A Zigzag Carbon Nanobelt

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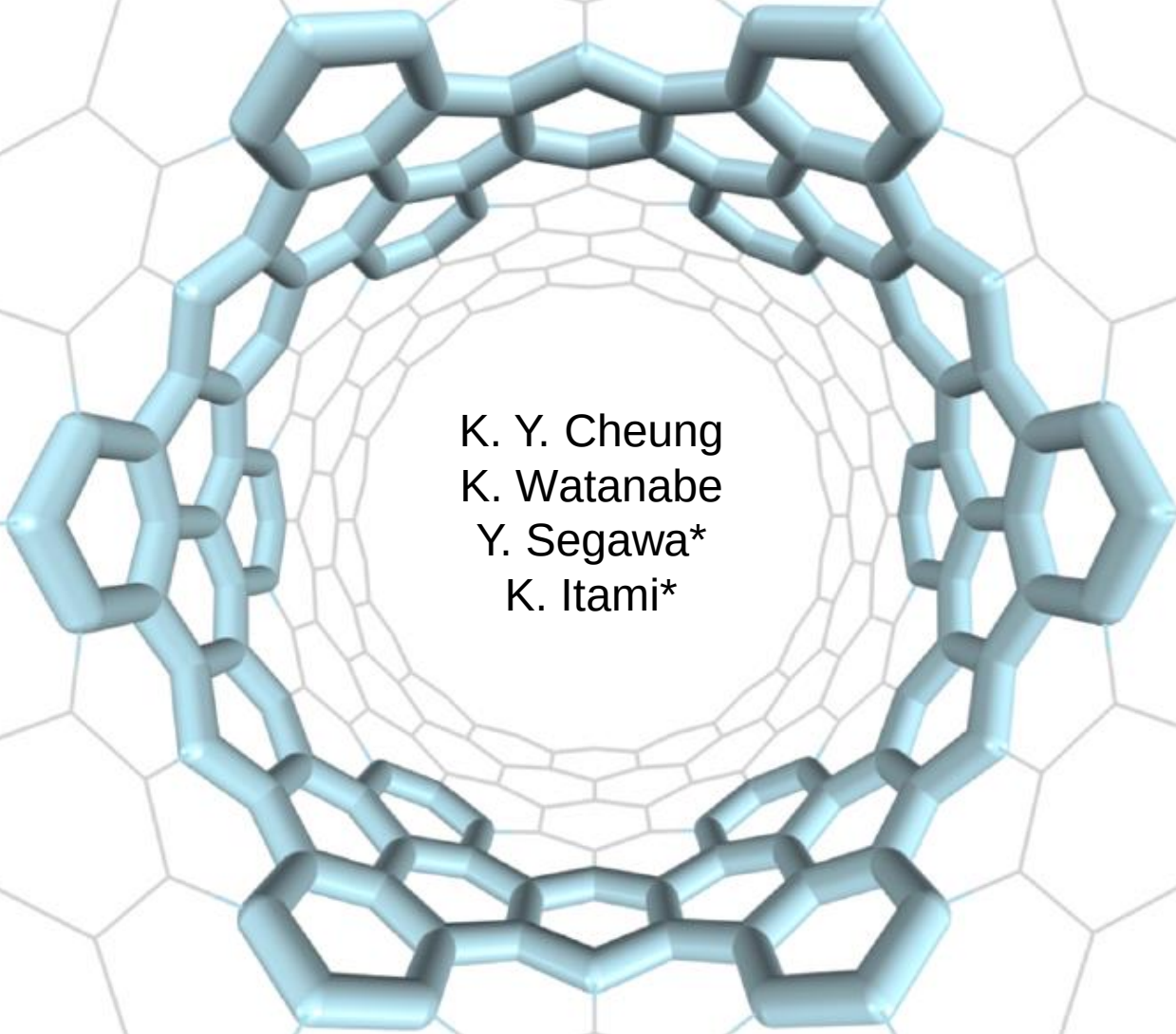
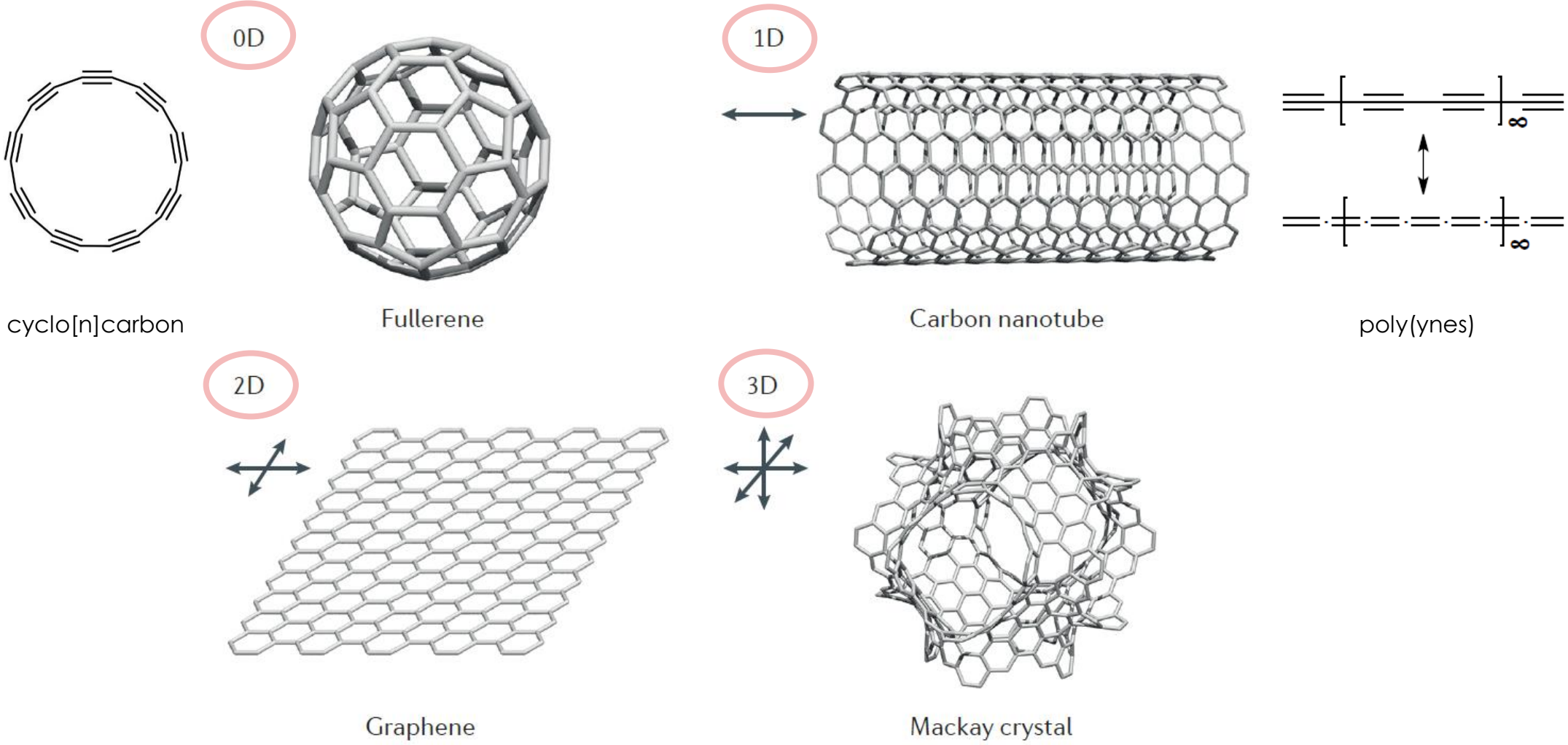


