PPGQ UFSC

GE|EM Grupo de Estrutura Eletrônica Molecular

A Brief Introduction to Single Supermolecule Electronics

MSc. Matheus C. Colaço

REVIEWS

[1]Department of Chemistry, Northwestern University, Evanston, IL, USA.

[2]Stoddart Institute of Molecular Science, Department of Chemistry, Zhejiang University, Hangzhou, China.

[3]ZJU-Hangzhou Global Scientific and Technological Innovation Center, Hangzhou, China.

[4]School of Chemistry, University of New South Wales, Sydney, New South Wales, Australia.

From molecular to supramolecular electronics

Hongliang Chen [1,2,3] ✉ and J. Fraser Stoddart [1,2,3,4] ✉

Chen, H., & Fraser Stoddart, J. (**2021**). *From molecular to supramolecular electronics.* ***Nature Reviews Materials*****, *6(9)*, *804–828.***

Summary

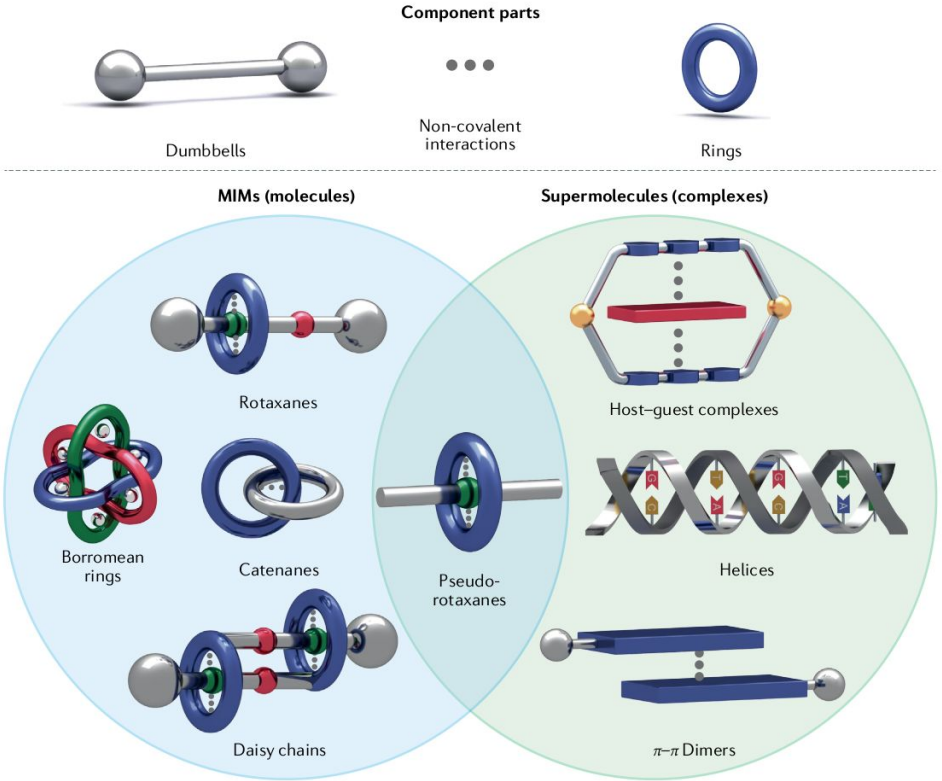
- Supramolecular Chemistry;
- From Single Molecule Electronics (SME) to Single Supermolecule Electronics (SSE);
- SSE Architectures:
  - Macrocyclic Architectures;
  - $\pi \cdots \pi$ Stacked Architectures;
  - Mechanical interlocked Molecule (MiM) Architectures;
- Challenges in the emerging field of SSE;
- Computational Chemistry in Action.

Supramolecular Chemistry

- Supramolecular chemistry was defined by Jean-Marie Lehn as "**chemistry beyond the molecule**", bearing on the organized entities of higher complexity that result from the association of two or more chemical species held together by **non-covalent interactions**.

- **Supermolecules** are complexes of two or more molecules that are bonded non-covalently.

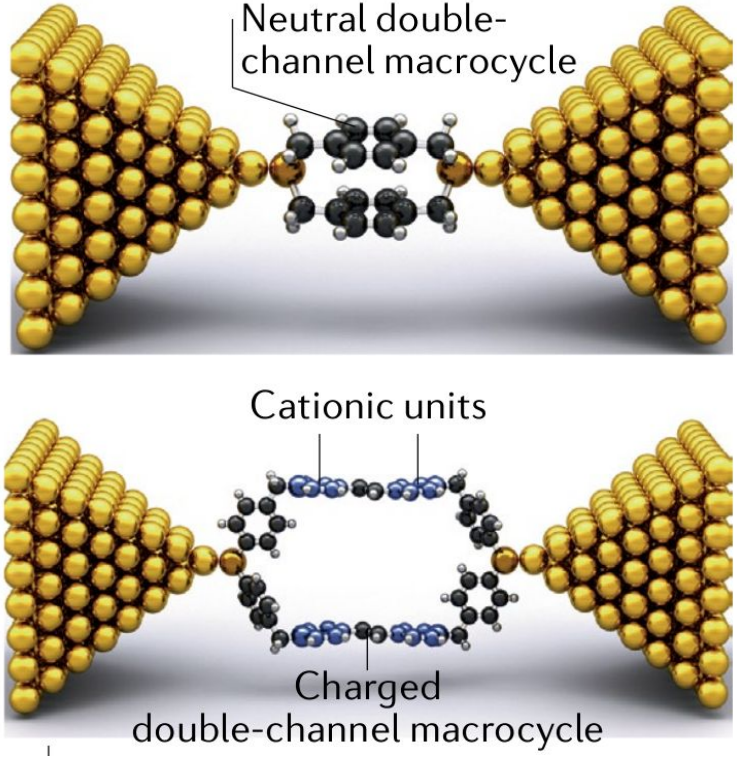
- **Mechanically interlocked molecules (MiMs)** are molecules with entanglements in space between two or more component parts such that they cannot be separated without breaking or distorting chemical bonds between atoms. MiMs, because of the presence therein of non-covalent interactions, exhibit many of the features of supermolecules.



