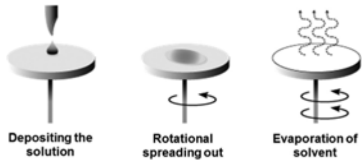
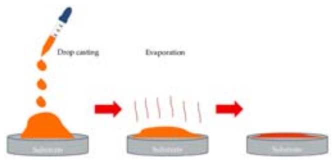
Paracyclophane derivatives and thin film coating via CVD process

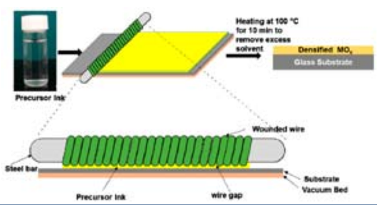
Department of Chemical Engineering and Applied Chemistry
Chungnam National University

Polymeric films onto surfaces

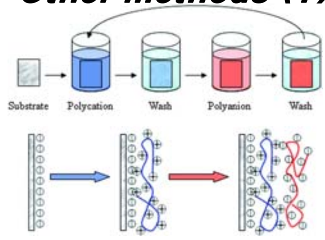
Conventional methods

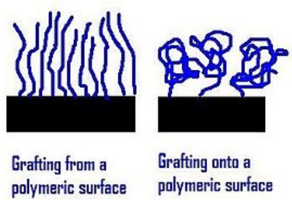






Other methods (?)





I. Vapor Deposition Polymerization

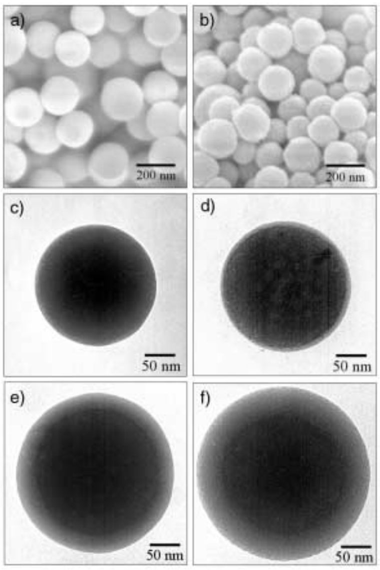
Advantages of Vapor Deposition Polymerization

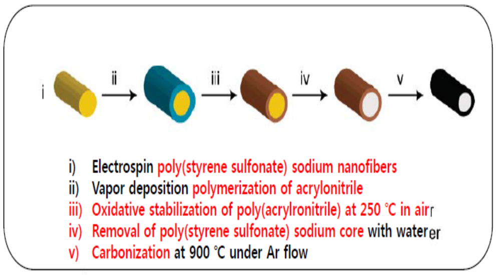
- **No Solvent (Environmental Friendly)**
- **No limitation on Monomers or Materials**
- **No limitation on surfaces (materials, morphology)**
- **Relatively Easy Process**
- **Good Processibility**
- **Conformal Coating**

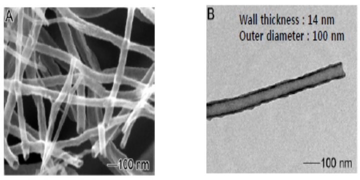
iCVD, oCVD, pyrolysis CVD, Vapor Deposition Polymerization

- **K. Gleason (MIT)**
- **J. Lahann (Michigan)**

Particle Coating

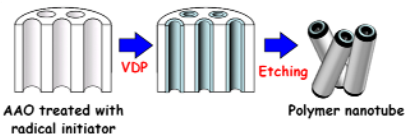


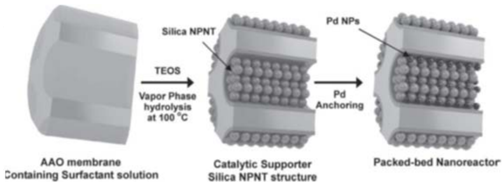




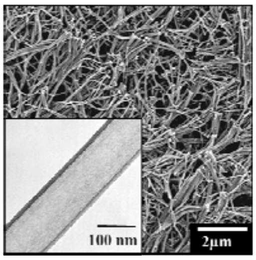
Once upon a time…

❖ My works about CVD in the past

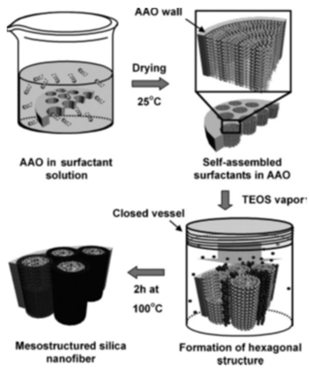




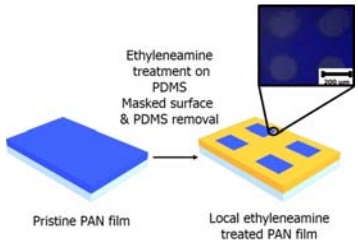
small 2010, *6*, No. 21, 2378–2382



Adv. Mater. 2006, *18*, 2216–2219

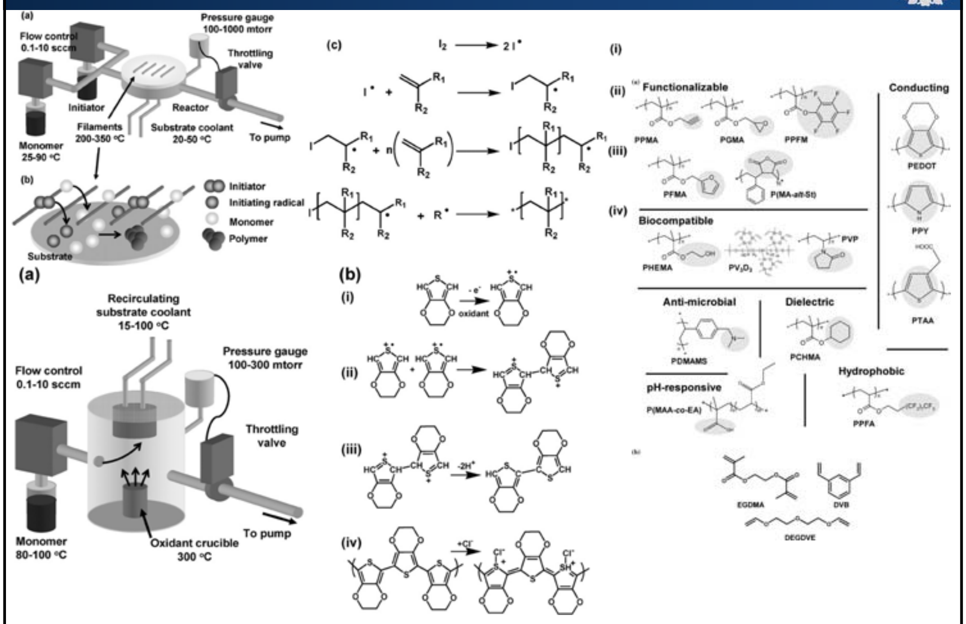


small 2008, 4, No. 11, 1945–1949

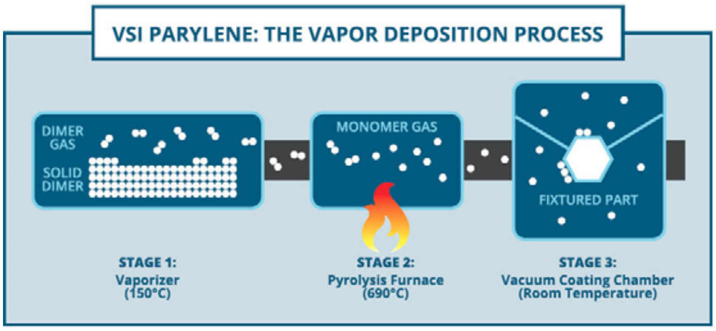


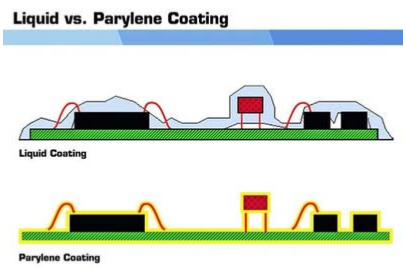
Macromol. Rapid Commun. 2015, *36*, 1192−1199

