Cyclic Tetrathiophenes Planarized by Silicon and Sulfur Bridges Bearing Antiaromatic Cyclooctatetraene Core: Syntheses, Structures, and Properties

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Tokyo Metropolitan Institute
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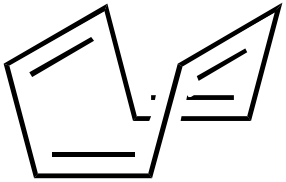
Cyclic Tetrathiophenes Planarised by Silicon and Sulfur Bridges Bearing Antiaromatic Cycloocatetraene Core: Syntheses, Structures, and Properties

Takeshi Ohmae, Tohru Nishinaga,* Mo Wu, and Masahiko Iyoda*
J. Am. Chem. Soc. **2010**, *132*, 1066–1074.

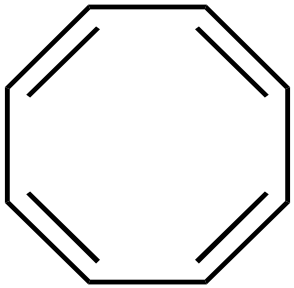
Organic Seminar, 2010-07-05
M1, Tsuyoshi Suzuki
Photoelectric Conversion Chemistry Laboratory

Introduction — Cyclooctatetraene (COT)



Actual COT

- **Tub-shape (nonplanar)**
- **Nonaromatic**



Imaginary COT

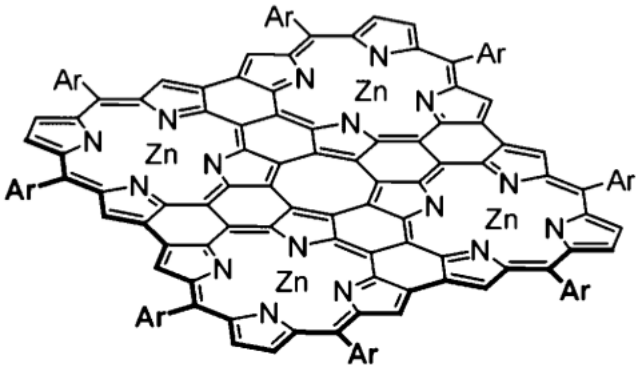
- **Planarized**
- **Antiaromatic**

Theoretical Predictions…
Narrow HOMO-LUMO gap
Antiaromatic–antiaromatic interaction

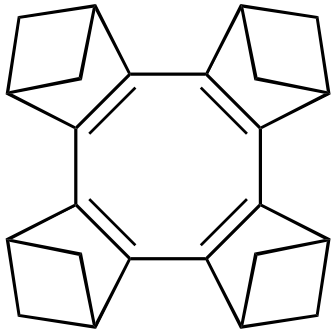
Jenneskens, L. W. *et al.*, *ACIE*, 2002, *41*, 1558–1560.

Introduction — Toward Planarized COT

■ Experimental Strategies



Annelation of rigid planar π-system to COT



Annelation of small membered rings to COT

■ Confirmation of Planar COT

Single Crystal Structure

^{1}H NMR

Characteristic weak absorption at long-wavelength area

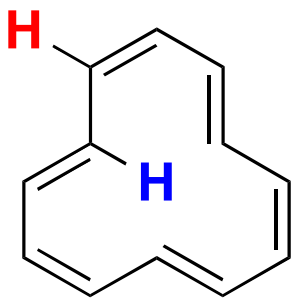
Kim, D.; Kobayashi, N.; Osuka, A. *et al.*, *JACS*, 2006, *128*, 4119–4127.

Komatsu, K. *et al.*, *JACS*, 2001, *123*, 1768–1769.

Introduction — Keywords

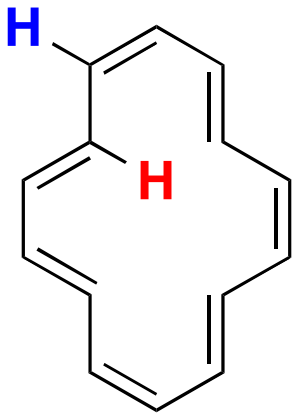
- **Paratropic**

  4nπ electron system
  Exocyclic H => upfield
  Endocyclic H => downfield



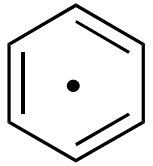
- **Diatropic**

  (4n+2)π electron system
  Exocyclic H => downfield
  Endocyclic H => upfield



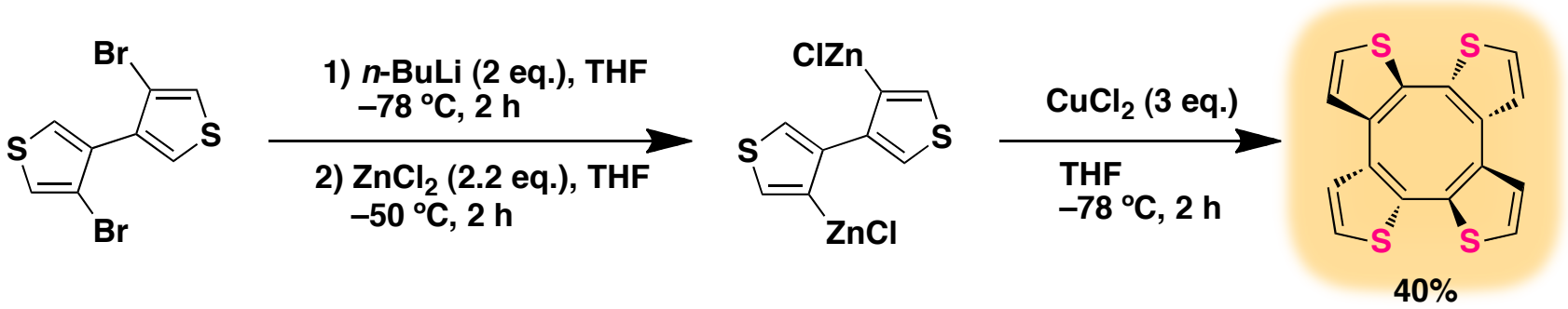
- **NICS (Nucleus Independent Chemical Shift)**

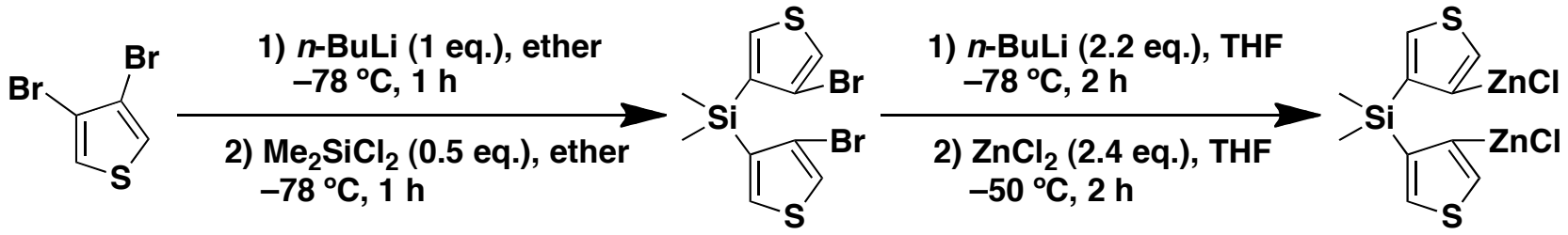
  Computing magnetic shielding
  Negative value => aromatic
  Positive value => antiaromatic

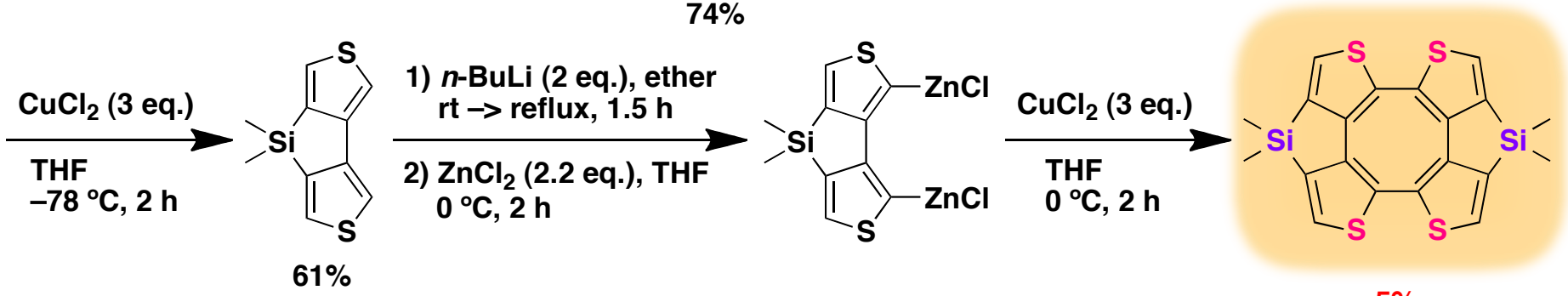


Schleyer, R. *et al.*, *JACS*, 1996, *118*, 6317–6318.

