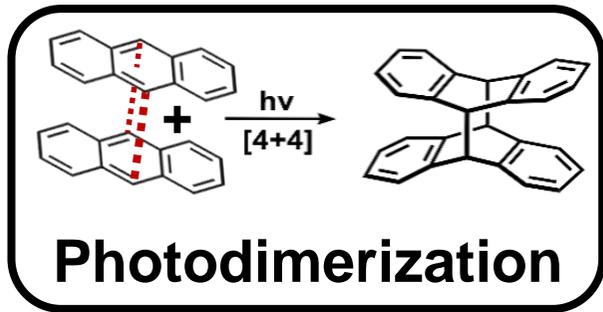
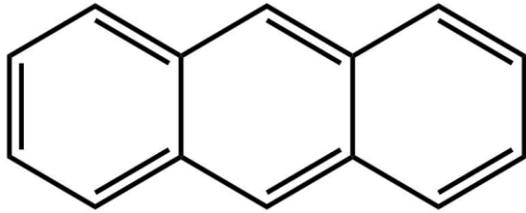
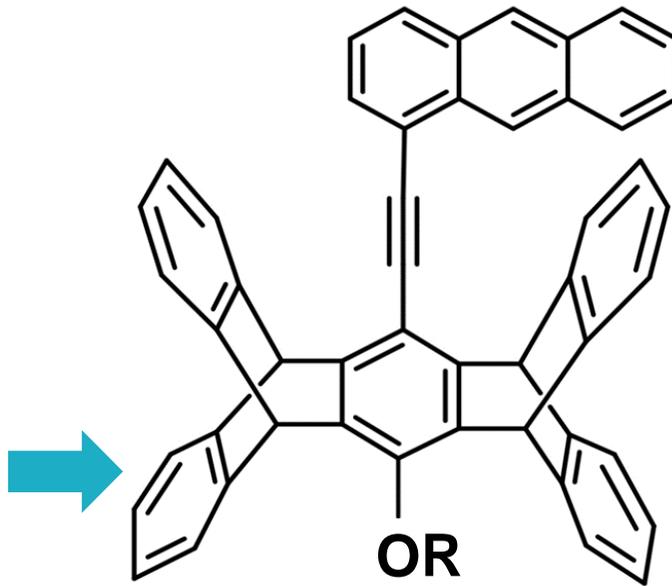


A Pentiptycene-Anthracene Hybrid Smart Fluorescent Material

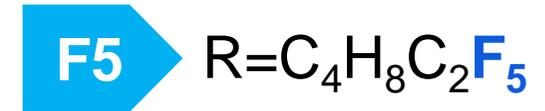
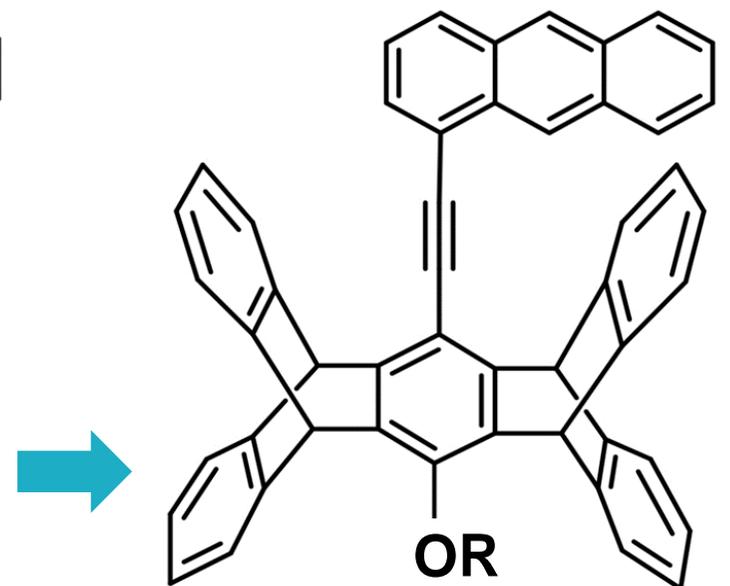
Introduction



Anthracene emits blue fluorescence under UV irradiation and undergoes [4+4] photodimerization. This reaction causes structural changes, allowing for applications.



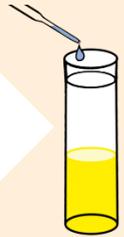
Scientists connected penta-1,3-diene on the anthracene to prevent anthracene aggregation. This one-side attachment promotes anthracene supramolecular pair formation.



There is a fluorine-substituted alkoxy chain compound. We believe this compound would have a different crystal structure from **C8** and hence unique photoactivities especially on the photomechanical effect.

Methods

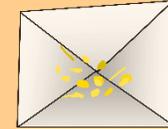
Crystal preparation



Layer MeOH in
F5 DCM solution



Wait for the
crystals to grow



Collect the
crystals

Fluorescence microscope



Observe the crystal's
fluorescence
changes under UV

$\lambda_{\text{ex}} = 340\text{-}390 \text{ nm}$
(180° between light source and camera)