K. Y. Cheung
K. Watanabe
Y. Segawa*
K. Itami*

Carbon Nanomaterials on all Dimension



Y. Segawa, H. Ito, K. Itami, *Nat. Rev. Mater.* **2016**, 15002

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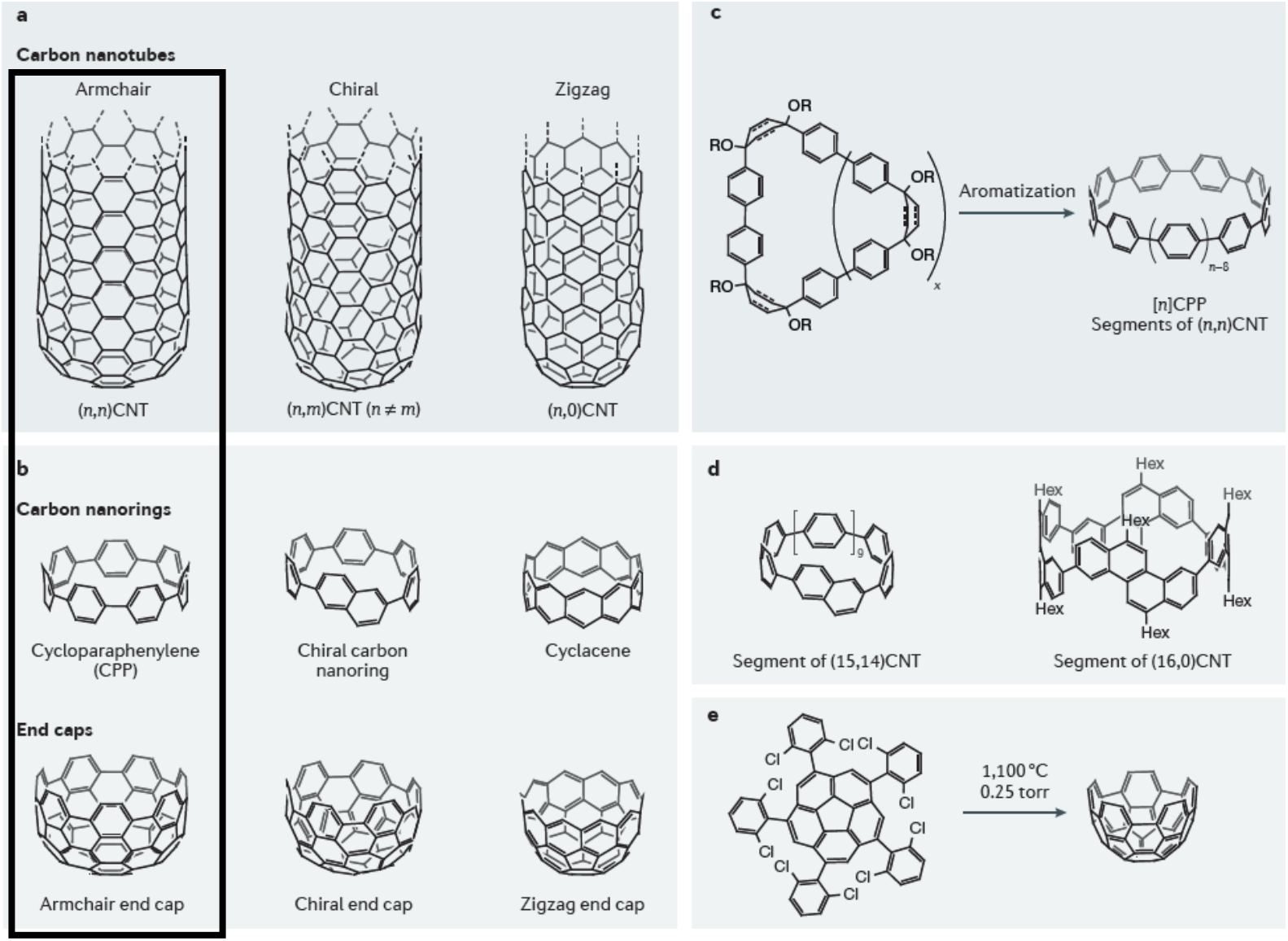
O.Dumele