Previous Work





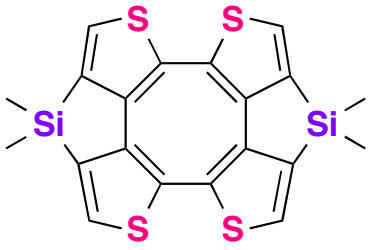


The yield was too low to characterize.

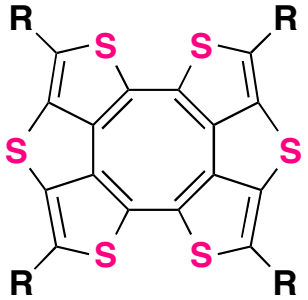
Iyoda, M. *et al.*, *Heterocycles*, 2000, *52*, 761–774.

This Work

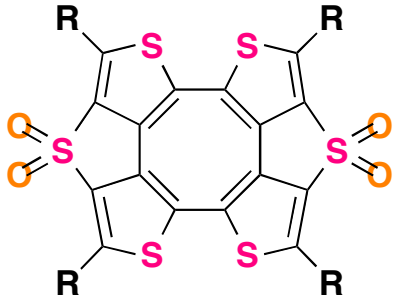
■ Molecular Design and Synthesis



1



2a: R = H
2b: R = TMS



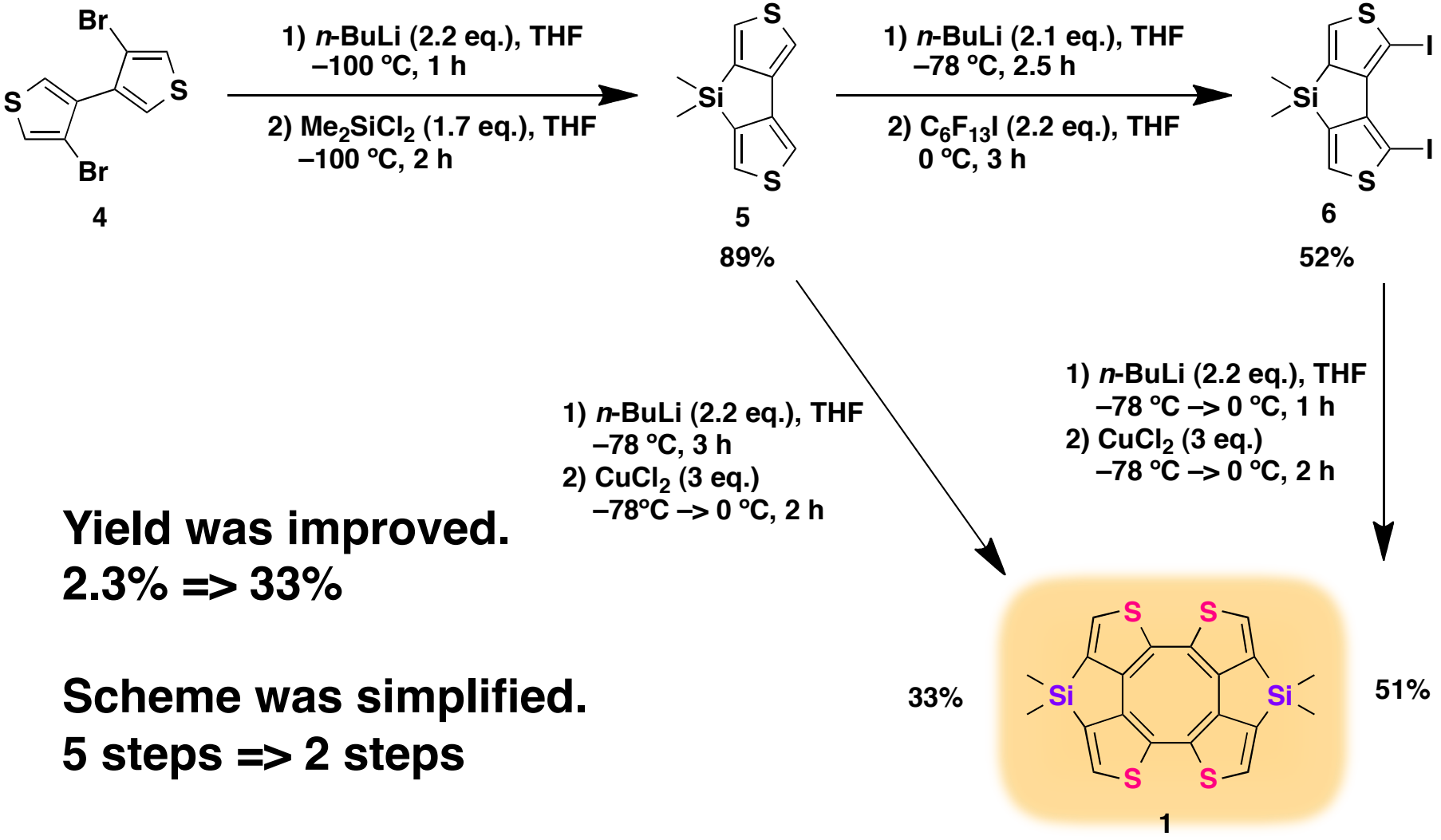
3a: R = H
3b: R = TMS

- The yield of compound 1 was improved.
- Small and planar polycyclic thiophene groups were introduced to planarize and stabilize the compounds.

■ Characterization

- Single Crystal –> to confirm planarity of COT directly
- Computational Studies –> antiaromatic properties
- Thorough NMR Investigation –> paratropic behaviors
- UV/vis Absorption Spectra –> HOMO-LUMO gap
- Redox Properties –> amphoteric property