iCVD/oCVD

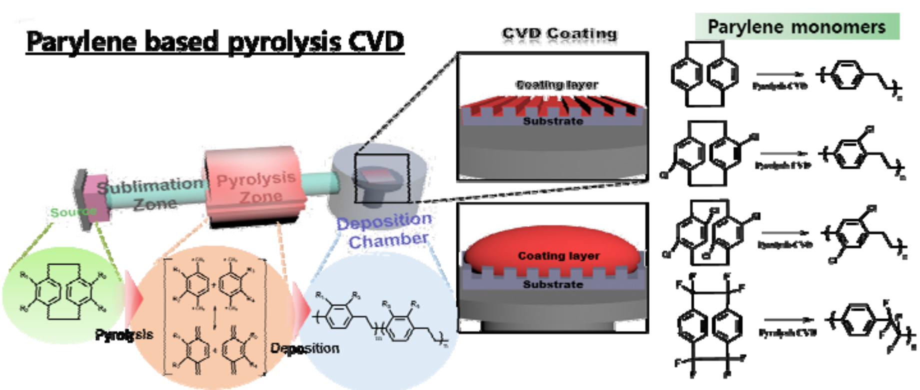


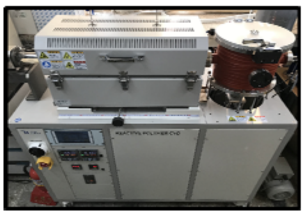
Parylene Coater





Parylene based pyrolysis CVD

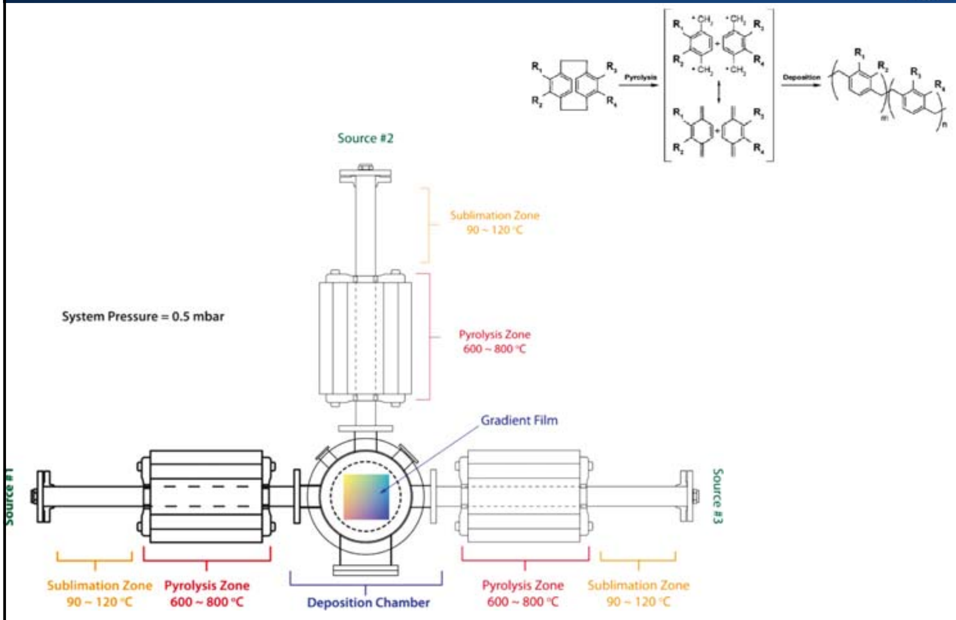


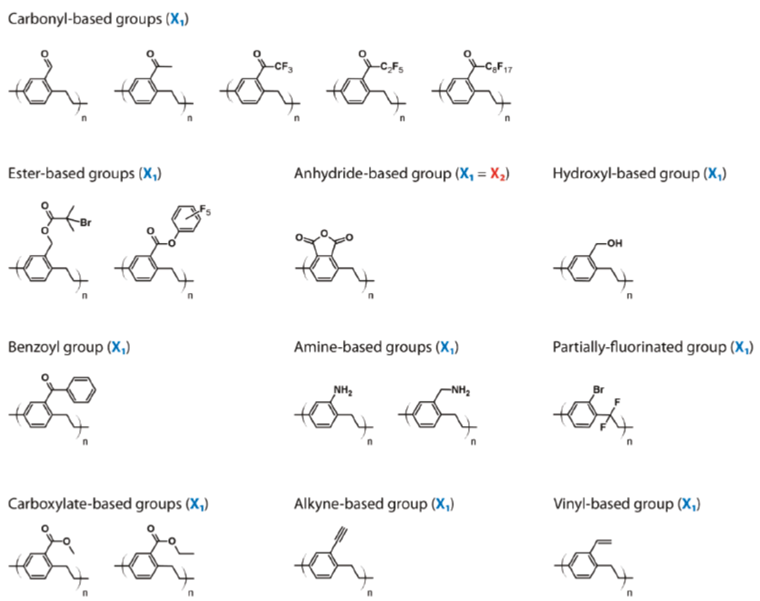


- ✓ 균일하고 얇은 코팅막 형성 및 피코팅체의 형상의 제한 없음
- ✓ 우수한 내식성 및 내화학성
- ✓ 우수한 절연성 및 낮은 유전률과 유전계수
- ✓ 다양한 관능화를 통한 고기능성 박막 고분자 코팅
- ✓ 박막 두께 조절 용이

8

p-cyclophane





REVIEW

Hall of Fame Article

ADVANCED MATERIALS INTERFACES

www.advmatinterfaces.de

Functionalization of Poly(*para*-xylylene)s—Opportunities and Challenges as Coating Material

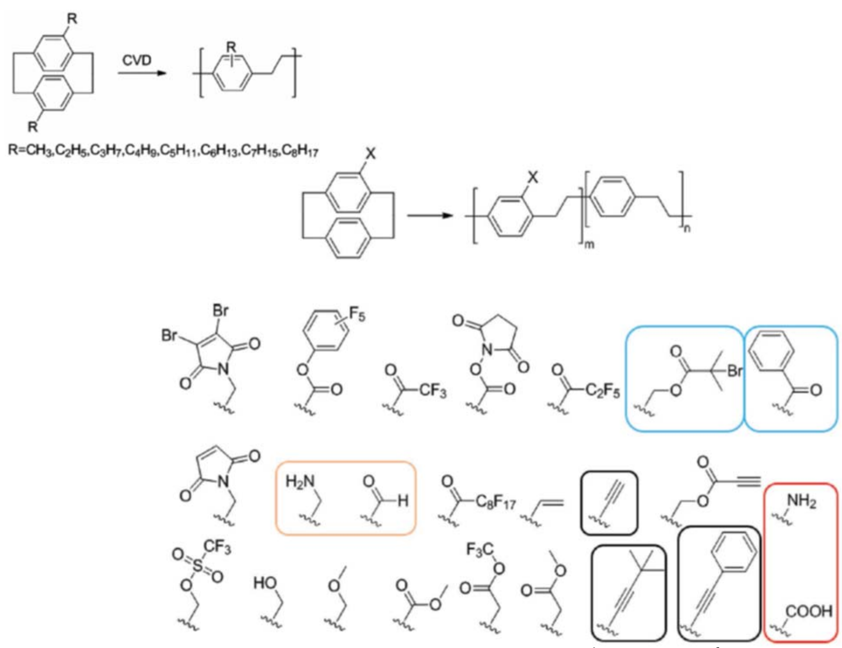
*Tobias Moss and Andreas Greiner**

The chemical vapor deposition (CVD) of poly(*para*-xylylene)s (PPX) is an enabling technology for materials design as well as for numerous high-performance applications. Additionally, PPX possesses of a unique set of structure–property relationships that can be tuned over a wide range. Different strategies vary from functionalization of the most used precursor [2.2] paracyclophane to the testing of new precursors and the copolymerization with various monomers. In this review, some recent developments on synthesis and properties of this unique class of polymers, the PPX, are reported.

systems,[14–16] organic light-emitting diodes,[17] or in biological and medical applications.[18–20] A relatively new area in the PPX research is the formation of reactive coatings. This can be achieved by the introduction of functional groups that are able to react in polymer analogous reactions.[21–23]

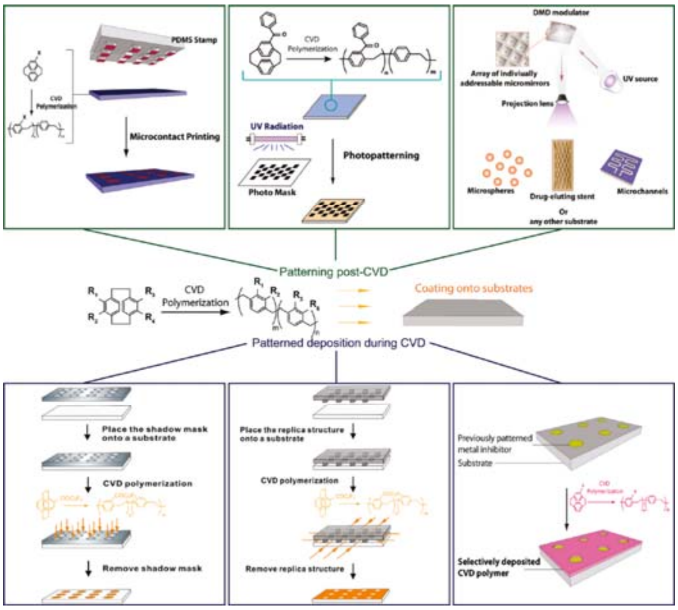
This review should also provide an overview of the opportunities that especially functionalized PPXs made by CVD provide. First, some general remarks and examples of PPX made by CVD will be given before functionalized PPX will be

Adv. Mater. Interfaces **2020**, *7*, 1901858

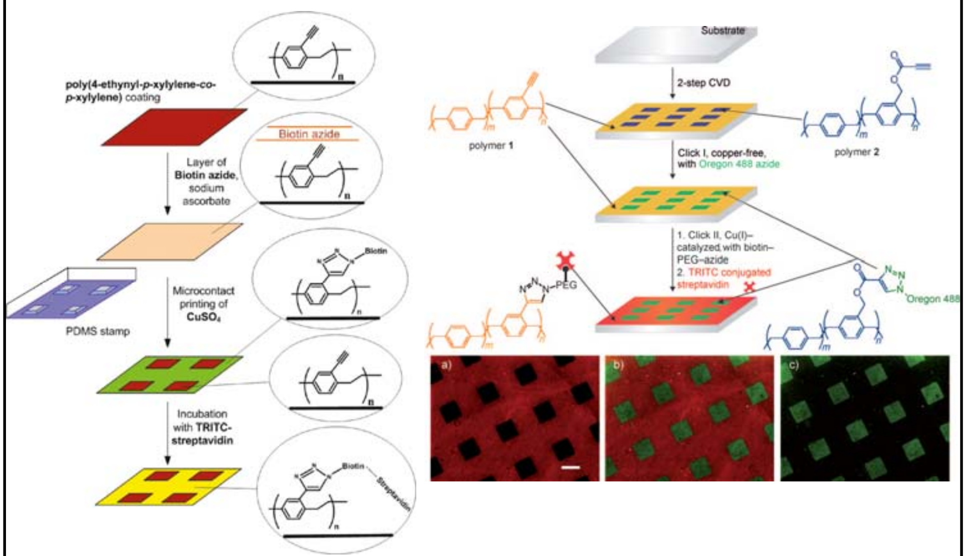


Adv. Mater. Interfaces **2020**, *7*, 1901858

CVD in Nanoscience- surface patterning

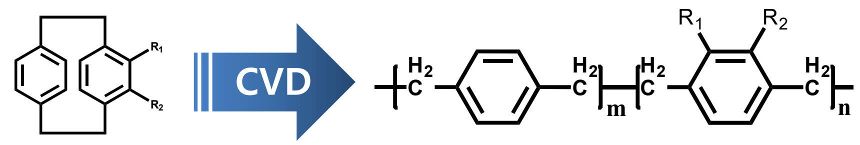


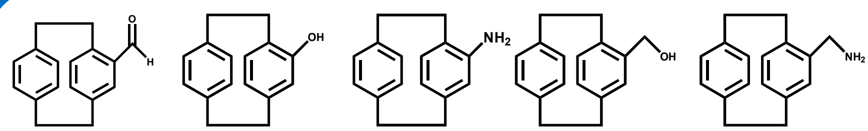
Can do many things with Simple Chemistry!!!



