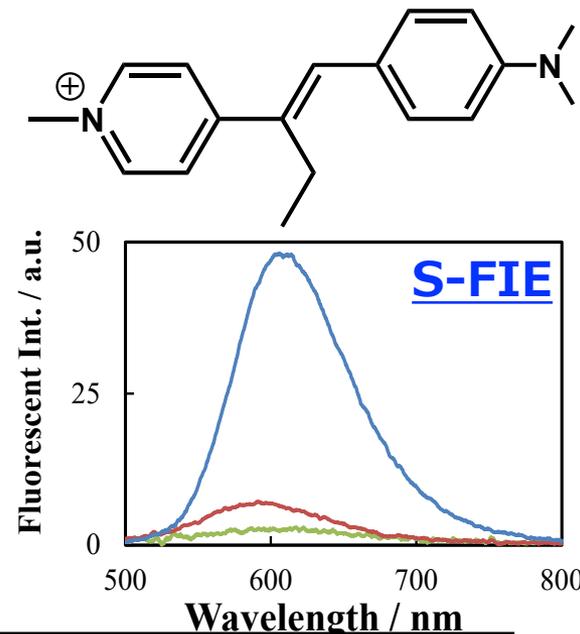
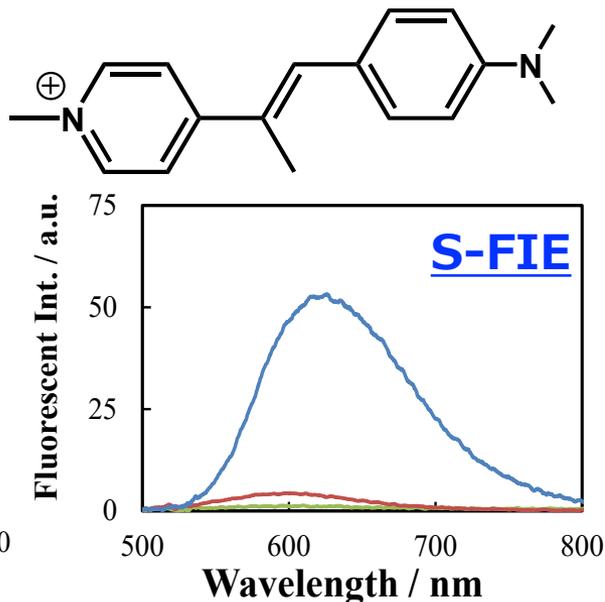
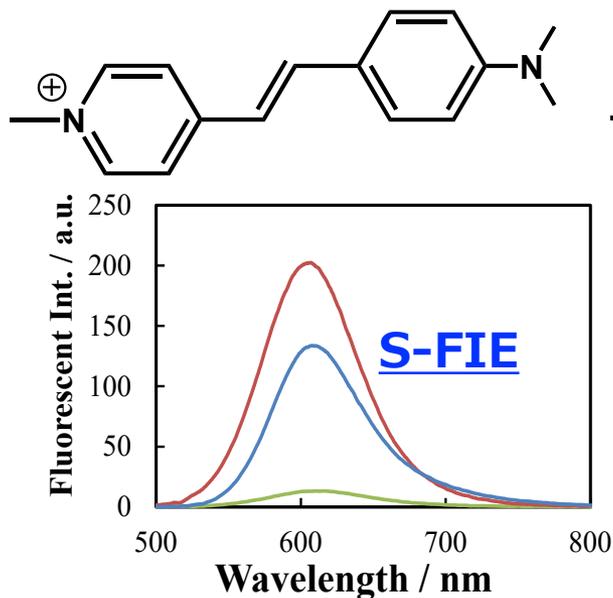


# S-FIE 拳動

**DASM**

**Me-DASM**

**Et-DASM**



DASM

Me-DASM

Et-DASM

$\Phi_f$  (In water)

$3.1 \times 10^{-3}$

**x30**

$\Phi_f$  (S-FIE)