From SME to SSE

- **SME** studies the way in which electrons propagate through a single molecule. It's ultimate goal is to use single molecules as the active species in sustaining CT in electronic circuitry;

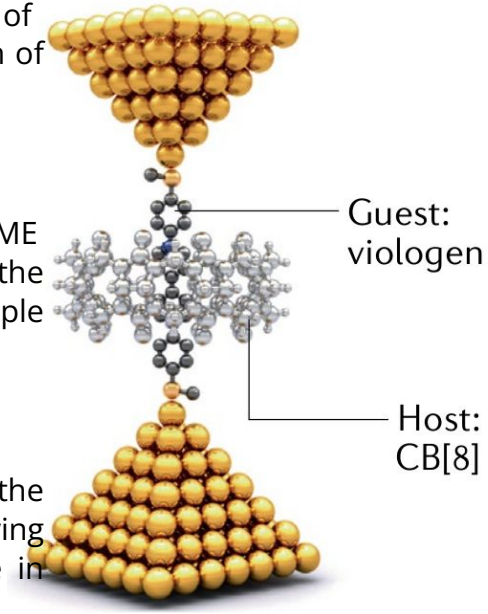
- However, to progress toward the fabrication of practical devices, opportunities could arise from the manipulation of weak multiple interactions on a supramolecular level;

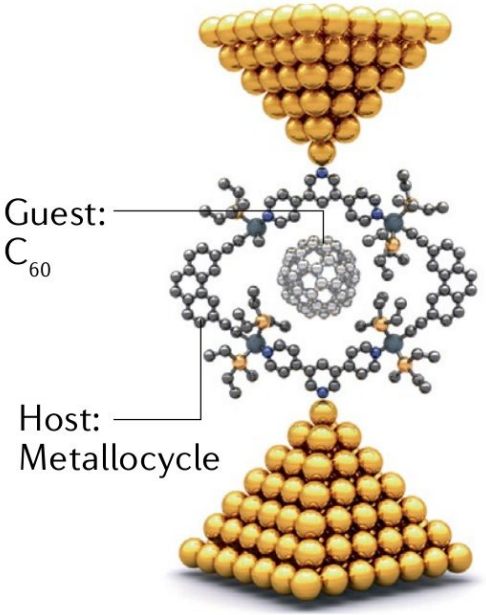


Chen, H., & Fraser Stoddart, J. ***Nat. Rev. Mater. 6(9)****, 804–828.* (**2021**)*;* Vazquez, H. et al. **Nat. Nanotechnol**. **7**, 663–667 (**2012**). ; Chen, H. et al. **Matter 2**, 378–389 (**2020**). ;

From SME to SSE

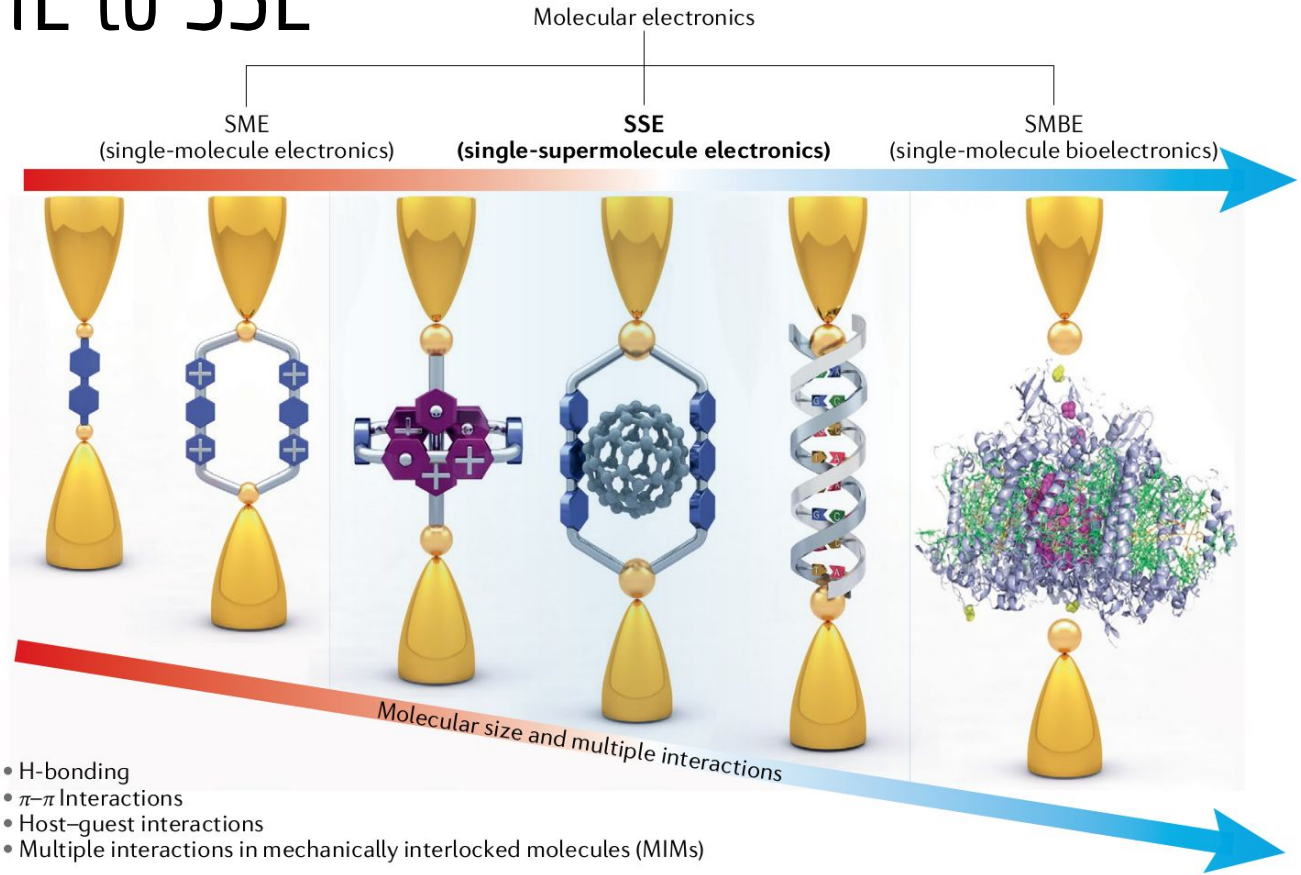
- **SSE** aiming the investigation and application of non-covalently bonded structures for the construction of electronic devices;
- **SSE** has the potential to expand the reach of SME because it not only focuses on the CT through the supermolecule, but takes into account the multiple non-covalent interactions within it.
- These multiple interactions can profoundly affect the conductances of electronic devices, giving supermulecules emergent properties not observable in their individual components.