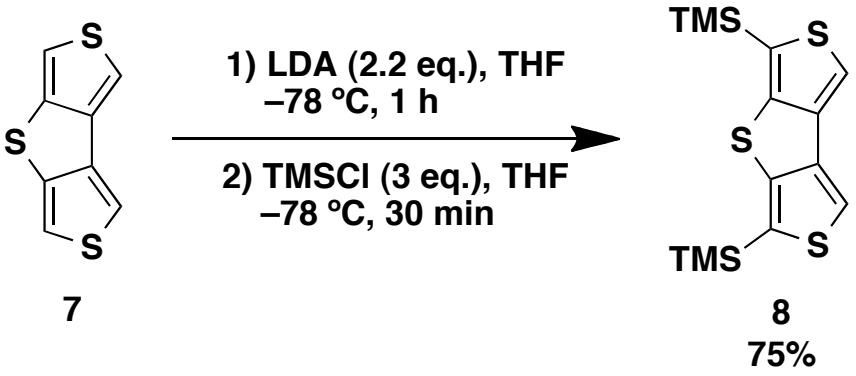
Synthesis 1



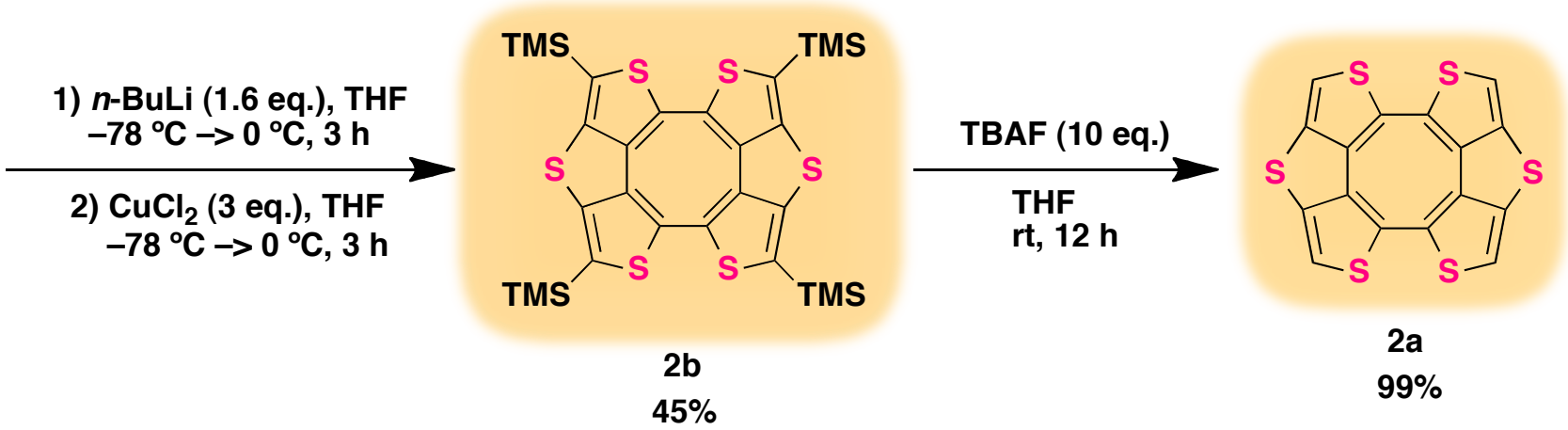
Yield was improved.
2.3% => 33%

Scheme was simplified.
5 steps => 2 steps

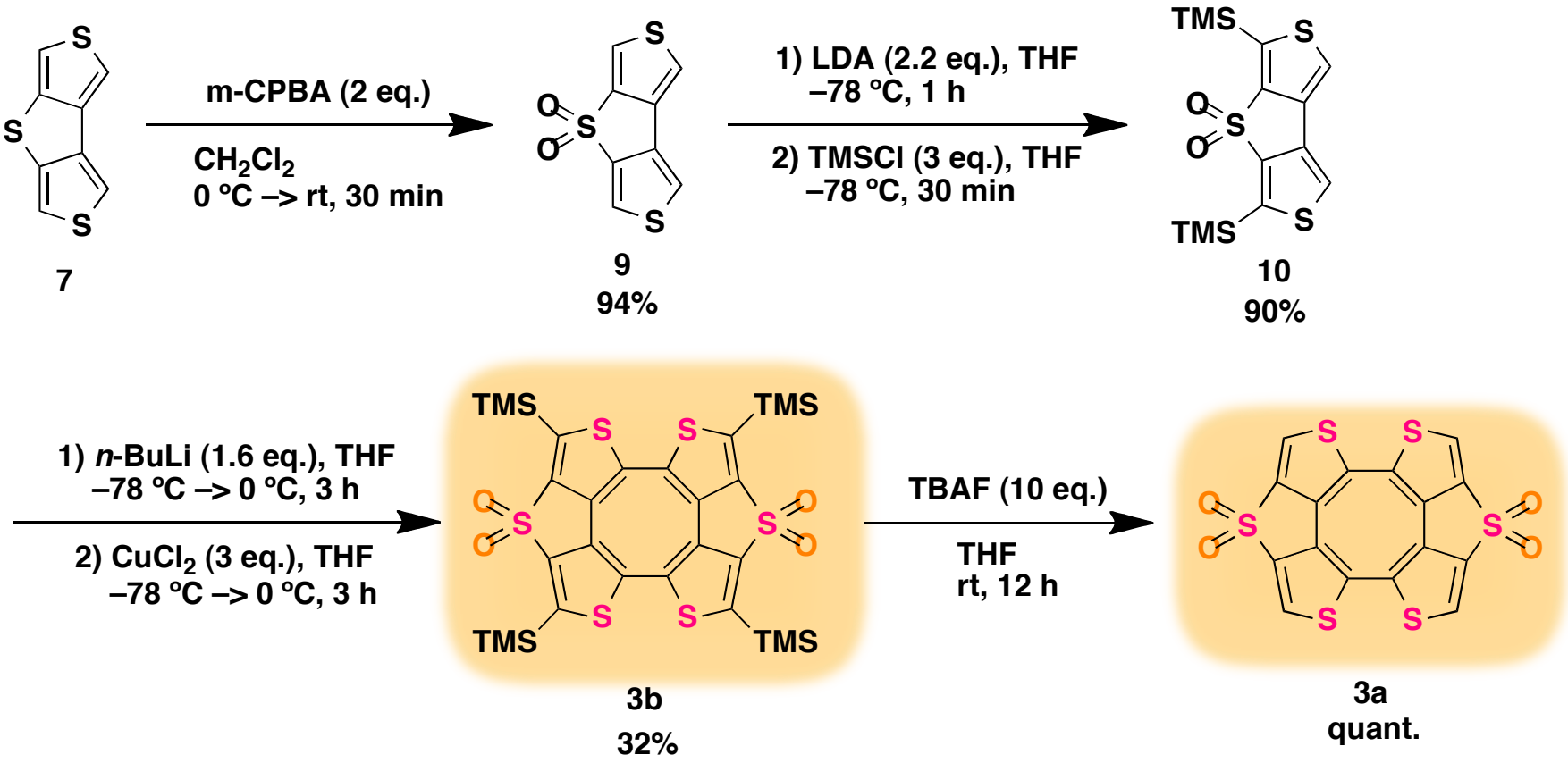
Synthesis 2



Rigid cycles were obtained in 2 and 3 steps

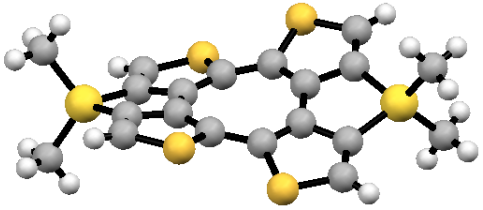


Synthesis 3



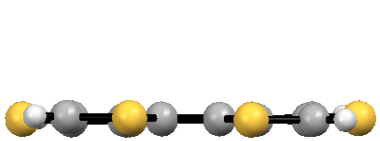
Polycyclic thiophene derivatives were synthesized easily.

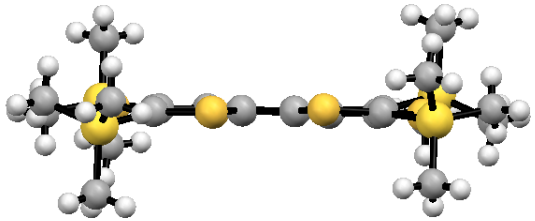
Crystal Structure for Obserbation of Planarity

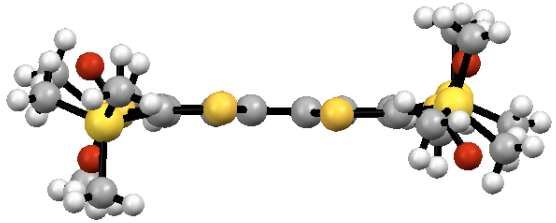


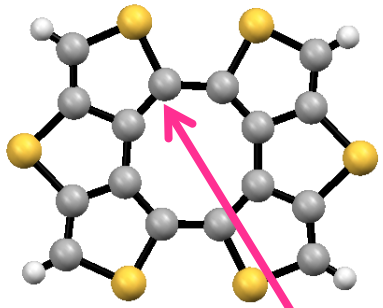
1

Compound 1 didn't form planar structure.
=> Bridging Si wasn't effective to constrain COT ring planar.



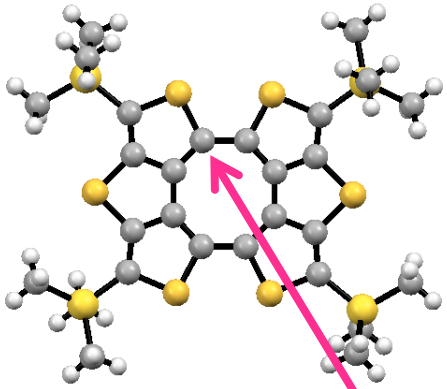






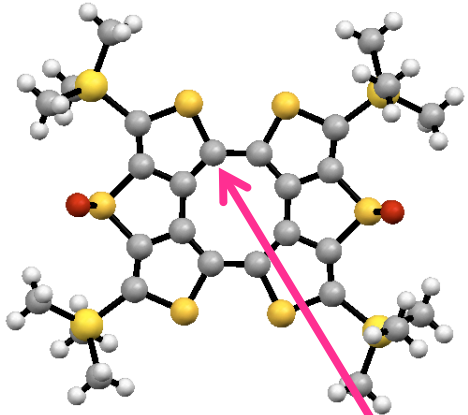
2a

135.0°



2b

135.0°

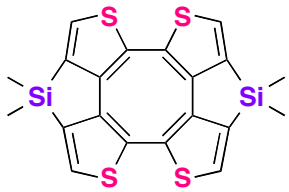


3b

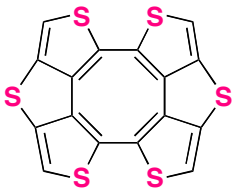
134.7°

Planar COT rings were formed successfully!