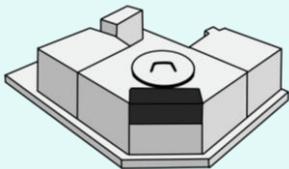


Observe **bending** of
crystals under UV



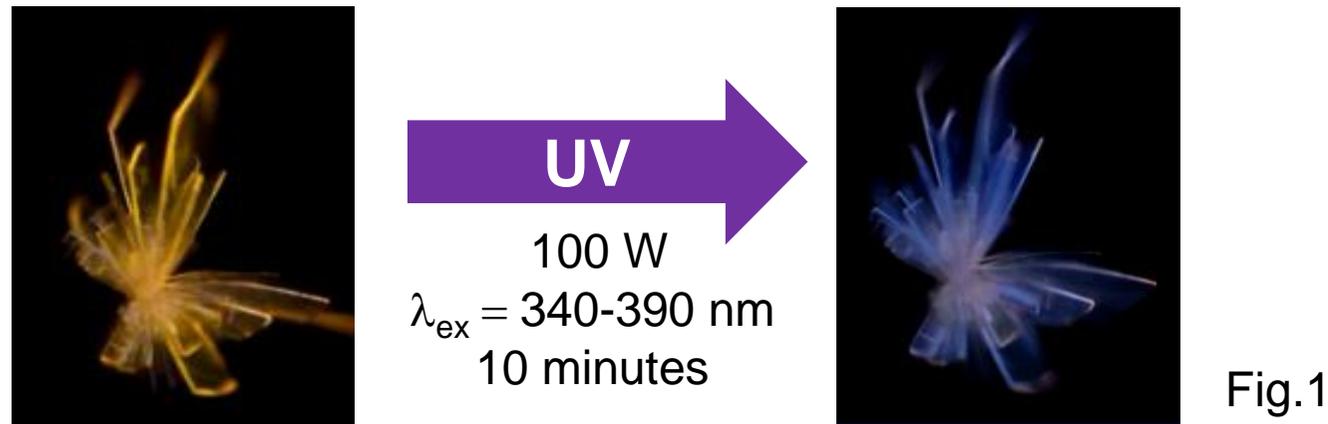
$\lambda_{\text{ex}} = 405 \text{ nm}$
(90° between light source and camera)

Fluorescence spectrometer

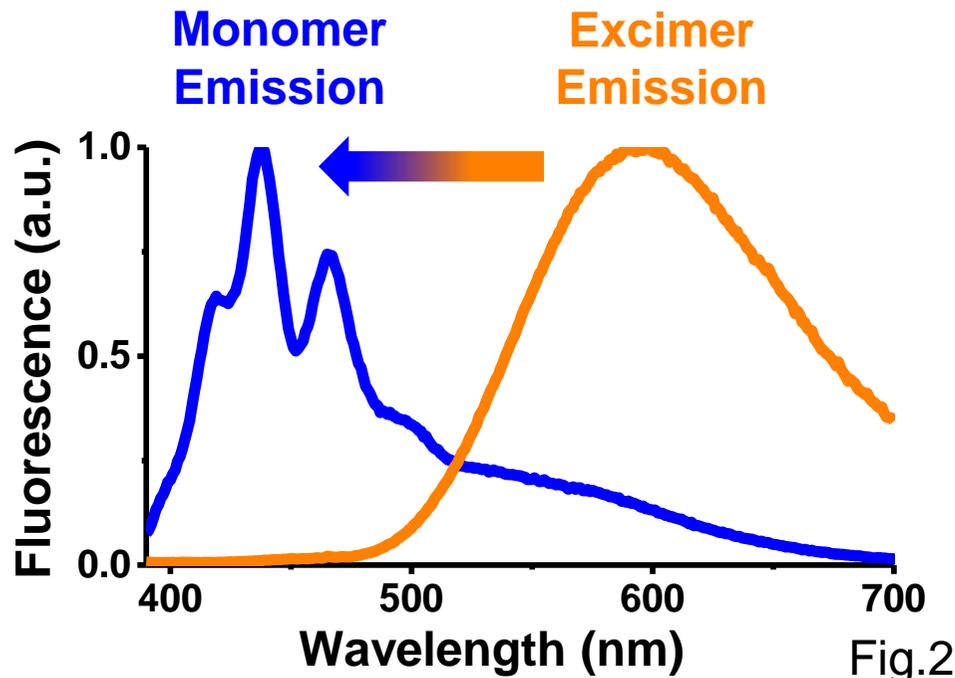


Measure the
emission spectra

Results and Discussion – PMFC (Photomechanofluorochromism)



The crystals of **F5** are generally needle shaped. A needle cluster is placed in the fluorescence microscope, the fluorescence changes from yellow to blue under UV.



From the emission spectra of **F5** crystals, we found that:

- The yellow fluorescence is a broad band excimer emission.
- The blue fluorescence exhibits the distinct monomer anthracene emission.

Results and Discussion – PMFC (Photomechanofluorochromism)