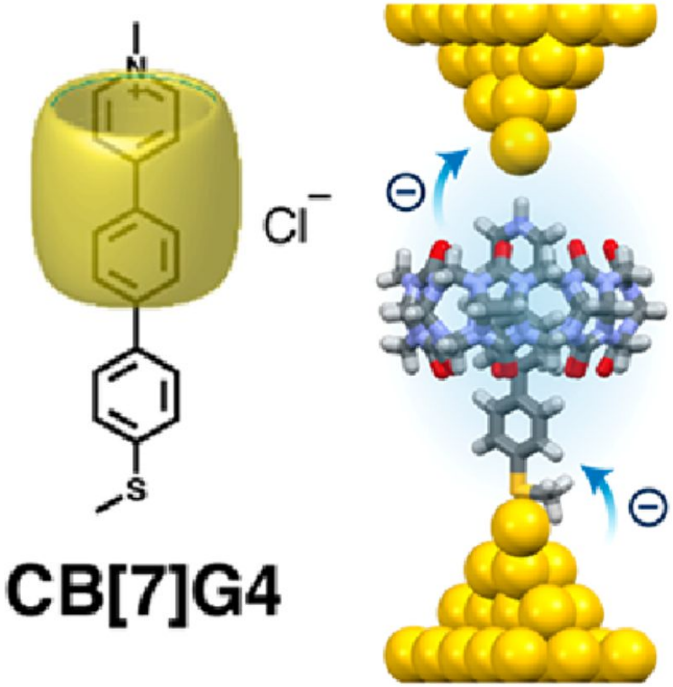


Chen, H., & Fraser Stoddart, J. ***Nat. Rev. Mater. 6(9)**, 804–828.* (**2021**); Tang, J. H. et al. **Nat. Commun**. **10**, 4599 (**2019**). ; Zhang, W. et al. **ACS Nano**, **10**, 5212–5220 (**2016**).

From SME to SSE

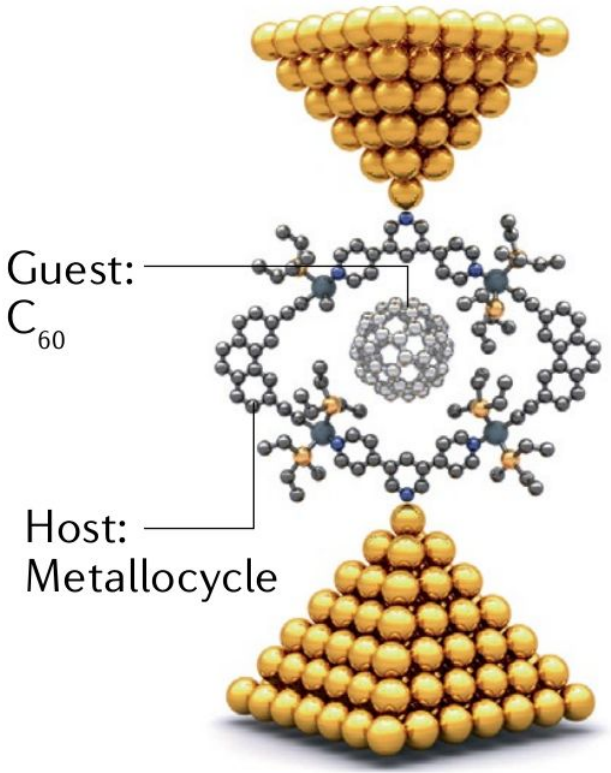


SSE Architectures



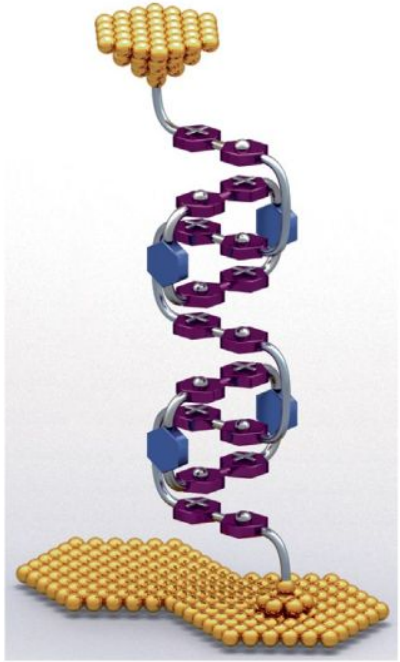
Yu, H. et al. ***J. Am. Chem. Soc.*** **144**, 7, 3162–3173 (**2022**)

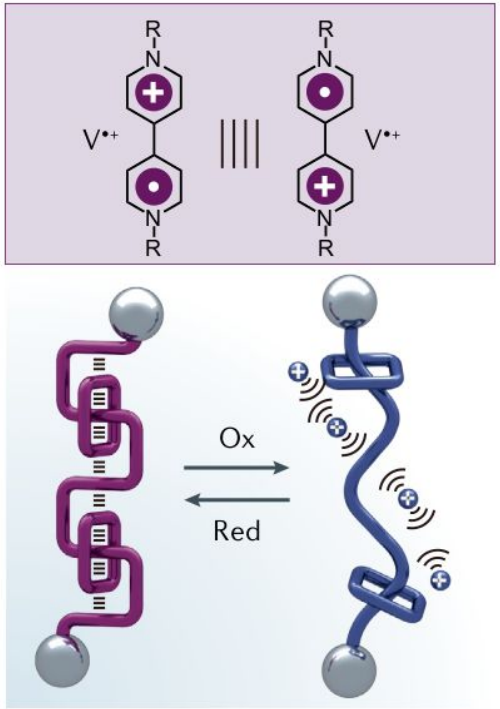
SSE Architectures



Tang, J. H. et al. **Nat. Commun**. **10**, 4599 (**2019**).