**0.091**

$3.0 \times 10^{-4}$

**x160**

**0.049**

$4.0 \times 10^{-4}$

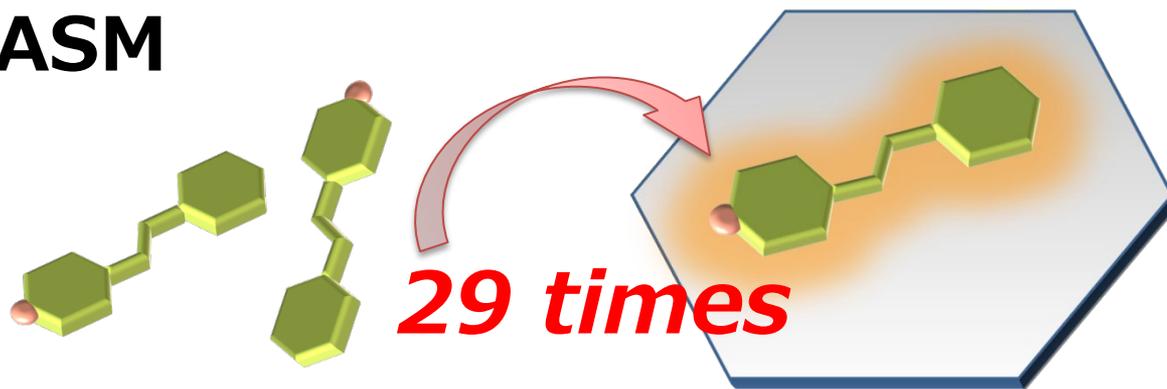
**x110**

**0.045**

# S-FIE メカニズムの解明

## 発光量子収率

### DASM



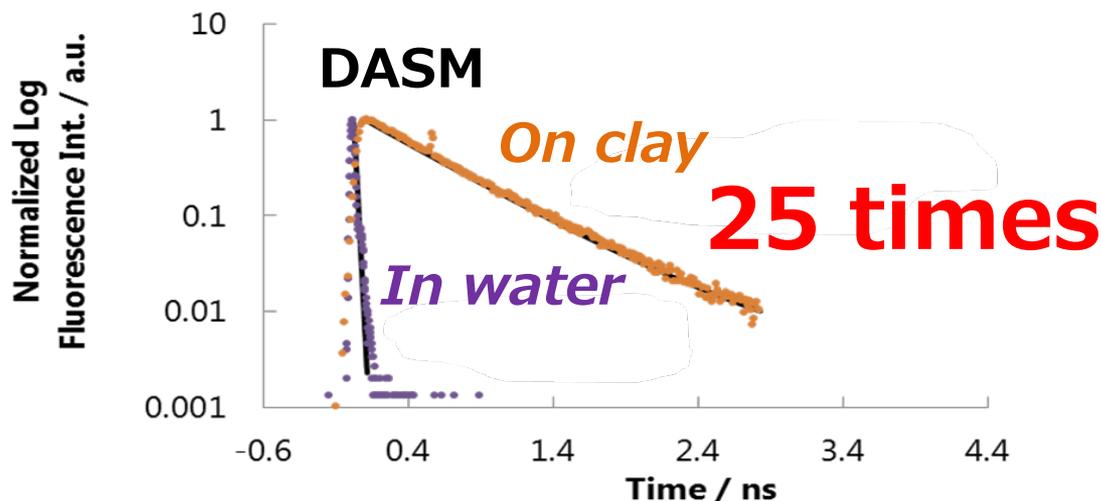
In water

$$\Phi_f = 0.0031$$

On clay (monomer)

$$\Phi_f = 0.091$$

## 発光寿命



In water

$$\tau = 0.02 \text{ ns}$$

On clay (monomer)

$$\tau = 0.5 \text{ ns}$$

# S-FIE メカニズムの解明

$$k_f = \lambda_f / \tau$$

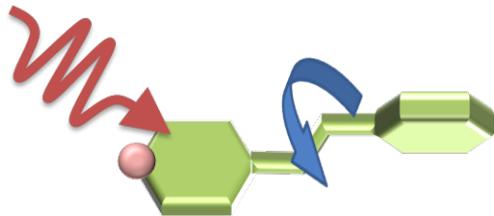
$k_f$  : fluorescence rate constant

$$k_{nr} = k_f / \lambda_f - k_f$$

$k_{nr}$  : nonradiative deactivation rate constant

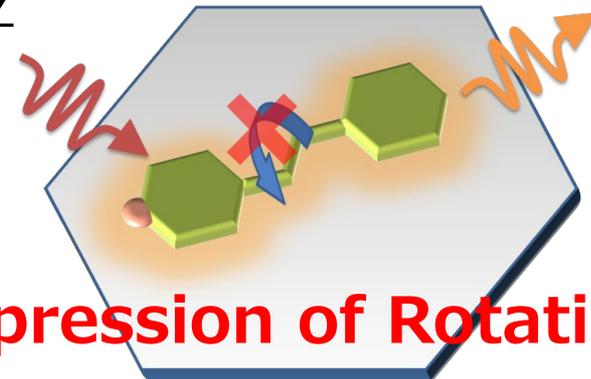
	$\Phi_f$	$\tau / ns$	$k_f / ns^{-1}$	$k_{nr} / ns^{-1}$
In water	0.0031	0.02	0.16	50
On clay	0.091	0.50	0.18 	1.8 

In water



Rotation

On clay



Suppression of Rotation

# ポルフィリン: $k_f$ and $k_{nr}$

$$k_f = \lambda_f / \tau$$

$$k_{nr} = k_f / \lambda_f - k_f$$

*RSC Advances, 2015, 5, 8479.*

radiative    non-radiative

	$\phi_f$	$\tau / \text{ns}$	$k_f / 10^8 \text{ s}^{-1}$	$k_{nr} / 10^8 \text{ s}^{-1}$
in water	0.052	1.3	0.4	7.3
on clay	0.079	0.9	0.87	10.2



In this case, an acceleration of  $k_f$  was observed.

# Surface-Fixation Induced Emission (S-FIE)

*ACS Applied Materials & Interfaces*, 2016, 8, 7522.

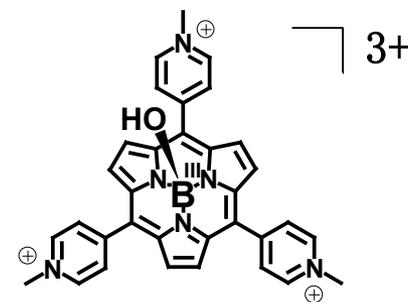
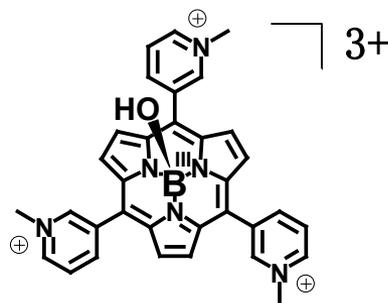
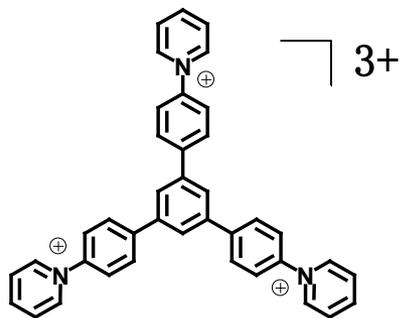
*RSC Advances*, 2015, 5, 8479.

*J. Phys. Chem. C*, 2014, 118, 20466.

*J. Phys. Chem. C*, 2013, 117, 2774.

*Langmuir (Invited Feature Article)*, 2013, 29, 2108.

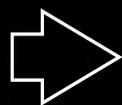
*J. Photochem. Photobiol. A (Invited Feature Article)*, 2017, 339, 67.



TPAB aqueous solution (365 nm irr.)

Without clay

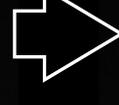
With clay



*m*-B<sup>III</sup>TmPySp aqueous solution (365 nm irr.)