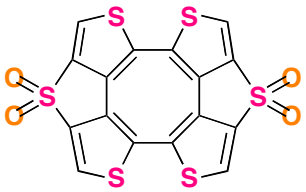
Computational Studies to Evaluate Paratropicity



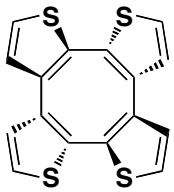
1 (D_2)



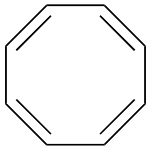
2a (D_2)



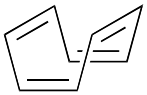
3a (D_2)



11 (D_2)



12 (D_{4h})



13 (D_{2d})

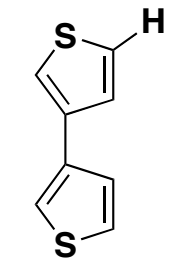
	1 (D_2)	2a (D_2)	3a (D_2)	11 (D_2)	12 (D_{4h})	13 (D_{2d})
NICS(0) (ppm)[b]	12.7	17.4	15.4	3.8	26.6	2.9
$NICS(1)_{zz}$ (ppm)[b]	33.3	44.8	40.2	13.2	62.5	7.4
HOMO-LUMO gap (eV)[a]	2.87	2.62	2.72	4.04	2.41	4.29

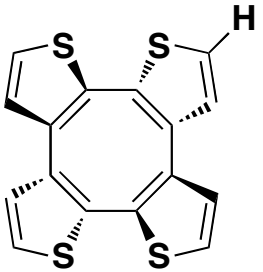
a: Calculated by RB3LYP/6-31G(d,p).
b: Calculated by GIAO/HF/6-311+G(d,p)//B3LYP/6-31G(d,p)

Compound 1, 2a, 3a were more paratropic than 11 and 13.
Aromatic thiophene ring caused a bit lower NICS values than 12.

Nenajdenko, V. G. *et al.*, *ACIE*, 2006, *45*, 7367–7370.
Awaga, K. *et al.*, *Chem. Eur. J.*, 2008, *14*, 6053–6056.

^{1}H NMR for Confirmation of Paratropicity

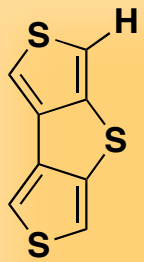


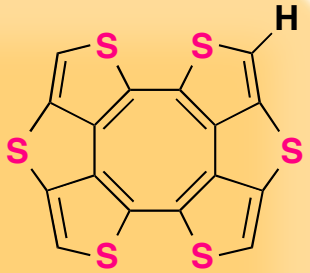


11

δ 7.20 **+0.17** δ 7.37

No paratropic ring current

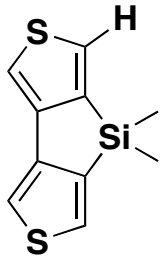


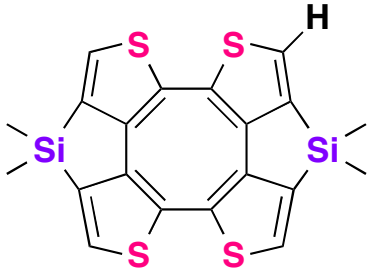


2a

δ 7.39 **–0.42** δ 6.97

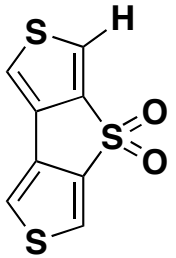
Largest upfield shift

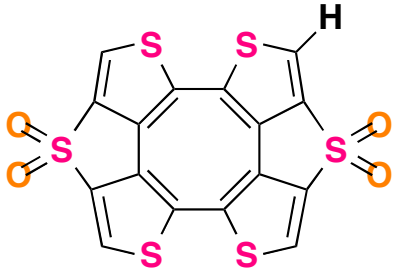




1

δ 7.53 **–0.27** δ 7.26



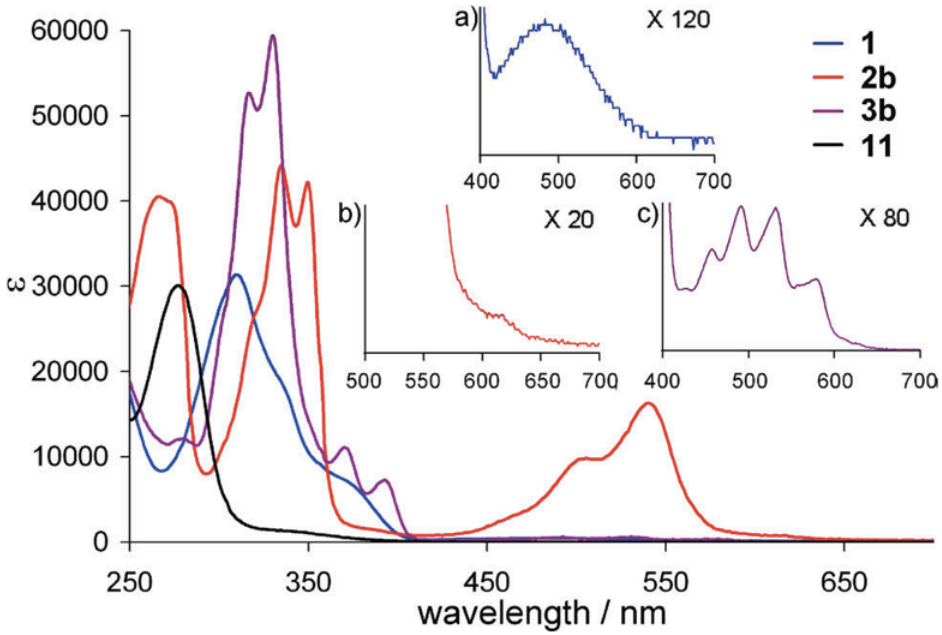


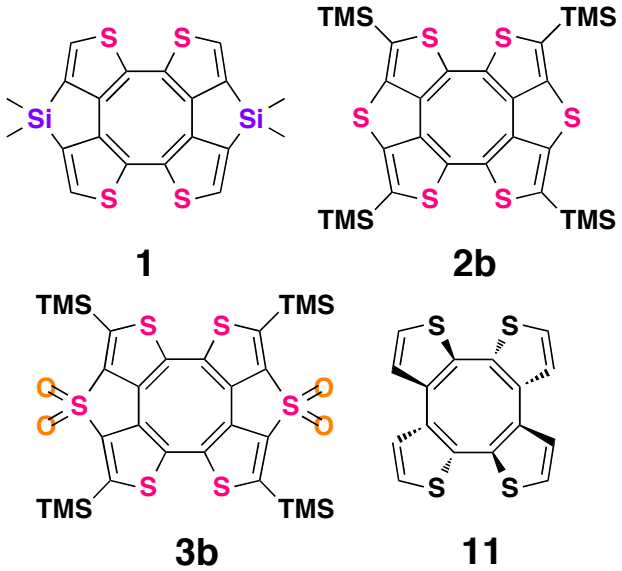
3a

δ 8.29 **–0.30** δ 7.99

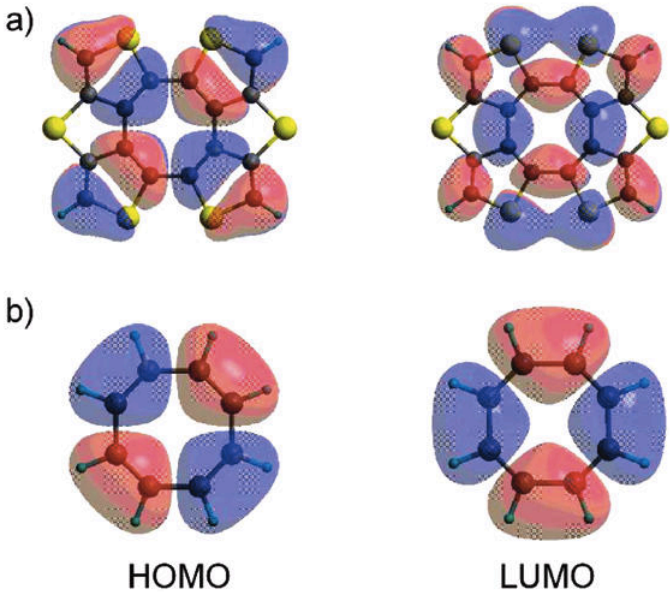
The results also supported that compound 2a was the most planar.

UV/vis Absorption of Planar COT





Planar COT has narrow HOMO-LUMO gap.