SSE Architectures

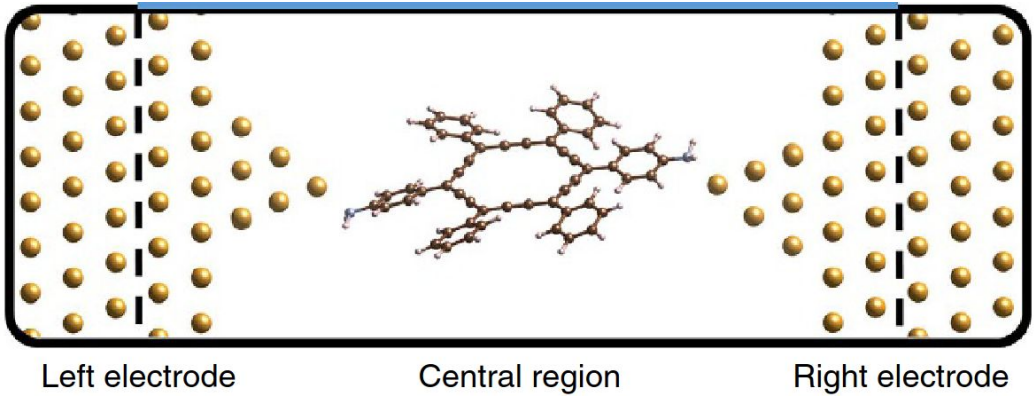


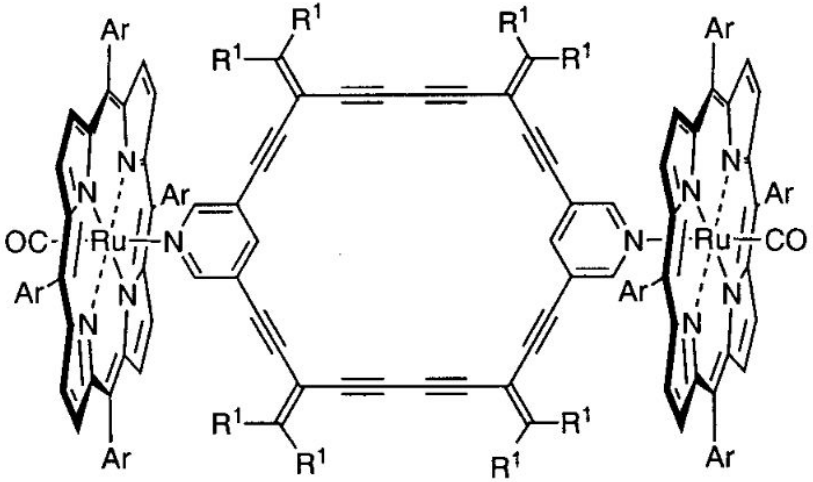


Wang, Y. P. et al. **ACS Cent. Sci**. **2**, 89–98 (**2016**).

SSE Architectures - Macrocyclic Supermolecules

- Quantum Interference between multiple conducting channels.





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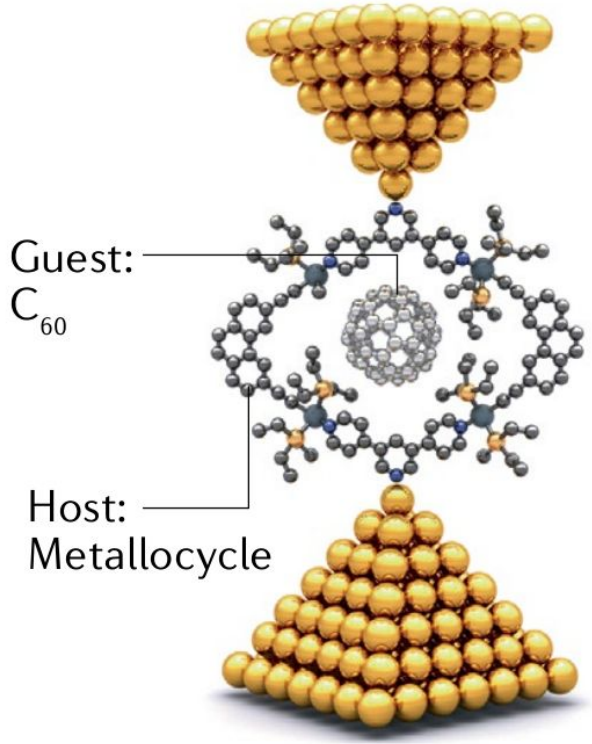
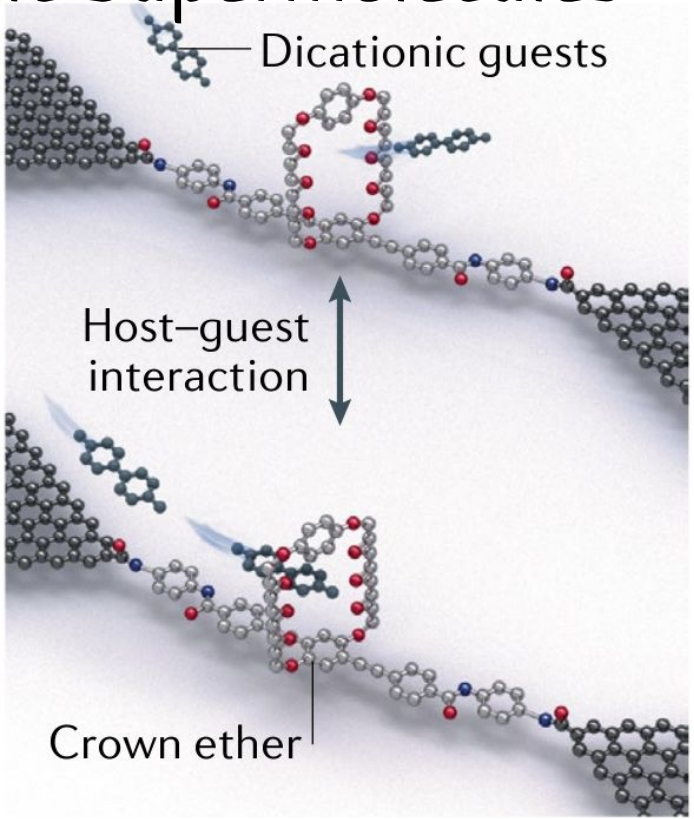
SSE Architectures - Macrocyclic Supermolecules

