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July 17-19, 2017 Chicago, USA

Nanjing University of Posts and Telecommunications

X L H Chemistry For Organic Nanogrids with "Plenty of Room"

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Outline



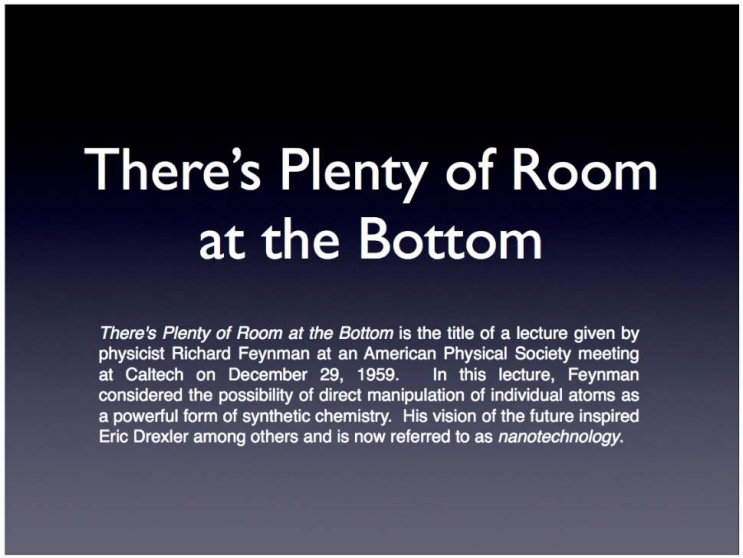
- Background
  - To Activate Molecular Nanoworlds
- From L-synthon to unit nanogrids and nanopolymers
- From X-synthon to spirodigrid and polygrids
- From H-synthon to fused digrids and polyladders
- Summary and Outlooks
- Acknowledgements

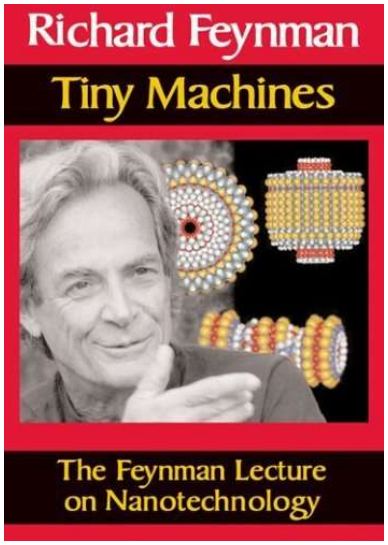


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Background——To Activate Molecular Nanoworlds

One Mission is to Challenge Feynman's Prediction

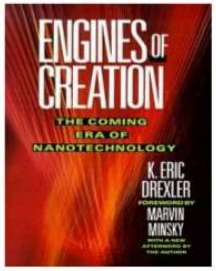




- Inspired by Feynman's concepts, **K. Eric Drexler** independently used the term "nanotechnology" in his **1986** book ***Engines of Creation: The Coming Era of Nanotechnology.***



- Also in **1986**, **Drexler** co-founded **The Foresight Institute** to help increase public awareness and understanding of nanotechnology concepts and implications.

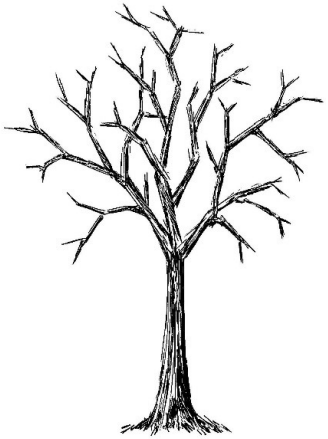


- All the science from inspiration of the real world at human scale such as a plane; and to creation of artificial systems is the role of human being as the unique wisdom on earth and in universe.
- The intrinsically key issue is to activate the molecular world by discovery of the knowledge at the nanoscale that is the key linkage between molecule and macroscale.

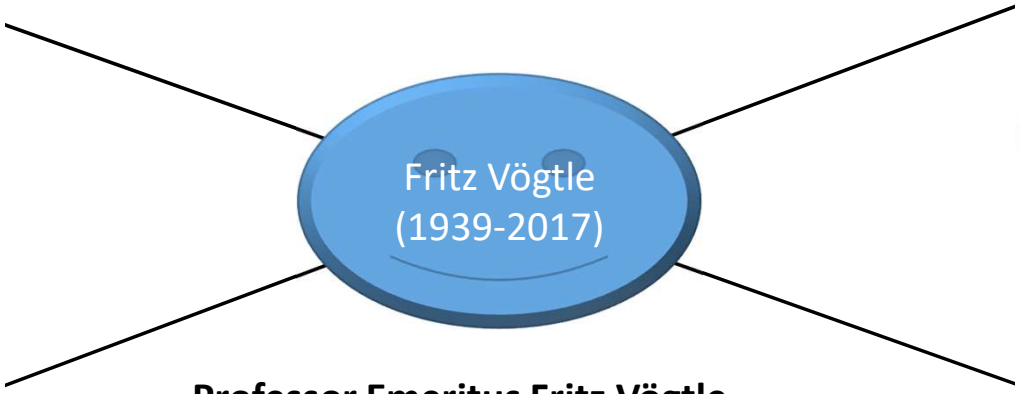
Nature Nanotechnology 4, 783 - 784 (2009). doi:10.1038/nnano.2009.357

To clone the structure in the real world
——Molecular Nanotechnology

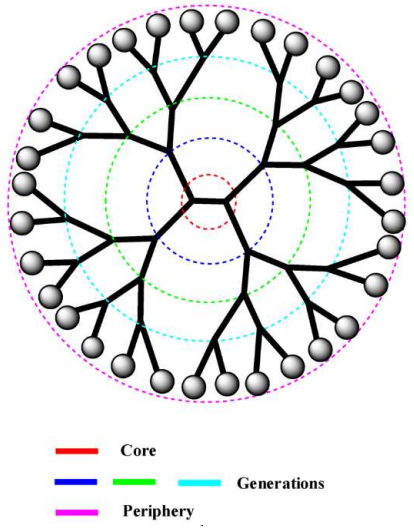
*Buhleier, Egon; Wehner, Winfried; Vögtle, Fritz (1978). ""Cascade"- and "Nonskid-Chain-like" Syntheses of Molecular Cavity Topologies". Synthesis. **1978** (2): 155–158. doi:10.1055/s-1978-24702.*



Nature is the wisdom of past



Professor Emeritus Fritz Vögtle, University of Bonn, Germany, passed away on January 3, 2017.



Fritz Vögtle in 1978

- **Dendrimer** is one of example to clone real worlds of the nature

https://en.wikipedia.org/wiki/Dendrimer

To clone the motion in the real world ——Molecular machines

The Nobel Prize in Chemistry 2016



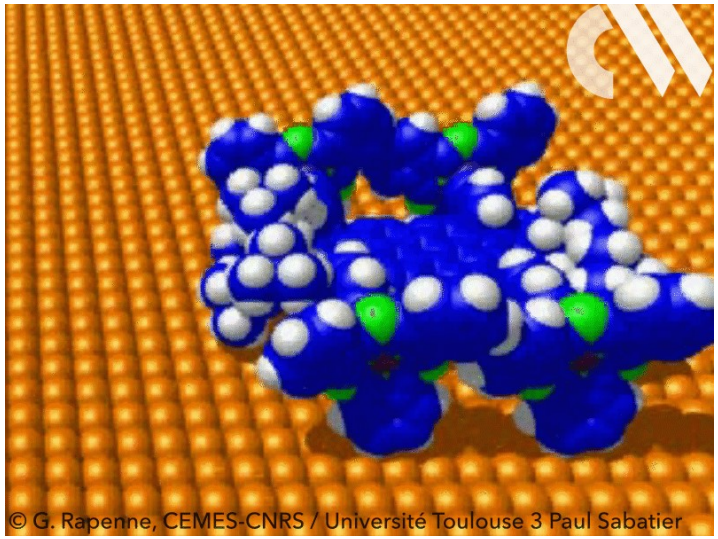
Photo: A. Mahmoud
Jean-Pierre Sauvage
Prize share: 1/3



Photo: A. Mahmoud
Sir J. Fraser Stoddart
Prize share: 1/3



Photo: A. Mahmoud
Bernard L. Feringa
Prize share: 1/3

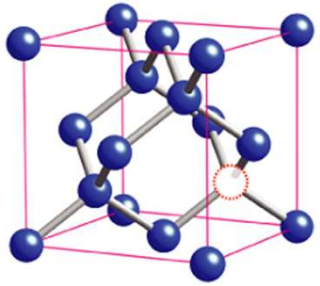


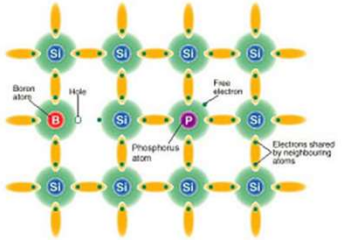
© G. Rapenne, CEMES-CNRS / Université Toulouse 3 Paul Sabatier

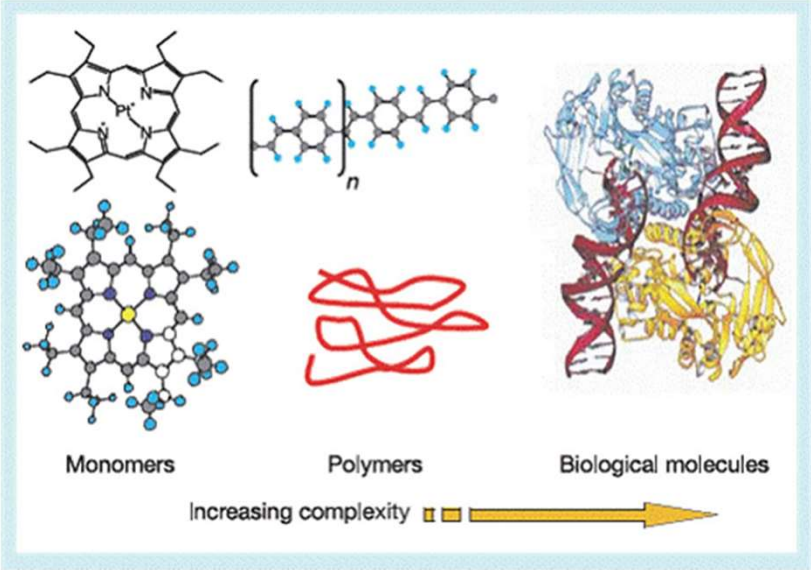
- The Nobel Prize in Chemistry 2016 was awarded jointly to Jean-Pierre Sauvage, Sir J. Fraser Stoddart and Bernard L. Feringa *"for the design and synthesis of molecular machines"*.

• **Nanocars gear up for first race of its kind** , 14 November 2016, France will host nanocar competition between six teams from around the world to test unique microscope

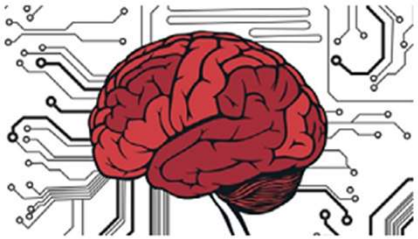
To clone the function from silicon to carbon
——Organic Electronics





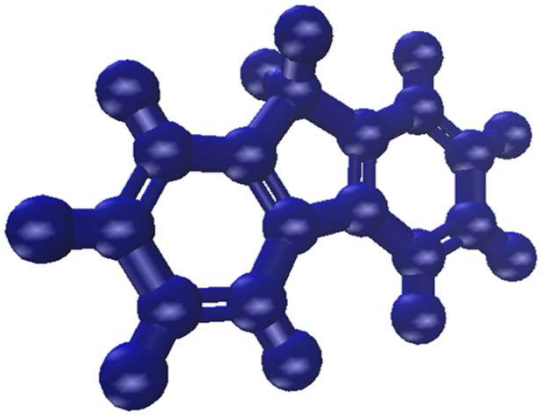


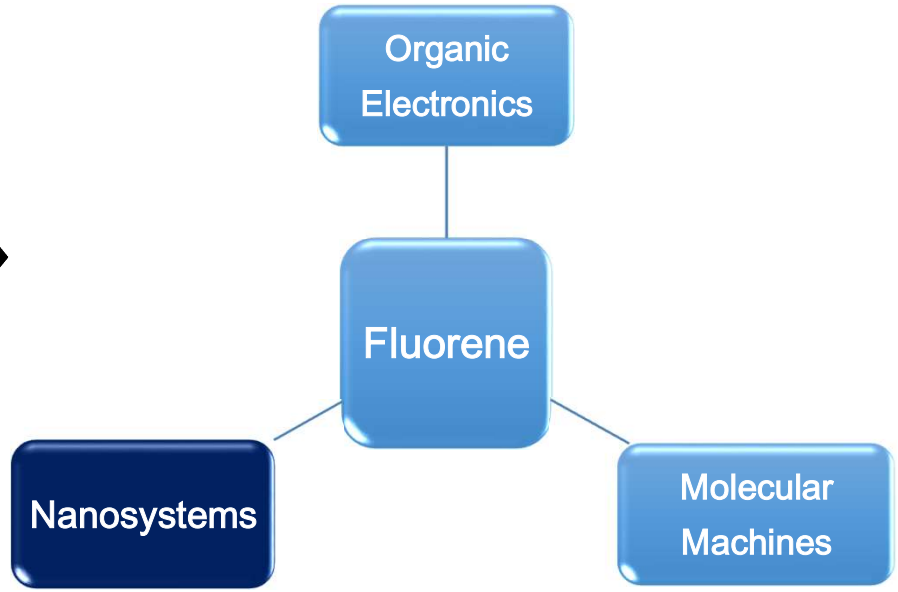




- Organic Electronics is another way to change the world of human beings; After silicon, carbon-based organics completely change the device morphology, procedures, as well as cost with the huge room for the application of mobile internet, virtual reality, Internet-of-thing (IoT), artificial intelligences and soft robots.