Without clay

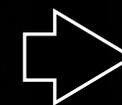
With clay



*p*-B<sup>III</sup>TmPySp aqueous solution (365 nm irr.)

Without clay

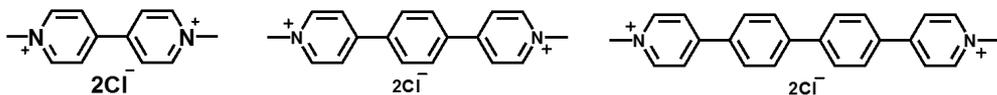
With clay



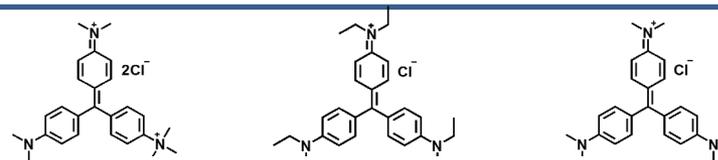
Fluorescence enhancement

Fluorescence color control

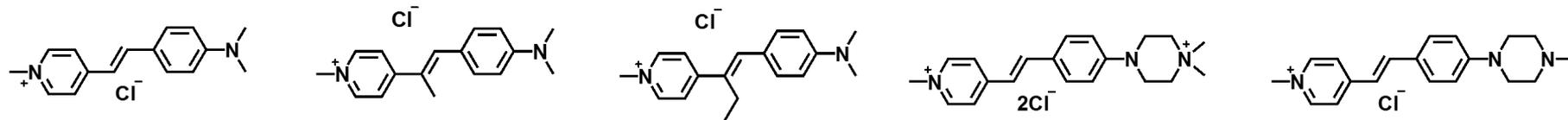
# S-FIEの普遍性



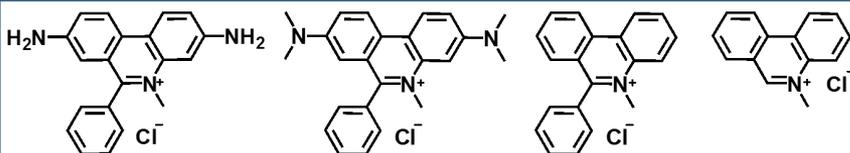
**Methylpyridinium**



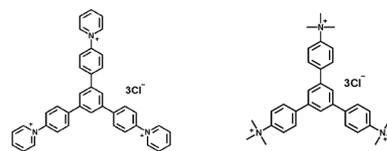
**Triphenylmethane**



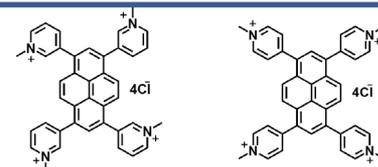