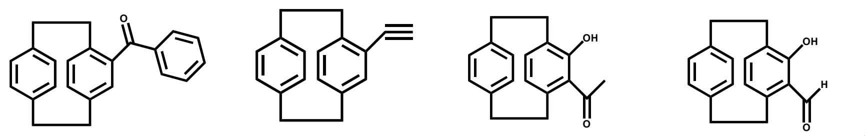
Currently Available Monomers in our Lab

Monomer Library



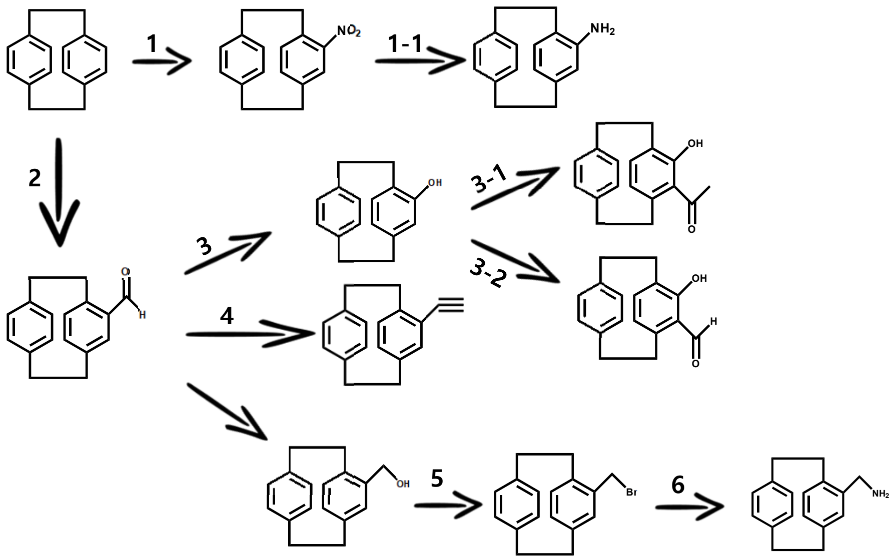


Aldehyde | Hydroxy | Amino | Hydroxy methyl | Amino methyl

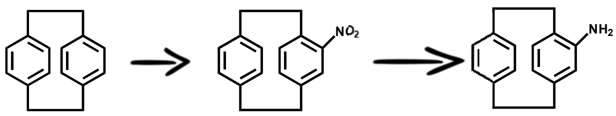


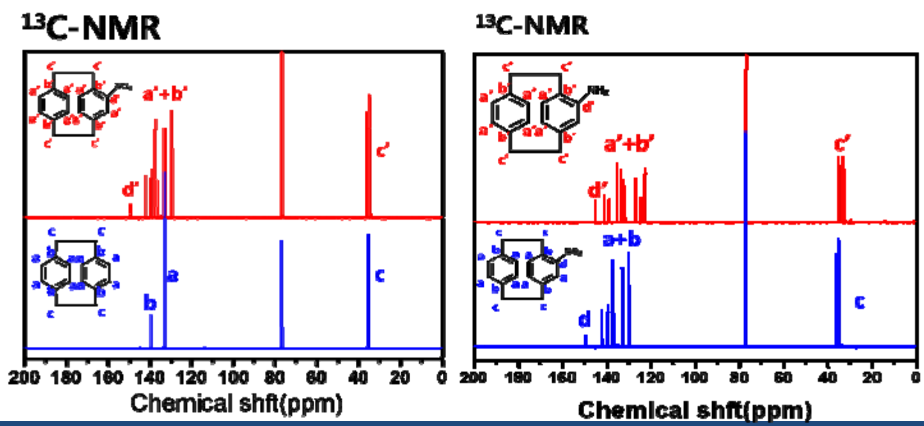
Benzoyl | Ethynyl | Acetyl, Hydroxy | Salicylaldehyde

Functionalized Parylene

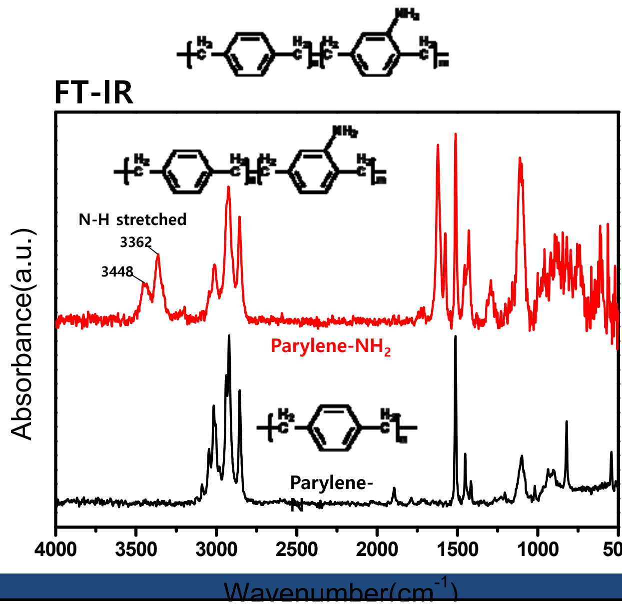


Amine

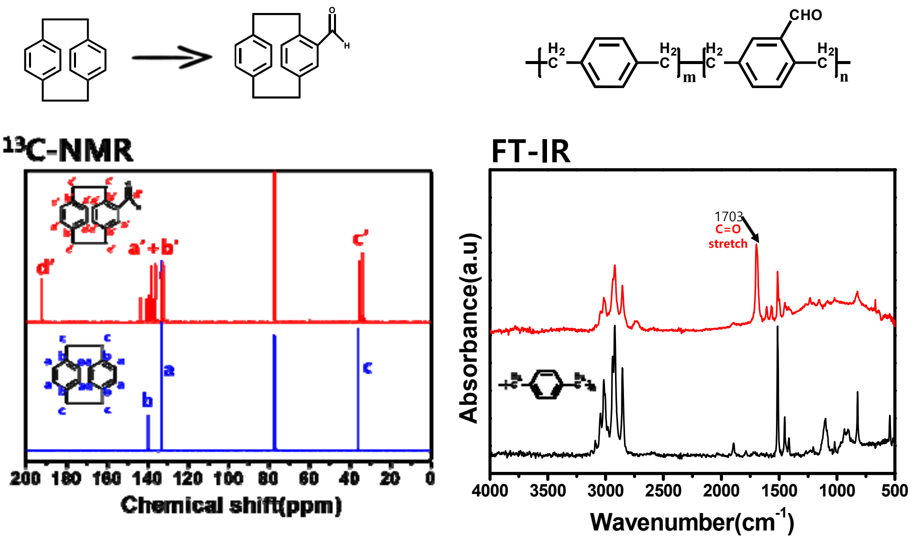




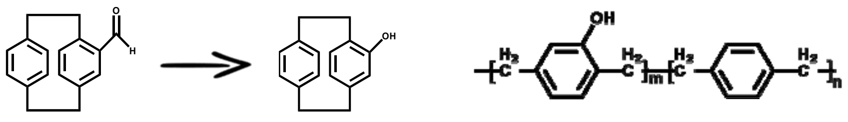
Amine



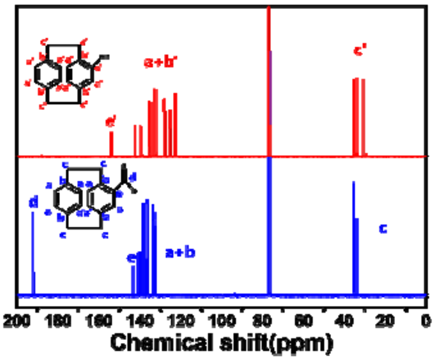
Aldehyde

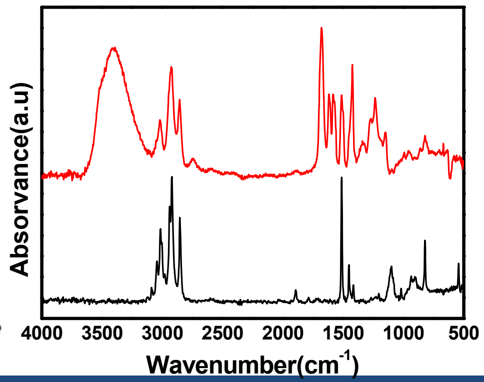


Hydroxyl

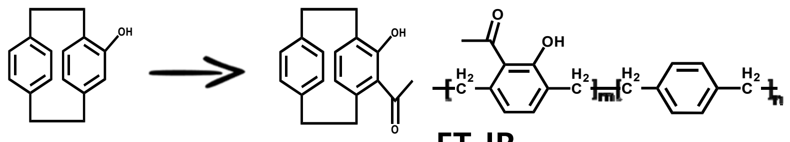


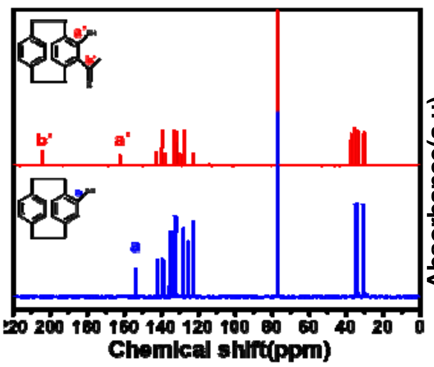
^{13}C NMR



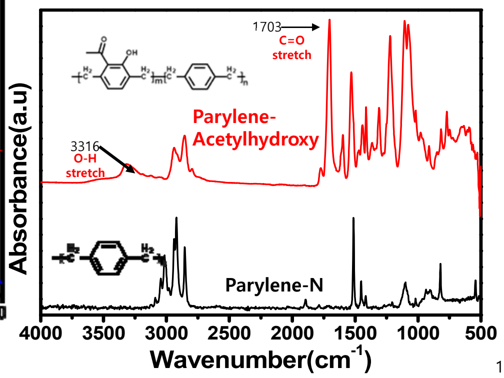


Dual (OH, Ketone)



