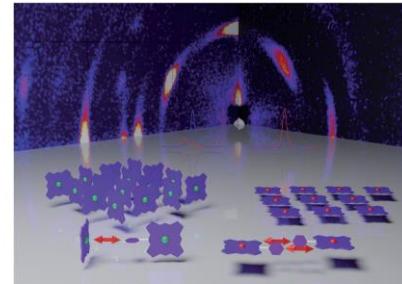
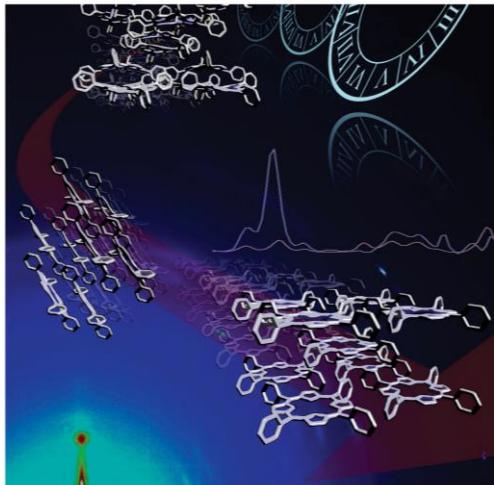
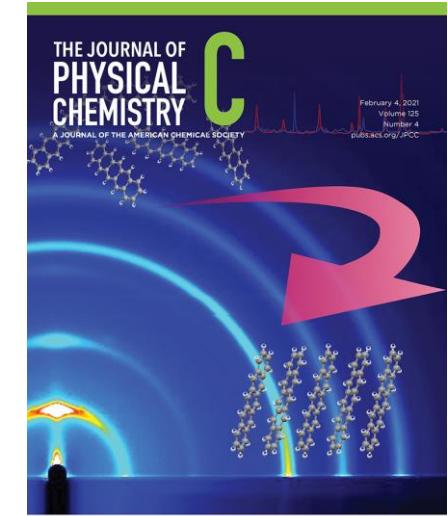


CRYSTAL GROWTH & DESIGN



Showcasing research from Professor Takeshi Hasegawa's laboratory at the Research Institute for Sustainable Materials, Kyoto University, Gokasho, Uji, Kyoto, Japan.
Image designed and illustrated by Kaito Tomita.
Control of supramolecular organizations by coordination bonding in tetrapyrrolylporphyrin thin films.
By changing the central metal ion of tetrapyrrolylporphyrin,



[Organic Semiconductor Group] 2022 Research Introduction

Projects

1 Selective control of molecular orientation

- ✓ *Sci. Rep.* **2019**, 9 (1), 579.

2 Understanding of crystal growth at the substrate interface

- ✓ *Appl. Phys. Express* **2020**, 13 (9), 095505.

3 Control and analysis of on-surface reactions

- ✓ *Sci. Rep.* **2022**, 12 (1), 4448.
- ✓ *J. Phys. Chem. C* **2021**, 125 (4), 2437–2445.

4 Porphyrin-based supramolecular organizations

- ✓ *Chem. Commun.* **2022**, 58 (13), 2116–2119.
- ✓ *Cryst. Growth Des.* **2021**, 21 (9), 5116–5125.
- ✓ *Chem. Eur. J.* **2016**, 22 (46), 16539–16546.

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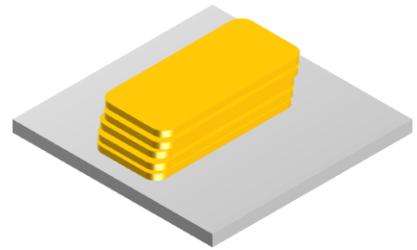
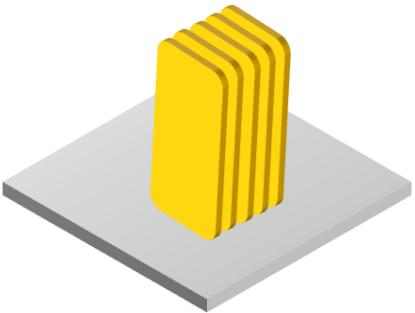
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4