Synthetic Carbon Scaffolding



Y. Segawa, H. Ito, K. Itami, *Nat. Rev. Mater.* **2016**, 15002

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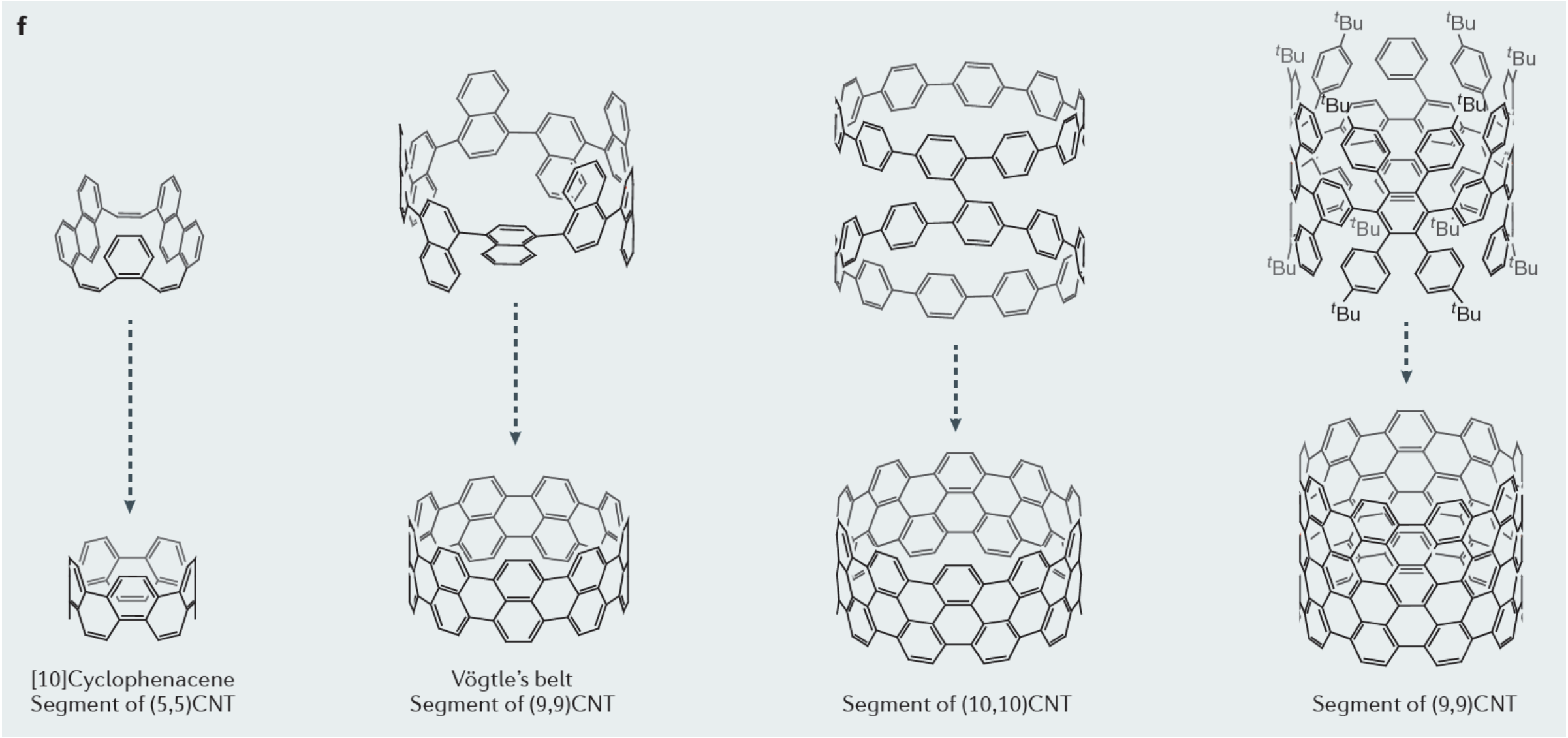
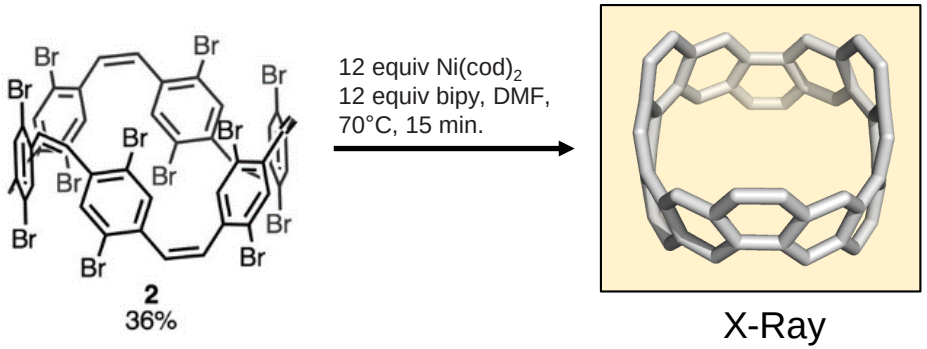
Armchair-Type Challenges