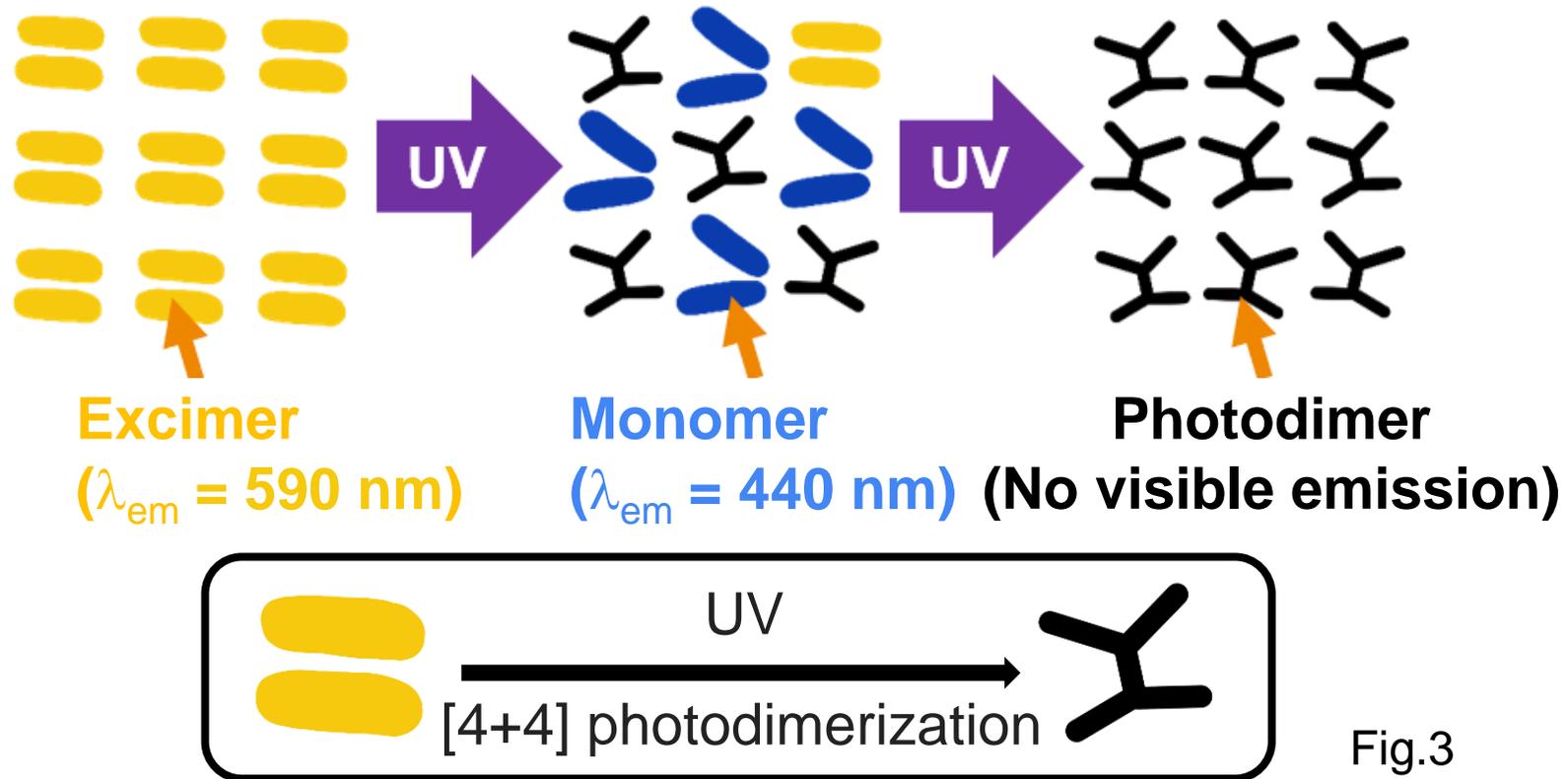
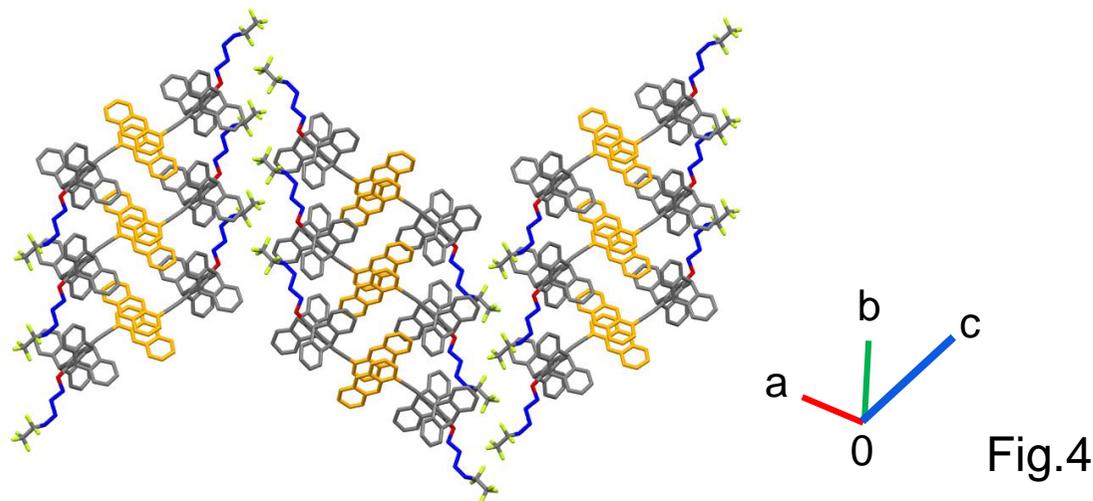


