Vilsmeier型反応を鍵とするピロール縮環アザナノグラフェンの合成

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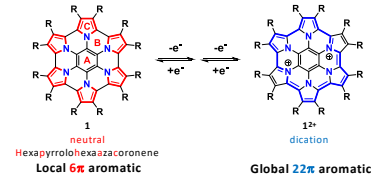
Introduction



Properties of HPHAC

- Nitrogen-incorporated π plane
- Hückel aromaticity in dication state

Application for organic electronics

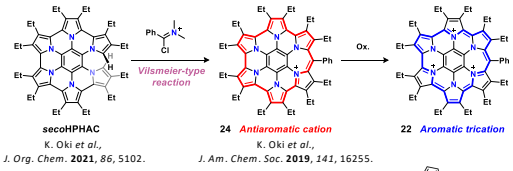
M. Takase *et al.*, *Angew. Chem. Int. Ed.* **2007**, *46*, 5524.

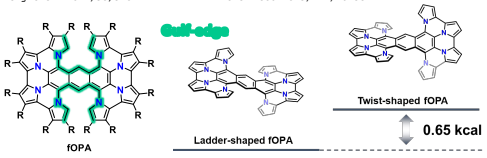
NICS(0) calculation (HPHAC-H)

	A	B	C
1	-13.0	4.6	-12.8
1^{2+}	-31.3	-20.7	-17.4

GIAO/HF/6-311+G(d,p)//B3LYP/6-31G(d)

Previous work

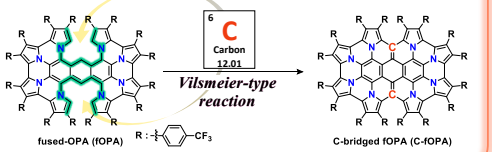




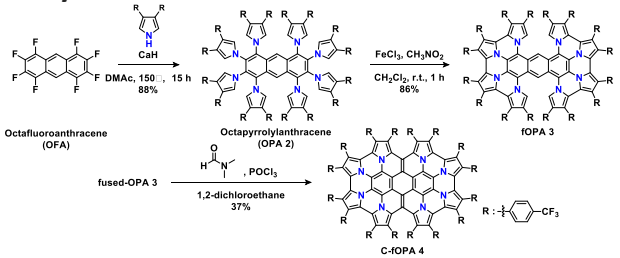
This work

- Carbon incorporation toward fOPA *via* Vilsmeier-type reaction
- Investigation of structural and physical properties