Y. Segawa, H. Ito, K. Itami, *Nat. Rev. Mater.* **2016**, 15002

Itami's 2017 Carbon Nanobelt



G. Povie, Y. Segawa, T. Nishihara, Y. Miyauchi, K. Itami; *Science,* **2017**, *356*, 172–175

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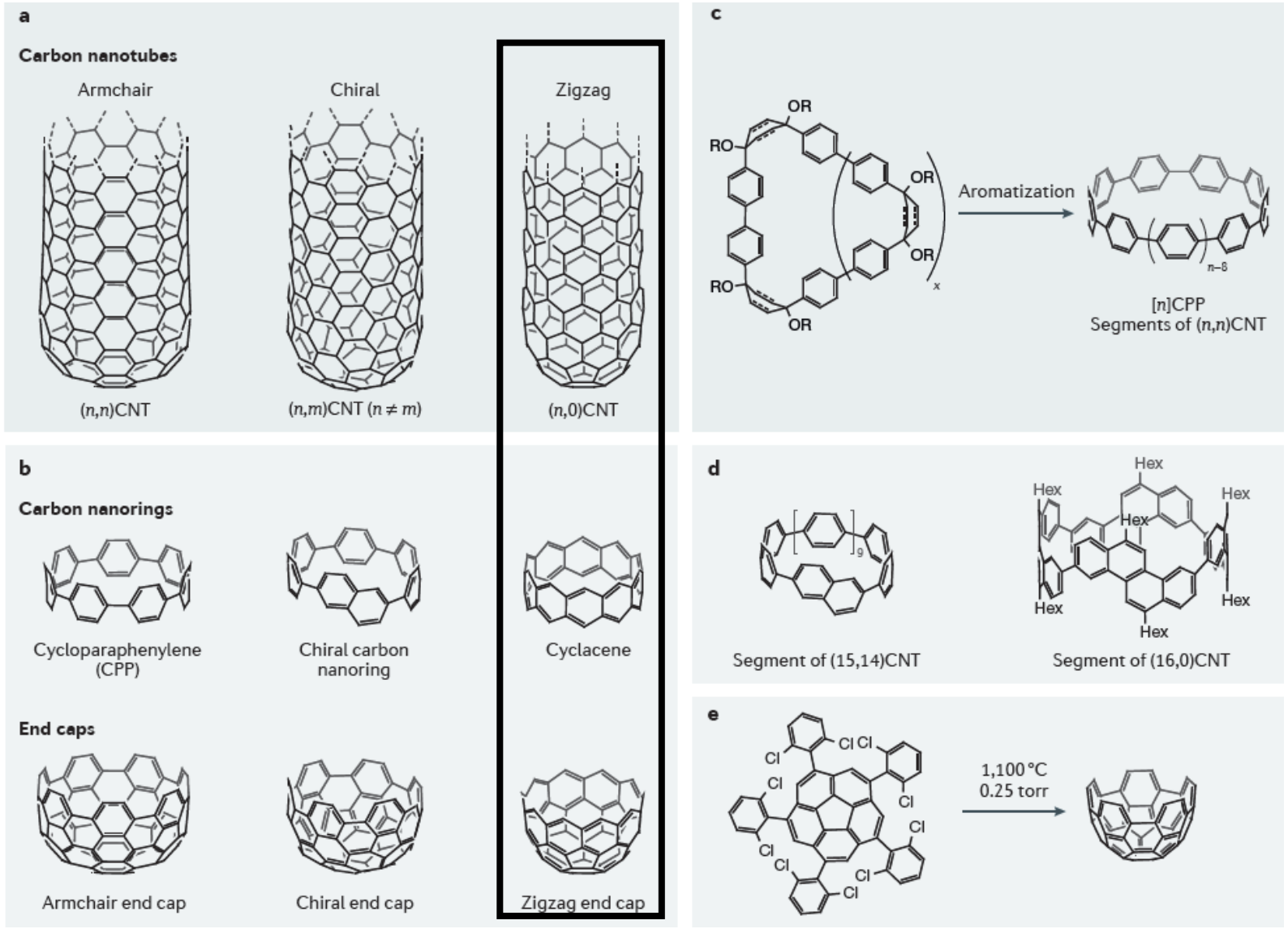
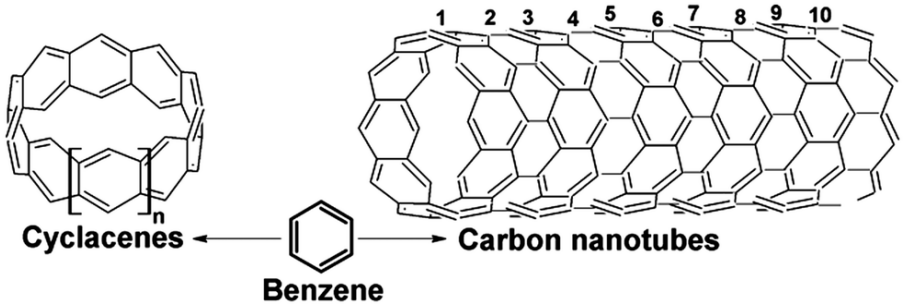
Synthetic Carbon Scaffolding

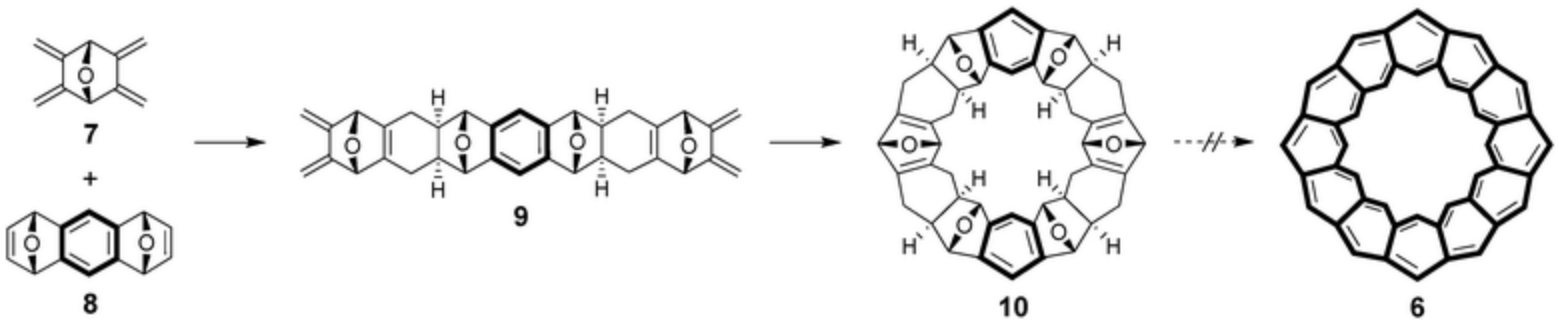


Y. Segawa, H. Ito, K. Itami, *Nat. Rev. Mater.* **2016**, 15002

The Cyclacene Family

first proposed by E. Heilbronner
Helv. Chim. Acta 1954, *37*, 921–935





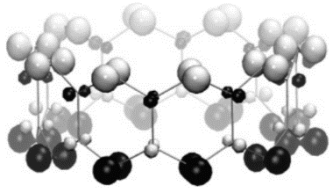
„Kohnkene“

early synthetic attempt:
F. H. Kohnke, A. M. Z. Slawin, J. F. Stoddart, D. J. Williams, *Angew. Chem. Int. Ed.* **1987**, *26*, 892–894

...also Schlüter and others tried

Are Cyclacenes Stable?