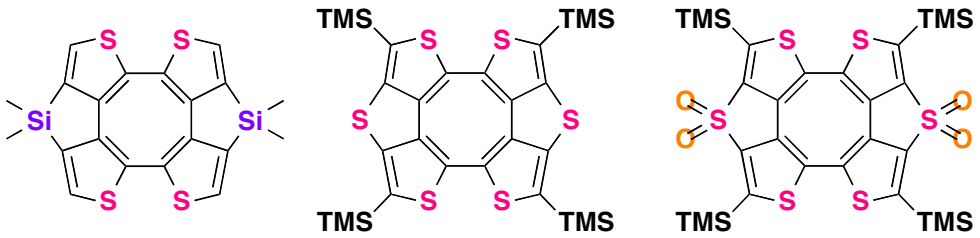


a) 2a
b) COT (D_{4h})

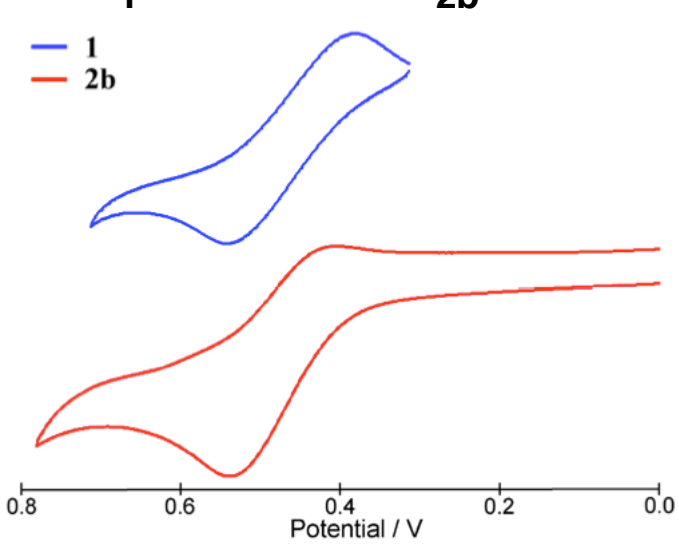
- Coefficients on sulfurs ~ 0
- HOMO and LUMO orbital shapes are identical with those of COT (D_{4h})

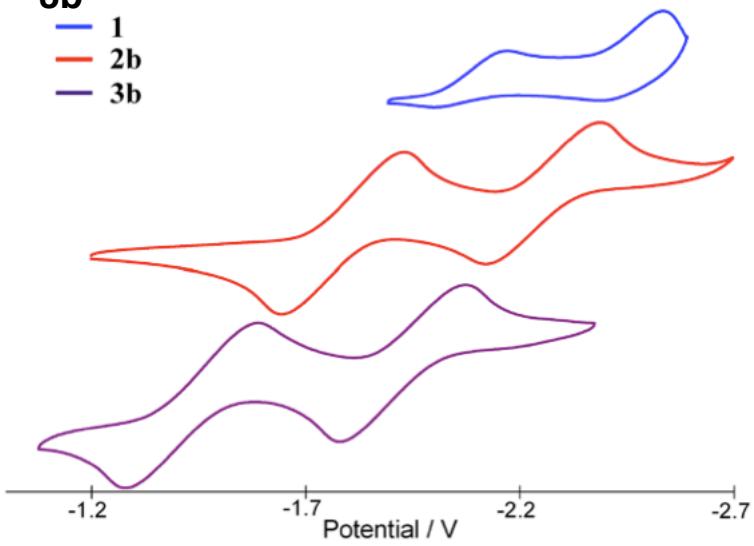
=> Planar COT is an important factor for long wavelength absorption

Redox Properties — CV



1 2b 3b





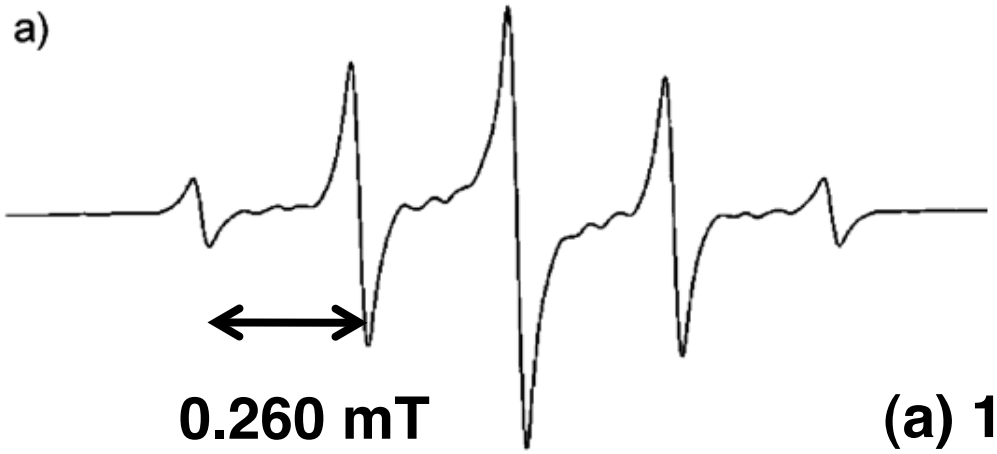
1, 2b ··· 2 step reduction waves & 1 step oxidation wave

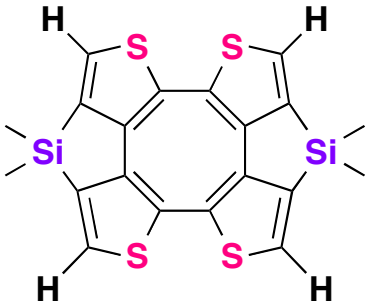
3b ··· 2 step reduction waves & no oxidation peak

=> due to low HOMO level

11 ··· only 1 irreversible oxidation wave

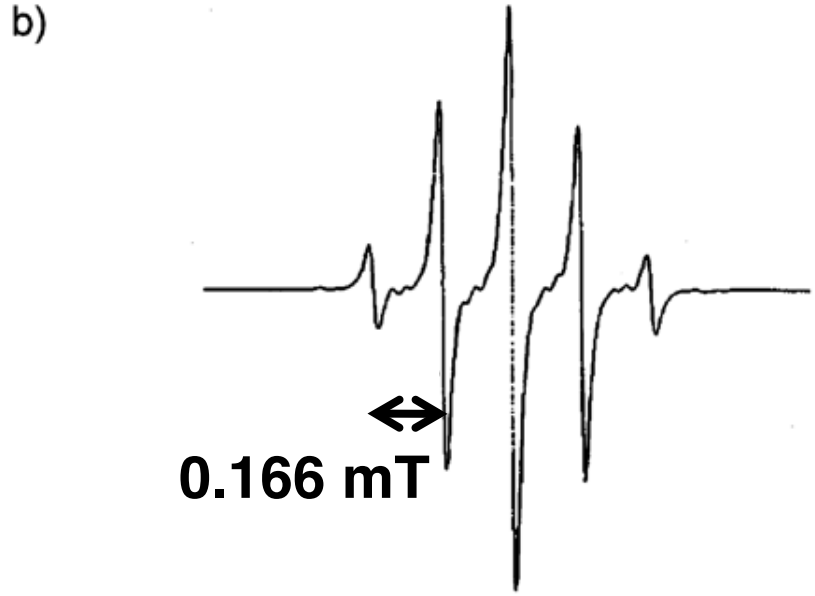
Redox Properties — ESR

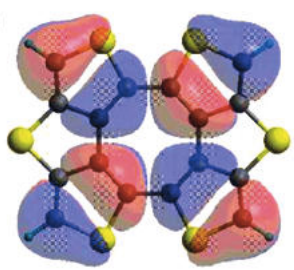




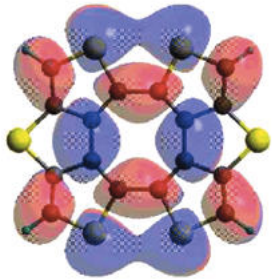
1

(a) $1^{\cdot+}$ in CH_2Cl_2 => g = 2.0032
(b) $1^{\cdot-}$ in THF => g = 2.0049





HOMO

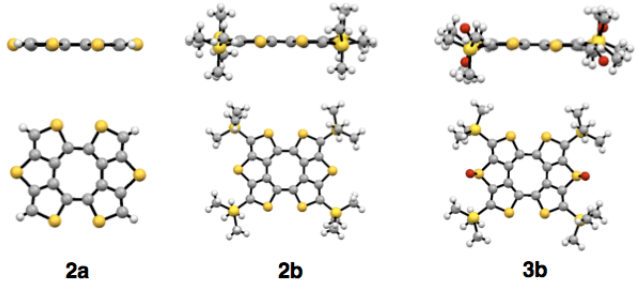


LUMO

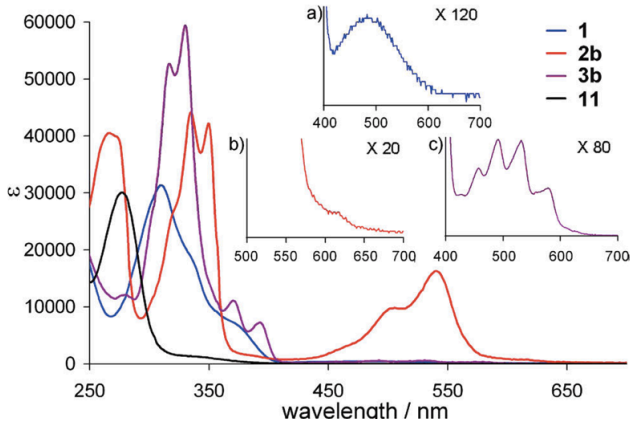
This difference comes from MO coefficients on carbons of C–H in HOMO and LUMO.