Porphyrin-based supramolecular organizations

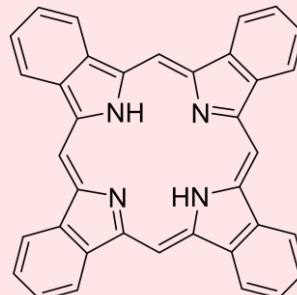
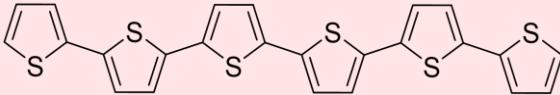
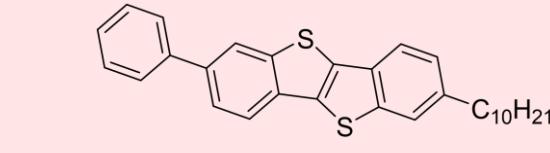
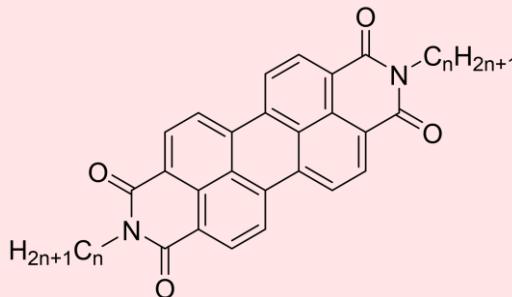
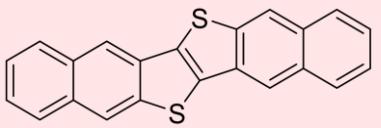
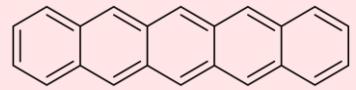
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Molecular orientation of organic semiconductors

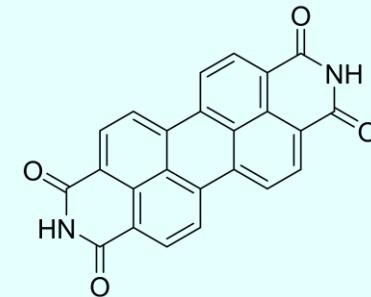
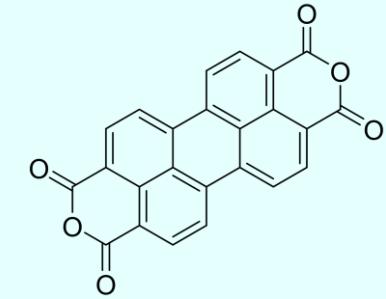
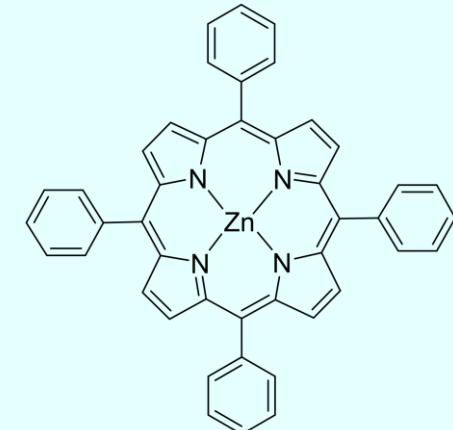