**Stilbazolium**



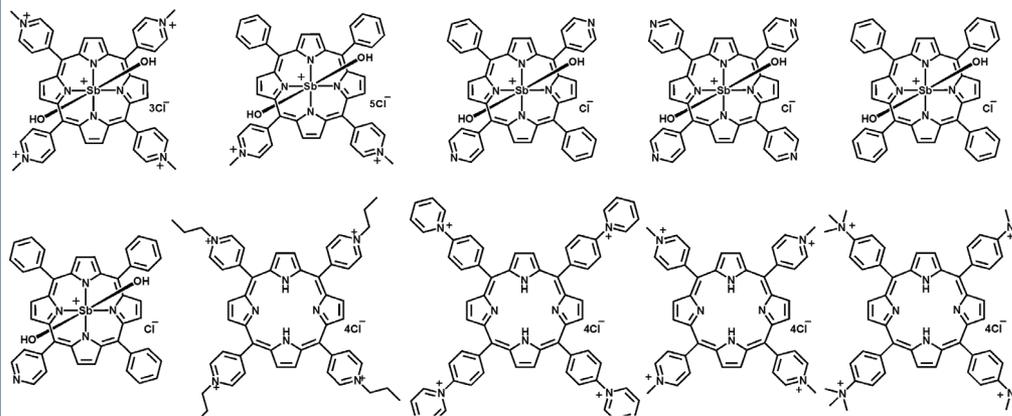
**Phenanthridine**



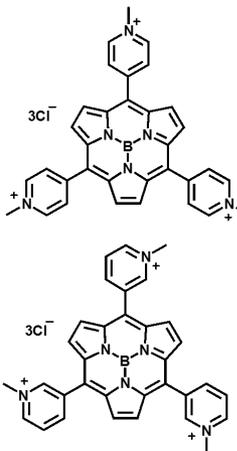
**TPB**



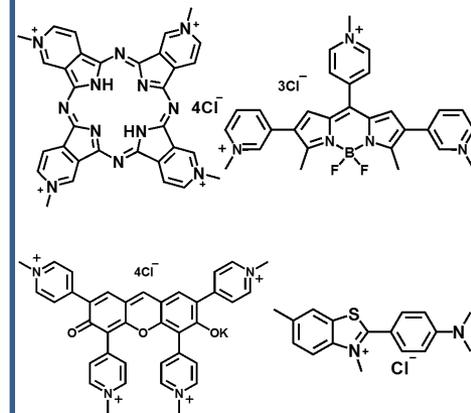
**Pyrene**



**Porphyrin**

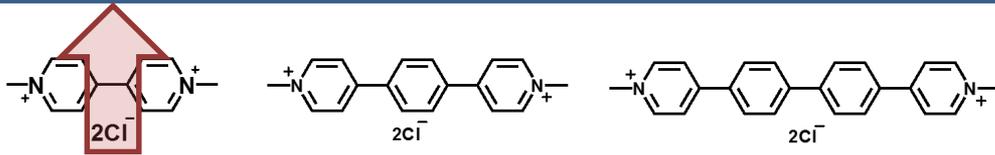


**Subporphyrin**

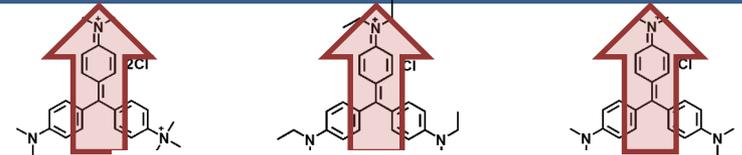


**Others**

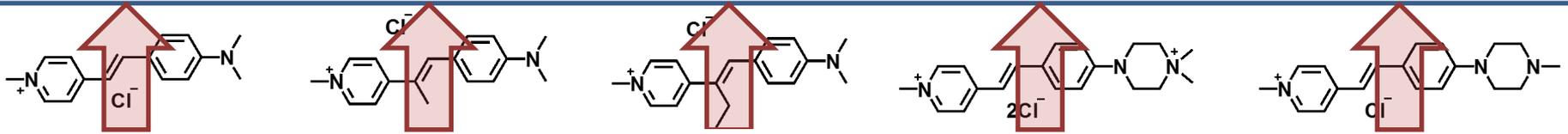
# S-FIEの普遍性



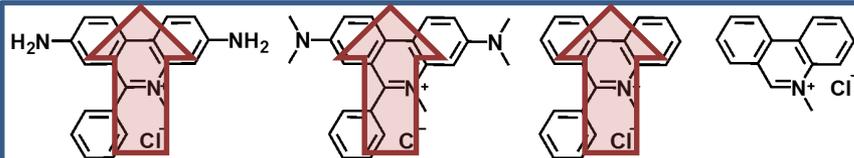
Methylpyridinium



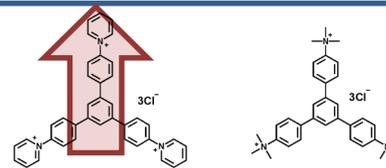