Conclusion / Future Views

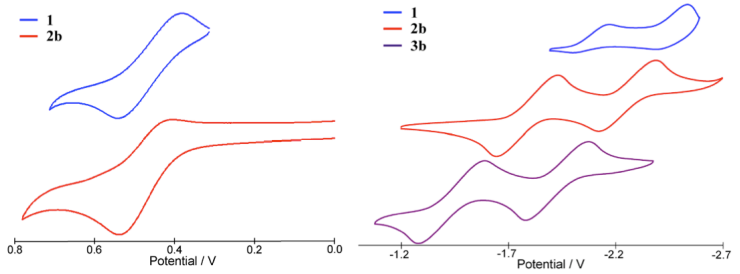
The authors obtained planar COT derivatives successfully.



They have experimentally demonstrated that planarity of COT ring is important for enhancement of antiaromaticity.



They showed amphoteric redox properties of compound 1.

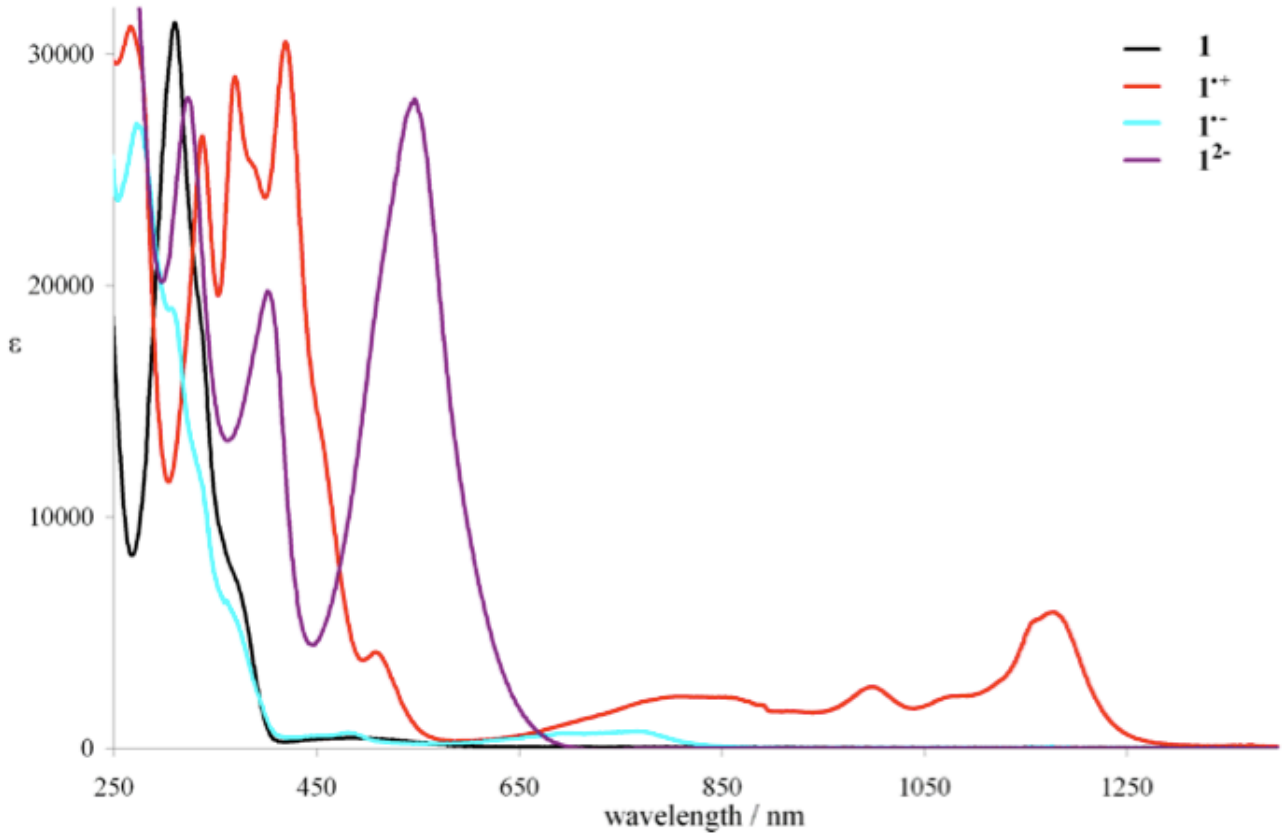


■ **Future View…**

Intermolecular antiaromatic–antiaromatic interaction => Organic semiconductors

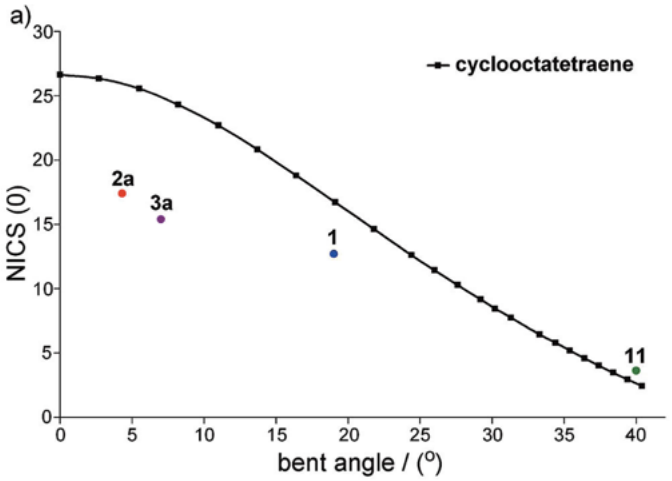
Title

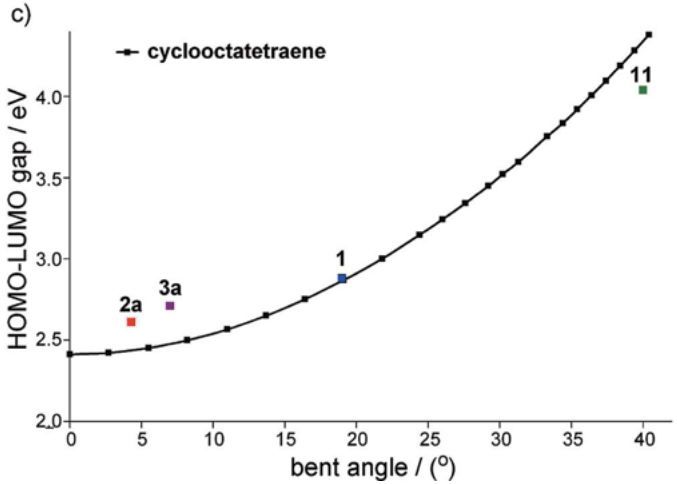
Redox Properties — UV/vis/NIR Spectra

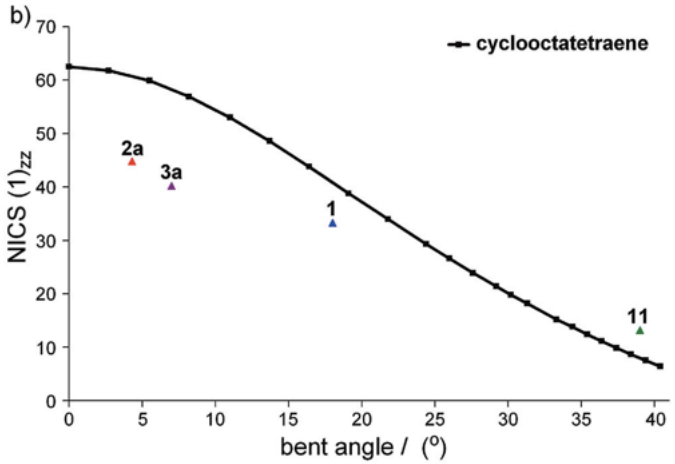


$1^{\cdot+}$ $SbCl_6^-$: black powder, yellow in CH_2Cl_2
$1^{\cdot-}$ K^+ : fate green in THF
1^{2-} K^+