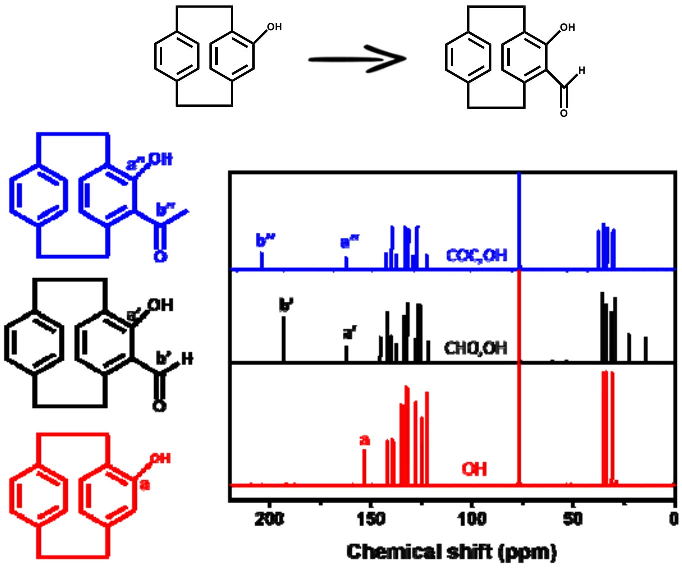


FT-IR

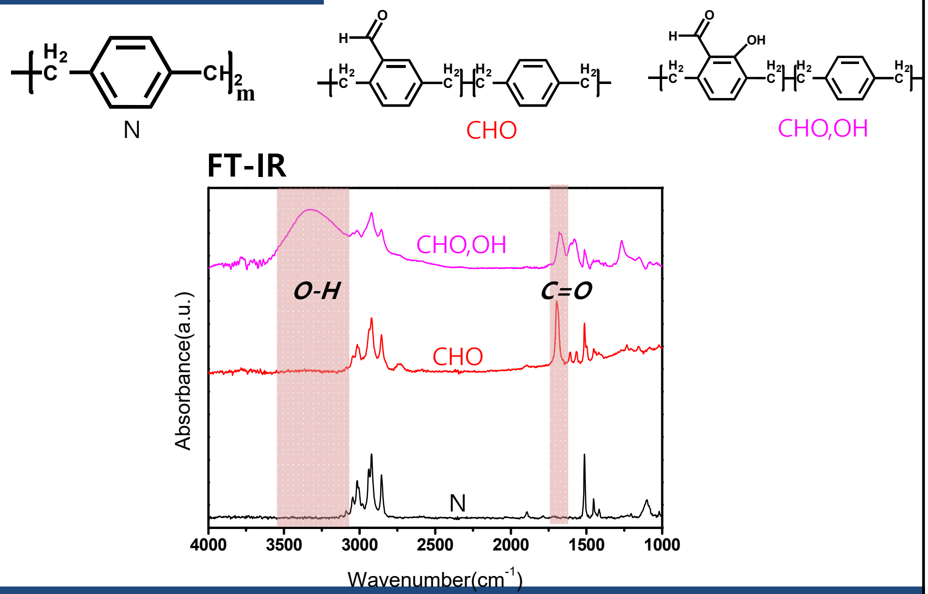


16

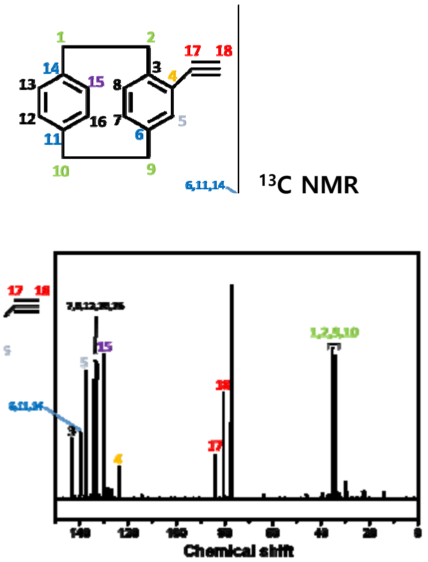
Dual (Salicyl Aldehyde)

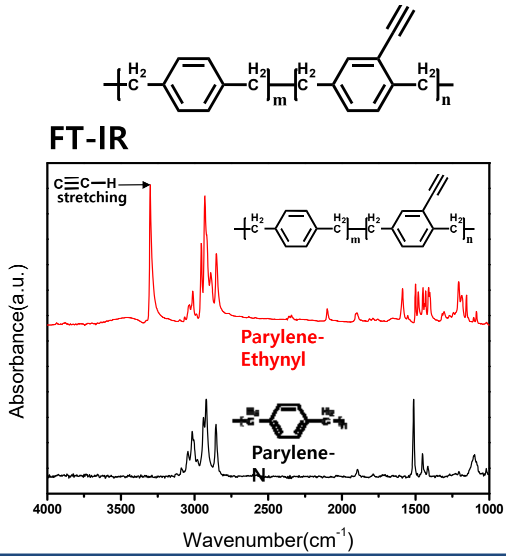


Dual (Salicyl Aldehyde)



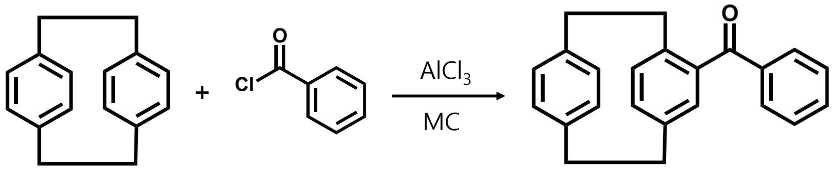
Alkyne



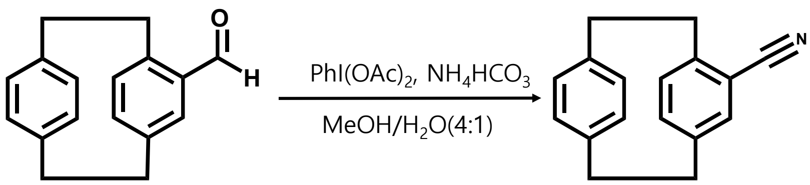


Benzoyl, Cyanide

<Benzoyl Parylene>

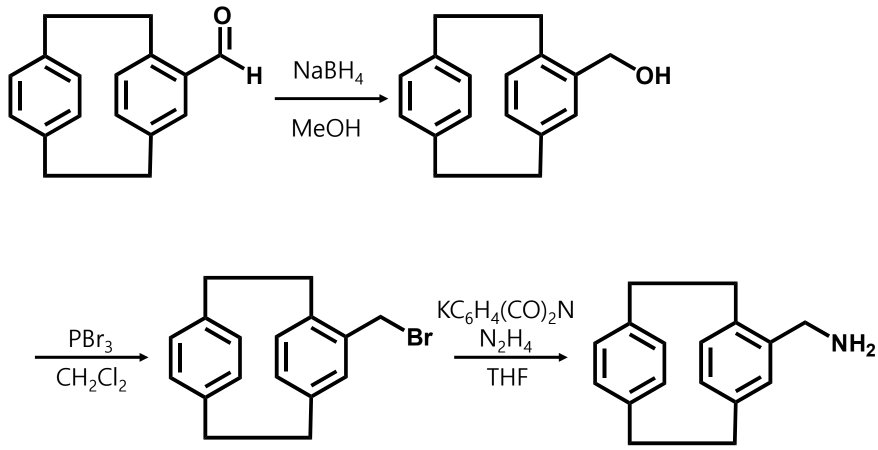


<Cyanide Parylene>

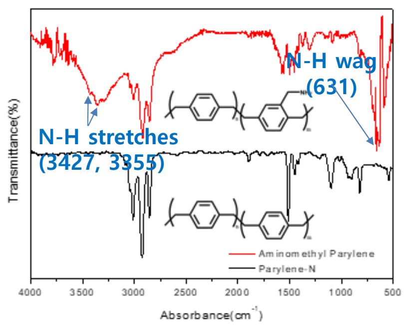


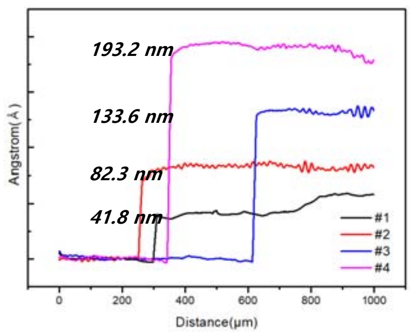
Methyl amino, Methyl hydroxyl

<Aminomethyl Parylene>



Aminomethyl Parylene

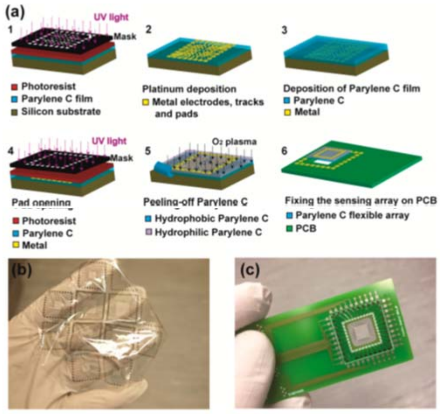


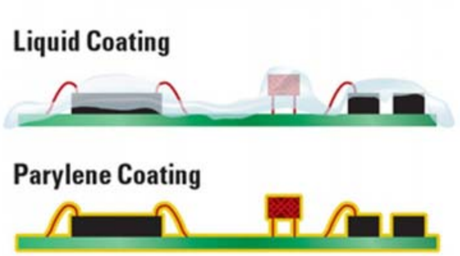


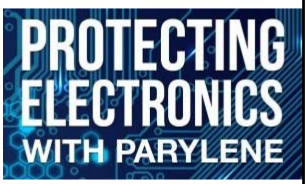
Gate dielectric Layer

Parylene works in Electronics

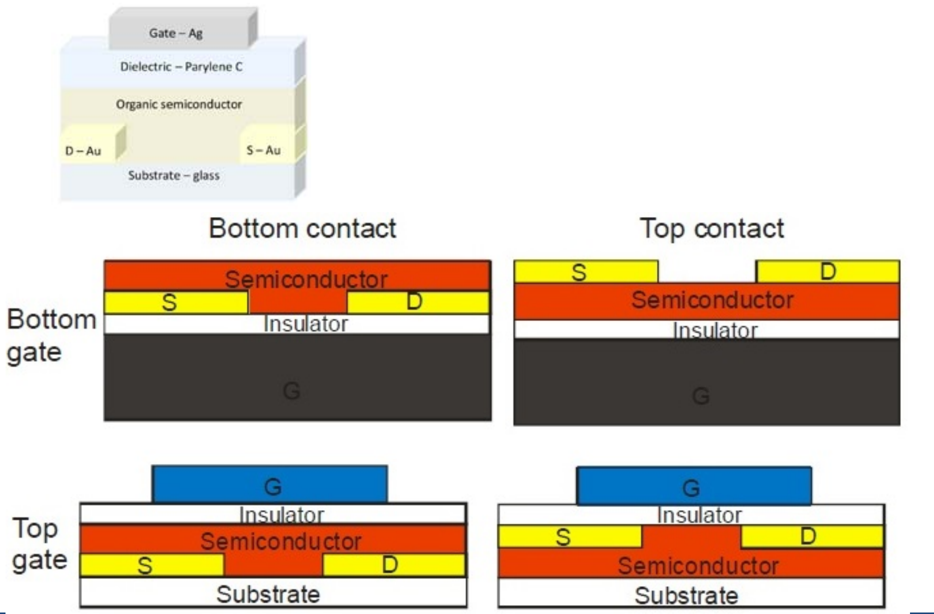
Majors are Encapsulation layer, Protection, and some of Dielectric layers in electronics!