Triphenylmethane



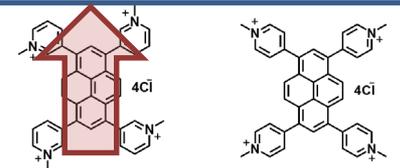
Stilbazolium



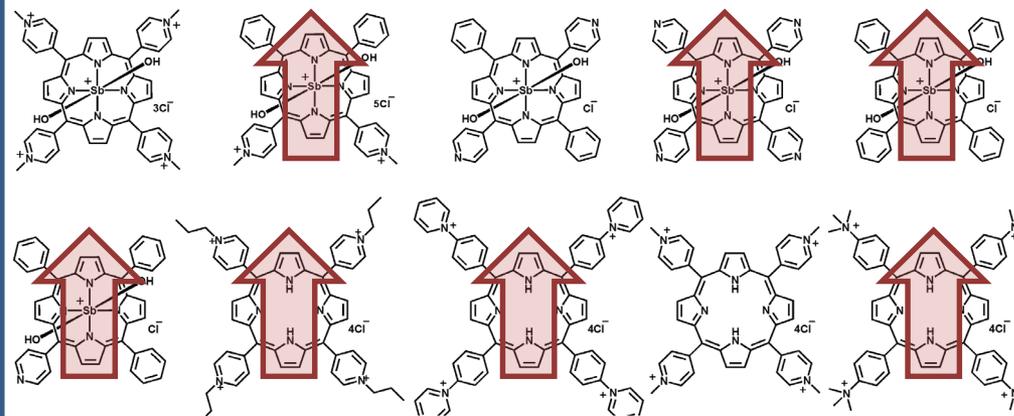
Phenanthridine



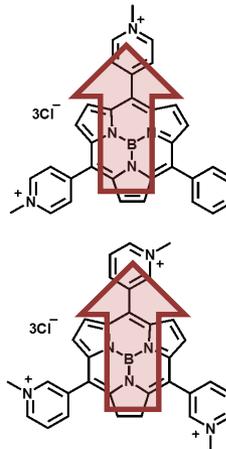
TPB



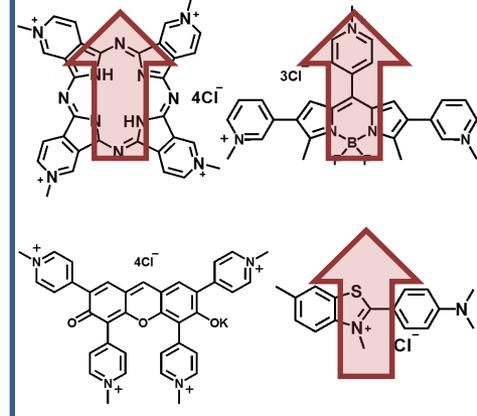
Pyrene



Porphyrin

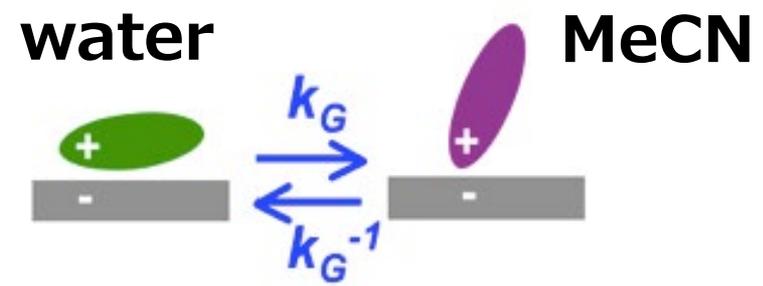


Subporphyrin

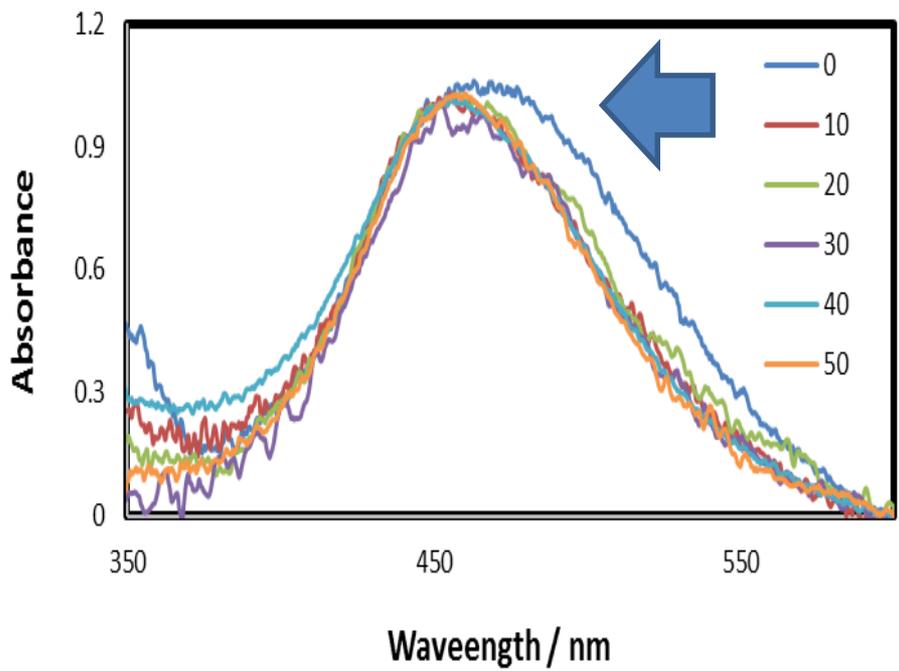


Others

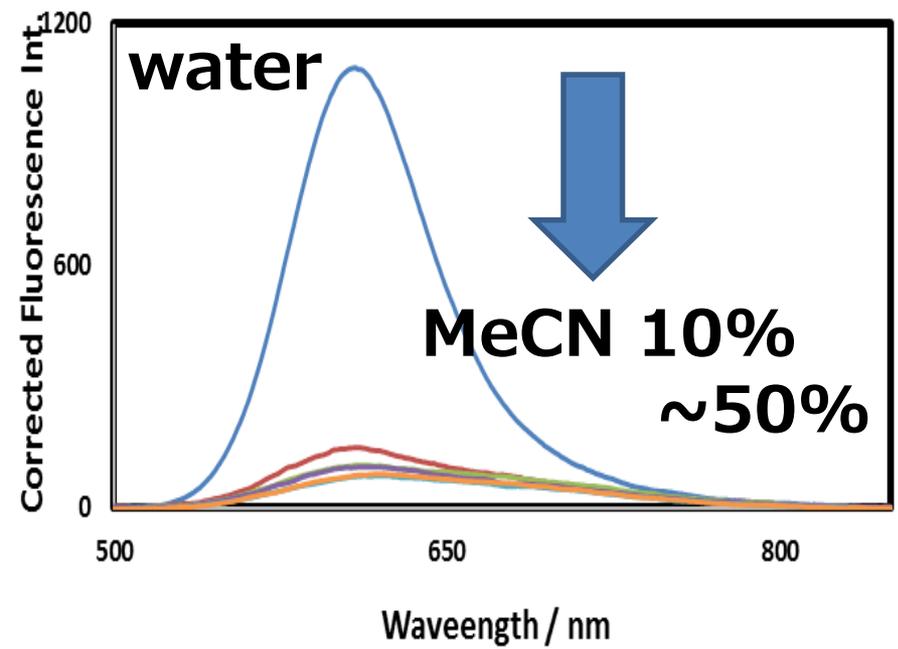
# 環境応答性



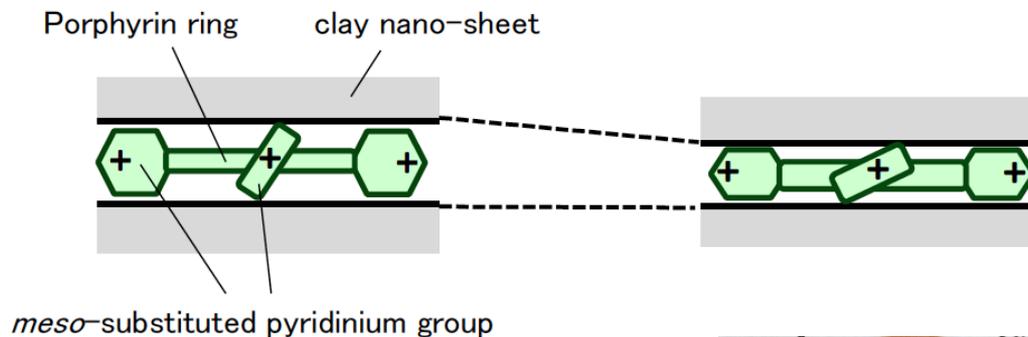
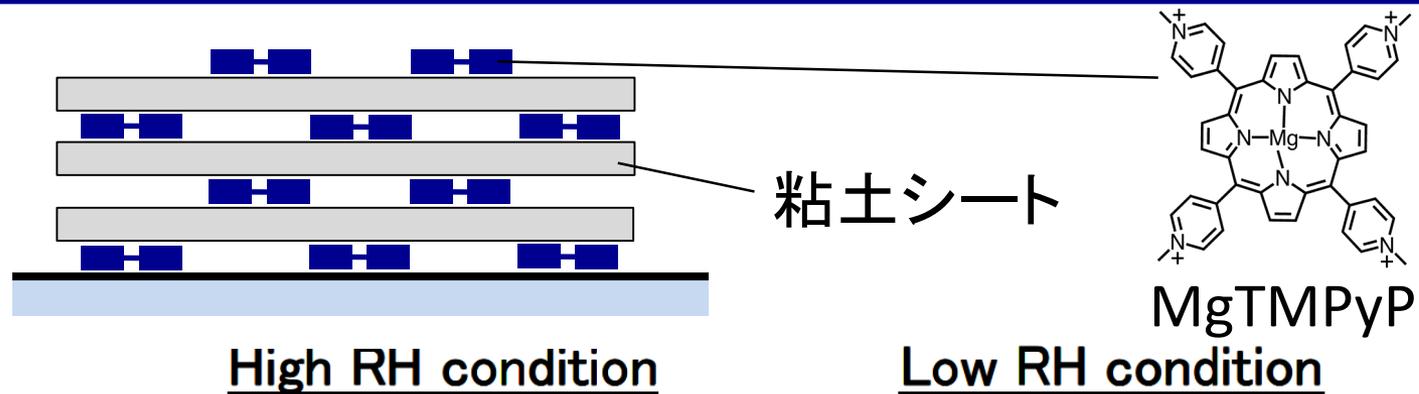
DASM with SSA