Fluorene-based Synthons as a versatile node for the uniform of three active areas

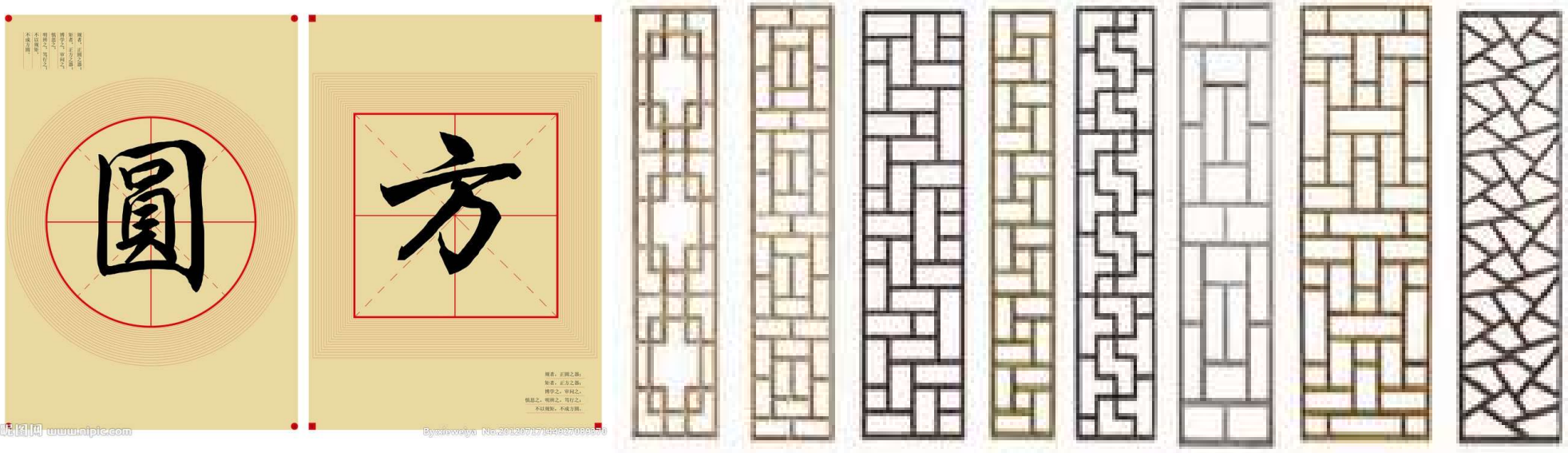




- **Ten years age, we get insight into fluorenes that can serve as the potential building blocks in nanosystems and nanoarchitectures, beside they have been explored in organic electronics and molecular machines**

Xie Ling-Hai, Huang Wei *et al.* *Org. Lett.* **2006,** *8* (7), 1363-1366.

Nanogrids with obvious advantage of expansibility over macrocycles

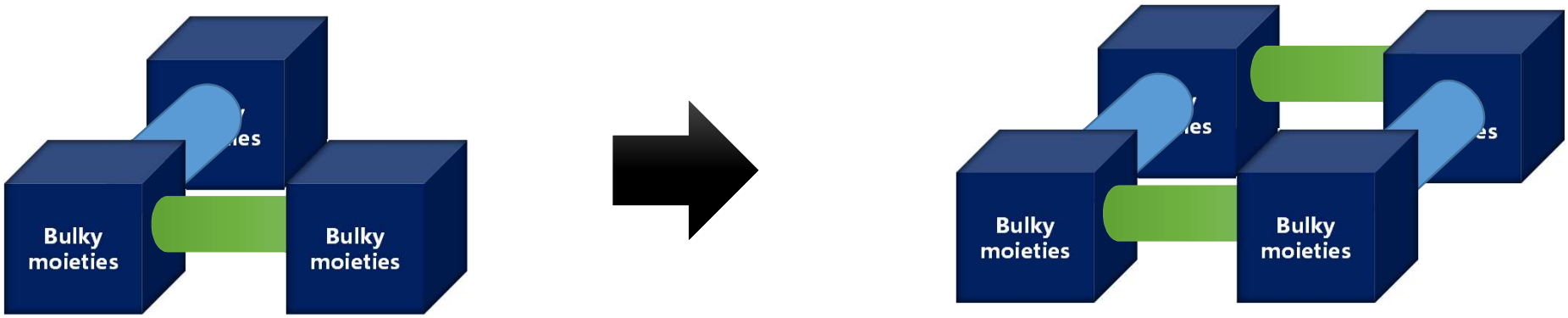


- Under the inspiration of ancient window patterns and FangYuan's culture, Nanogrids have been proposed in order to integrate three aspects into one system
- Different from the macrocycles, nanogrids have obvious vertexes that facilitate the linkage with the controllable direction

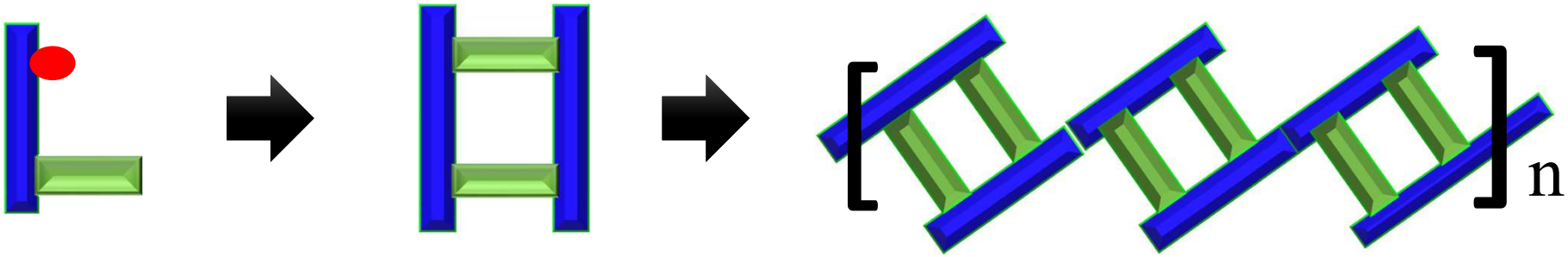
L. Wang, L.-H Xie,* W. Huang,* et al., *Org. Lett.*, **2014**, *16*, 1748.

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From L-synthon to unit nanogrid and nanopolymers



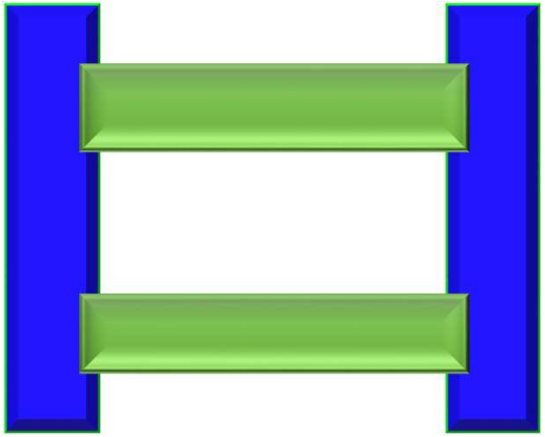
A first paradigm of nanogrids and nanopolymers

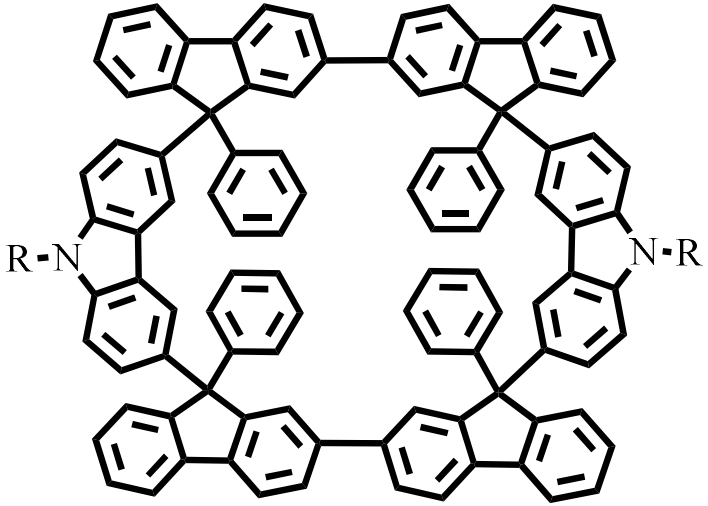


- We give a basic paradigm of L-type synthon, square nanogrids with KOU shape and polygrids from the fluorenes.
- In this paradigm, various functional groups such as molecular machines, optoelectronic groups as well as ionic redox groups and any other segments can be integrated, although the detailed design should be further demonstrated.

Wei Ying et al., *Mater. Chem. Front.* **2017** *1* (3), 455-459.

A general formal of ladder-like nanogrid and one typical fluorene-based nanomolecule

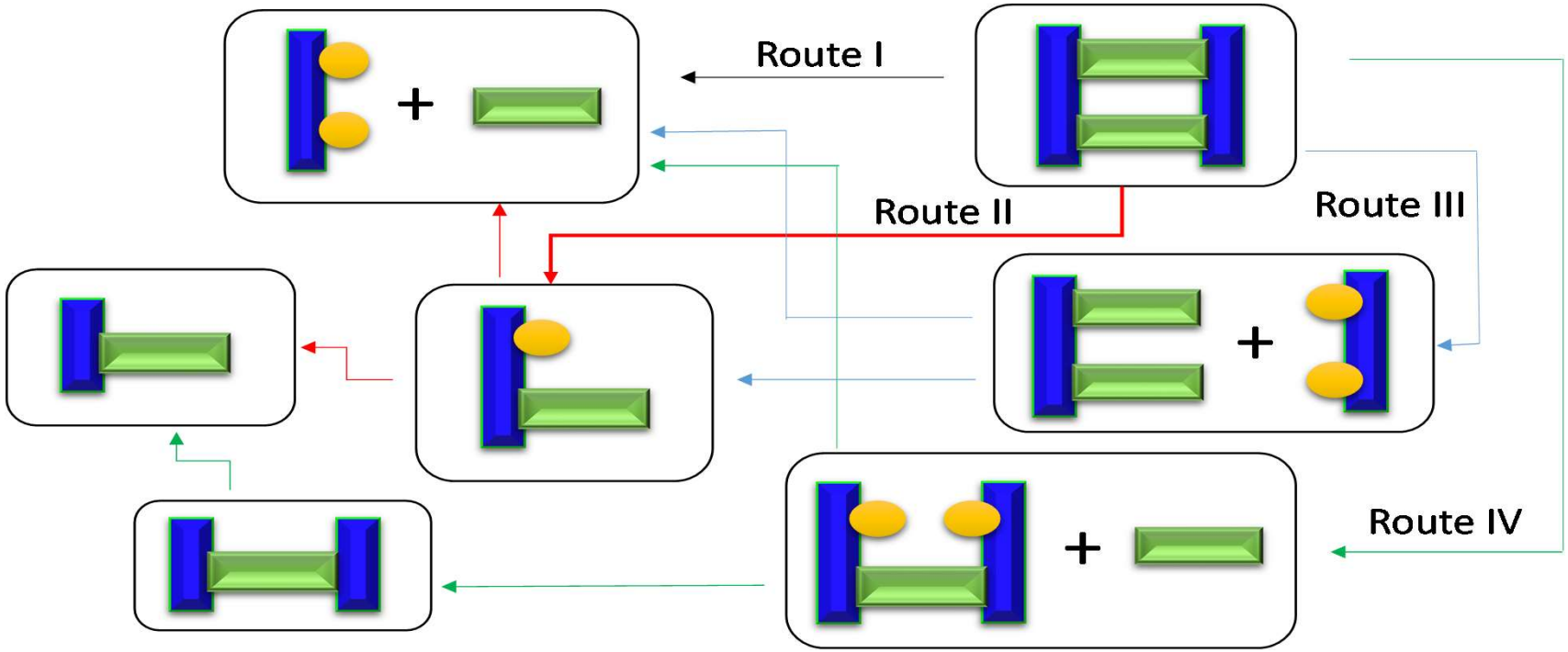




- A nanogrid that consists of four fluorenes and two carbazoles has been successfully designed with the unique 2/9 linkage pattern.

Wei Ying *et al.*, *Mater. Chem. Front.* **2017** *1* (3), 455-459.