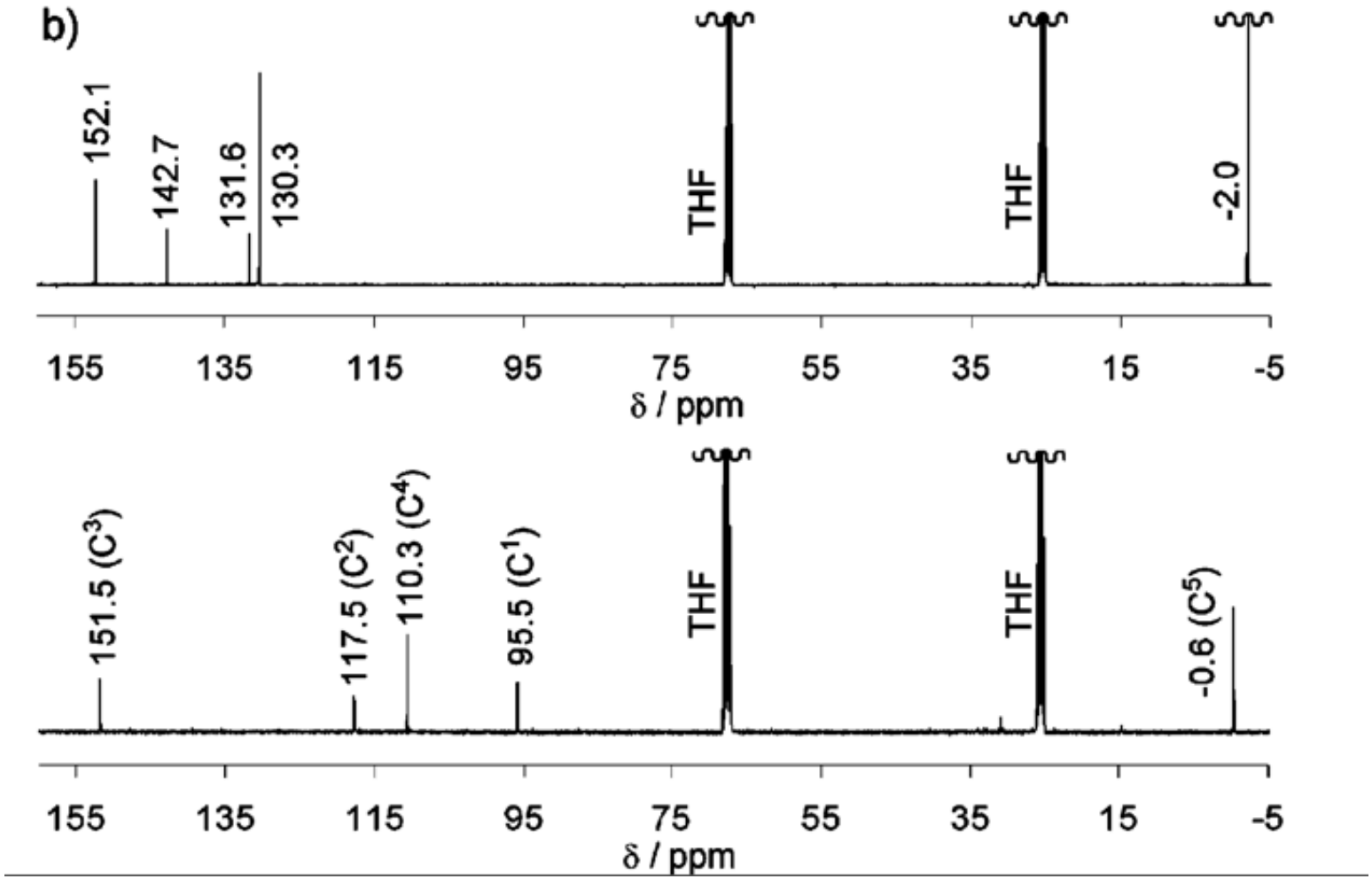
Title


a)
cyclooctatetraene
2a
3a
1
11
NICS (0)
bent angle / (°)

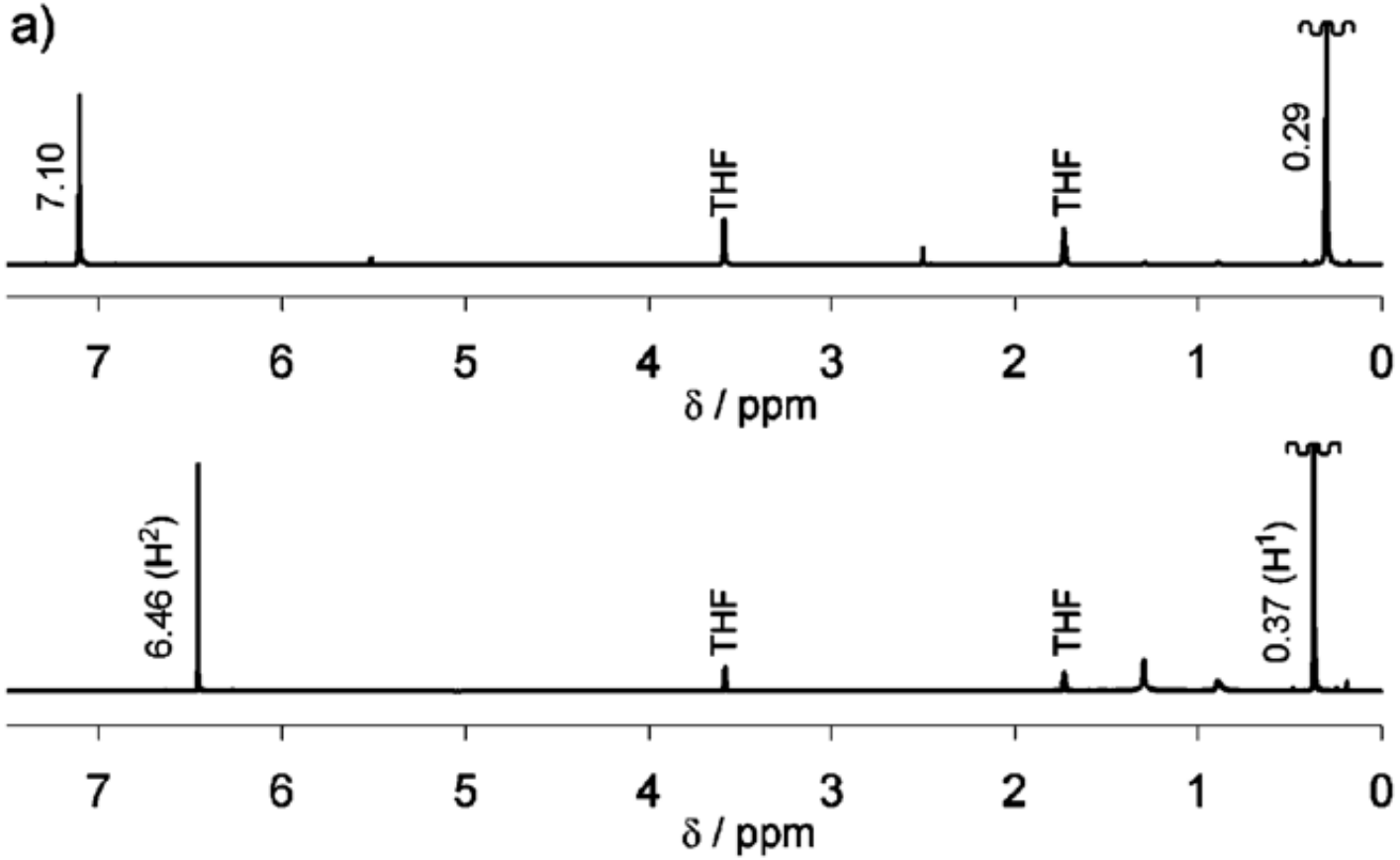

c)
cyclooctatetraene
2a
3a
1
11
HOMO-LUMO gap / eV
bent angle / (°)


b)
cyclooctatetraene
2a
3a
1
11
NICS (1)zz
bent angle / (°)