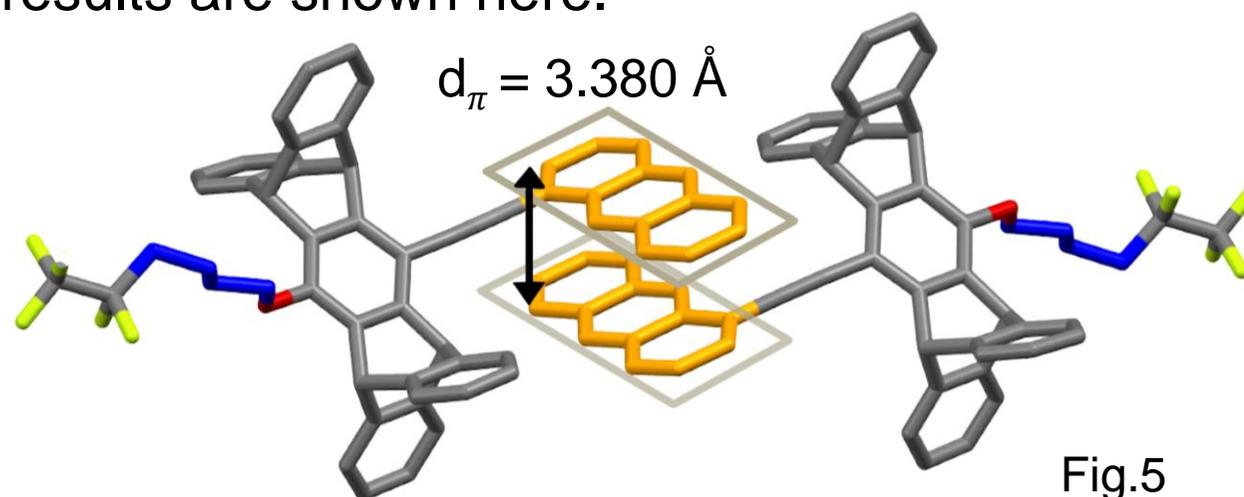
Fig.3

We believe the fluorescence change is due to the dimerization of the supramolecular pairs under UV irradiation. The products require larger space, and give mechanical stress on nearby molecules, causing them to move apart, becoming monomers.

Results and Discussion – Crystal Structure

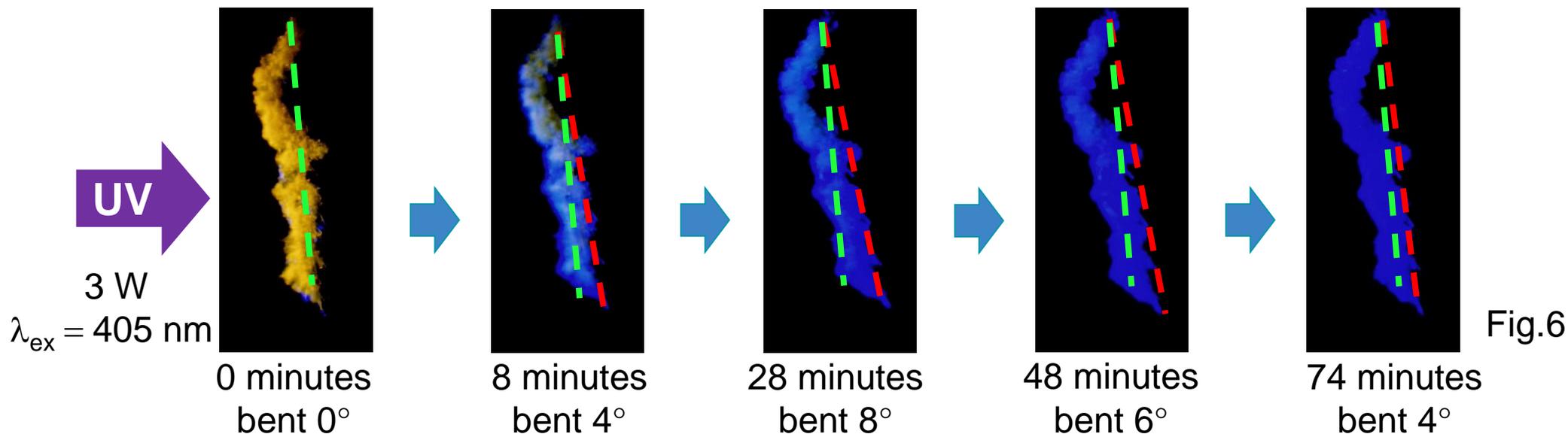


To verify our hypothesis, we submitted the crystal for X-ray structure analysis, the results are shown here.

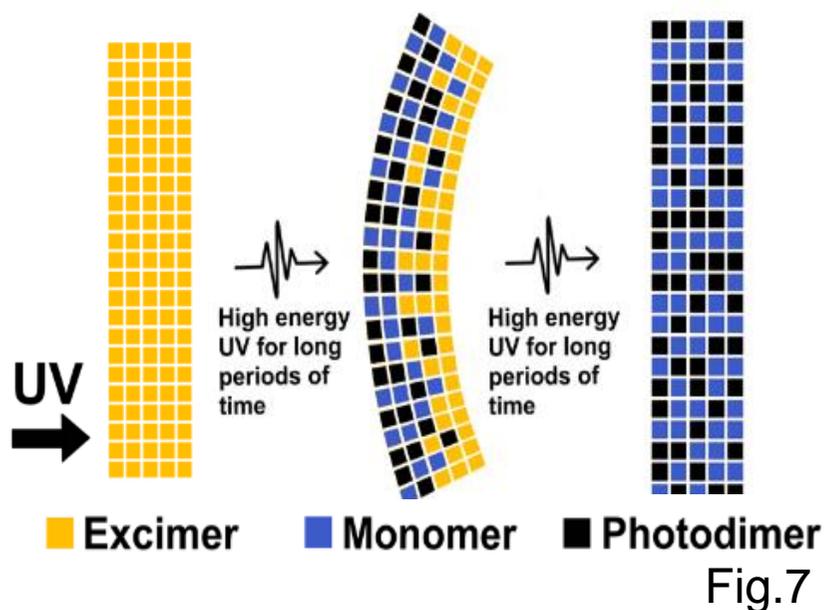


It is clear that pentiptycene promotes anthracene supramolecular pair formation. The distance between two anthracene planes is far for ground state interactions, but close enough for excited state dimerization.

Results and Discussion – The Photomechanical Effect



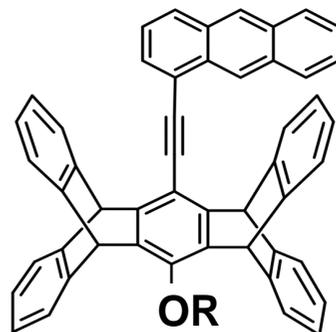
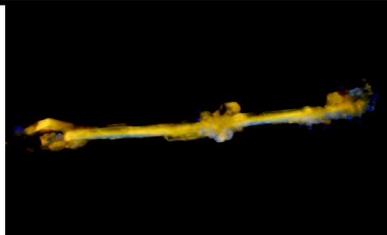
We observed that needle-shaped crystals bended away from UV light, then back to its original position.