Retrosynthetic Analysis of molecular grids

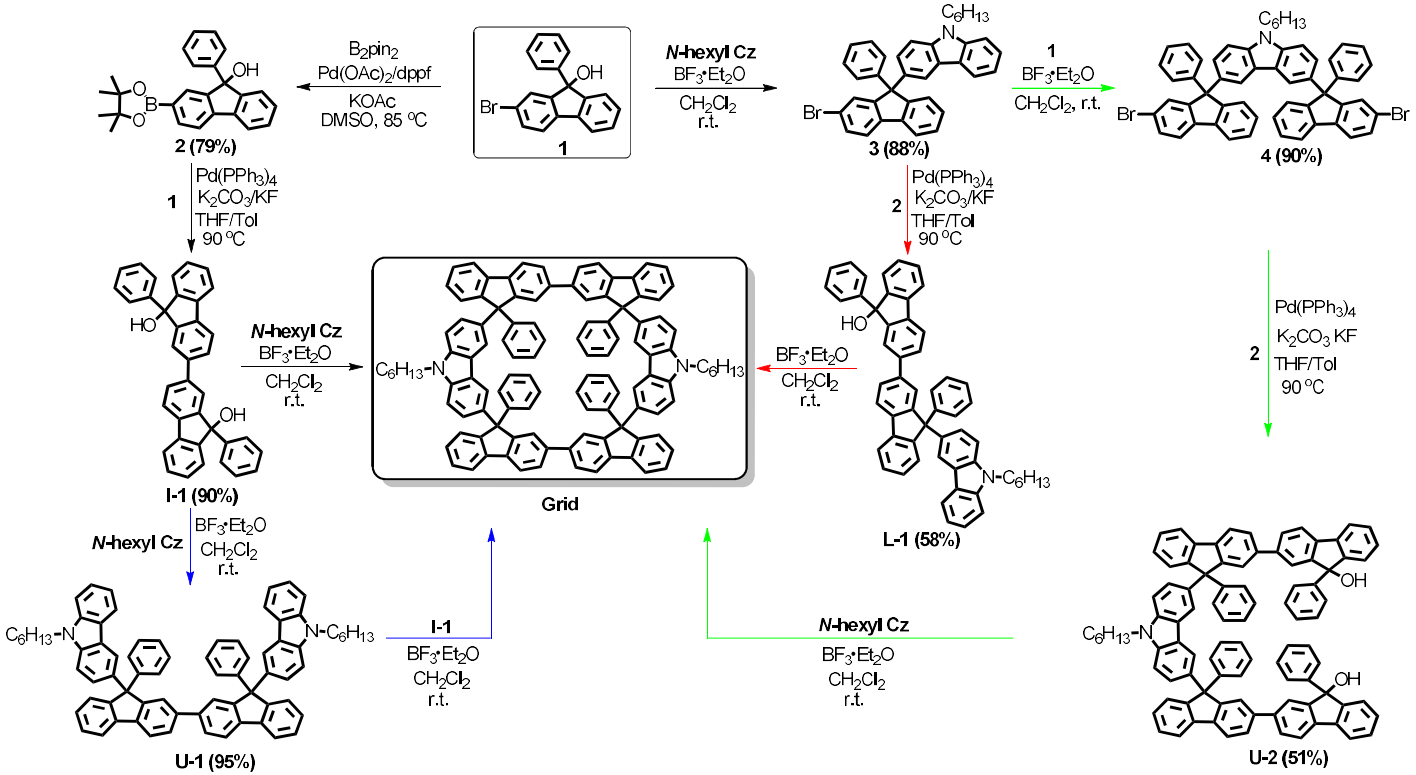


- Four Routes to Grids: 1) I-type one-pot, 2) L-shape method, 3) U-shaped methods

Wei Ying *et al.*, *Mater. Chem. Front.* **2017** *1* (3), 455-459.

Bottom-up fabrication of a molecular unit grid via molecular installing technology (MIT)

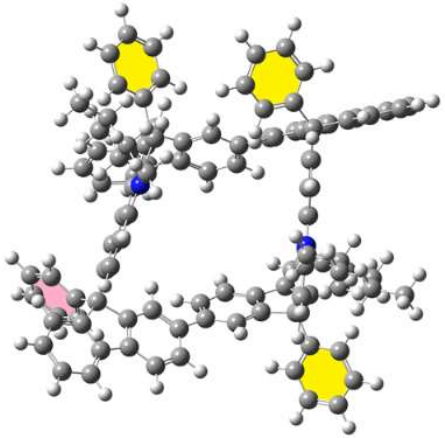
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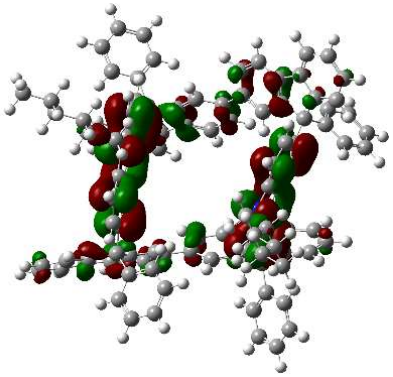
Grids were synthesized from L-shape synthon via molecular installing technology at a total yield of 21% that is higher than the one-pot route of I-shape synthon in 10% yield .

Wei Ying *et al.*, *Mater. Chem. Front.* **2017** *1* (3), 455-459.

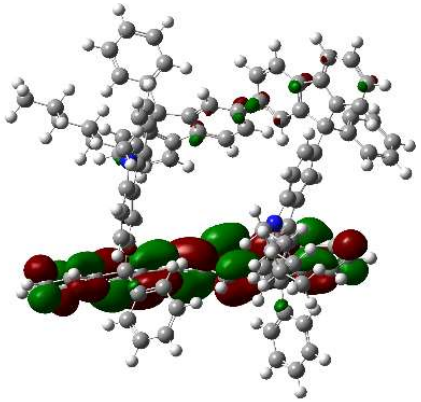
Theoretical calculation of square nanogrids



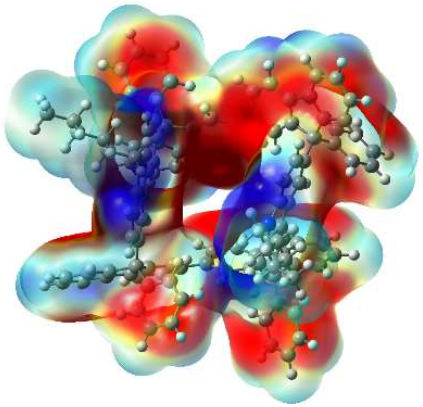
Conformation



HOMO



LUMO

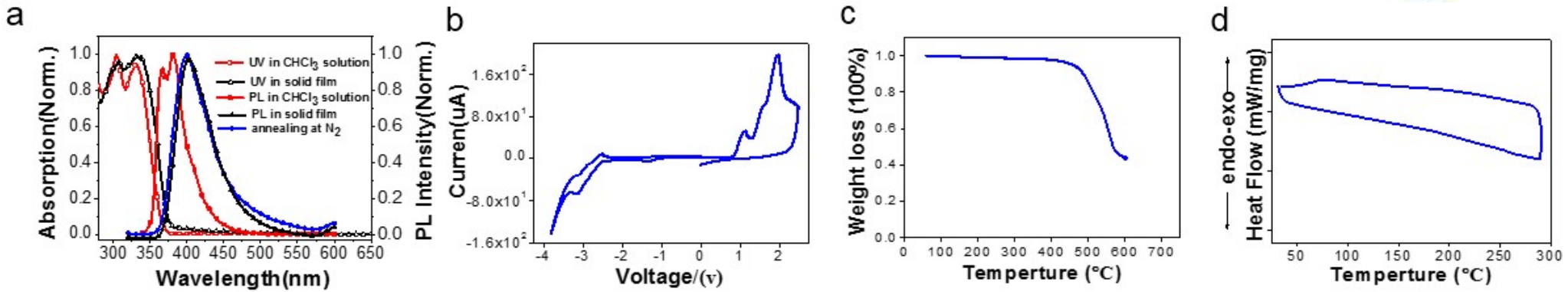


ESP

- Optimized conformations, HOMO and LUMO, electrostatic potential (ESP)
- The target grid has the size of about the length × width of 1.7 nm × 1.2 nm, with a cave of about 0.77 nm × 0.73 nm.

Wei Ying *et al.*, *Mater. Chem. Front.* **2017** *1* (3), 455-459.

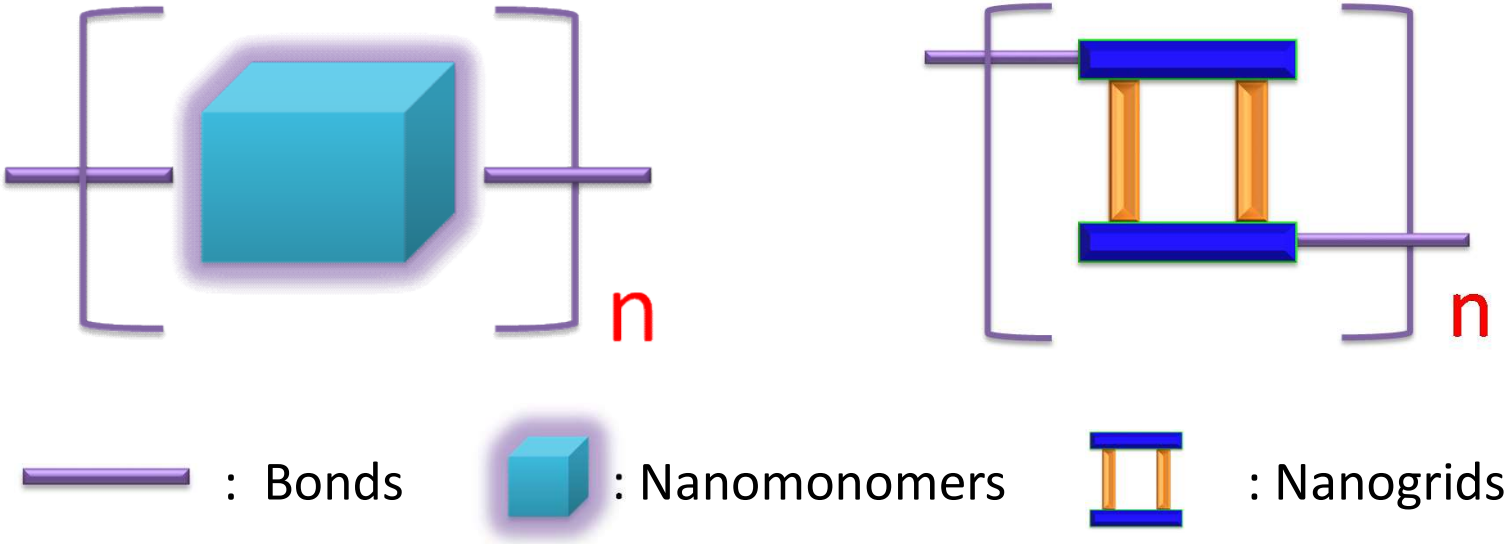
Basic photo-physics and physicochemical properties



- (a) Absorption spectra and emission spectra of **Grid**; (b) TGA curves of **Grid**; (c) CV curves of **Grid** (10 successive scans for anode processes); (d) DSC curves of **Grid**.
- **Grid** exhibit almost the same UV with absorption bands located at 304 nm and 331 nm in dilute $CHCl_3$ solution and in film. **Gird** in dilute $CHCl_3$ solution exhibits emission spectra with peaks at 367 and 380 nm.
- The HOMO energy level of **Grid** was −5.58 eV, LUMO energy level of **Grid** was −2.20 eV and electrochemical band gap is 3.38 eV;
- The decomposition temperatures were 458.2 °C for Grid (Figure 5c). DSC of **Grid** shows that no obvious glass transition temperature can be observed below 250 °C.

Wei Ying *et al.*, *Mater. Chem. Front.* **2017** *1* (3), 455-459.

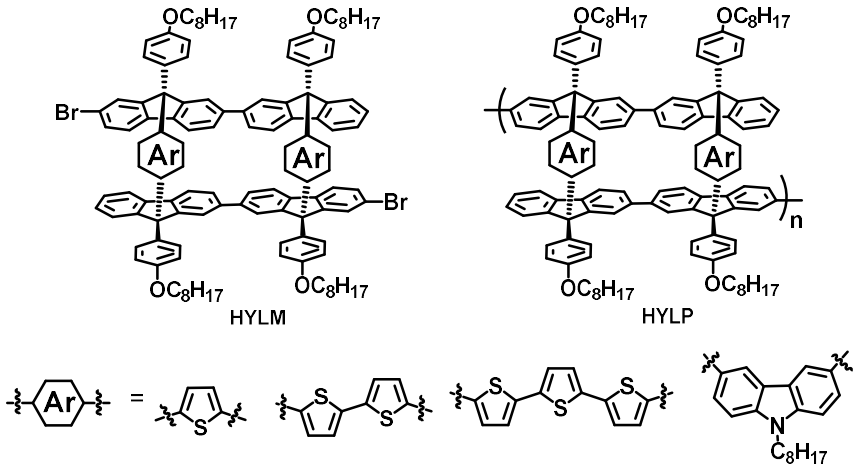
A Platform of Soluble Nanopolymer

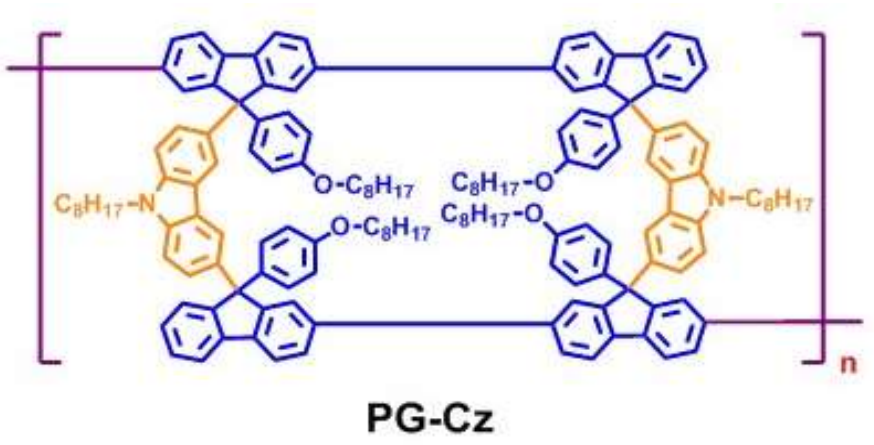


- A cartoon of nanopolymers with the both merits of CNT and conjugated polymers

Feng Q. Y. *et al*, C*hinese Journal of Polymer Science* **2017** 35(1), 87–97.