Selective control of molecular orientation

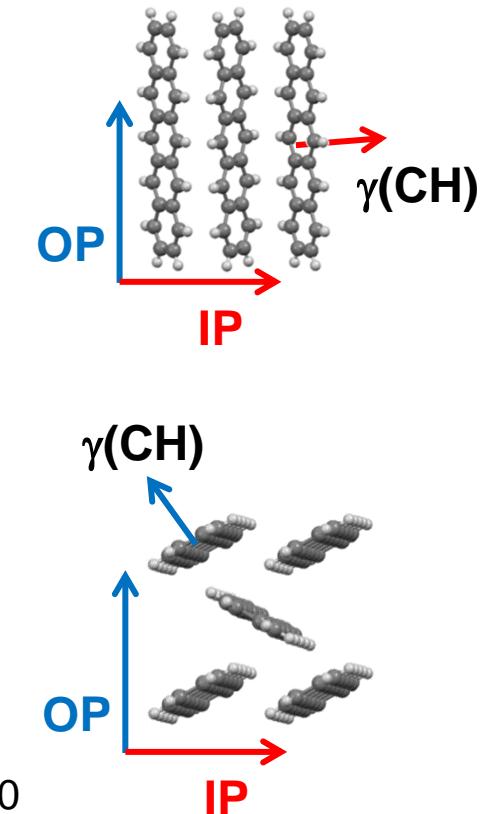
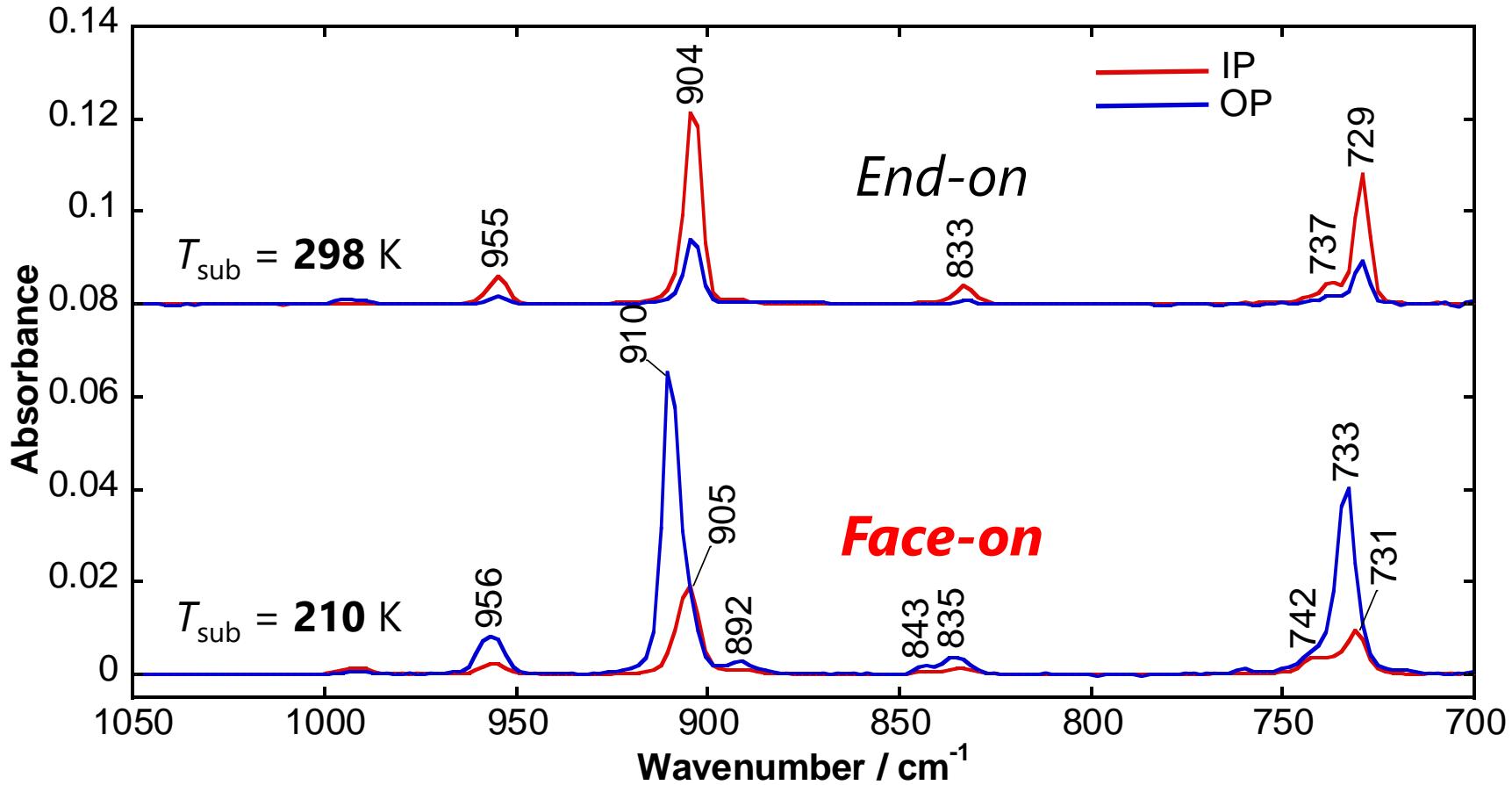
End-on



Face-on



Alternative face-on thin film structure of pentacene



Achievement of **face-on orientation** of pentacene on silicon

Sci. Rep. 2019, 9, 579.