We believe this is due to uneven photoreactions. The near-side formed more photodimers than the far side in the beginning. Since they take up more space, the crystal bended away from light. After a while, the far side also photodimerized, and the crystal bended back to its original position.

Results and Discussion – The Photomechanical Effect

F5 R = C₆H₈F₅



C8 R = C₈H₁₇



Fig.8

Comparing the crystals' morphology. **F5** is needle-like and **C8** is plate-like.

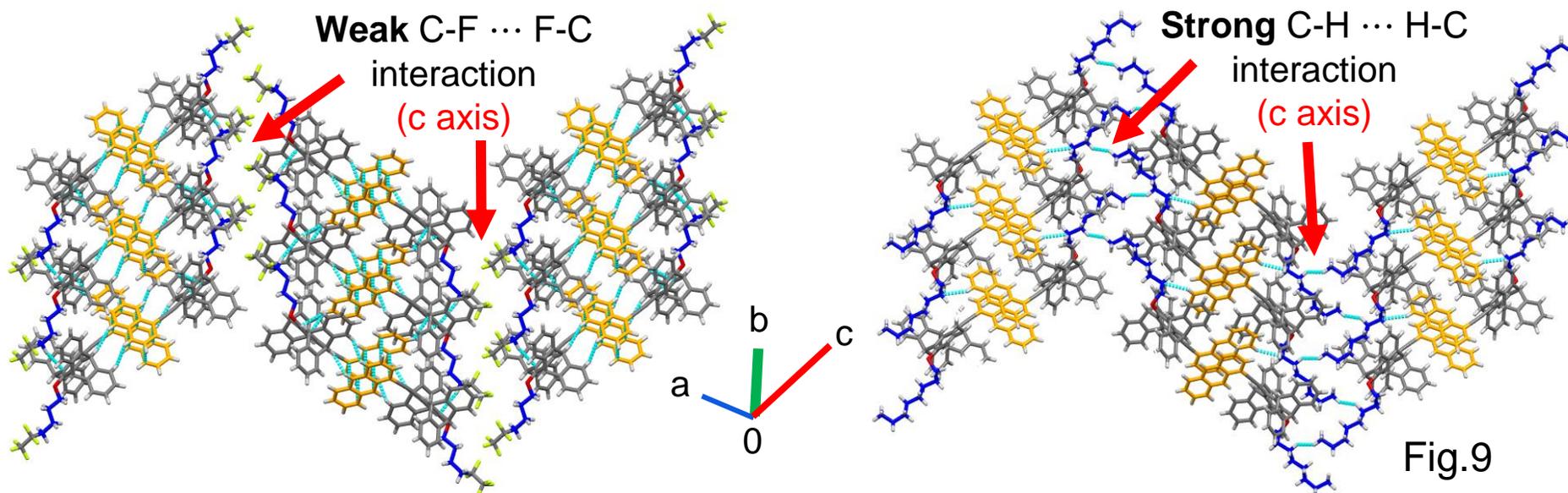


Fig.9

Both crystals grow along the anthracene packing (b axis). Strong interactions between hydrocarbon alkoxy chains (c axis) in **C8**, result in two dimensional crystals (b, c axes). Fluorine substituents in **F5** weaken the interactions along the c axis, resulting in one dimensional crystals (b axis only). The bulky plates inhibit **C8** crystal bending. The needle crystal of **F5** is the key for bending.