Basic of Basic for Thin Film Field Effect Transistor



Issues in Dielectric layers?

- ✓ *Low operation voltage*
- ✓ *High capacitance with Perfect Thin Film*

- ✓ *Low leakage current*
- ✓ *Stability*
- ✓ *Reliability*
- ✓ *Flexibility*

- *Chemical Composition*
- *Molecular Design*

- *Film Properties*
- *Processing Optimization*

Parameters

-Monomer structure

-Molecular weight and MW distribution

-Density of film (number of pinhole)

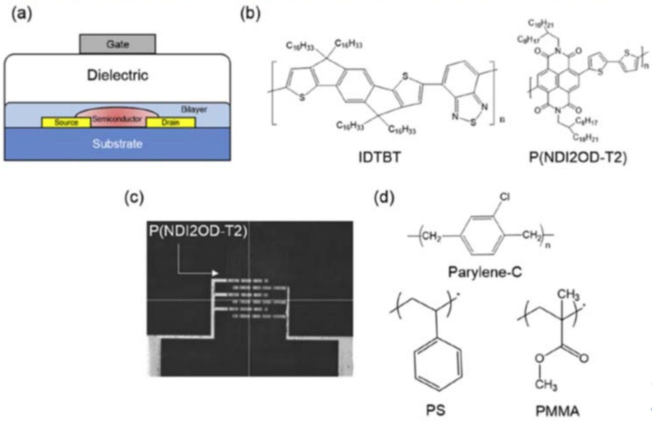
-No Chemical reaction with organic semiconductors

Previous works with Parylene as dielectric layer

Parylene based bilayer flexible gate dielectric layer for top-gated organic field-effect transistors

Eul-Yong Shin [a], Eun-Young Choi [b, **], Yong-Young Noh [a, *]

[a] Department of Energy Materials Engineering, Dongguk University, 30, Pildong-ro 1-gil, Jung-gu, Seoul, 04620, Republic of Korea
[b] Korea Atomic Energy Research Institute, Daedoek-daero 989-111, Yuseong-gu, Daejeon, 34057, Republic of Korea



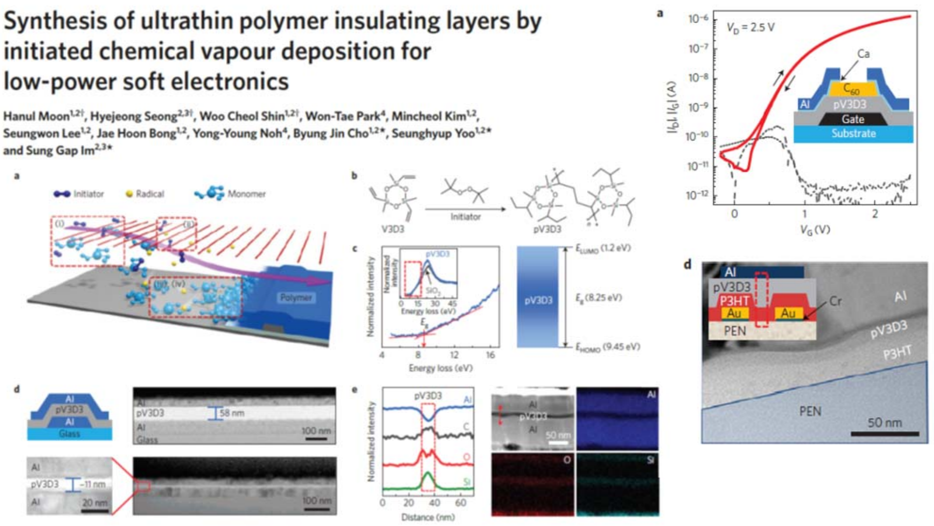
Organic Electronics 46 (2017) 14–21

Previous works with CVD polymer films in Dielectric

ARTICLES
PUBLISHED ONLINE: 9 MARCH 2015 | DOI: 10.1038/NMAT4237
nature materials

Synthesis of ultrathin polymer insulating layers by initiated chemical vapour deposition for low-power soft electronics

Hanul Moon[1,2†], Hyejeong Seong[2,3†], Woo Cheol Shin[1,2†], Won-Tae Park[4], Mincheol Kim[1,2], Seungwon Lee[1,2], Jae Hoon Bong[1,2], Yong-Young Noh[4], Byung Jin Cho[1,2*], Seunghyup Yoo[1,2*] and Sung Gap Im[2,3*]



In addition to High dielectric constant, high capacitance, low leakage current, operation stability…etc

→ Interfacial Optimization with f- Parylene
→ Obtaining InGaZnO (CVD based) semiconductor devices with Top or Bottom gate from

Cowork with Prof. Kim H

CNU 충남대학교
CHUNGNAM NATIONAL UNIVERSITY

2018

101. Hyoung-Do Kim, Jong-Heon Kim, Kyung Park, Jozeph Park*, and **Hyun-Suk Kim***, *corresponding author, "Highly Stable Thin-Film Transistors based on Indium Oxynitride Semiconductor" (In preparation).

100. Jong Heon Kim, Kyung Park, Su-Ho Cho, Yun Chang Park, Jung Hyun Kim, Chunjoong Kim, Il-Doo Kim, Jozeph Park, and **Hyun-Suk Kim***, *corresponding author "Effect of annealing temperature on the interfacial interaction of $LiNi_{0.5}Mn_{1.5}O_4$ thin film cathode with stainless-steel substrate", Thin Solid Films (Under review).

99. Dae Soo Park, Won Seok Choi, Hyunil Kang, Seung-Wook Baek,**Hyun-Suk Kim**, Abul K. Azad, Jun-Young Park, Jung Hyun Kim*, "X-ray Photoelectron Spectroscopic Study of Impregnated $La_{0.4}Sr_{0.6}Ti_{0.8}Mn_{0.2}O_{3±d}$ Anode Material for High Temperature-Operating Solid Oxide Fuel Cell", Ceramics International (Under review)

98. Kyung Park, Jong-Heon Kim, Hyun-Woo Park, Ju-Heyuck Baeck, Jonguk Bae, Kwon-Shik Park, Inbyeong Kang, Kwun-Bum Chung, **Hyun-Suk Kim***, and Jang-Yeon Kwon*, *corresponding author, "Highly Reliable Amorphous In-Ga-Zn-O Thin Film Transistors Through the Addition of Nitrogen Doping", IEEE Transactions on Electron Devices (Under review).

97. Ho-Hyun Nahm, Kanghoon Yim, **Hyun-Suk Kim**, and Seungwu Han, "Electron Effective Mass Increased by Interstitial Impurities in Zinc Nitride: A Band-Gap Uncertainty Theory", Advanced Materials (Under review).

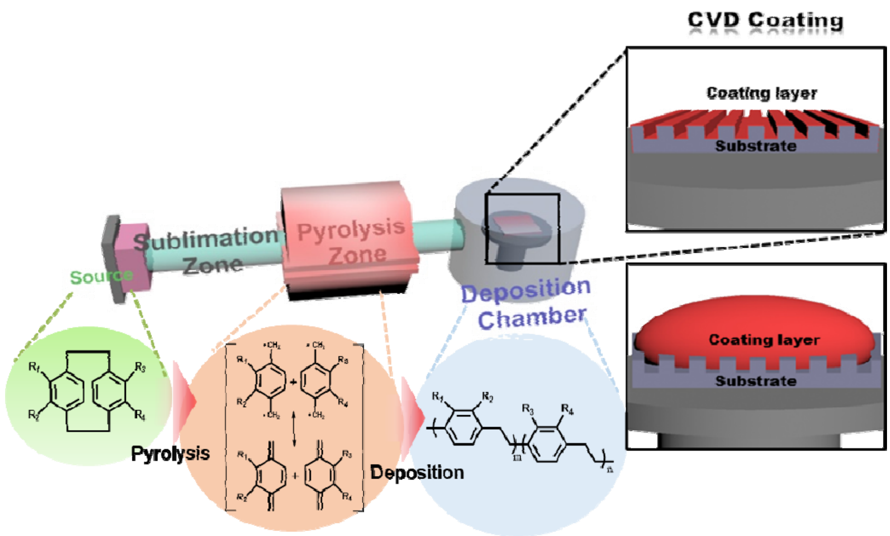
96. Jin Young Kim, Yu Kyoung Ryu, Javier Martinez, Marta Tello, Ramses V. Martinez, **Hyun-Suk Kim**, Yun Tang, Erio Tosatti, Ricardo Garcia, and Francesco Stellacci, "Nano 'crystal radio' receivers as a femtoWatts tunable infrared room-temperature photodetectors", Nature Materials (Under review).