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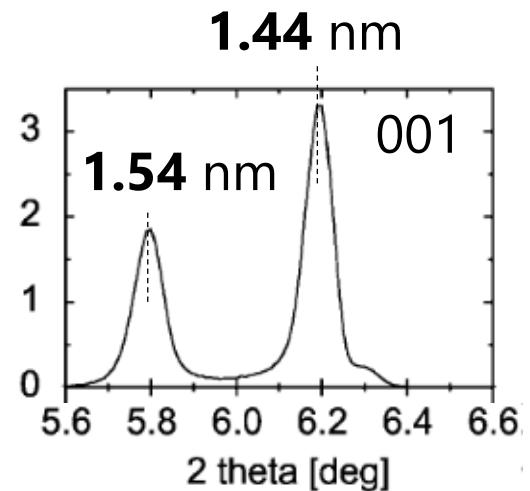
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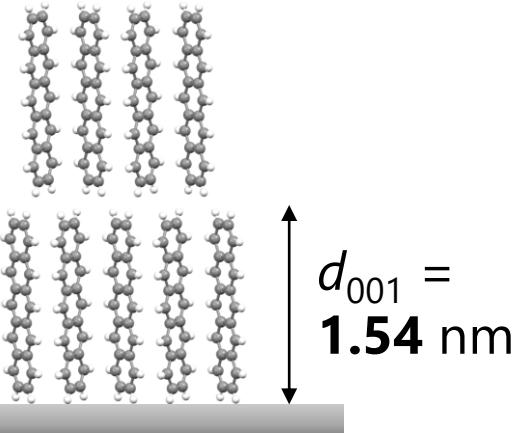
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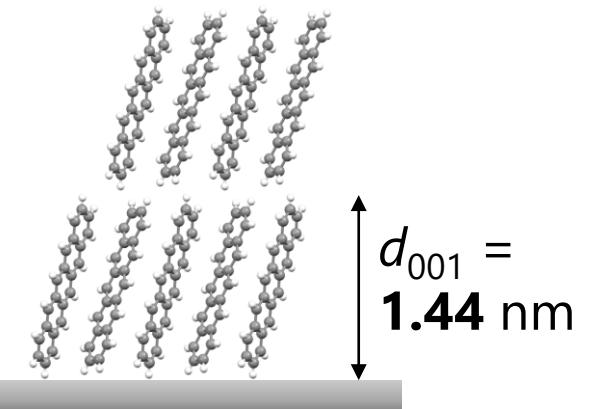
Thin-film phases of organic semiconductors



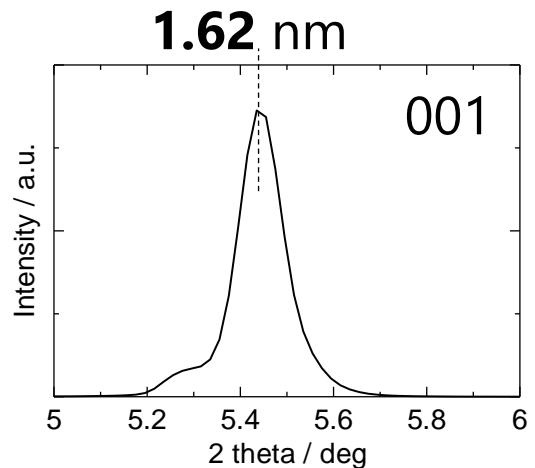
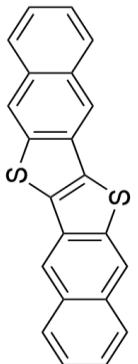
Thin-film phase