Application – Organic Vapor Detection

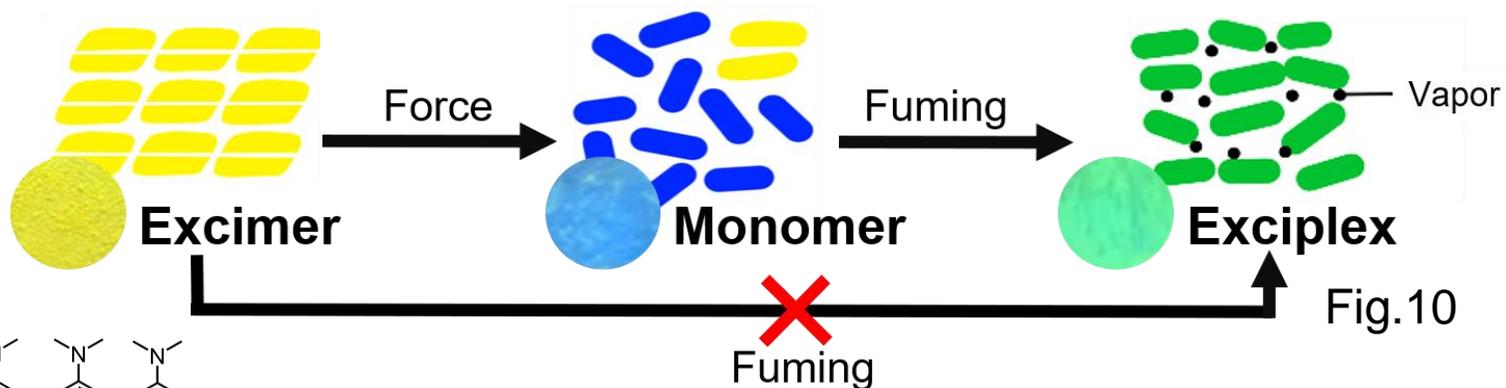


Fig.10

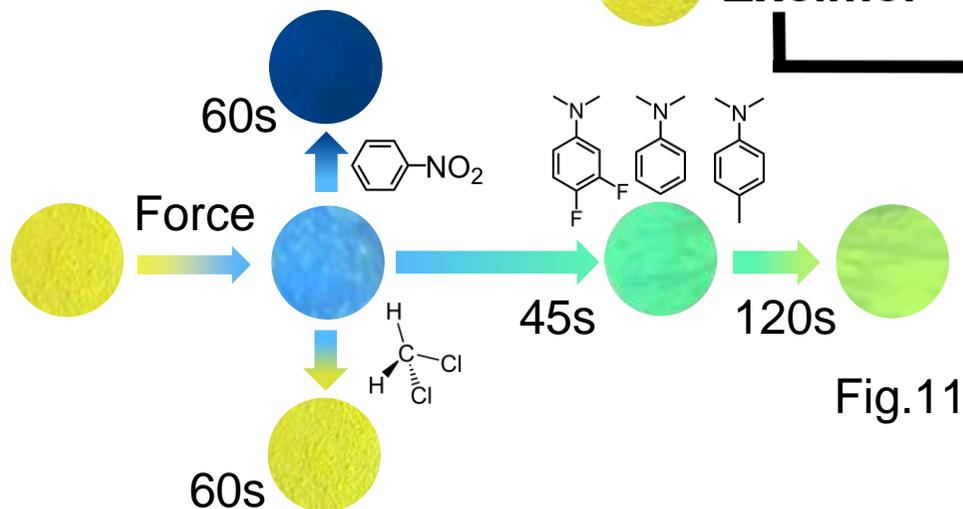


Fig.11

The crystalline powder with yellow excimer emission shows no change with organic molecules. However, after grinding, the crystalline powder changes to an amorphous powder with some blue monomer emission.

This monomer emission responds to organic compounds. Adding aniline derivatives changes fluorescence to green. Adding dichloromethane recrystallizes the amorphous powder. Adding nitrobenzene results in fluorescence quenching.

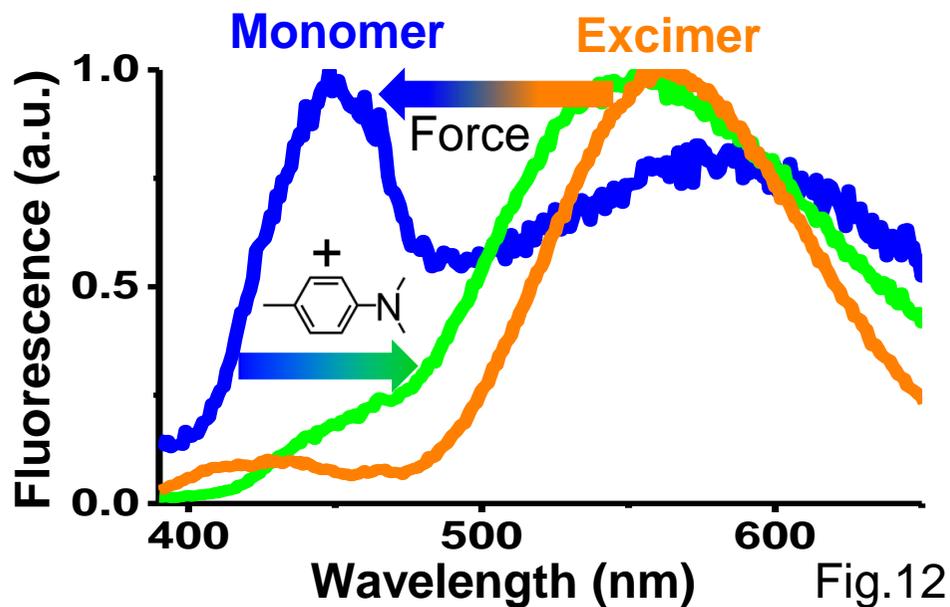
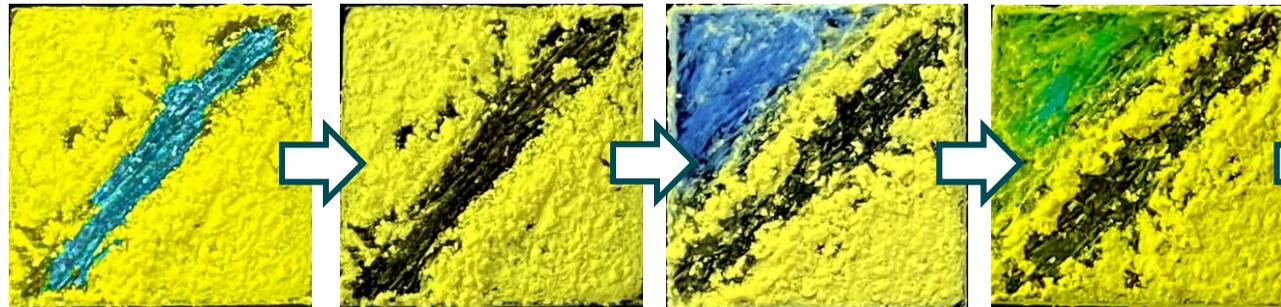
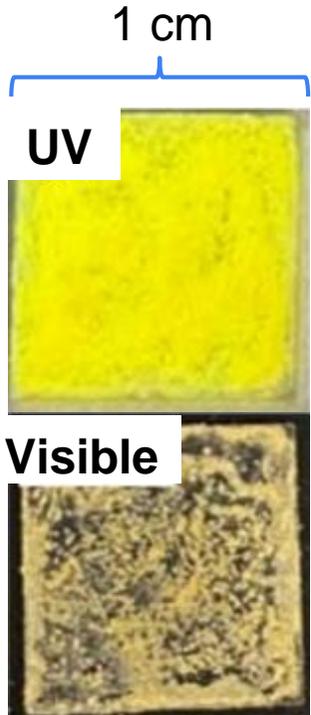


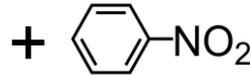
Fig.12

Application – Multicolor Drawings

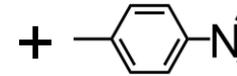
Rich organic vapor detection properties enable a multicolor drawing.