Schleyer & Houk:

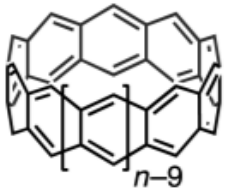


spin density; [10]cyclacene

Open-shell singlet character of cyclacenes

Z. Chen, D.-e. Jiang, X. Lu, H. F. Bettinger, S. Dai, P. von R. Schleyer, K. N. Houk, *Org. Lett.* ***2007****, 9*, 5449–5452

Segawa, Ito, Itami:



C_n

$1324.3 \cdot n^{-1}$ kcal mol^{-1}

$R^2 = 0.99708$

A theoretical study on the strain energy of carbon nanobelts.

Y. Segawa, A. Yagi, H. Ito, K. Itami, *Org. Lett.* **2016**, *18*, 1430–1433

→ *cyclacenes may not be stable*

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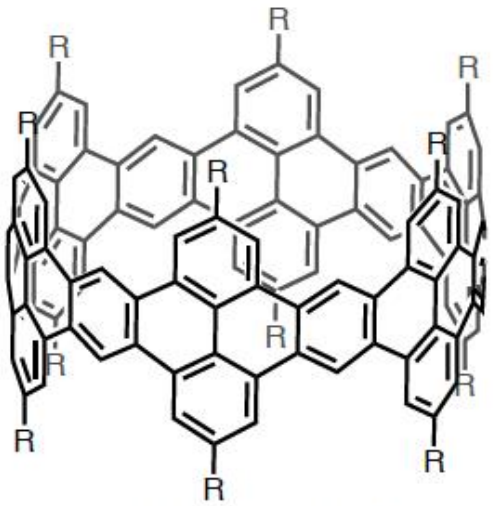
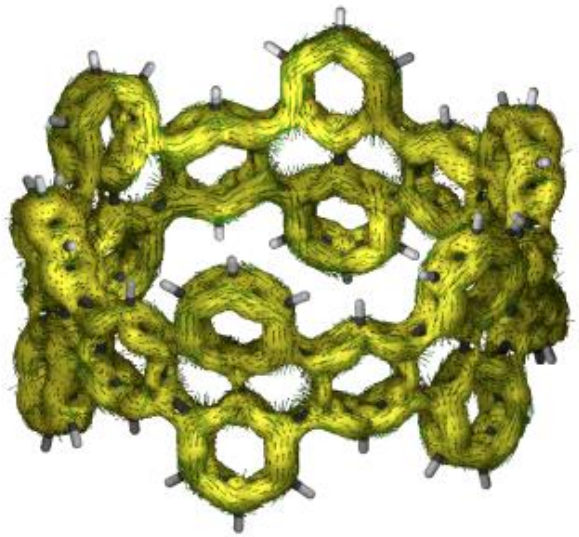
New Itami approach: Pyrene Subunits

a



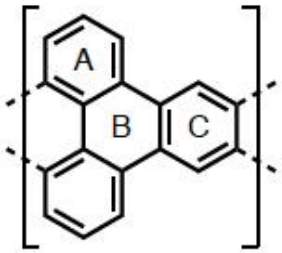
(18,0) zigzag CNB
1 (R = ^{t}Bu), **1'** (R = H)

b



ACID plot
(ring current)

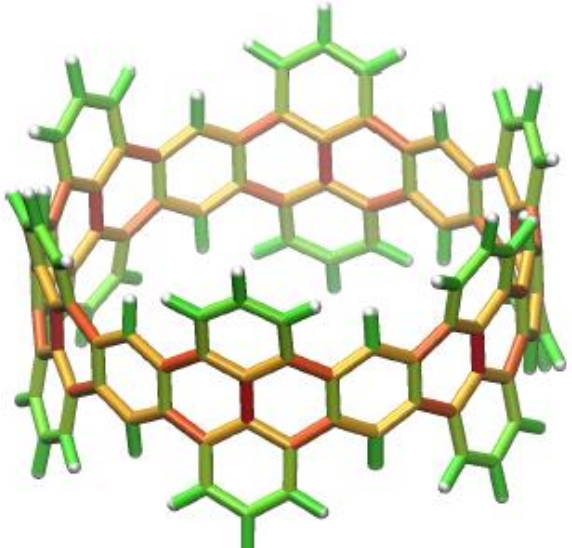
c



	NICS(0)
A	−7.54
B	0.99
C	−7.44

Nucleus independent chem. shift
(NICS values in ring centroid)