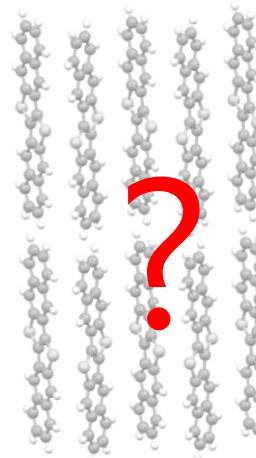
Bulk phase



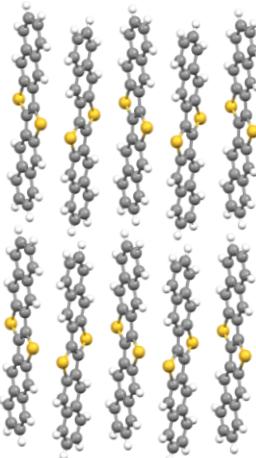
Mattheus et al., *Synth. Met.* **2003**, 138, 475.



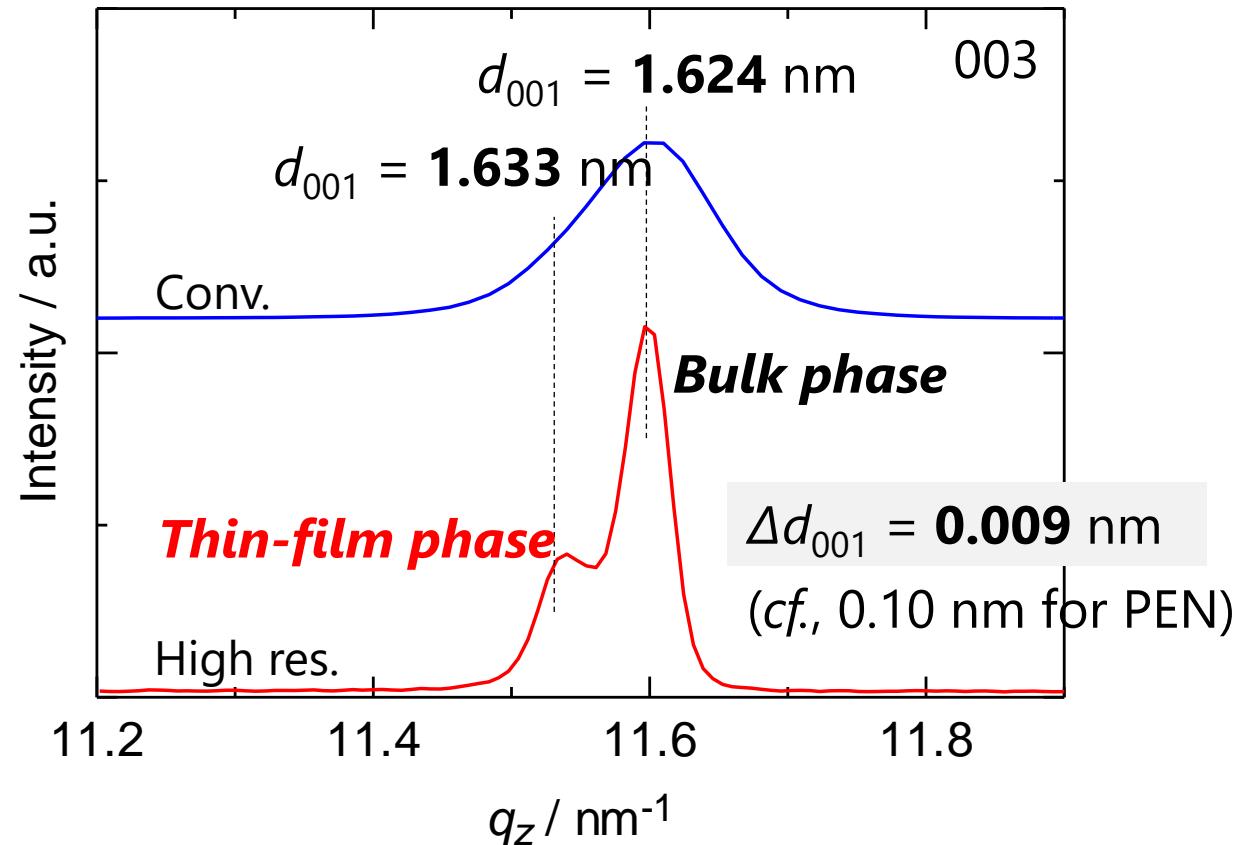
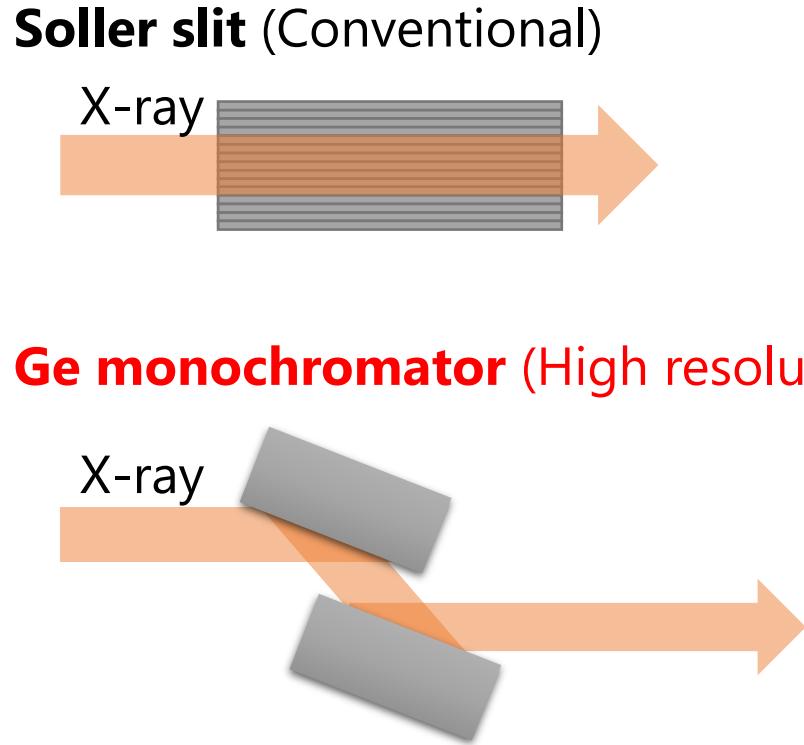
?