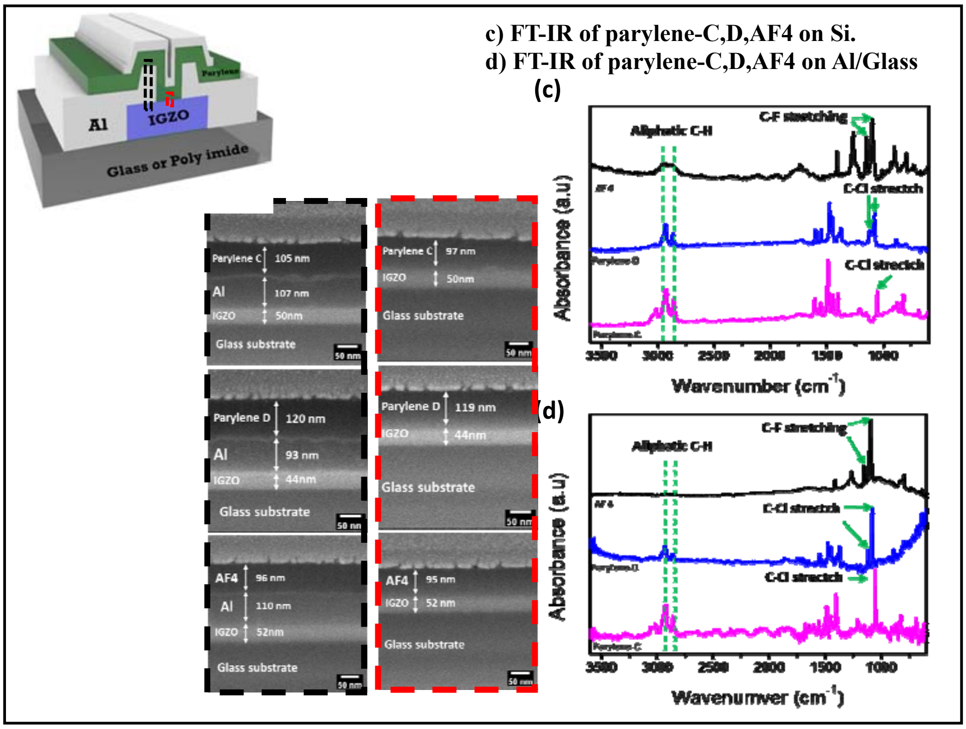
2017

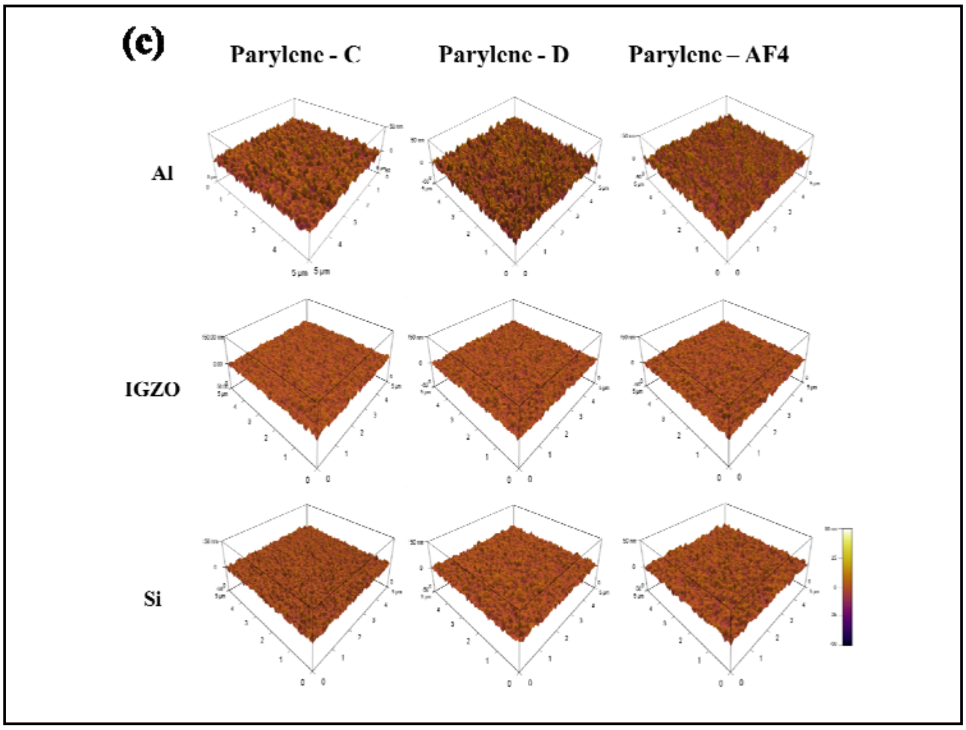
95. Jong Heon Kim, Hyoung-Do Kim, Dae-Gyu Yang, **Hyun-Suk Kim***, *corresponding author, "High-Voltage $LiNi_{0.5}Mn_{1.5}O_4$ Thin Film Cathode Prepared by RF Sputtering", ECS Transactions, vol. 80 (Accepted).

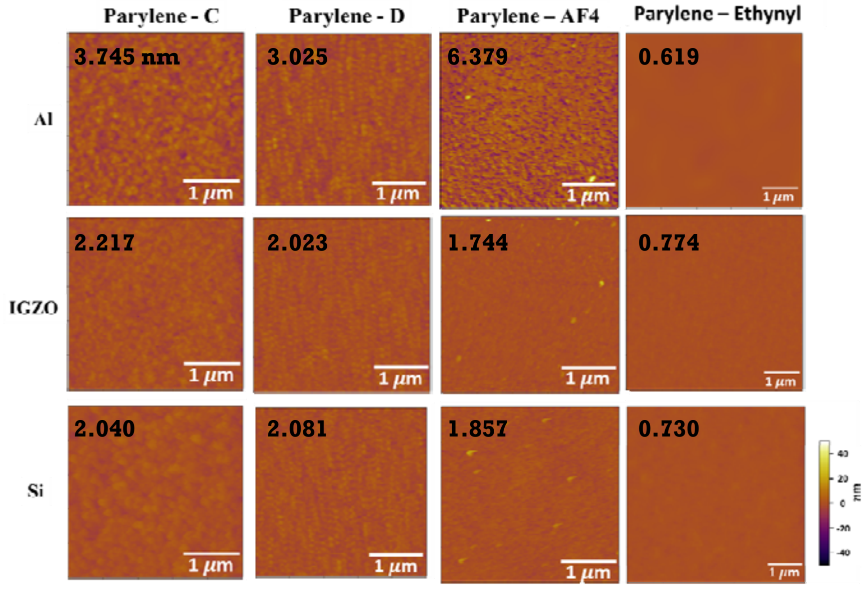
94. Na Liu, Jongyeol Baek, Seung Min Kim, Seongin Hong, Young Ki Hong, Yang Soo Kim, **Hyun-Suk Kim***, Sunkook Kim*, and Jozeph Park*, *corresponding author, "Stability improvement of High-Performance Multilayer MoS_2 Field-Effect Transistors", ACS Applied Materials & Interfaces, vol. 9, 42943-42950 (2017) [JCR 10%] [IF = 7.504]

Schematic diagram of parylene coating with several monomer

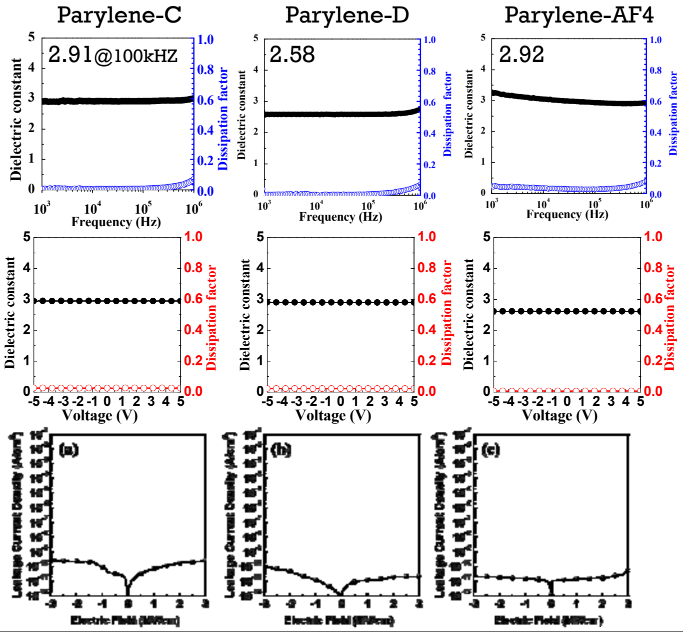



c) FT-IR of parylene-C,D,AF4 on Si.
d) FT-IR of parylene-C,D,AF4 on Al/Glass
(c)
(d)
Al
IGZO
Glass or Poly imide
Parylene C 105 nm
Al 107 nm
IGZO 50nm
Glass substrate
Parylene C 97 nm
IGZO 50nm
Glass substrate
Parylene D 120 nm
Al 93 nm
IGZO 44nm
Glass substrate
Parylene D 119 nm
IGZO 44nm
Glass substrate
AF4 96 nm
Al 110 nm
IGZO 52nm
Glass substrate
AF4 95 nm
IGZO 52 nm
Glass substrate
Aliphatic C-H
C-F stretching
C-Cl stretch
Absorbance (a.u)
Wavenumber (cm-1)
Wavenumver (cm-1)

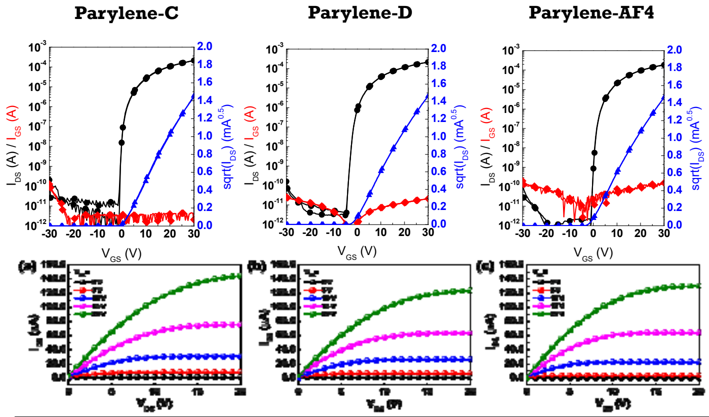

(c)
Parylene - C
Parylene - D
Parylene – AF4
Al
IGZO
Si



TFT – MIM (100 nm thickness)