d

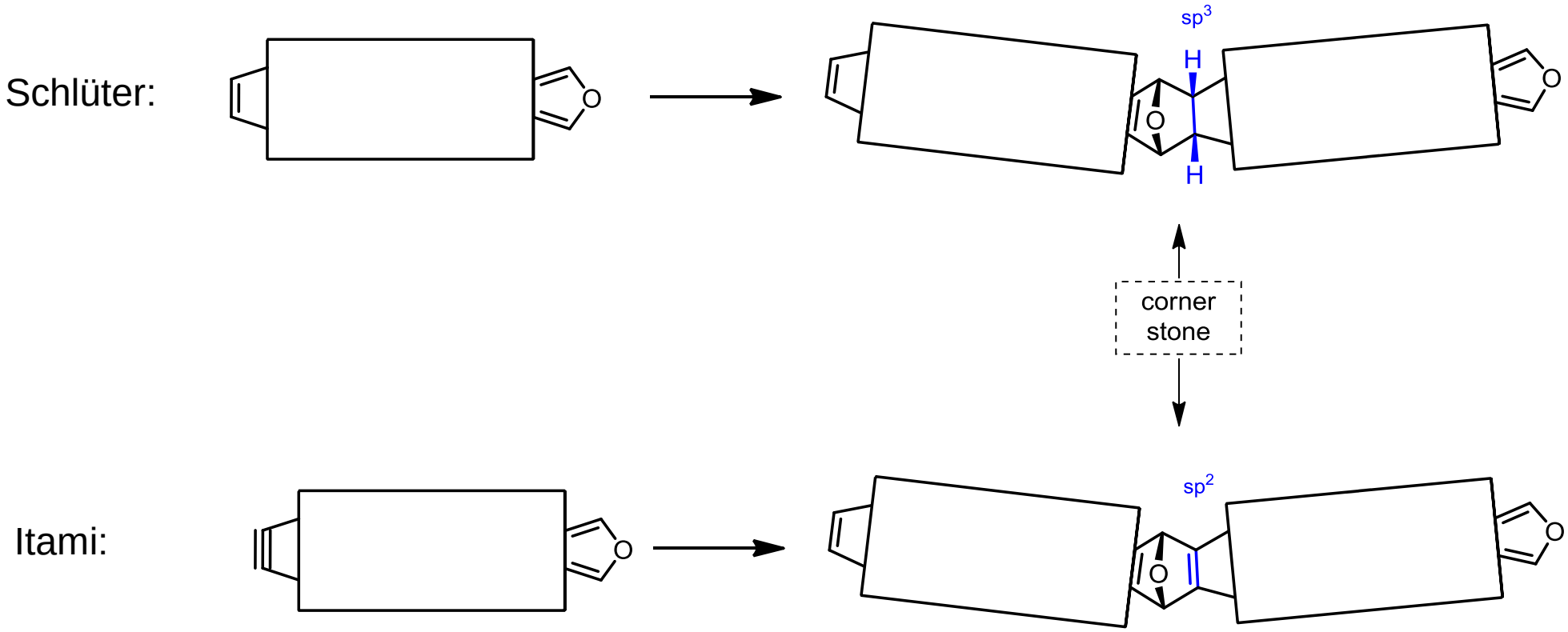


StrainViz analysis

Synthetic Approach: Consecutive Diels–Alder & Rearomatizations

similar to Schlüter approach

Schlicke, B.; Schirmer, H.; Schlüter, A. D. *Adv. Mater.* **1995**, *6*, 544.



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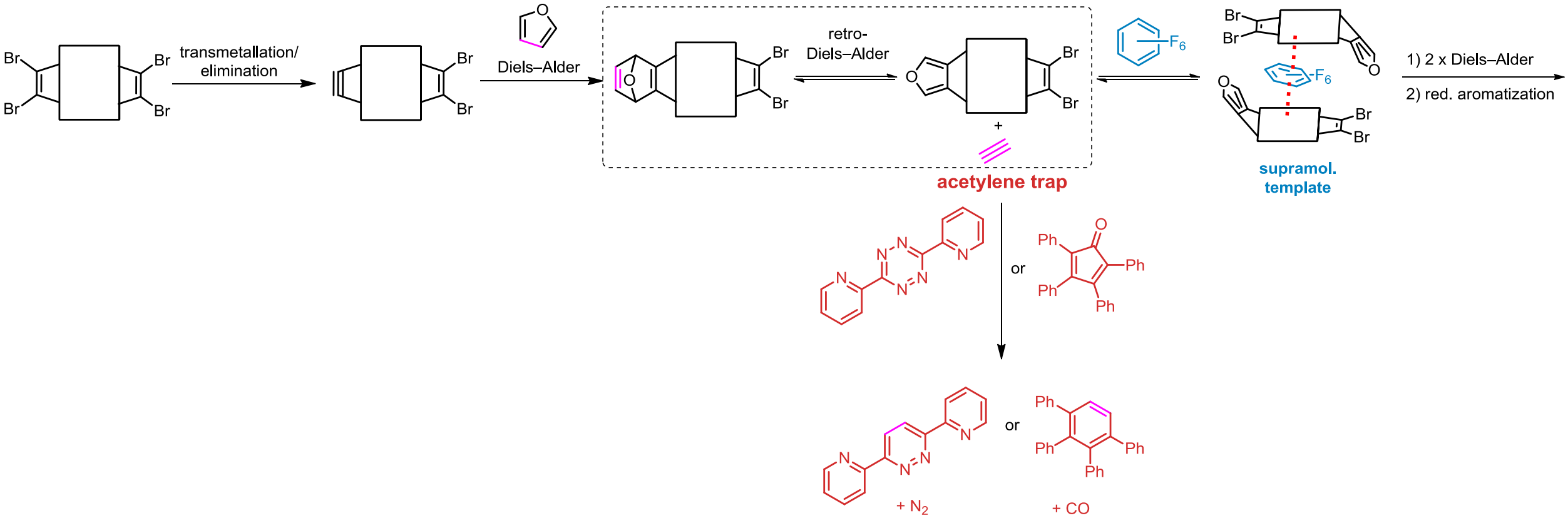
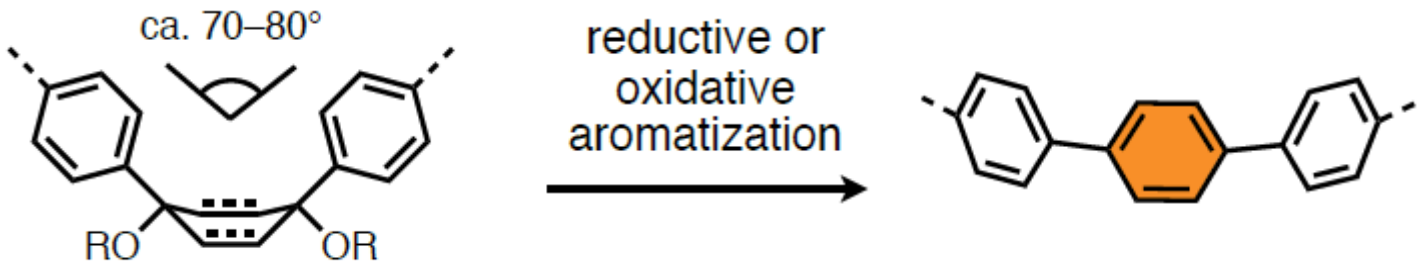
Key Step: retro-Diels–Alder to remove “excess of carbon” and reactivate for next DA