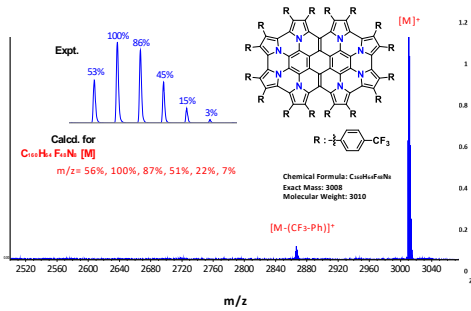
New azananographene



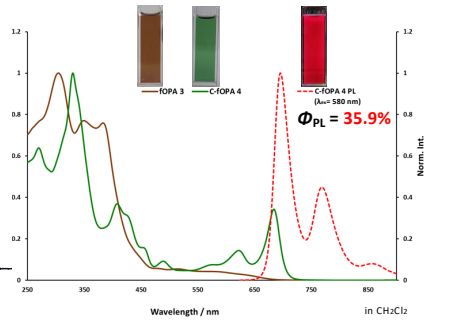
Synthesis



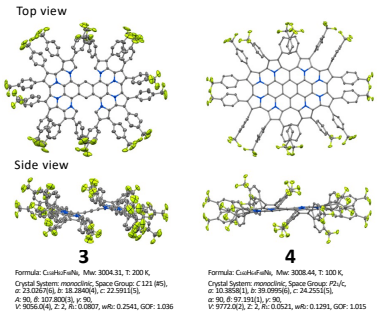
MALDI-TOF MS



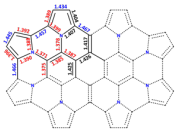
Absorption and PL



Crystal structures of 3 and 4

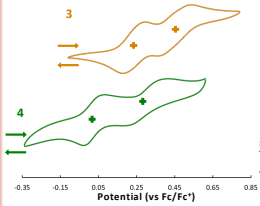


Bond length of **4**



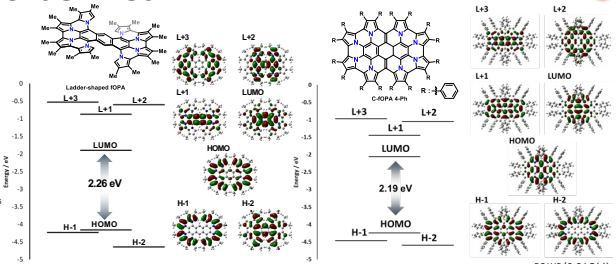
1.430 < Bond length
1.400 ≤ Bond length ≤ 1.430
Bond length < 1.400 (Å)

CV

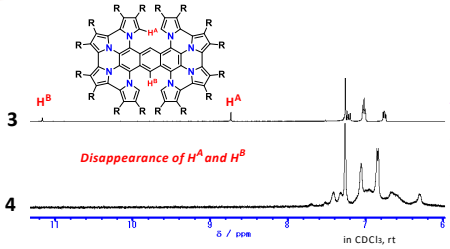


Cyclic voltammograms of **4** in benzonitrile (1.0 mM), **3** in CH_2Cl_2 (1.0 mM) Conditions: supporting electrolyte, 0.1 M TBAPF$_6$; working electrode, Pt; reference electrode, Ag/AgNO$_3$; counter electrode, Pt wire; scan rate, 100 mV/s, potentials, vs Fc/Fc+.

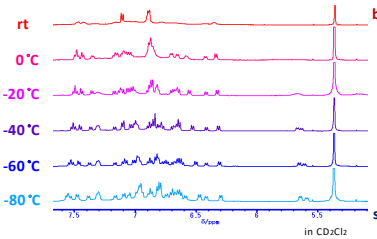
Frontier MOs



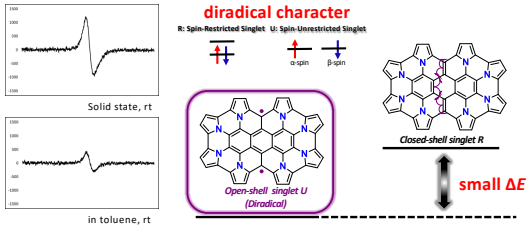
^{1}H NMR of 3 and 4



VT ^{1}H NMR of 4

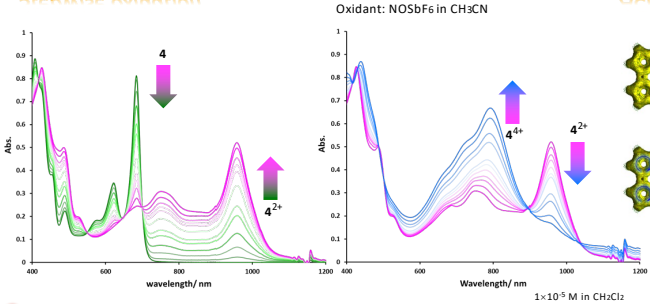


ESR

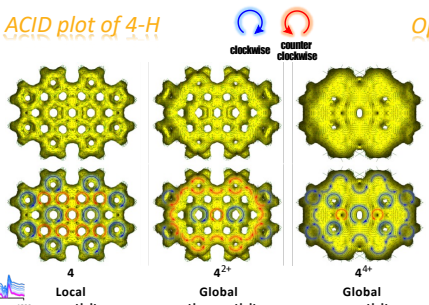


Oxidized species

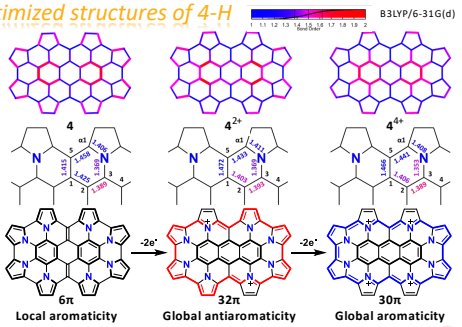
Stepwise oxidation



ACID plot of 4-H



Optimized structures of 4-H



Summary

- Compound **3** was synthesized *via* S_NAr reaction and intramolecular oxidative coupling reaction and carbon incorporated **4** was obtained *via* Vilsmeier-type reaction from **3**.
- Compound **4** was suggested to be diradical and emissive in the neutral state.