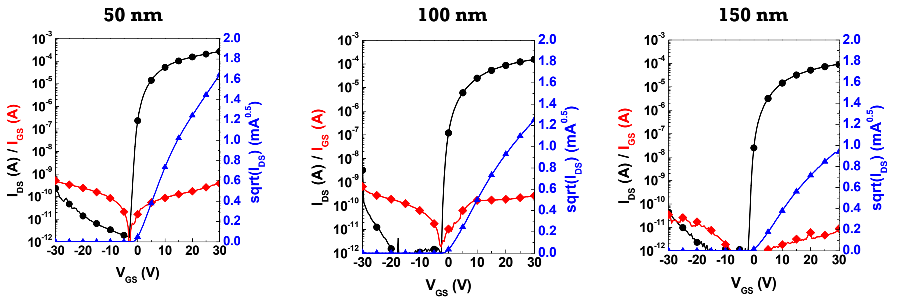
TFT - Transistor



Gate dielectric	Thickness [nm]	Semiconductor	Mobility [cm^2/Vs]	V_{on} [V]	S.S [V/dec]	N_{it} [/cm^2 eV]
SiO_2	100	IGZO	2.39	-2.81	0.48	8.60×10^{11}
Parylene-C	100	IGZO	6.22	-0.52	0.21	4.11×10^{11}
Parylene-D	100	IGZO	5.81	-3.31	0.58	1.39×10^{12}
Parylene-AF4	100	IGZO	6.23	0.02	0.41	9.42×10^{11}
Parylene-Ethynyl	74	IGZO	7.08	-3.72	0.20	6.02×10^{11}

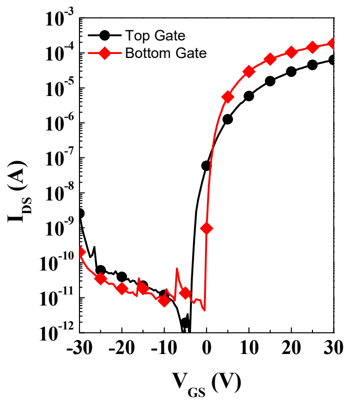
TFT - Transistor

Parylene-AF4

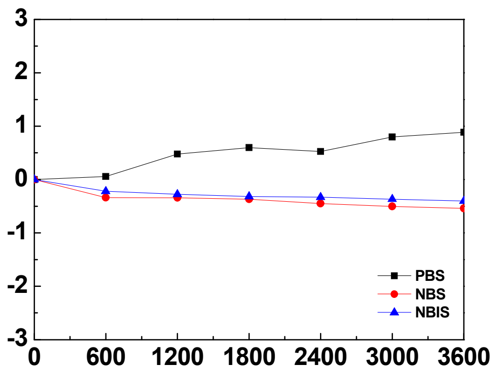


Gate dielectric	Thickness [nm]	Semiconductor	Mobility [cm^2/Vs]	V_{on} [V]	S.S [V/dec]	N_{it} [/cm^2 eV]
Parylene-AF4	50	IGZO	5.14	-1.69	0.46	2.15×10^{12}
Parylene-AF4	100	IGZO	5.06	-1.62	0.41	9.42×10^{11}
Parylene-AF4	150	IGZO	4.83	-0.93	0.30	4.32×10^{11}

SiO_2 Reference

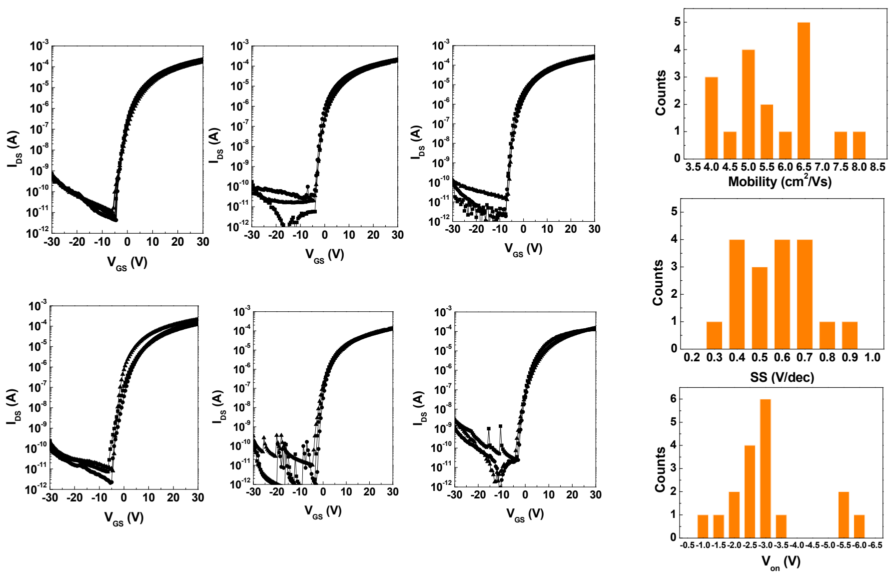


PBS/NBS/NBIS

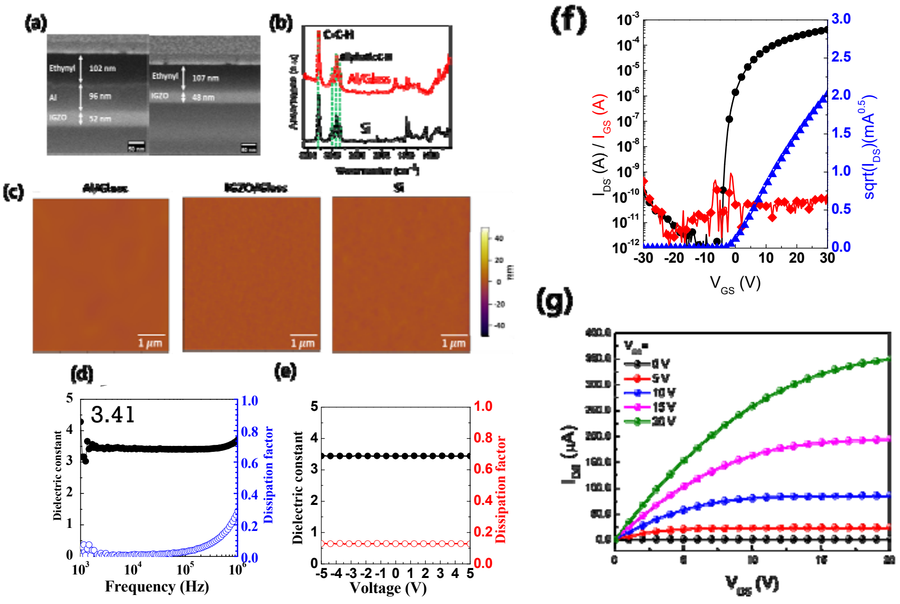


	Top Gate	Bottom Gate
Mobility	2.39	5.47
V_{on}	-2.81	0
S.S	0.48	0.42
N_{it}	8.60×10^{11}	1.17×10^{12}