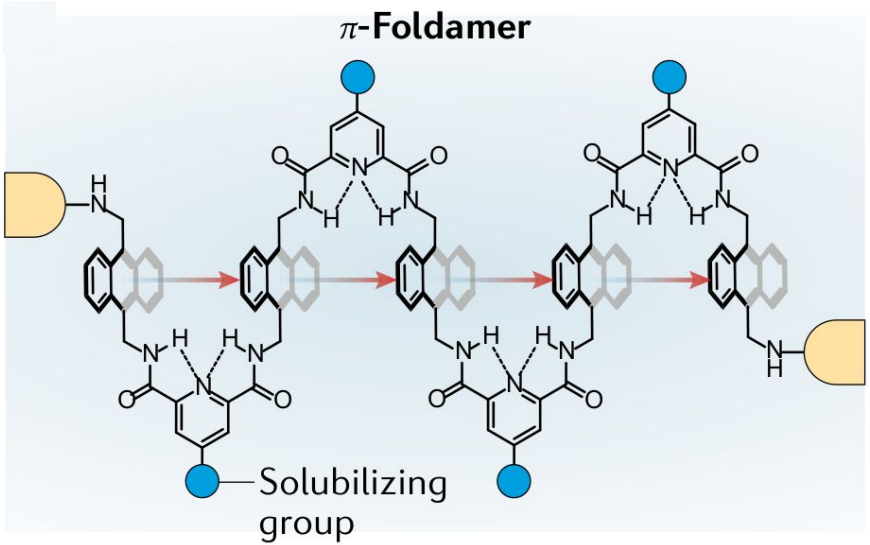


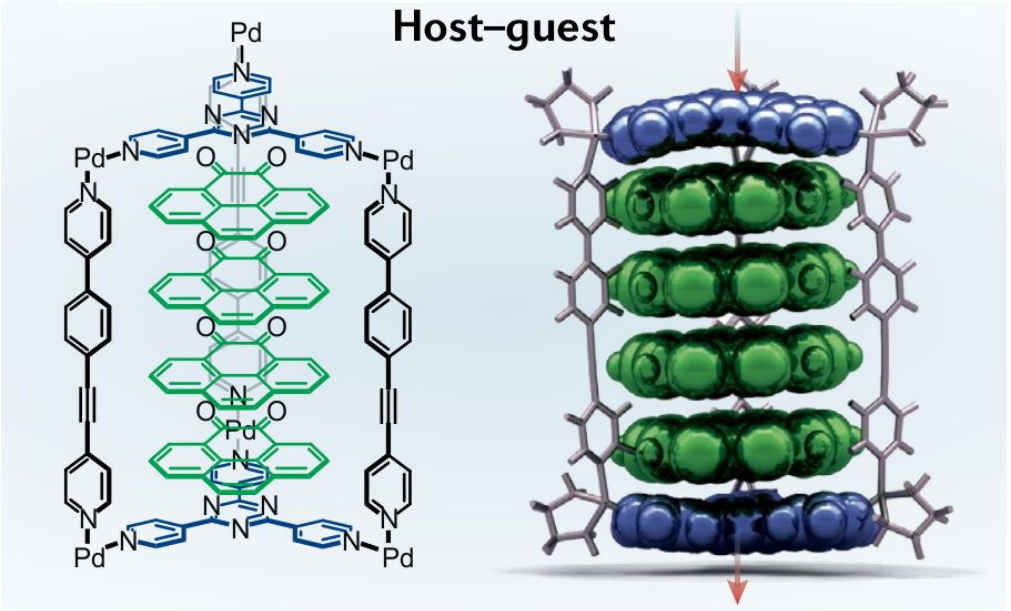


Tang, J. H. et al. **Nat. Commun**. **10**, 4599 (**2019**) ; Chen, H., & Fraser Stoddart, J. ***Nat. Rev. Mater. 6(9)****, 804–828.* (**2021**)

SSE Architectures - $\pi\cdots\pi$ Stacked Supermolecules

- Through-space interactions.

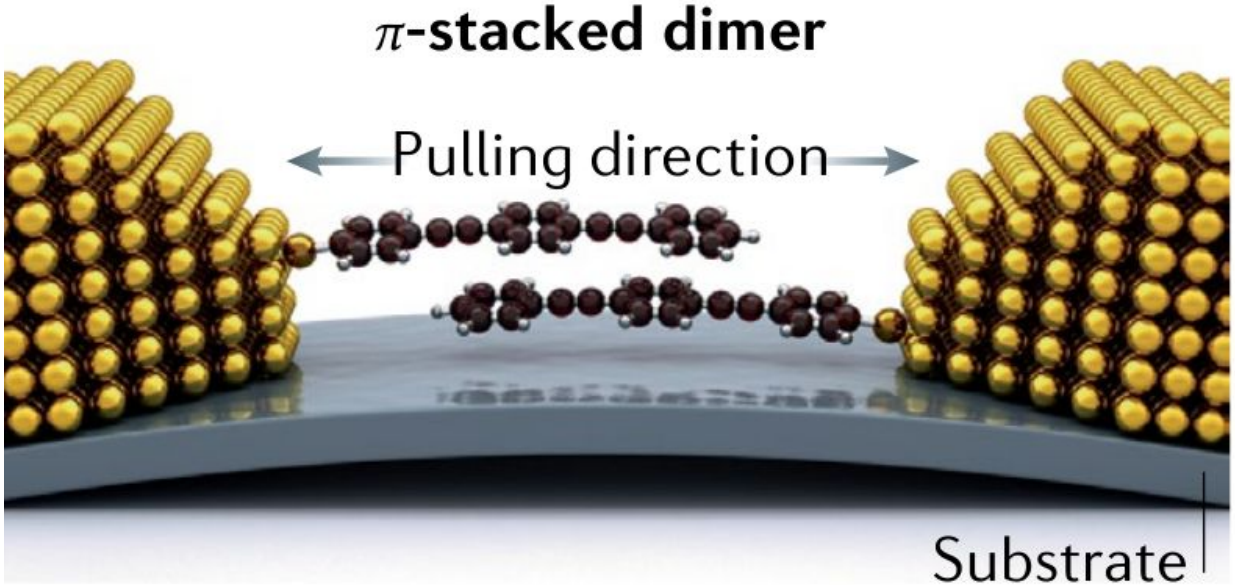




Carini, M. et al. **Nat. Commun. 8**, 15195 (**2017**). ; Kiguchi, M. et al. **Angew. Chem. Int. Ed. 50**, 5708–5711 (**2011**).