DASM with SSA



# 透明Mgポルフィリン粘土膜



LANGMUIR

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Optical Humidity Sensing Using Transparent Hybrid Film

Composed of Cationic Magnesium Porphyrin and Clay Mineral

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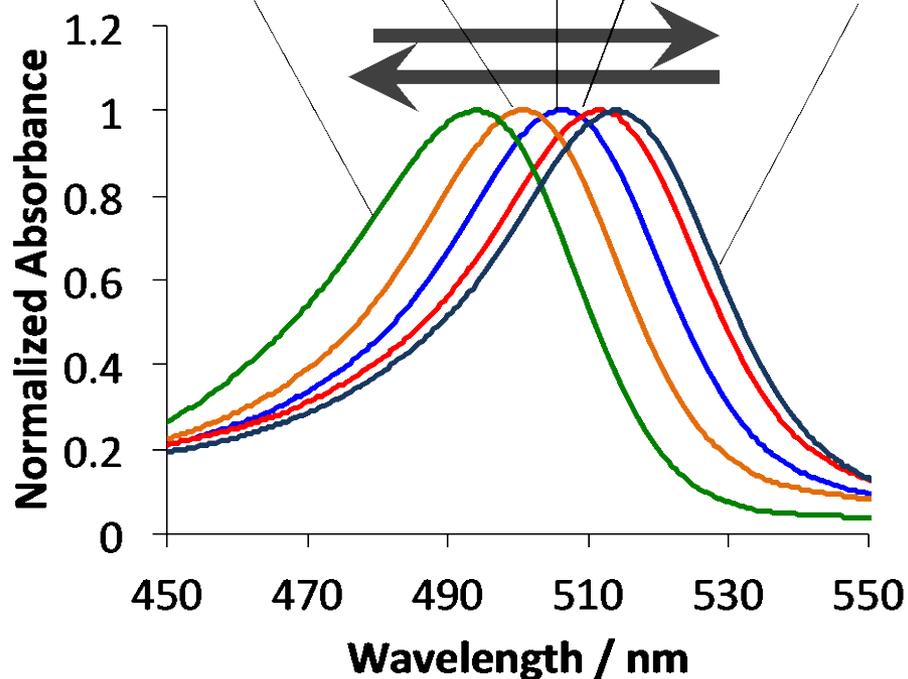
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# 可逆な色調変化



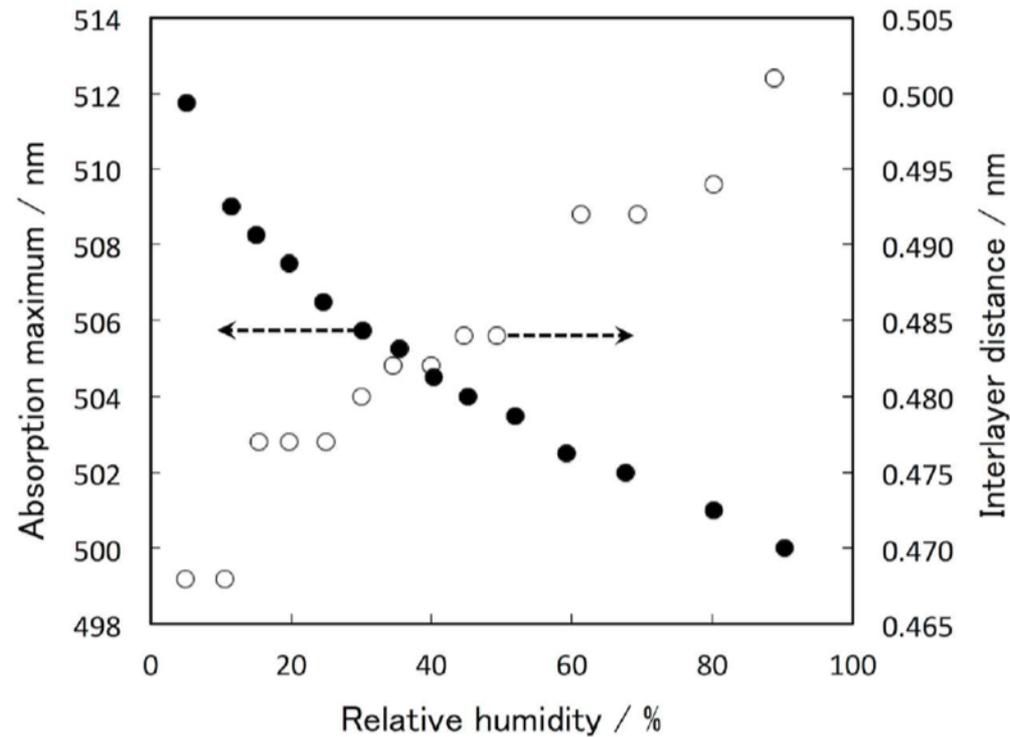
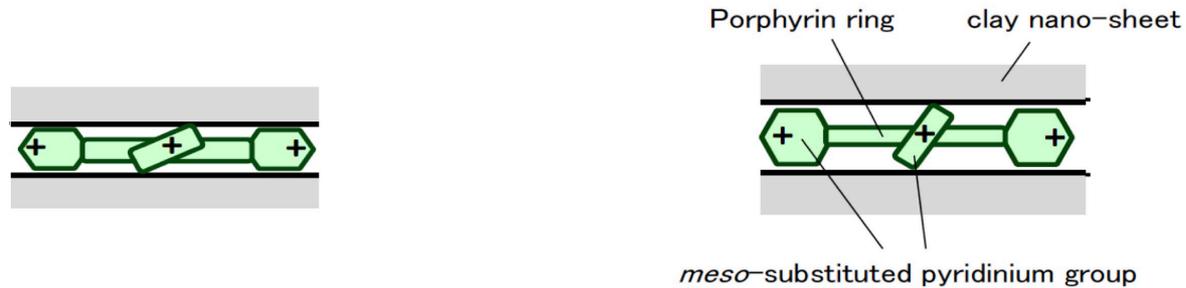
RH(%) 5 11 15 20 25 30 36 40 45 52 59 68 80 90