Grinding



Grinding



Reverse by fuming dichloromethane

Reverse by heating

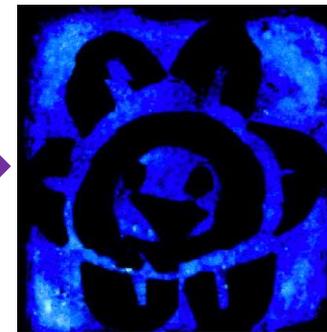
Final F5 drawings



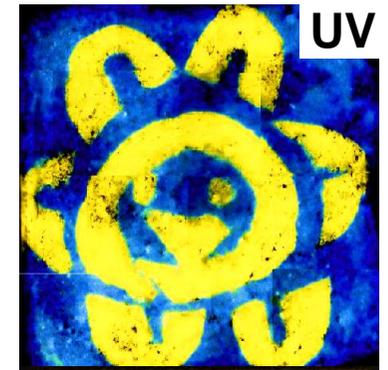
Black tape
+
slide glass



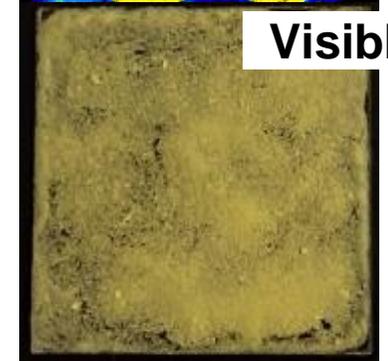
Before irradiation



After irradiation



UV



Visible

Photomechanofluorochromic properties make a different type of multicolor drawing.

Application – F5 in Polymer Thin Film

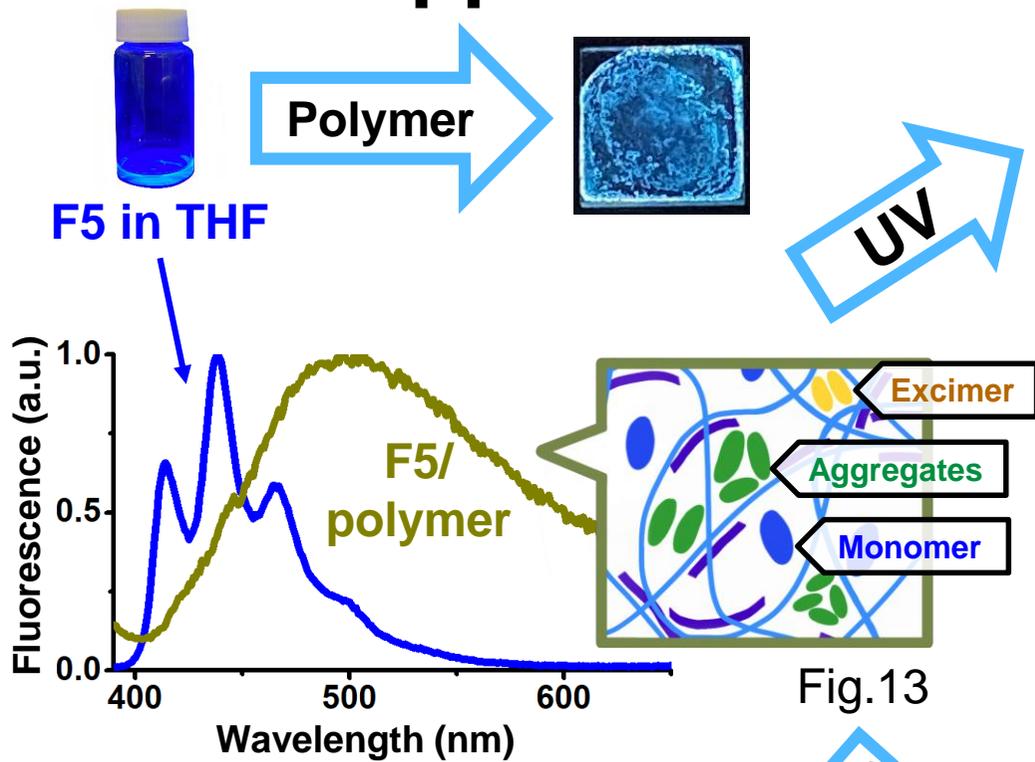


Fig.13

We believe polymer strands coil up to form chambers. Some molecules remain monomers while others form aggregates or supramolecular pairs. The mixture of all species gives this broad band emission.