SSE Architectures - $\pi\cdots\pi$ Stacked Supermolecules

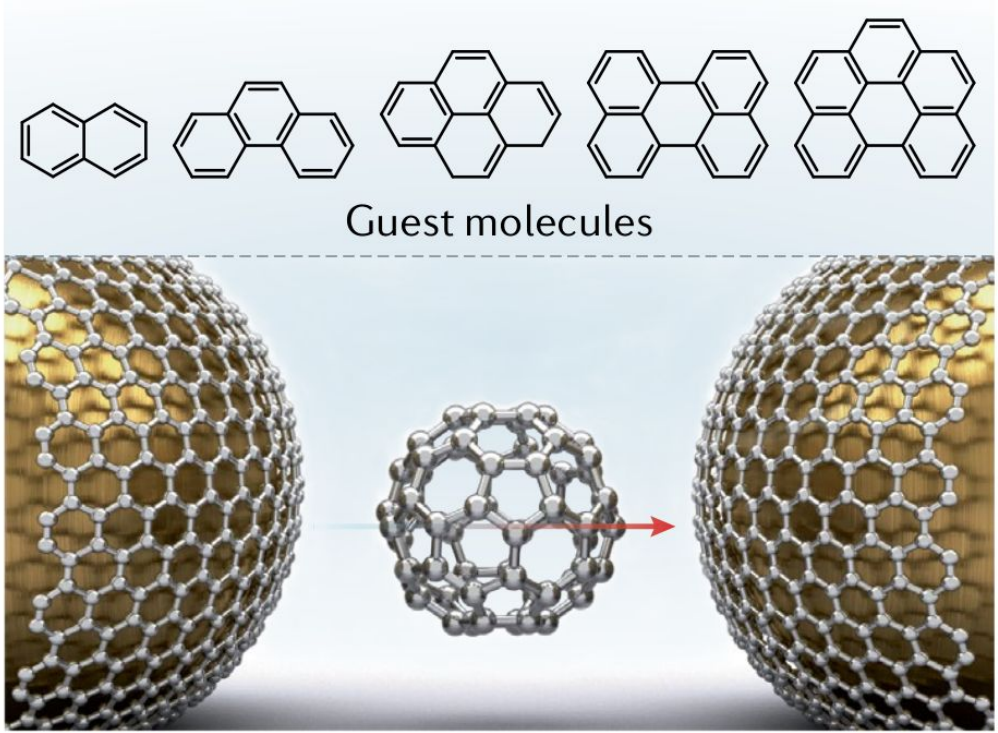
- $\pi\cdots\pi$ interaction are strong enough to sustain current



Wu, S. et al. **Nat. Nanotechnol. 3**, 569–574 (**2008**). ; Caneva, S. et al. **Nat. Nanotechnol. 13**, 1126–1131 (**2018**).

SSE Architectures - $\pi\cdots\pi$ Stacked Supermolecules

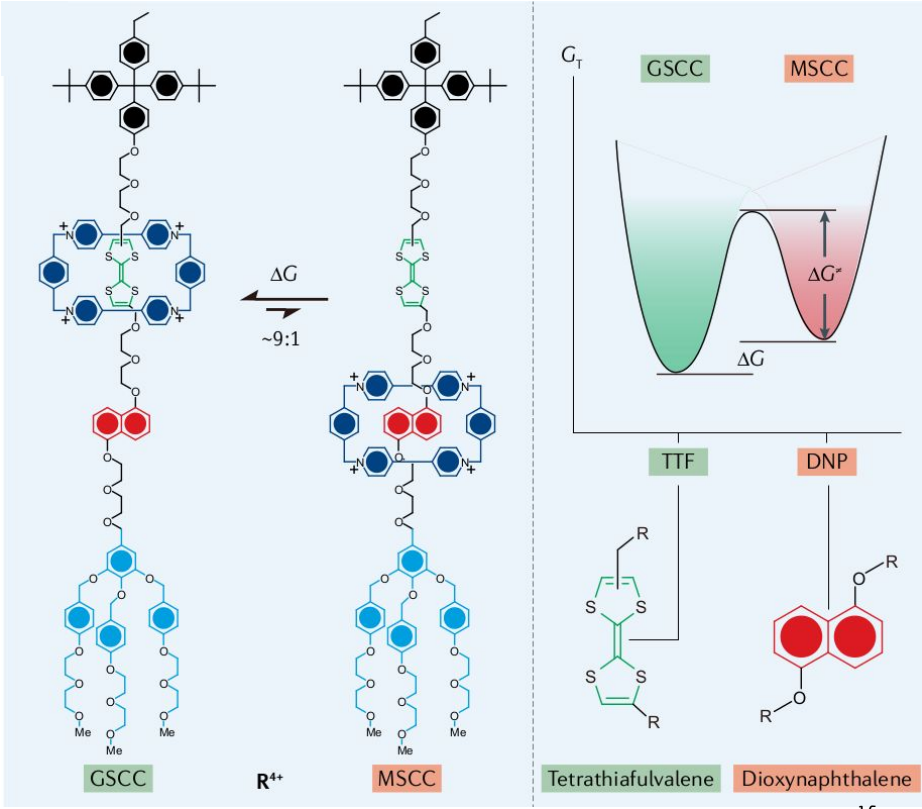
- Increase connectivity



Tan, Z. et al. **Nat. Commun. 10**, 1748 (**2019**).