In water 55% 16% 4.4% Under vacuum

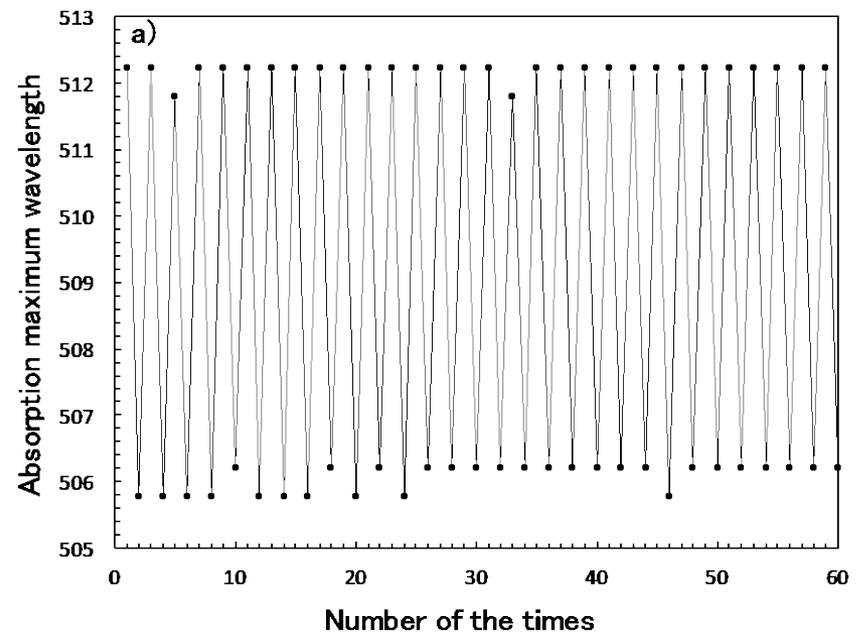
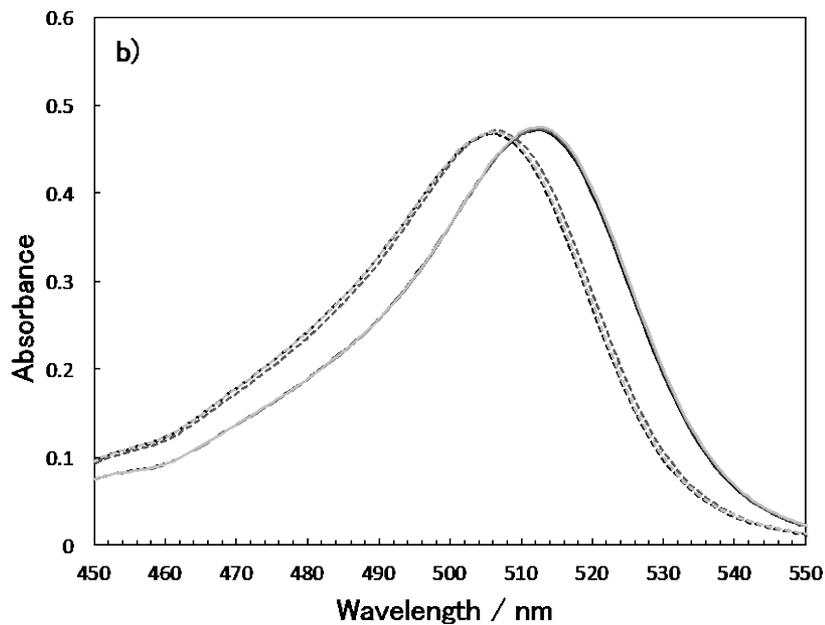
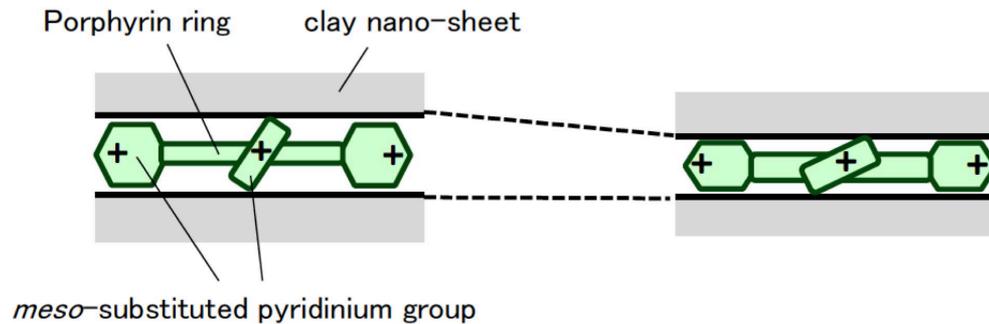


RH(相对湿度) / %(25 °C)	$\lambda_{max}$ / nm
(Under vacuum)	<b>514.0</b>
4.4	511.5
16	507.0
55	501.5
(In water)	494.0

# 吸収波長 vs 層間距離



# 高い繰り返し耐久性



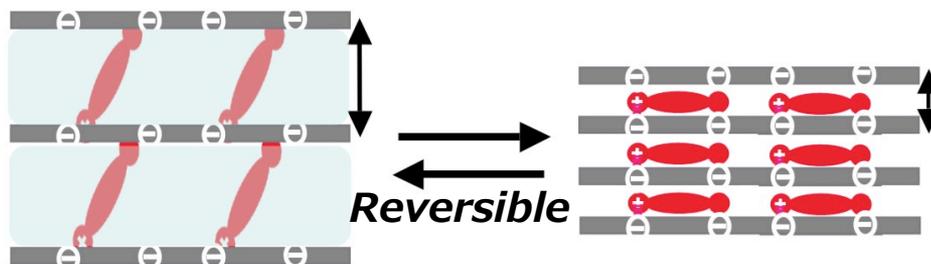
**Figure S6.** (a)  $\lambda_{\max}$  of MgTMPyP/SAP hybrid film under vacuum or wet air (RH30%) and (b) absorption spectra of MgTMPyP/SAP hybrid film under vacuum condition (solid line) and under wet air (RH30%, broken line), and repeated count is one (black line), fifty (dark gray line) and one hundred (gray line) times.