$d_{001} = 1.62 \text{ nm}$



Hidden thin-film phase of DNTT



*Identification of **thin-film phase** of DNTT on silicon*

Appl. Phys. Express **2020**, 13, 095505.



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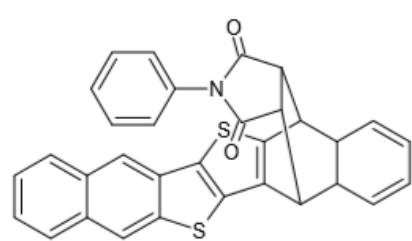
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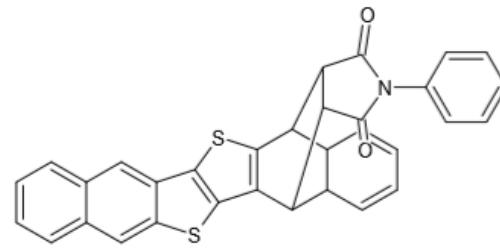
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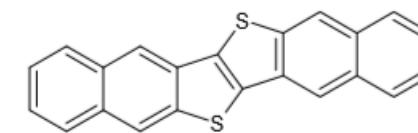
Thermal conversion of DNTT precursors



Endo-isomer



Exo-isomer

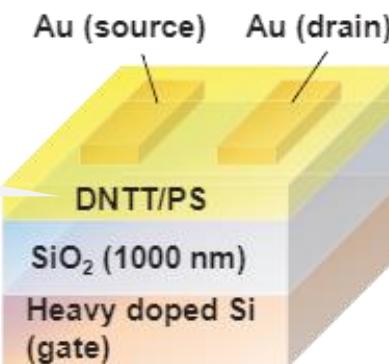


DNTT

3.35 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

OFET
mobility

0.94 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

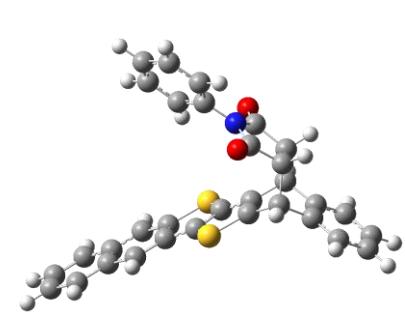


[1] Hamaguchi, A. et al. *Adv. Mater.* **2015**. 27, 6606.