SSE Architectures - MiM Architectures

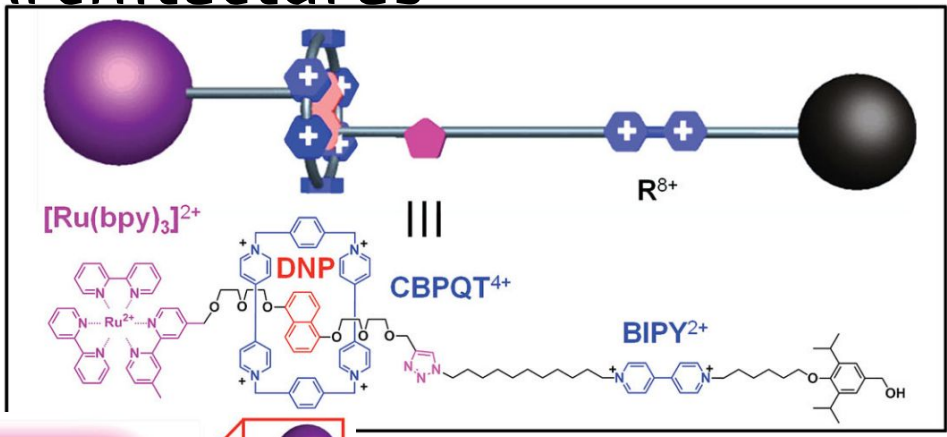
- Bistable co-constitutional changes;



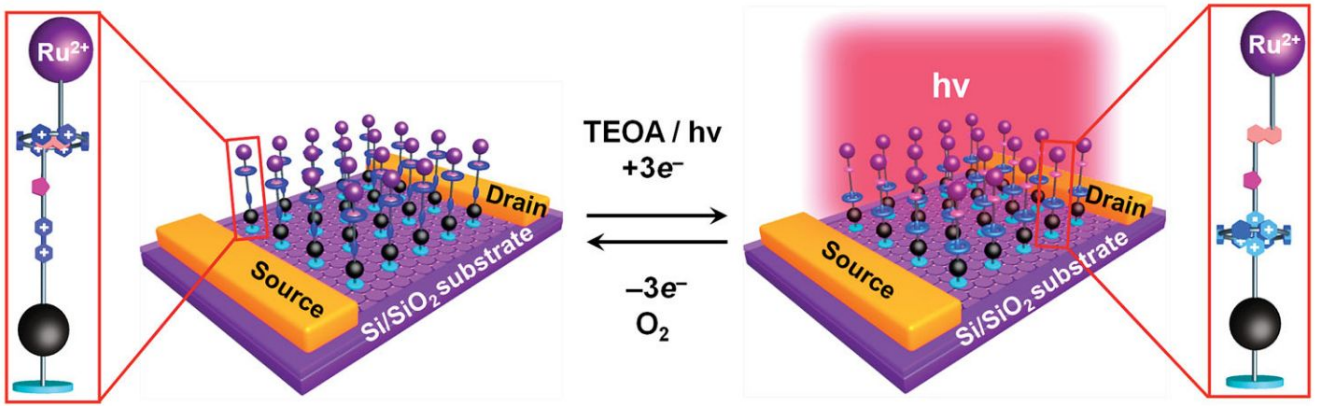
Choi, J. W. et al. **Chem. Eur. J. 12**, 261–279 (**2006**).

SSE Architectures - MiM Architectures

- Bistable co-constitutional changes;



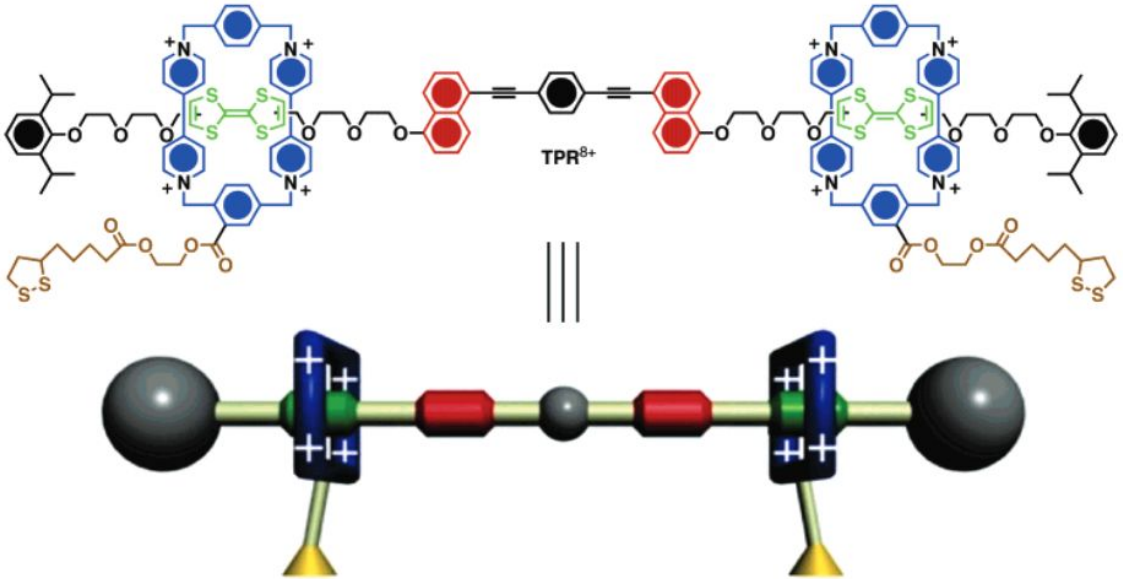
- Photo-switches;



Jia, C. et al. **Adv. Mater. 25**, 6752–6759 (**2013**).