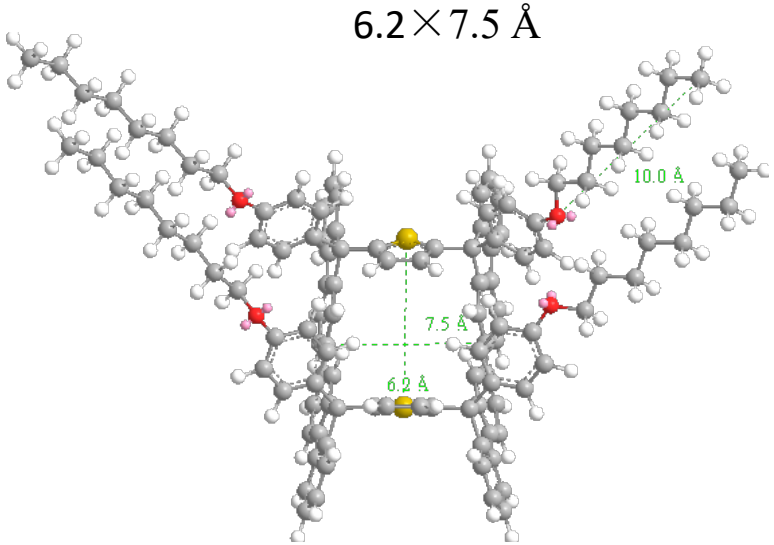
A series of chemical structures of fluorene-based polygrids

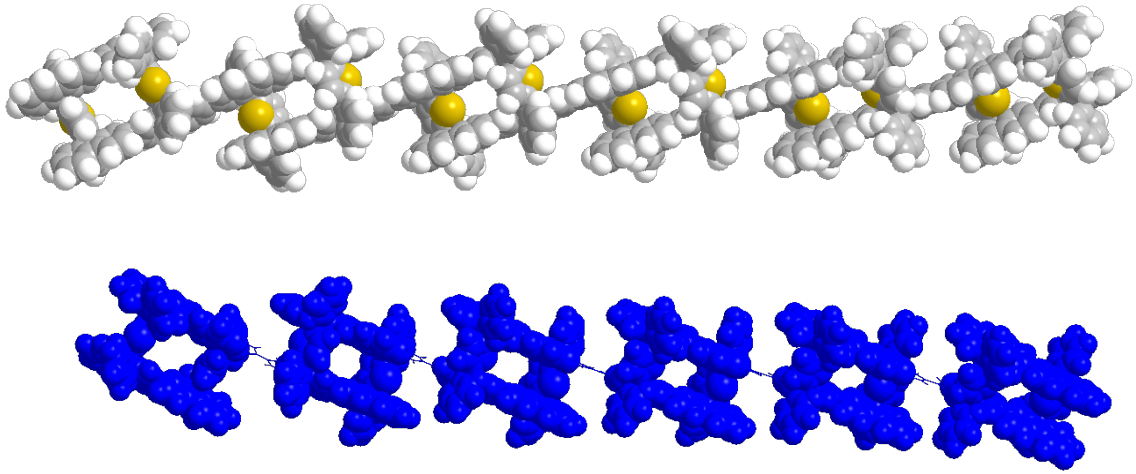




Q. Y. Feng, L.-H. Xie,* W. Huang,* *et al.,* A Robust and Soluble Nanopolymer Based on Molecular Grid-Based Nanomonomer. C*hinese Journal of Polymer Science* **2017** 35(1), 87–97.

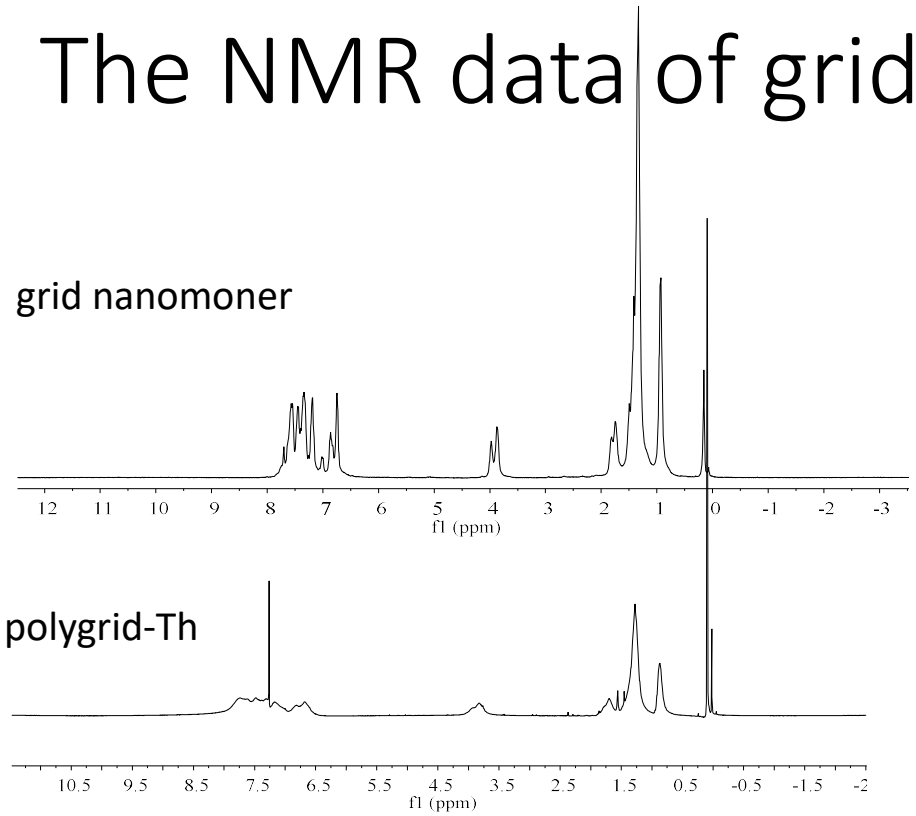
A typical rigid conformation of polygrids without alkyl side chains



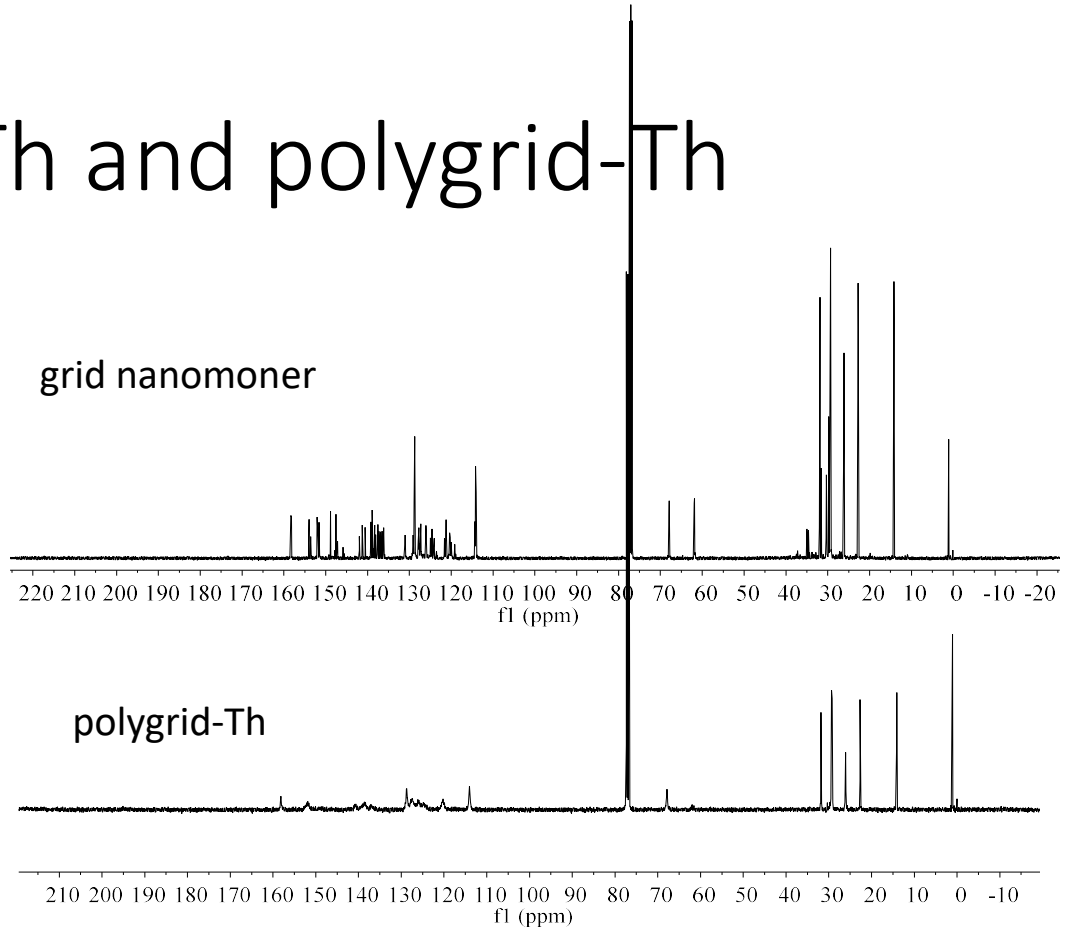


- Before nanosynthesis, we examined the rigidity of backbone by the MM2 model simulation, the rigid and shape persistent conformations reduce the complexity of polymer materials.

The NMR data of grid-Th and polygrid-Th



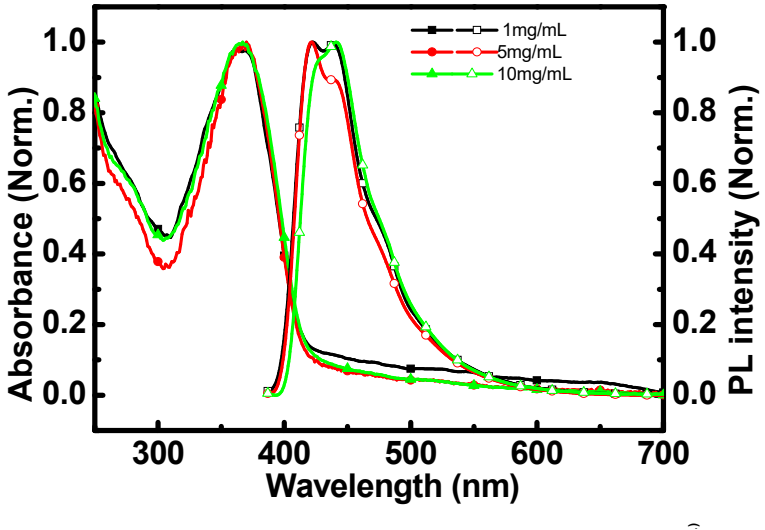
氢谱，^{1}H-NMR spectra



碳谱, ^{13}C-NMR spectra

- NMR show the polygrid have the similar chemical shift value with unit grid, and GPC with a molecular weight of 2.5×10^4 and PDI of 2.2, indicating with more than 7 repeat units in the polygrids-Th.