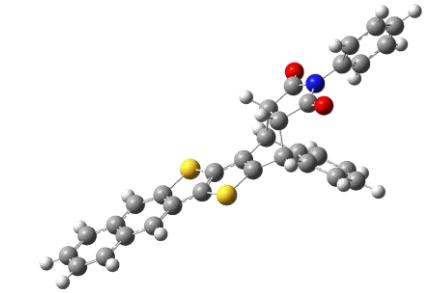
[2] Kimura, Y. et al. *Adv. Mater.* **2015**. 27, 727.

The structure-property relationship remains unresolved.

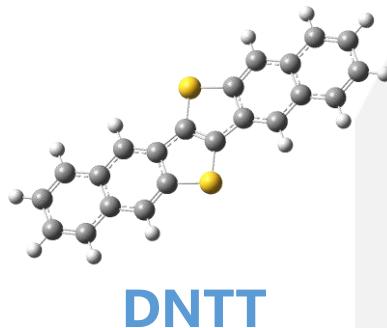
Stereoisomer-dependent conversion



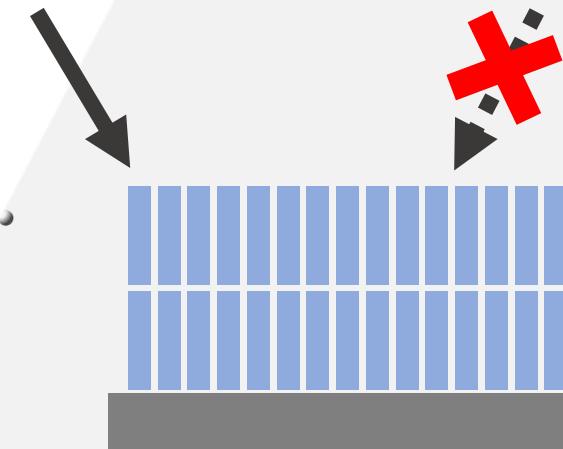
Endo-isomer
(High mobility)



Exo-isomer
(Low mobility)



DNTT



*Control of **on-surface reactions** of DNTT precursors*

Sci. Rep. 2022, 12, 44448.



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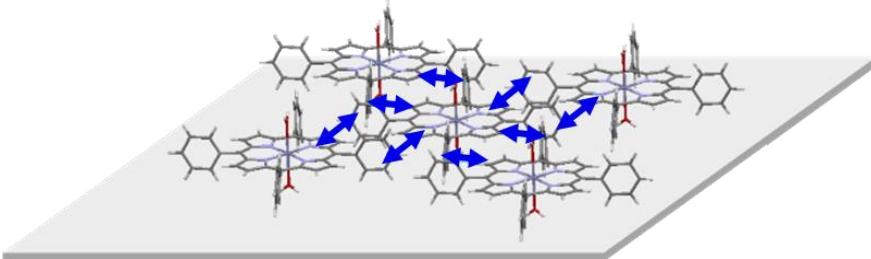
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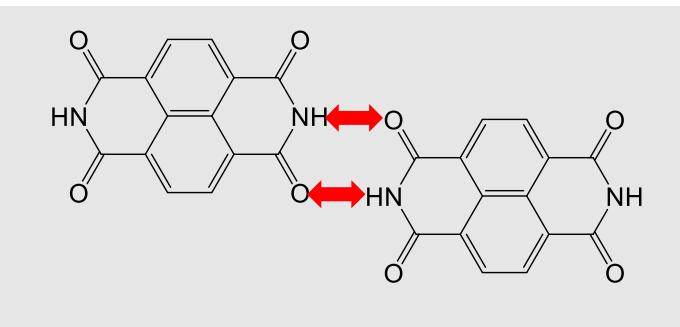
Supramolecular organizations in thin films