# ソルバトクロミズム挙動



DMF Dioxane EtOH Acetone Water  $\text{H}$  Air

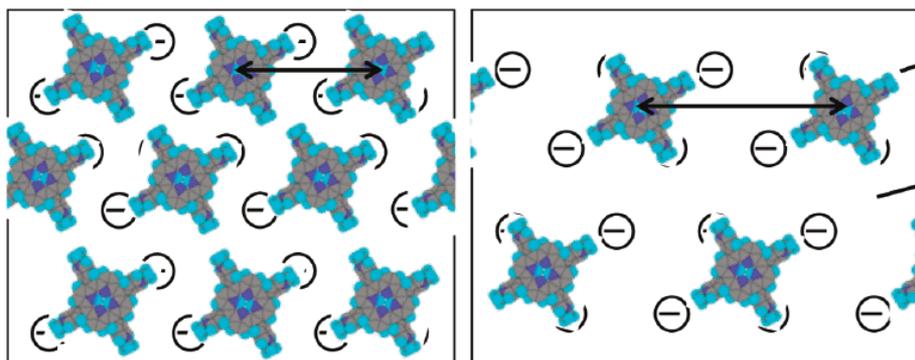


DMF, Dioxane, etc.

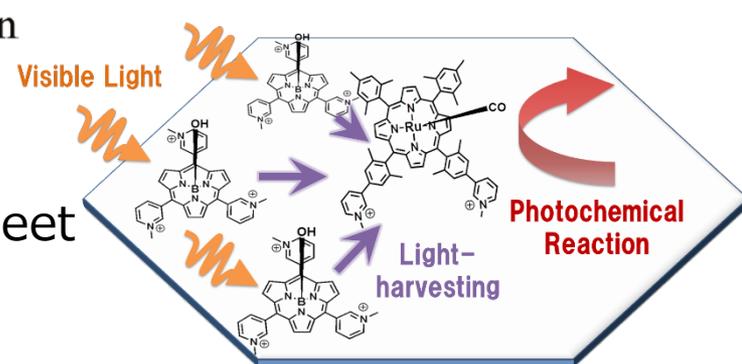
Air, water, etc.

# 人工光合成型システム

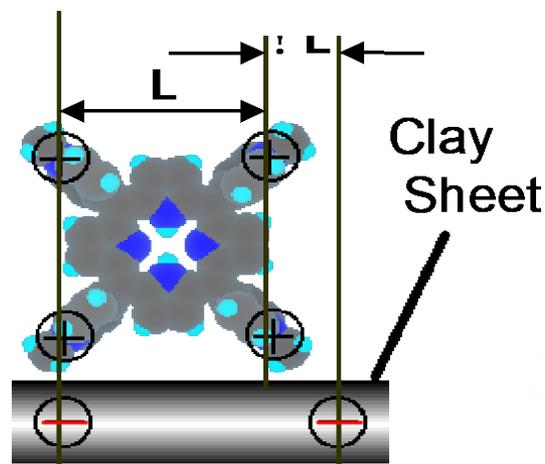
## “Size-Matching Effect”



Intermolecular Distance  
= 2.3 ~ 3.0 nm

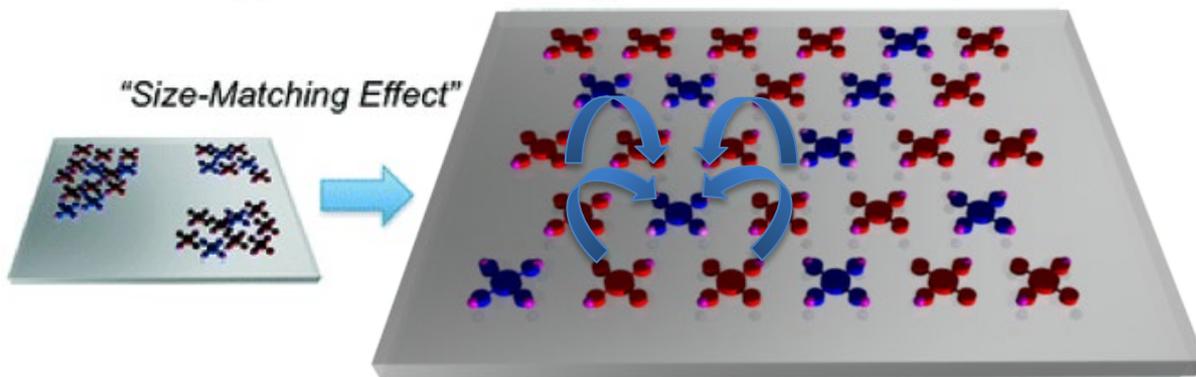


*J. Am. Chem. Soc.* 2011, 133, 14280.  
*J. Phys. Chem. C*, 2013, 117, 9154



1.20 nm

## Artificial Light Harvesting System on the Clay Surface



c.a. 100% Energy Transfer



## 企業への期待

- 色素に関わる開発を行っている企業との共同研究を希望。
- 用いている色素の構造式がわかれば、本技術がどこまで有効かの予想ができるので、お気軽にお問い合わせ下さい。
- 日本発の技術を育てて欲しい。



# 本技術に関する知的財産権

- 発明の名称 : 発光性組成物の発光調節方法  
およびこれを用いたセンサー
- 出願番号 : 特願2018-077347
- 出願人 : 首都大学東京
- 発明者 : 高木慎介、嶋田哲也、工藤奈々



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