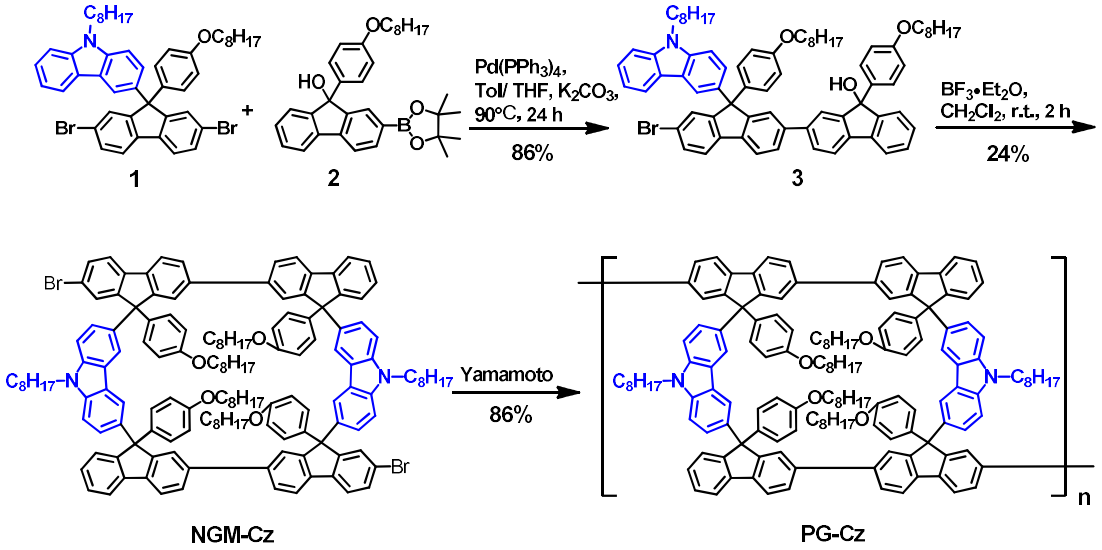
UV and PL spectra in film

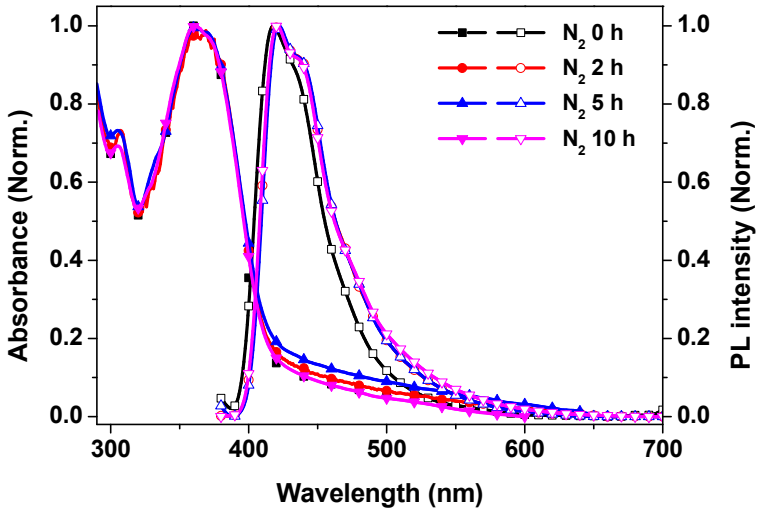


Concen（mg/mL）	λ_{abs}(nm)	λ_{pl}(nm)
1	367	422, 439
5	370	421, 438
10	363	428, 441

- Film obtained by spin-coating from the different concentration of toluene solution with a speed of 1500 rpm and a time of 30 s.

Another detailed nanosysthesis of polygrid-Cz

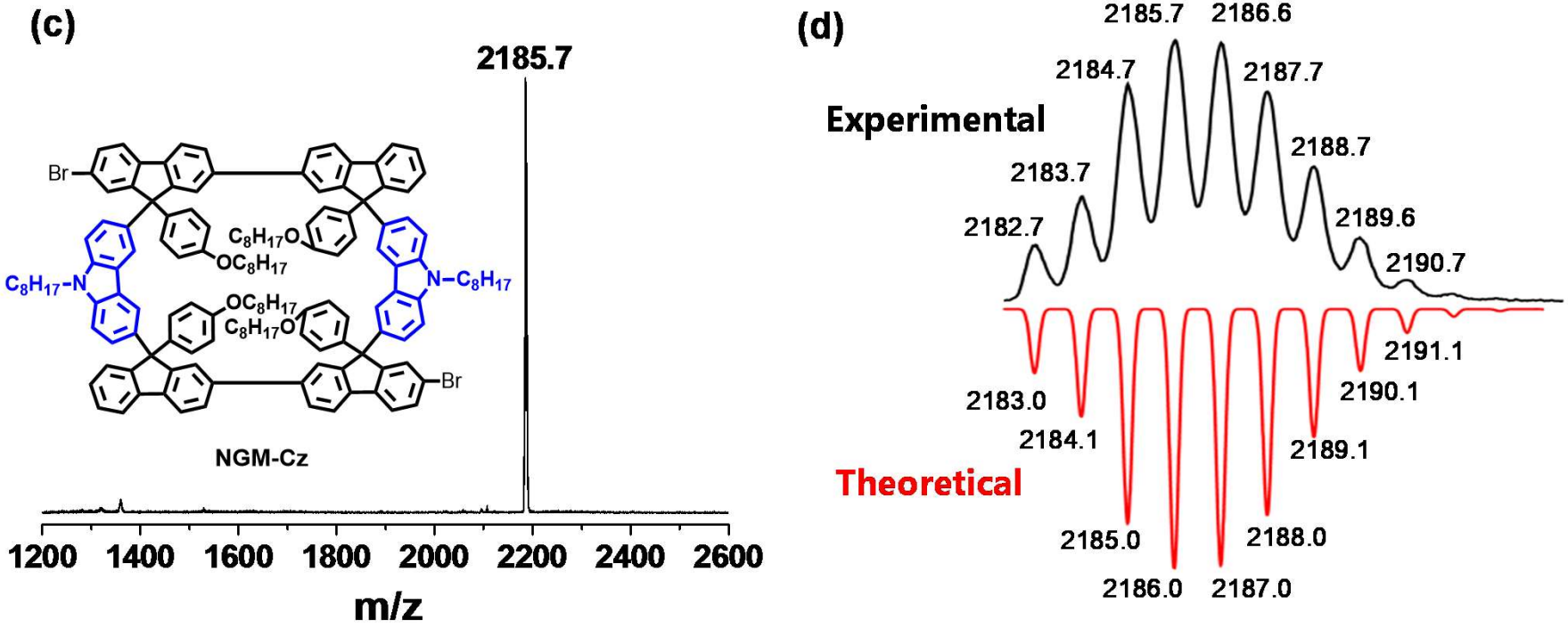




- PG-Cz with shape persistent chain backbones show excellent spectral stability.

Feng Q. Y. *et al*, C*hinese Journal of Polymer Science* **2017** 35(1), 87–97.

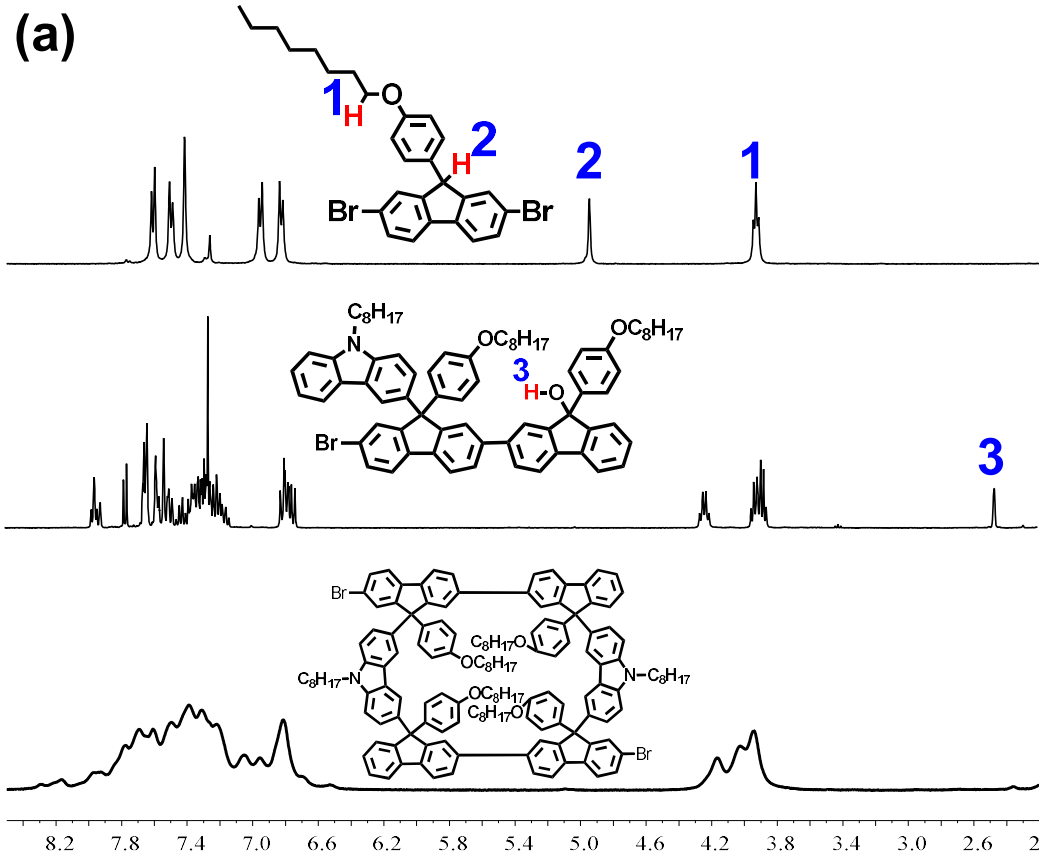
MALDI-TOF-MS of Nanomonomers

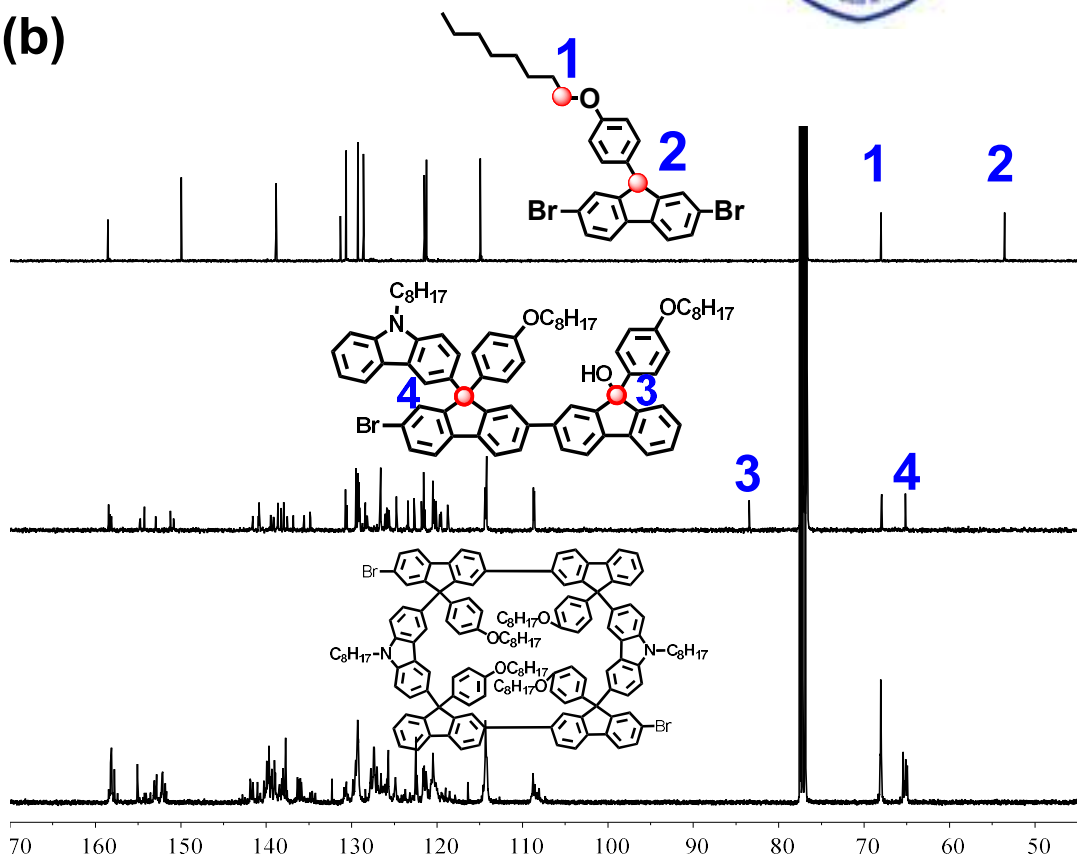


- Molecular weight of nanomonomer with 2185.7 that consistent with theoretical value

Feng Q. Y. *et al*, C*hinese Journal of Polymer Science* **2017** 35(1), 87–97.

The NMR characterization of Nanomonomers-Cz

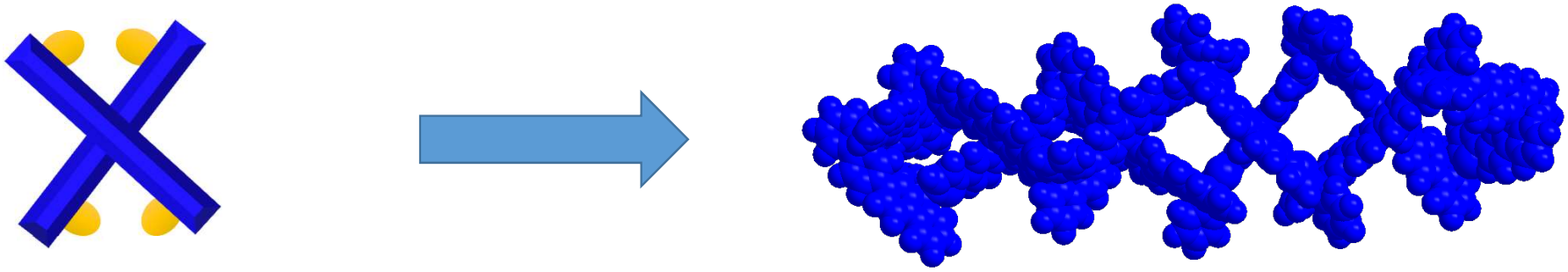




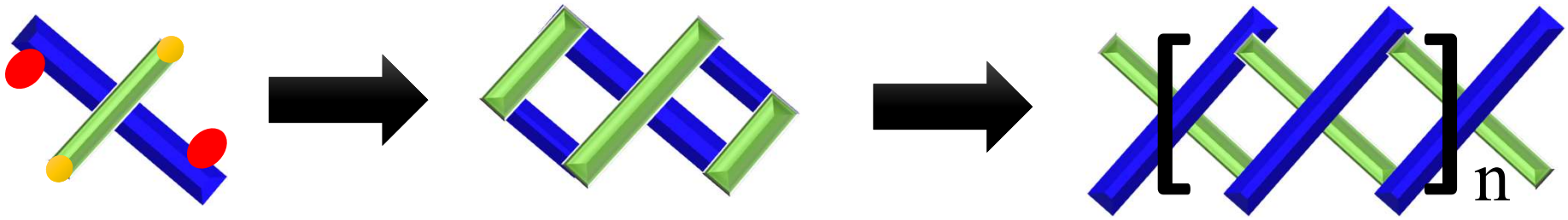
Feng Q. Y. *et al*, C*hinese Journal of Polymer Science* **2017** 35(1), 87–97.