- ✓ Molecular design strategy for **face-on** orientation

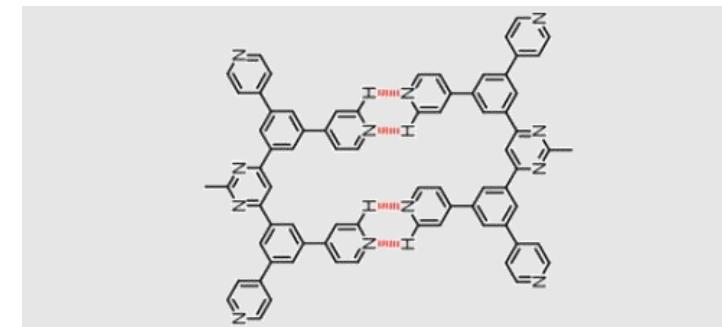
C-H/π interaction



Hydrogen bonding



C-H/N interaction

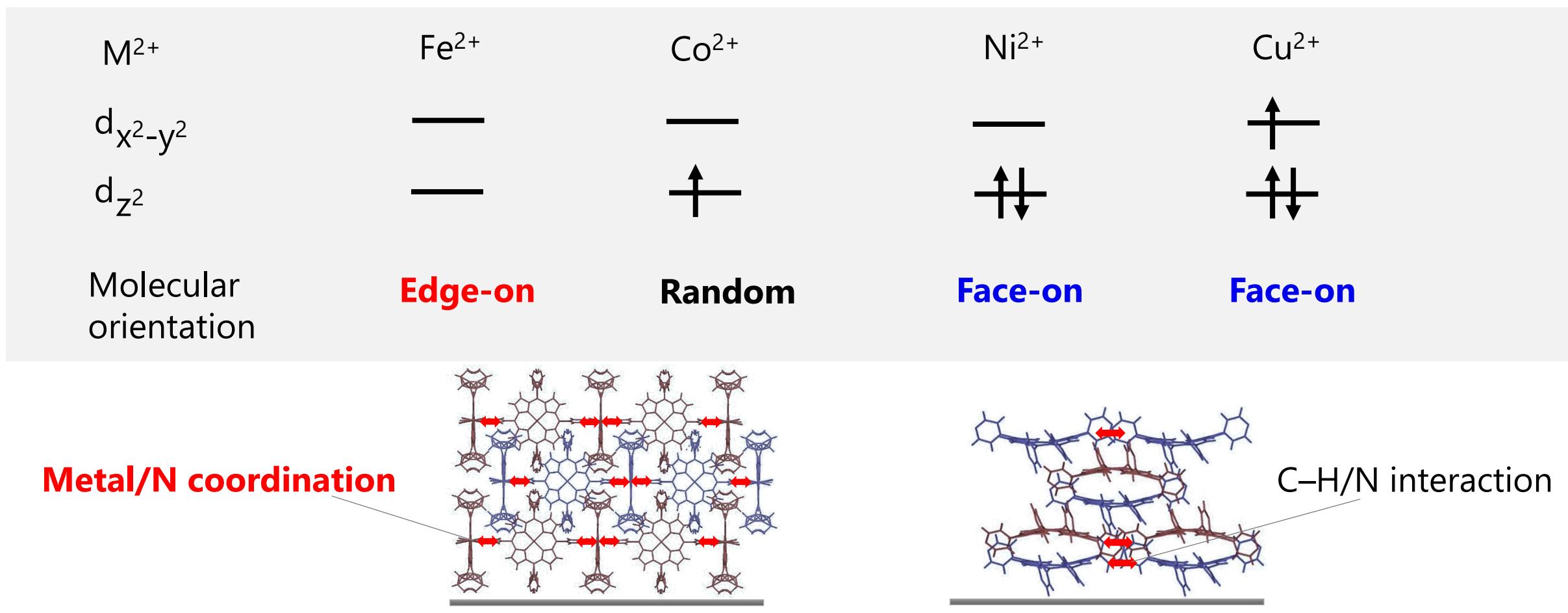


Yokoyama, D. et al. *Adv. Funct. Mater.*
2011, 21, 1375.

- ✓ Molecular design strategy for **edge-on** orientation

No report!

Control of supramolecular organizations



Achievement of ***edge-on orientation*** of porphyrins

Chem. Commun. **2022**, 58, 2116.