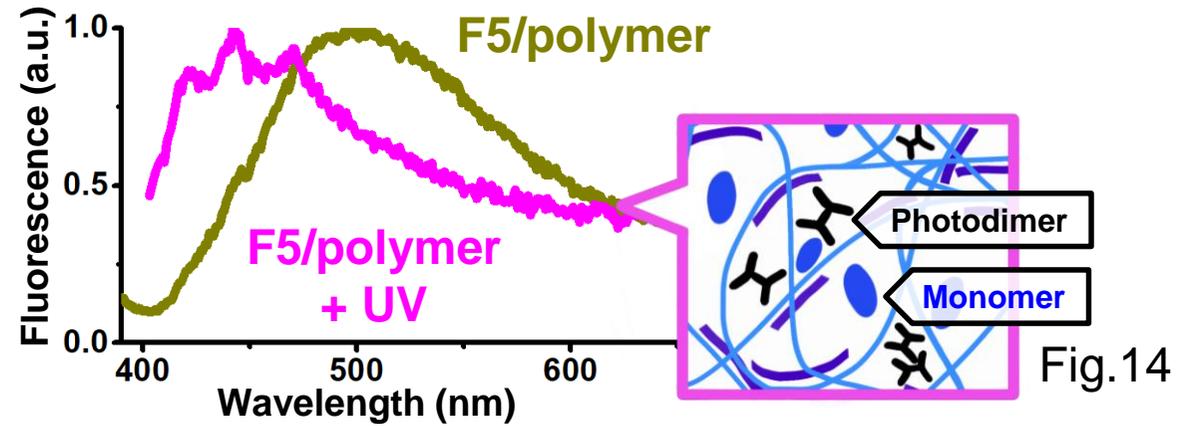
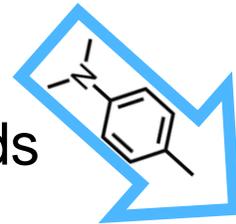


Fig.14

After UV irradiation, the monomer emission was more distinct. This is due to the photodimerization of aggregates and supramolecular pairs reducing the broad band emission.

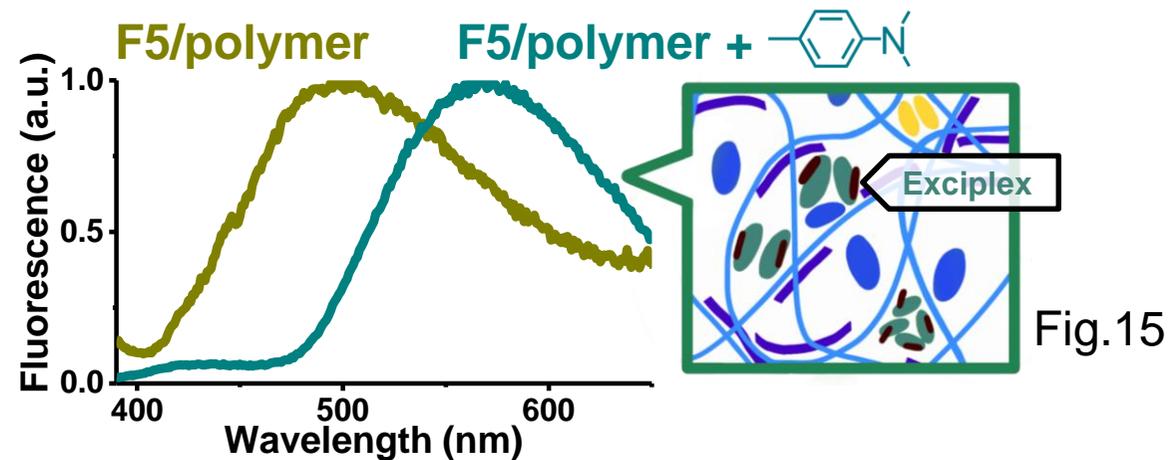


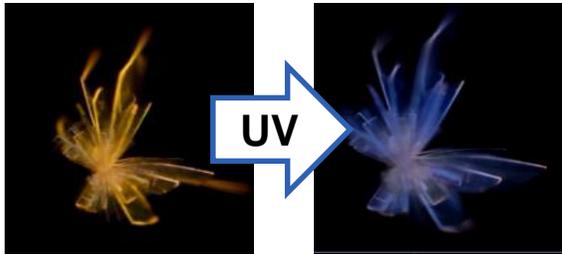
Fig.15

After fuming aniline derivatives, the broad band emission redshifted to green, similar to amorphous powder.

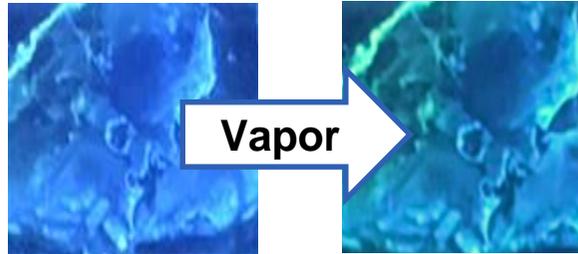
Conclusions

Smart Material F5

Fluorochromism



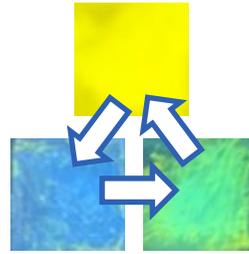
PMFC



Polymer thin film

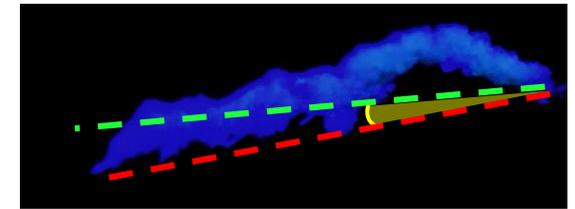
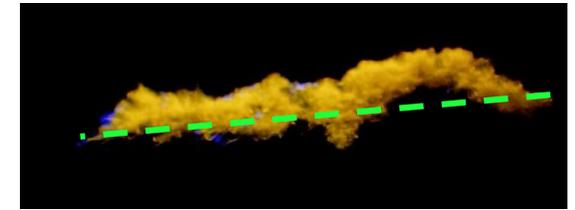


Multicolor drawings



Organic vapor detection

Photomechanical effect



Photomechanical bending

References

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- Kim, T., Zhu, L., Al-Kaysi, R. O., and Bardeen, C. J. (2014) Organic Photomechanical Materials. *Chemphyschem.*, **15(3)**, 400-414.