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From X-synthon to spirodigrid and polygrids

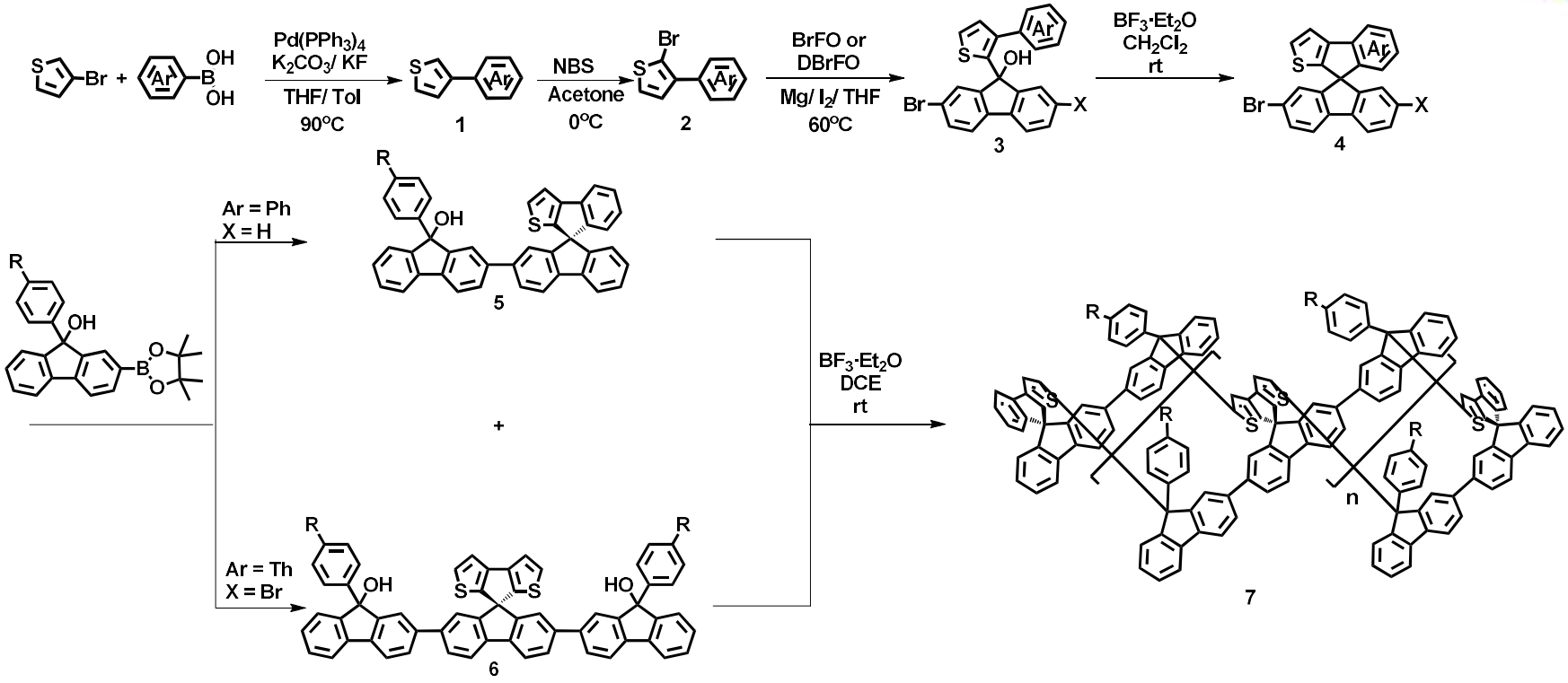


A second paradigm of spirodigrids and nanopolymers

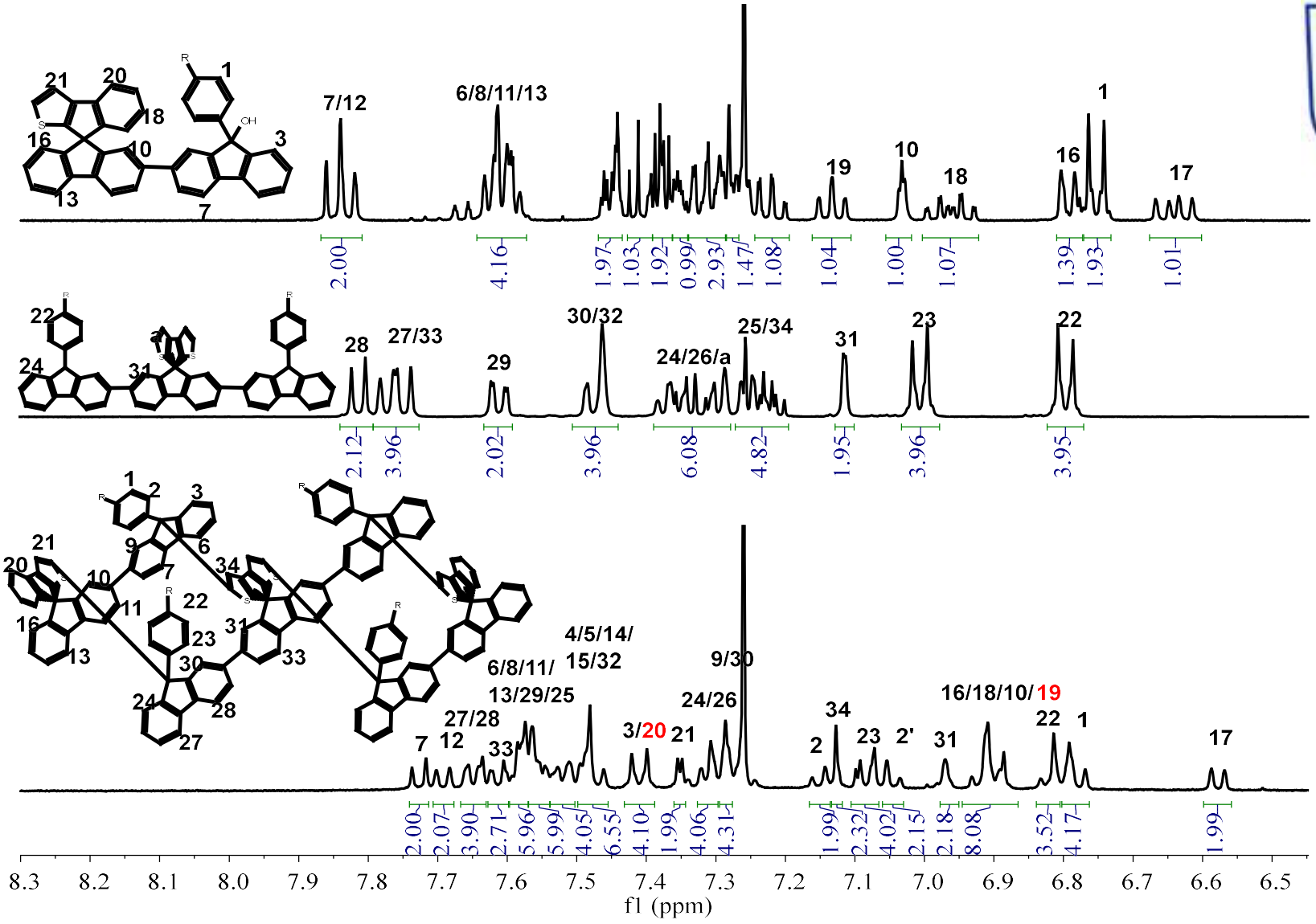


- Digrid have the key feature of extension that differ from the macrocycle dramatically.
- X-type synthons have shape geometry advantage that are favorable for the gridization for the digrids that is one type of rhombus-type nanogrids
- This pattern make possible by polymerization of A2B2-type synthon for the nanopolymers, that is , rhombus-type polygrids.

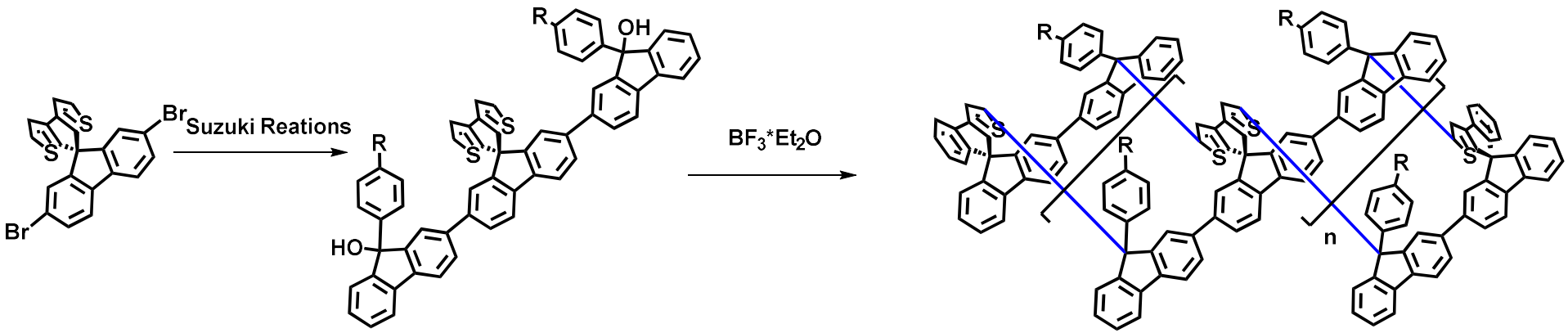
A2B2-type synthon for the spirodigrid and polygrids



- A detailed route starting from the small arenes to give the nanopolymers

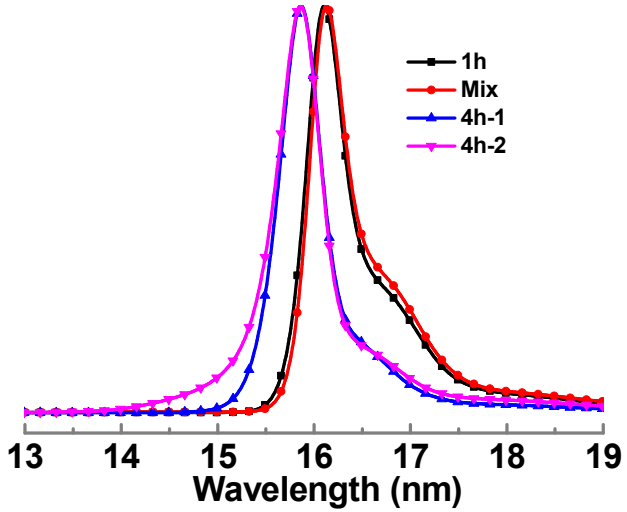

7/12
6/8/11/13
19
10
18
16
1
17
28
27/33
29
30/32
24/26/a
25/34
31
23
22
4/5/14/
15/32
6/8/11/
13/29/25
27/28
3/20
21
24/26
9/30
34
2
23
2'
31
16/18/10/19
22
1
17
7
12
33
f1 (ppm)

Polygrids from A2B2-type synthon



- To obtain spiropolygrids via the Friedel–Crafts polymerization of A2B2-type synthons at the room temperature
- We examine the polymerization time and capped synthon effects on molecular weights, including 1 hour, 1 hour with a mixture of caped synthon, 4(2-2) hours and 4 hours

GPC Measurement of Polygrid



	Mn	Mw	PDI
1h	64979	98481	1.516
Mix	62729	93219	1.486
4h-1	1.11×10^5	1.61×10^5	1.45
4h-2	9.69×10^4	2.32×10^5	2.39

The most molecular weight of spiropolygrid is near 100 k that is completely successful for the FC polymerization at the room temperature

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Nanjing University of Posts and Telecommunications

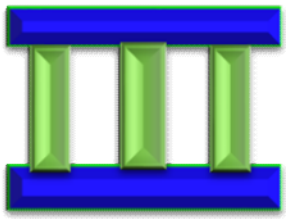
From H-synthon to Ladder-type nanogrids and nanopolymers



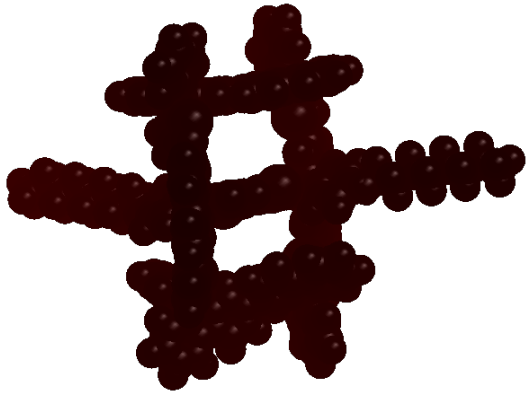
H shape[ref 16]