SSE Architectures - MiM Architectures

- Bistable co-constitutional changes;
- Artificial muscles;

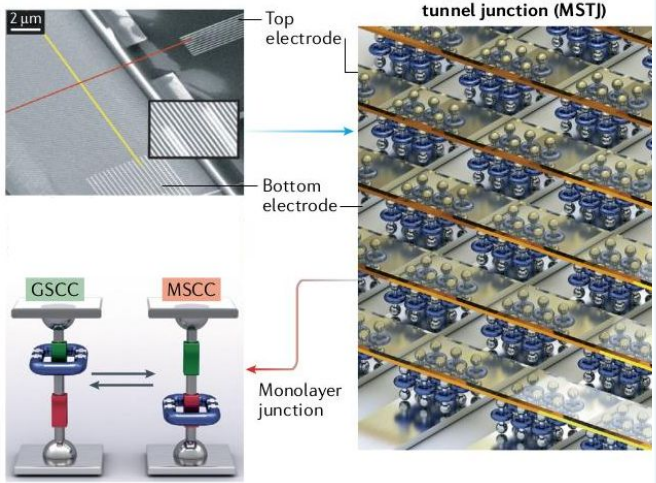


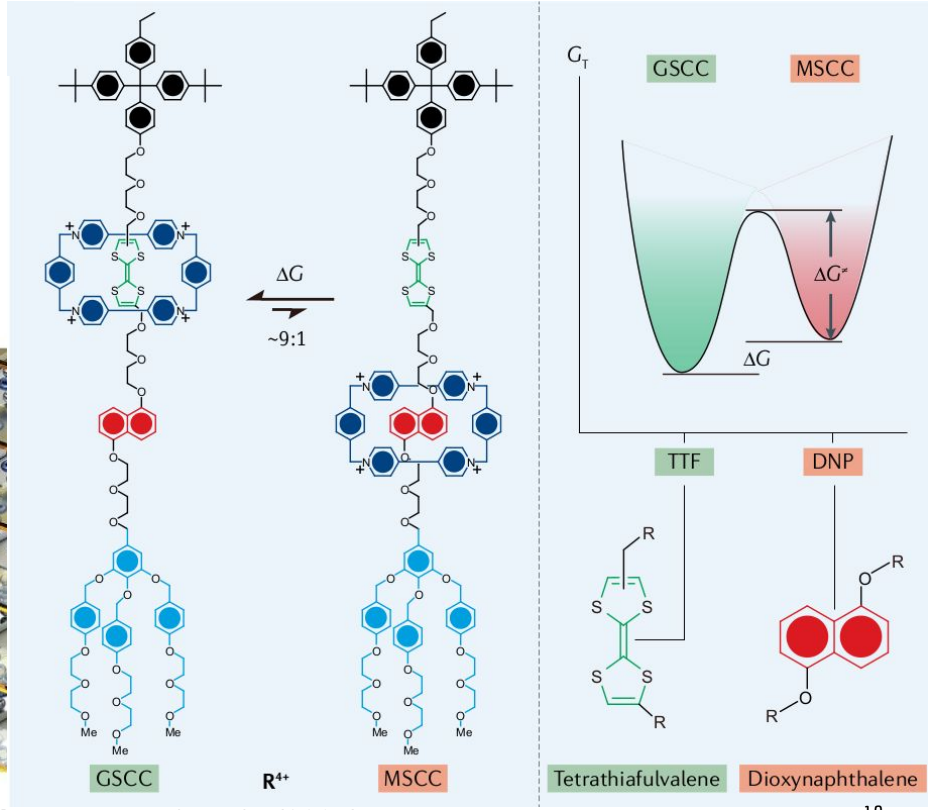
Liu, Y. et al. **J. Am. Chem. Soc. 127**, 9745–9759 (**2005**).

SSE Architectures - MiM Architectures

- Bistable co-constitutional changes;

- Random-access memories;

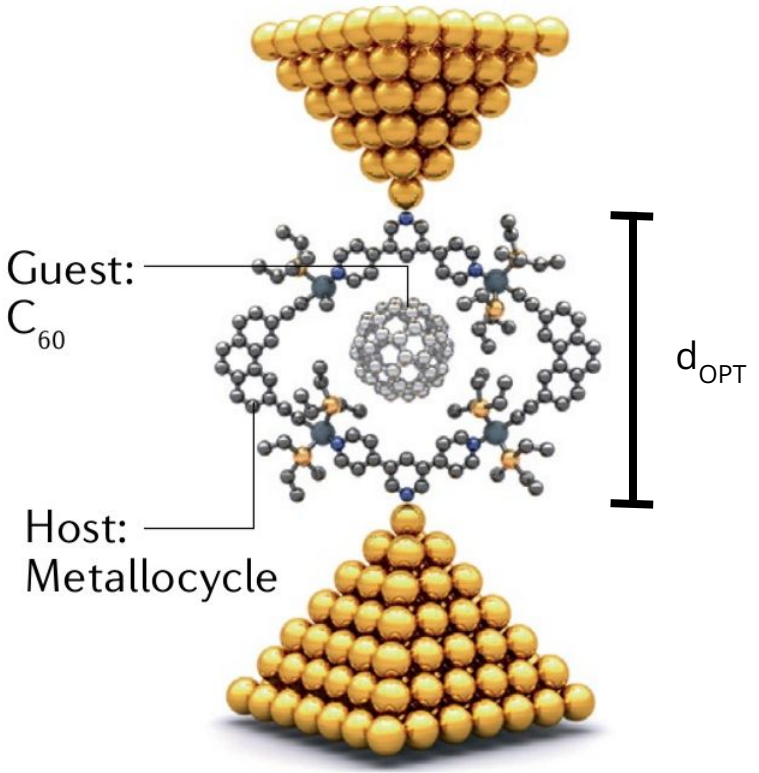




Choi, J. W. et al. **Chem. Eur. J. 12**, 261–279 (**2006**). ; Green, J. E. et al. **Nature 445**, 414–417 (**2007**).

Main Challenges in the SSE

- Optimize the distance between the electrodes;
- Understand the role played by the multiple non-covalent interactions in the charge transport through supermolecules and how to modulate it;
- Understand the electronic effects in supermolecules, such as quantum interference, and how to use them to build functionalized electronic devices.



Tang, J. H. et al. **Nat. Commun**. **10**, 4599 (**2019**).

Computational Chemistry in Action

- Use DFT to predict the d_{OPT} for the connection of different supramolecular architectures;
- NEGF-DFT formalism to evaluate the electron transport through these systems;
- NCI, QTAIM and electron density analysis to understand the role played by non-covalent interactions in supermolecules when they are placed between metallic electrodes.


That's all Folks!

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