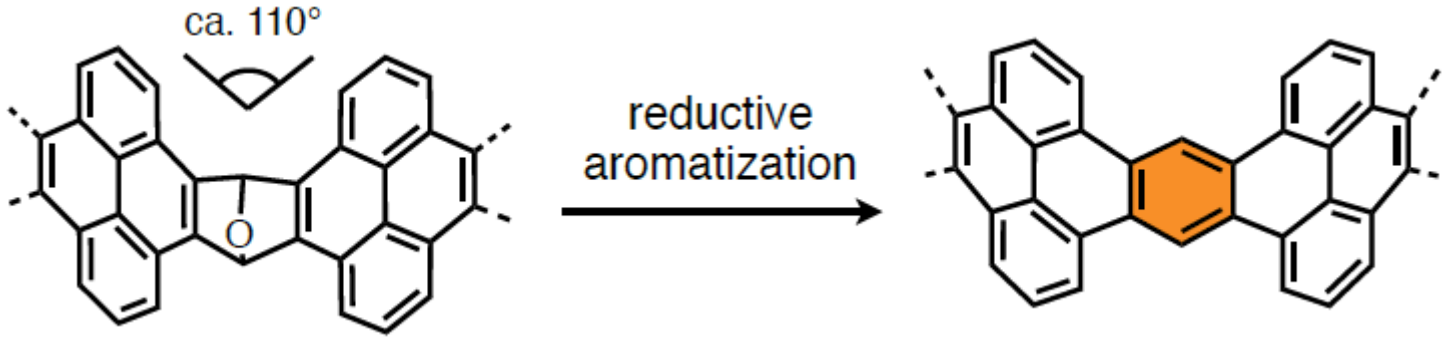
examples of alkyne–triazine cycloaddition and the role of the pyridyl substituents:
J. Prescher and co-workers, *Chem. Sci.* **2019**, *10*, 9109–9114

Strain Step:

for CPP's



Now Itami,
similar to Stoddart's
Kohnkene...



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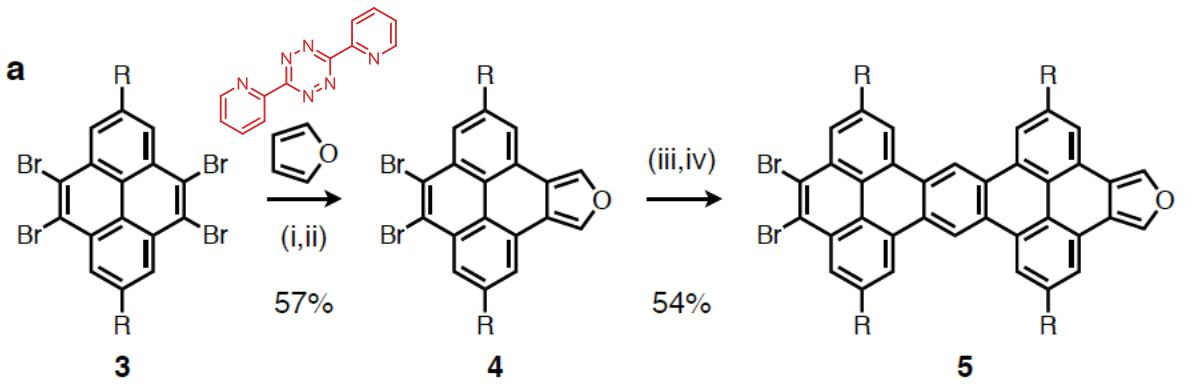
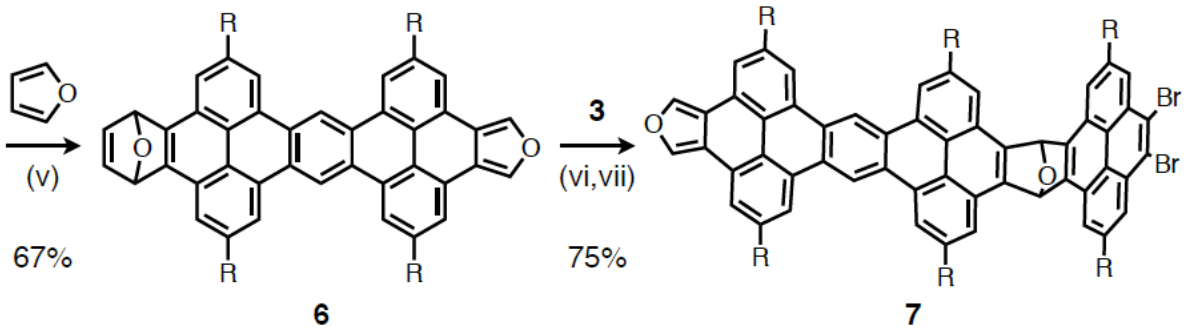
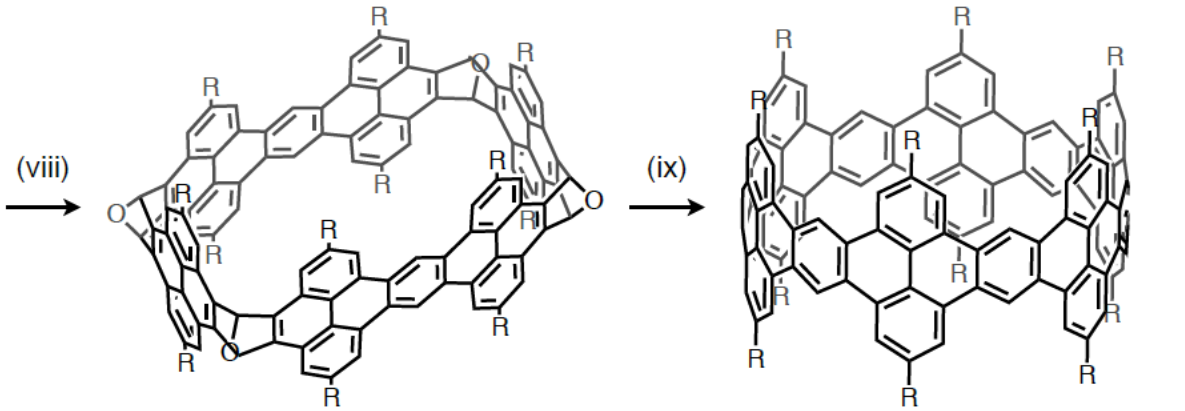
Synthesis: Plenty of Unconventional Key Steps!