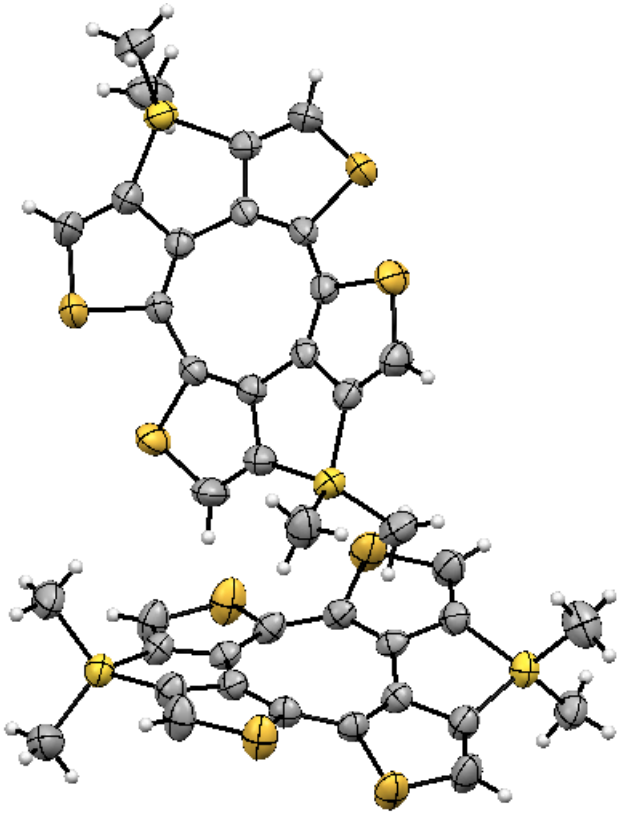
^{13}C NMR of 1 vs 1^{2-}

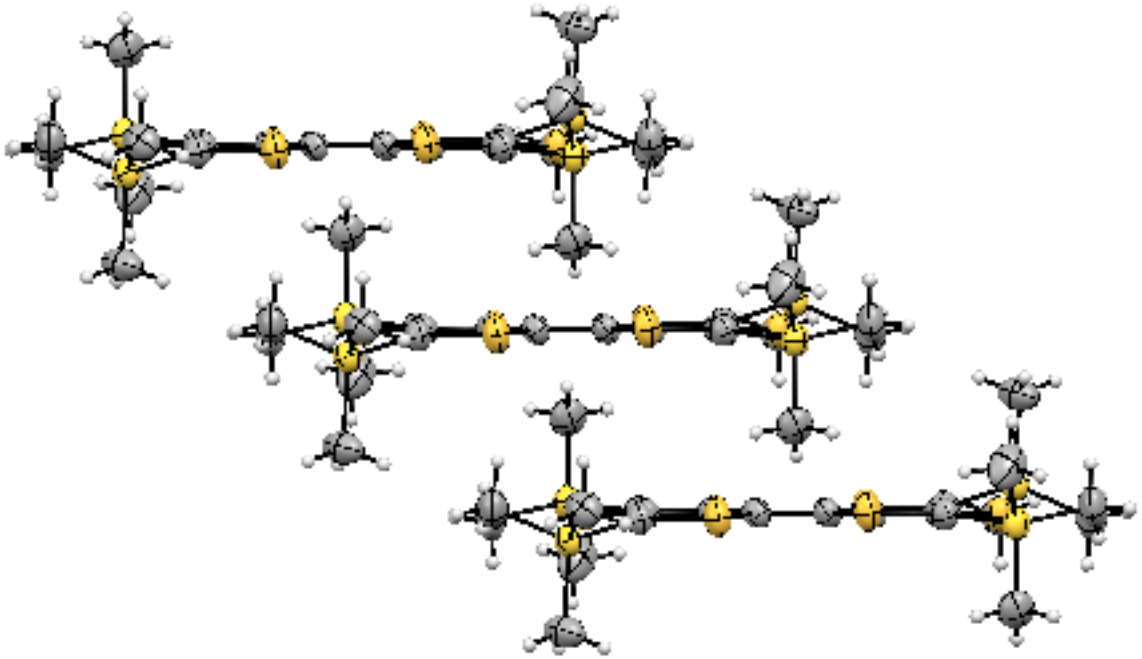


^{1}H NMR of 1 vs 1^{2-}

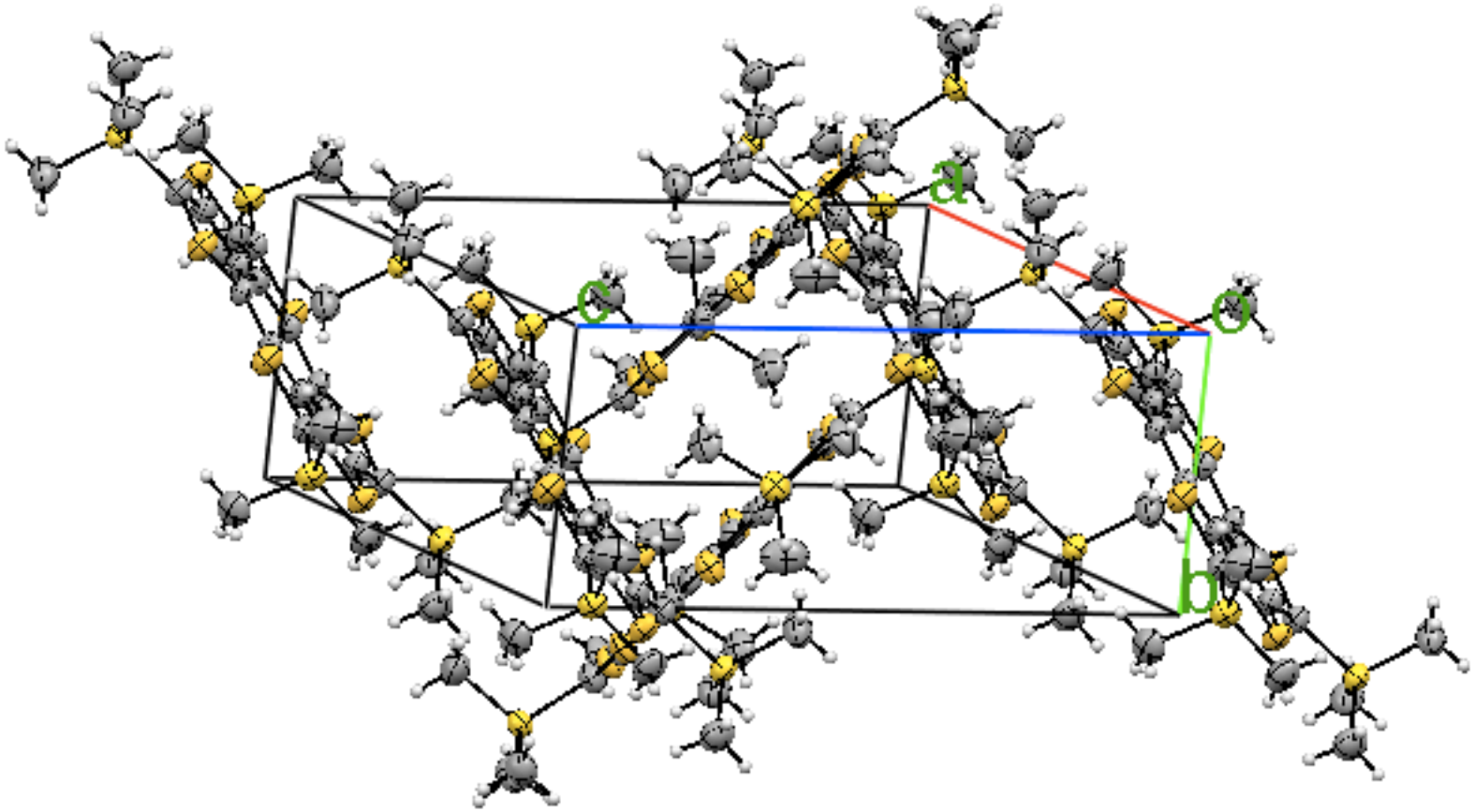


Packing Structure of 1 vs 2b





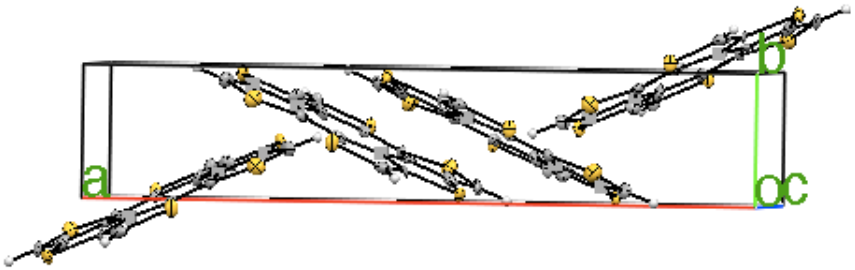
Packing Structure of 2b



herringbone

π-π: 3.710 Å

Packing Structure of 2a



π-π: 3.541 Å