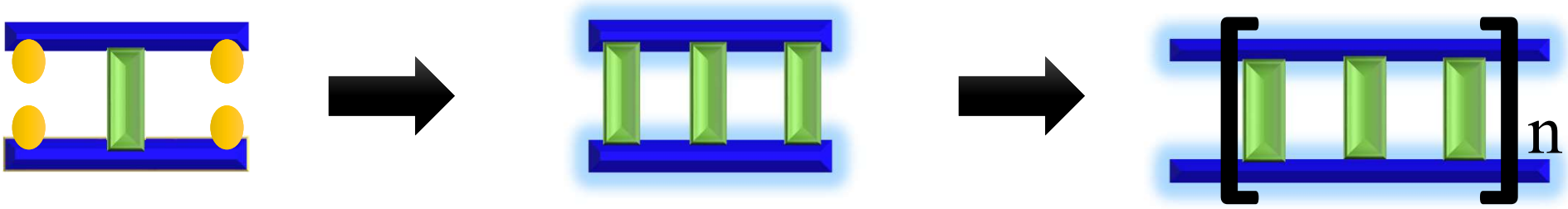
This work 口shape



日shape[ref 7]



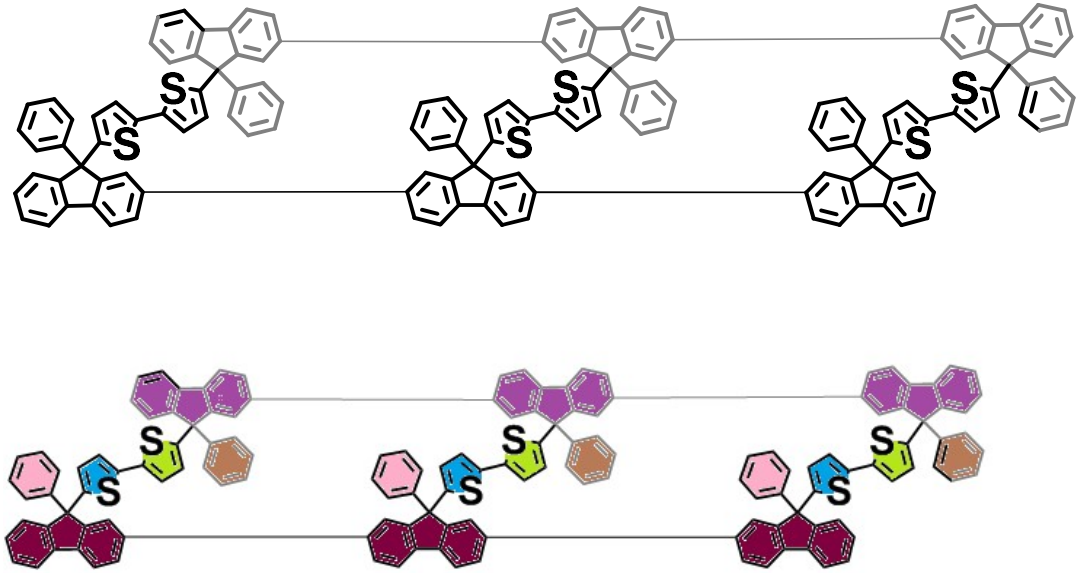
A third paradigm of fused Digrids and nanopolymers

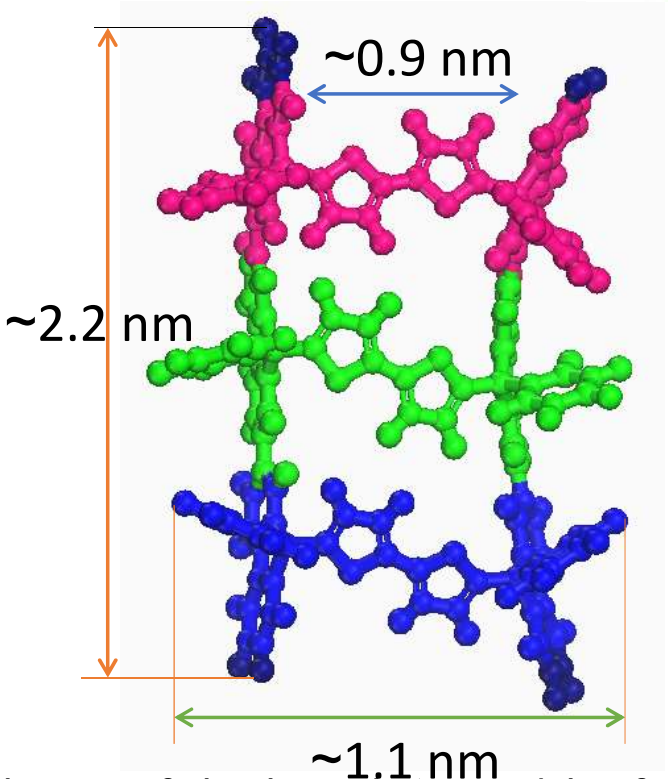


- H-type synthon with a role of covalent restriction to surport the gridization and make two-direction and four- terminal extension to give the ladder-type grids;
- H-type synthons offer one type of fused digrids that is another type of digrids after rhombus-type digrids
- The extension of H-type and digrids leads to one kind of polyladders

Wang Long et al., Org. Lett. **2014**, 16, 1748−1751

Fused grid are typical models of complex molecules

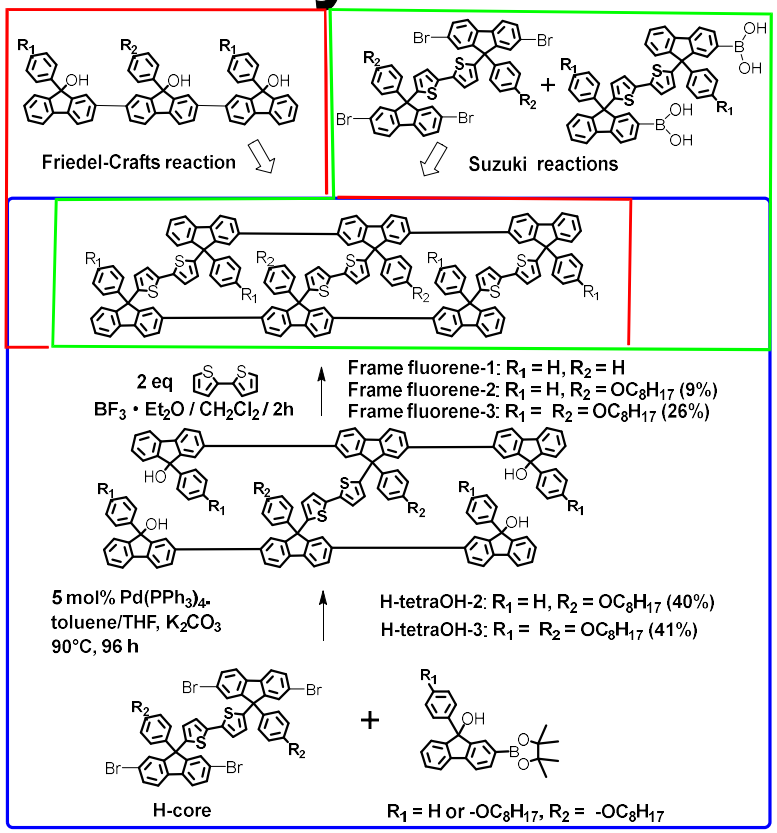


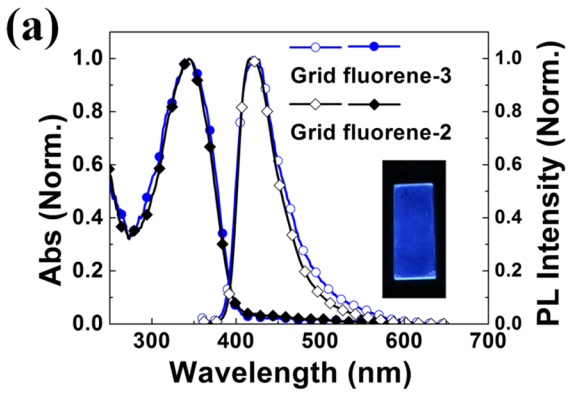


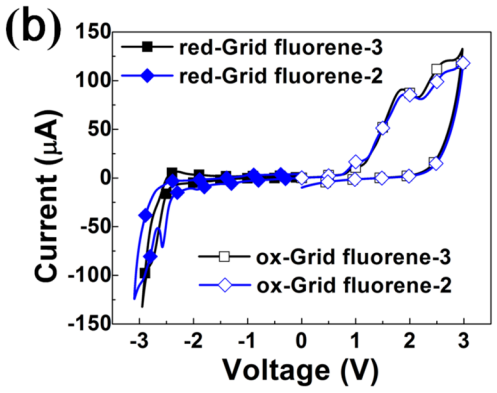
- **Fused grid** are typical models of nanomolecules with size of the length × width of 2.2 nm × 1.1 nm and two cave of less than 1 nm^2

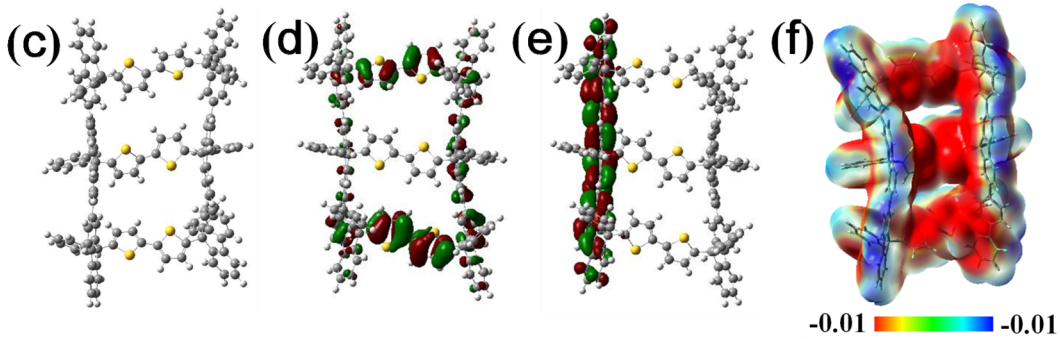
Wang Long et al., Org. Lett. **2014**, 16, 1748−1751

Friedel-Crafts Bottom-up NanoSynthesis of fused digrids





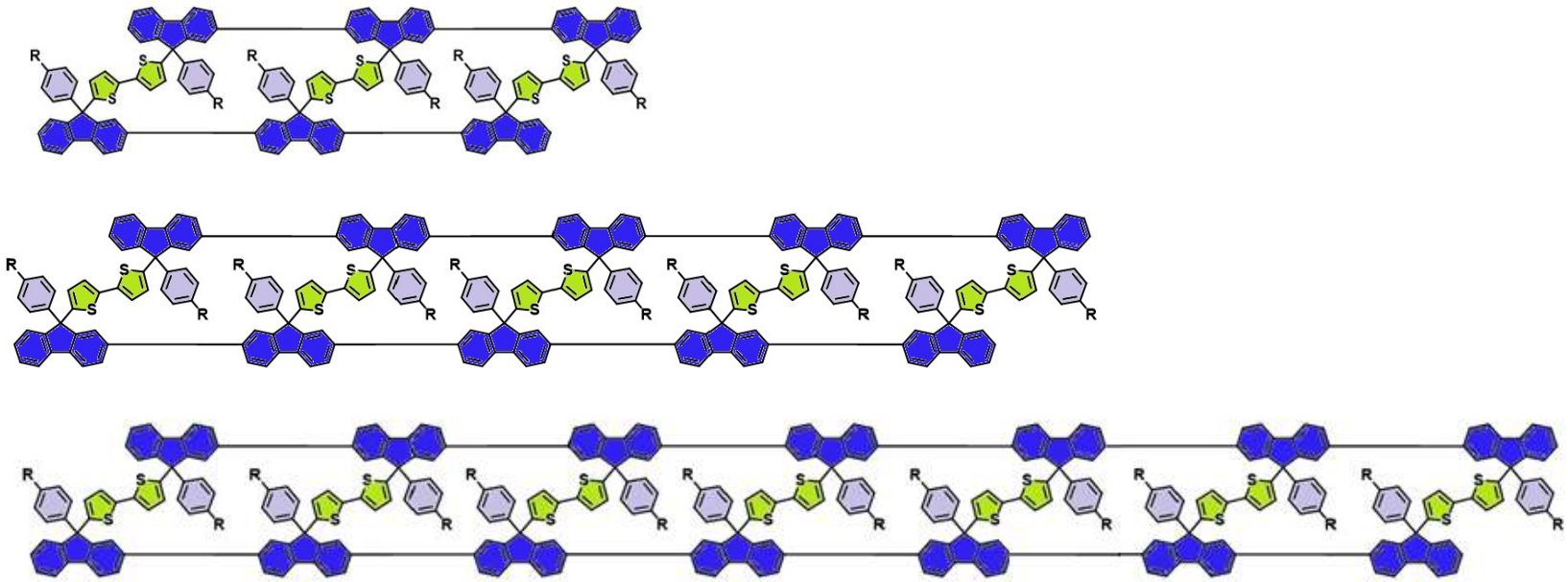




- Starting from H-shaped precursors via the alternative Friedel-Crafts reactions of fluorenols and Suzuki cross-coupling reactions with the key cyclization yield of up to 26%.