(i) furan (10 equiv.), *i*PrMgCl·LiCl (1.1 equiv.), THF, –46 °C, overnight;

(ii) 3,6-di-2-pyridyl-1,2,4,5-tetrazine (1.05 equiv.), $CHCl_3$, 60 °C, overnight.

(i) *n*-BuLi (0.35 equiv.), toluene, –78 °C, 2 h;

(iv) $P(OPh)_3$ (1.5 equiv.), NH_4ReO_4 (5 mol%), Na_2SO_4 (1 equiv.), toluene, 100 °C.

(v) furan (50 equiv.), *n*-BuLi (1.3 equiv.), PhCl/THF, –78 °C, 1.5 h;

(vi) **3** (4 equiv.), *i*-PrMgBr (3.5 equiv.), THF, 0 °C, 3 h;

(vii) tetraphenylcyclopentadienone (1.05 equiv.), toluene, 130 °C, overnight;

(viii) hexafluorobenzene (5 equiv.), *n*-BuLi (4 equiv.), PhCl/toluene, –46 °C, 1 h;

(ix) Cp_2TiCl_2 (10 equiv.), Mn powder (50 equiv.), THF, 60 °C, overnight.

comments:
red: alkyne trapping reagents
blue: supramolecular template

green box: methodology key step

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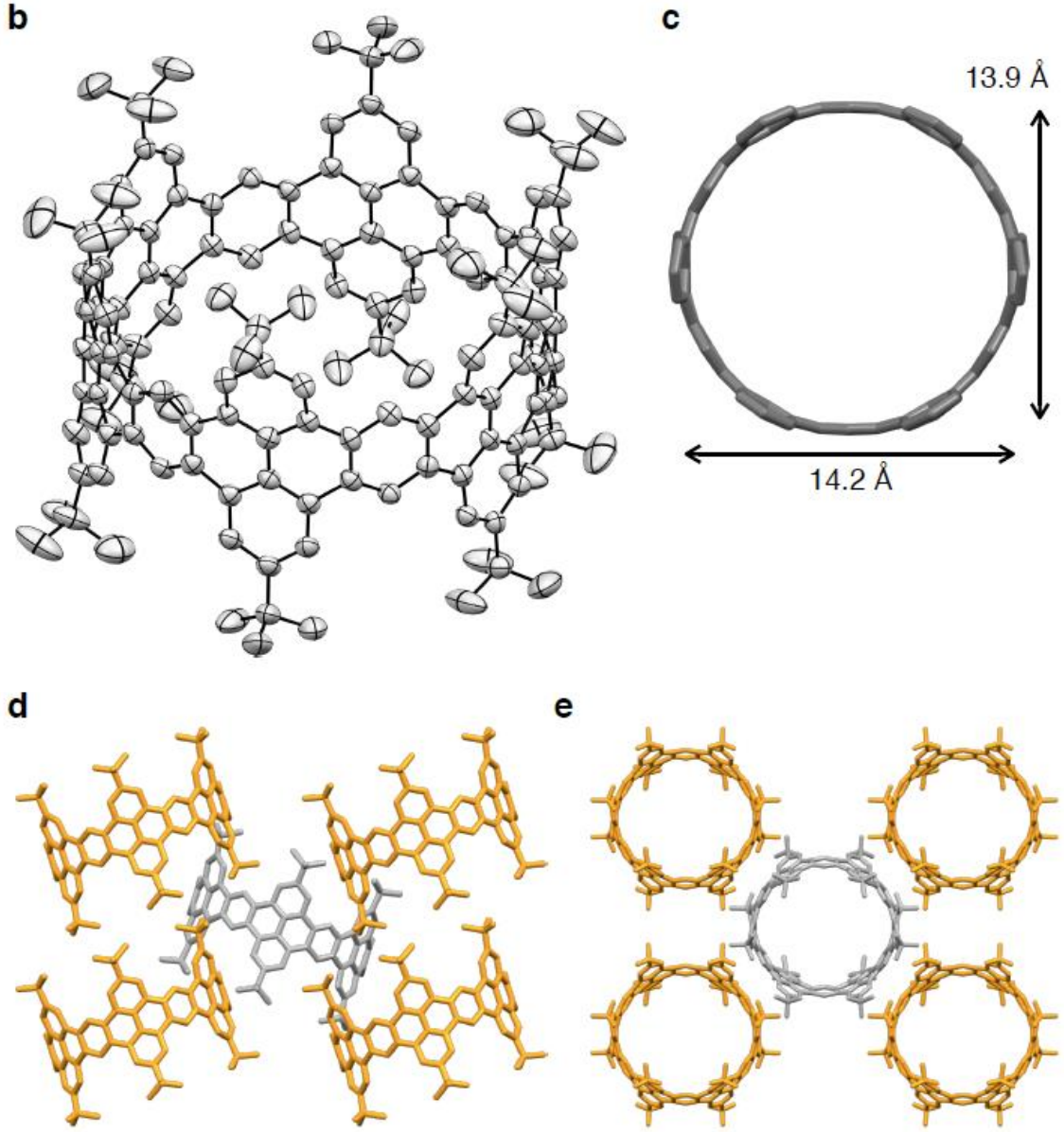
X-ray Structure



Opto-electronic Properties