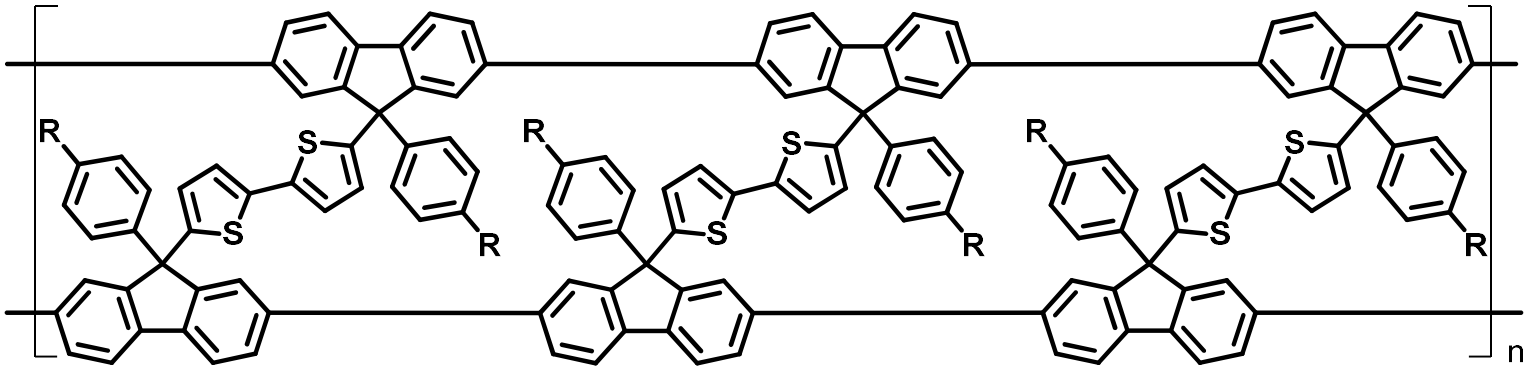
Wang Long et al., Org. Lett. **2014**, 16, 1748−1751

Step-by-step extension of polyladders



- From the square grid unit to digrid ladder, trigrid ladder and 7-node ladder by the step-by-step gridization

Challenge is still exist to synthesize polyladders via polymerization



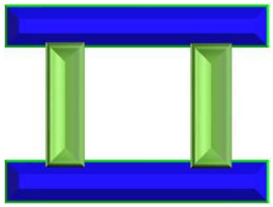
- Until now, we demonstrated the oligonanoladders, but the polyladder is still difficult to obtain by the design of effective synthons and pathway in high yields.

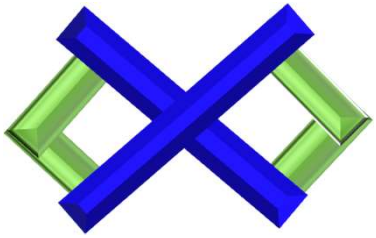


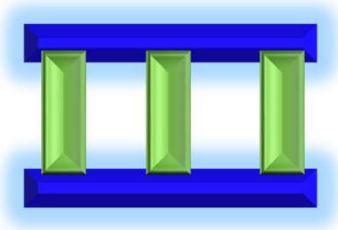
南京郵電大學
Nanjing University of Posts and Telecommunications

Summary and Outlooks

Summary-Grid[n]Fluorene make New DAO

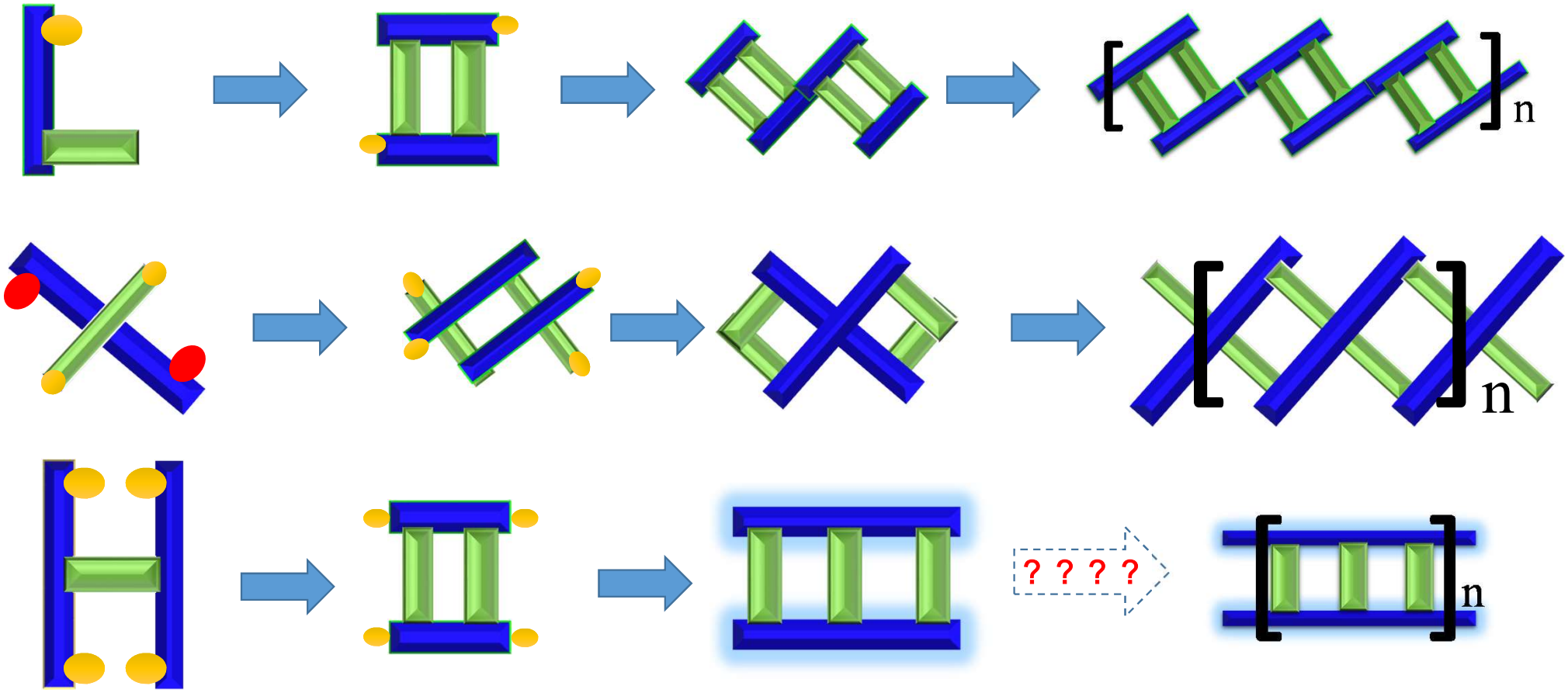




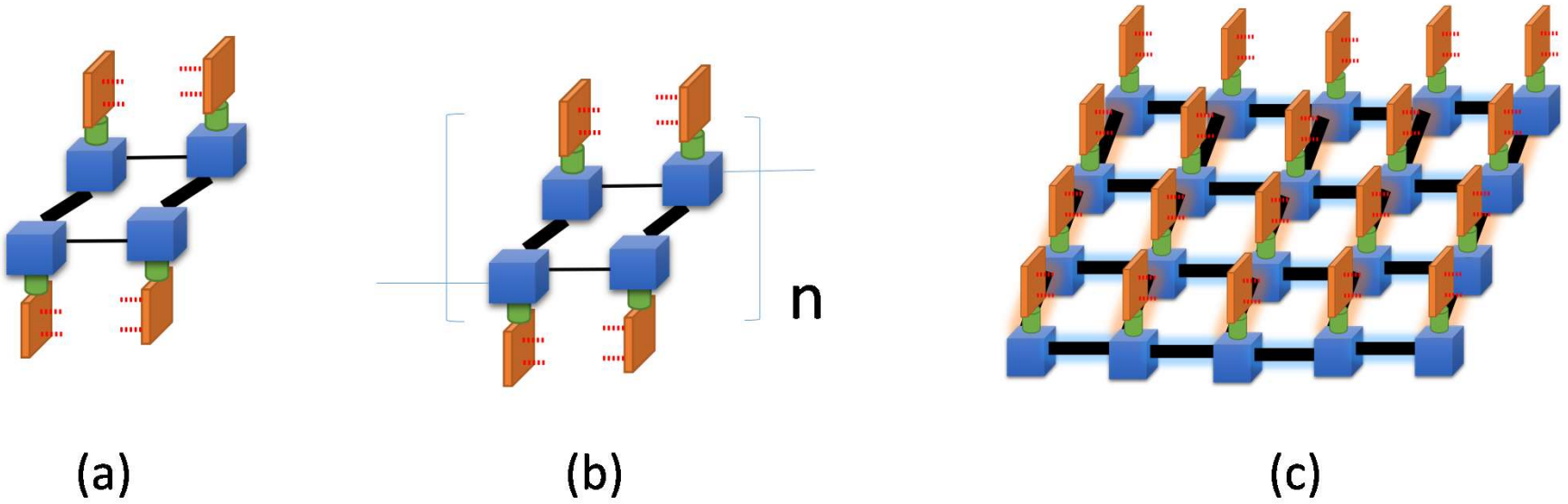


- We proposed nanogrids and polygrids in order to integrate various functon, such as exciton-electron-mechanon-ion coupling systems into single-molecule cells
- Nanogrid unit and digrids have been achieved with the feature of fluorene as a versatile building blocks.

Outlook-I: To challenge the polyladders



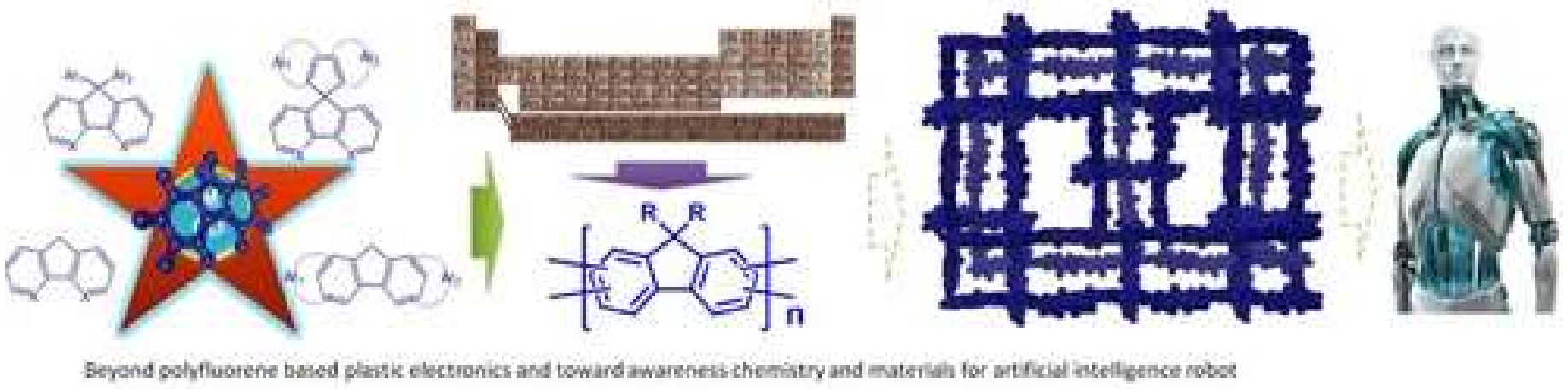
Outlook-II: Organic Supramolecular Nanopolymers (OSNPs)



- Supramolecular nanogrids with potentially smart and multifunctional features as well as self-assembly and other function groups will be introduced into grids.

Xie, L.-H. and Huang, W. (2016) Supramolecular Steric Hindrance at Bulky Organic/Polymer Semiconductors and Devices, in Non-covalent Interactions in the Synthesis and Design of New Compounds (eds A. M. Maharramov, K. T. Mahmudov, M. N. Kopylovich and A. J. L. Pombeiro), John Wiley & Sons, Inc, Hoboken, NJ. doi: 10.1002/9781119113874.ch25

Outlook-III: Nanogrids pushing toward the era of consciousness



- Xie L-H, Huang W.*et al.* Prog Polym Sci 2012, 37, 192- 1264 (Highlighted by advances in engineering);
- https://advanceseng.com/electrical-engineering/polyfluorene-based-semiconductors-combined-with-various-periodic-table-elements-for-organic-electronics

Advances In ENGINEERING



Members from Center for Molecular Systems and Organic Devices (CMSOD@IAM): Wei Huang (Academician); Prof. YI Ming-Dong, QIAN Yan, SHI Nai-En, SONG Juan; Staff: LIU Yuyu, Wei Xue, Yongzhong Chang; ZHAO Jian-Feng, YIN Cheng-Rong, LIN Jin-Yi, **Ying Wei**, **FENG Qiangyou**, BIAN Linyi, ZHAO Wei; PH D. SUN Mingli, LIN Zong-Qiong, LI Wei-Jie, LI Wen, LING Haifeng, LIU Bin, OU Changjin, WANG Laiyuan, YU Yang…….

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