TFT – Batch-to-Batch

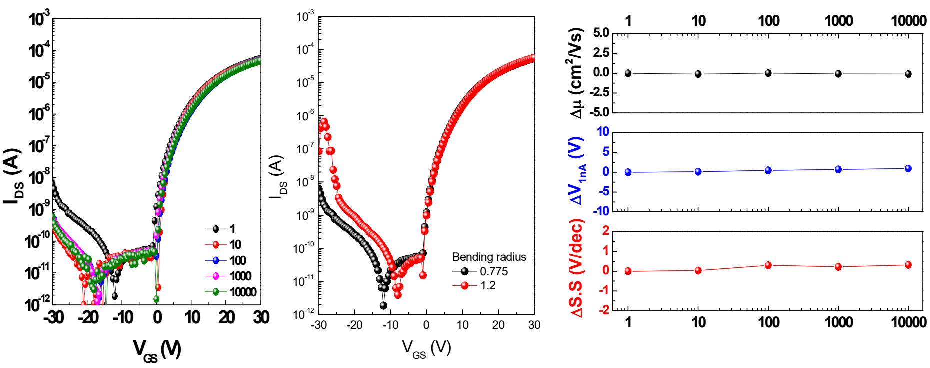


Parylene - ethynyl



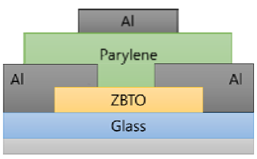
TFT - Flexible

- **Bending radius of 0.775 mm, calculated strain 0.68 %**

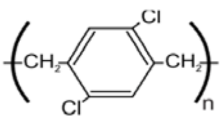


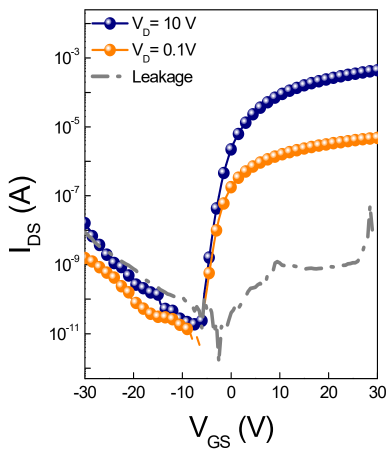
On-going Researches

TFT – High Mobility



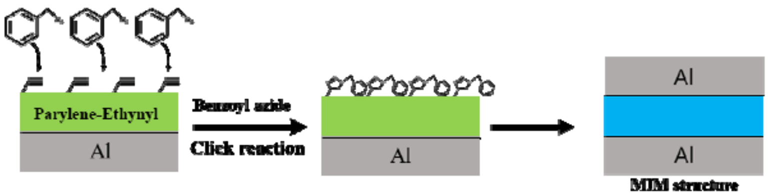
Gate dielectric
⇒ **Parylene D**

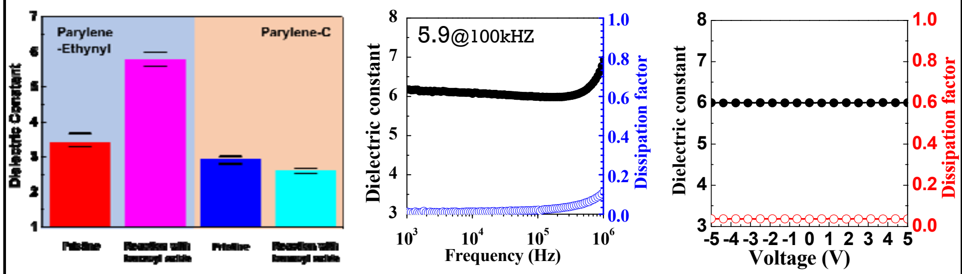




μ_{FE} (cm2/Vs)	S.S (V/dec)	V_{TH} (V)	I_{on}/I_{off}
17.57	0.85	-1.79	~10^7

TFT – Click Reaction



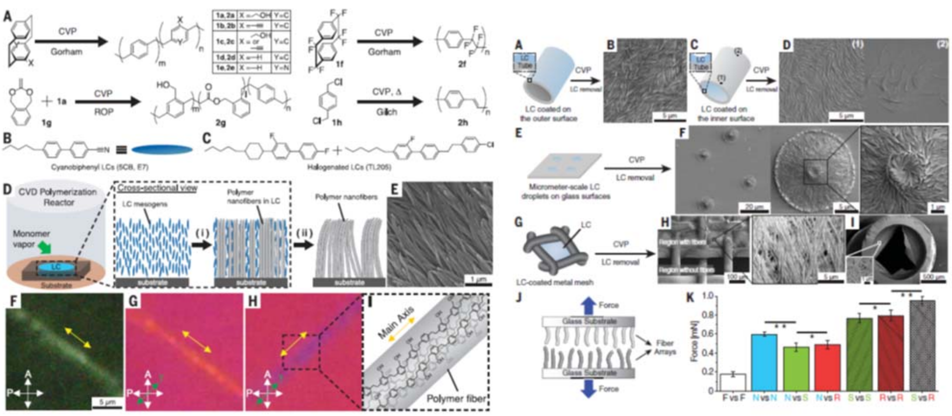


REPORT

POLYMERS

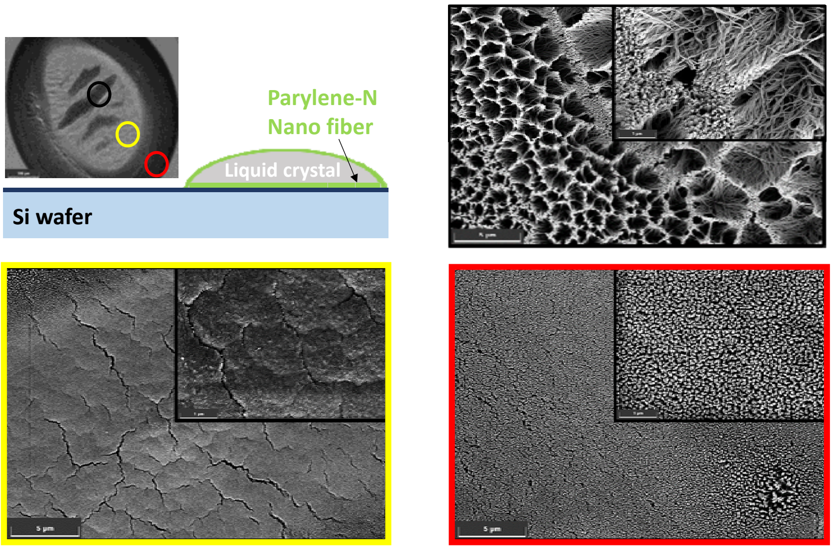
Templated nanofiber synthesis via chemical vapor polymerization into liquid crystalline films

Kenneth C. K. Cheng, Marco A. Bedolla-Pantoja, Young-Ki Kim, Jason V. Gregory, Fan Xie, Alexander de France, Christoph Hussal, Kai Sun, Nicholas L. Abbott, Joerg Lahann

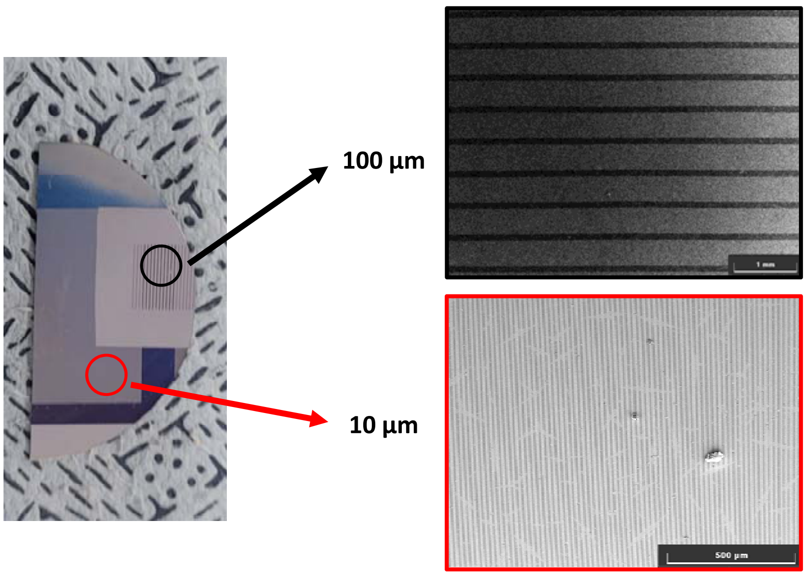


Cheng et al., Science 362, 804–808 (2018)

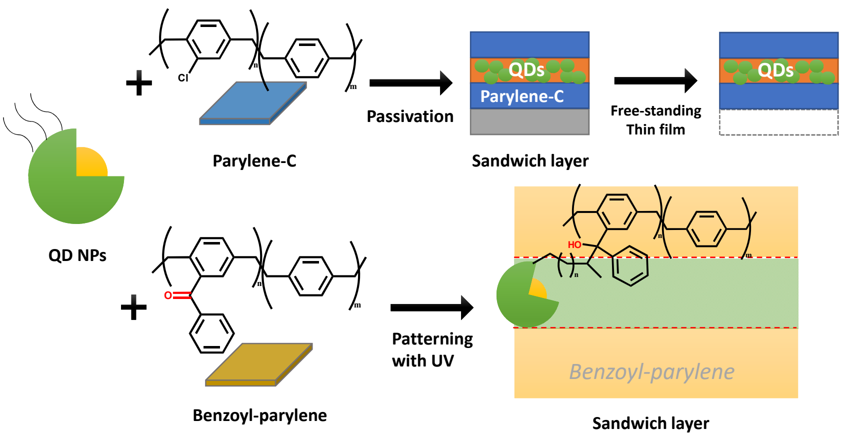
Nano Fiber



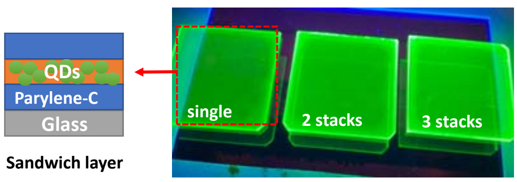
Photoreactive parylene



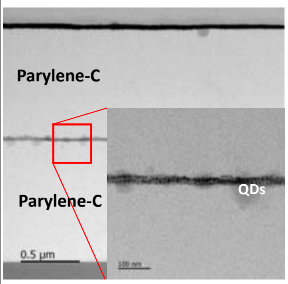
PL(Quantum dots) Film



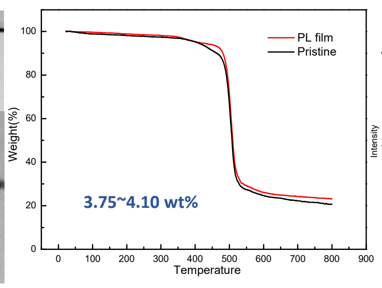
PL(Quantum dots) Film



<TEM-cross section image>



<TGA>



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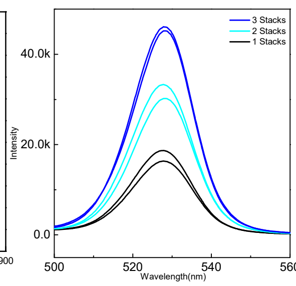
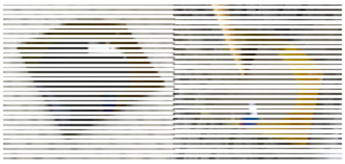


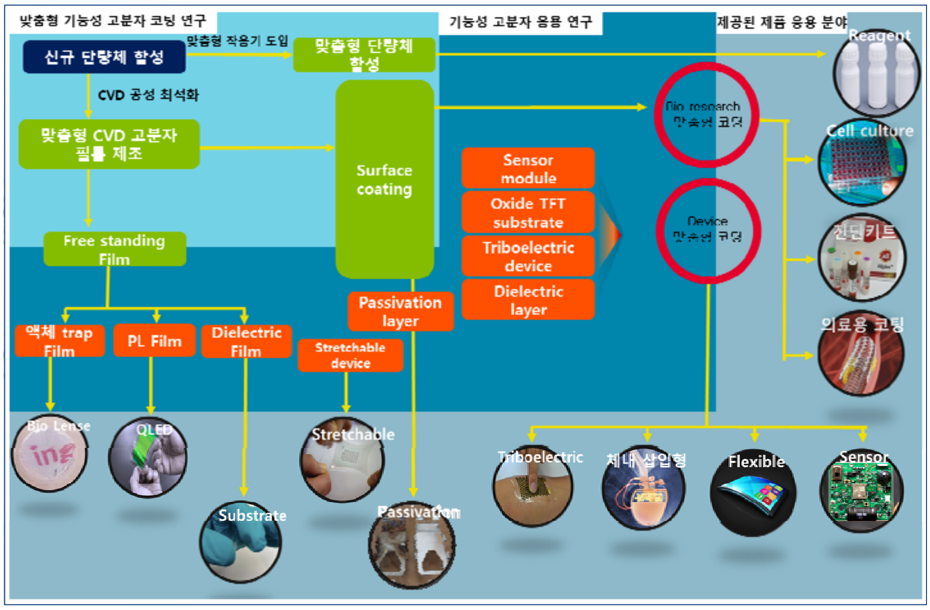
Liquid Material Encapped Parylene

Liquid electrolyte



Liquid Polymer(PEG)

연구개발 목표



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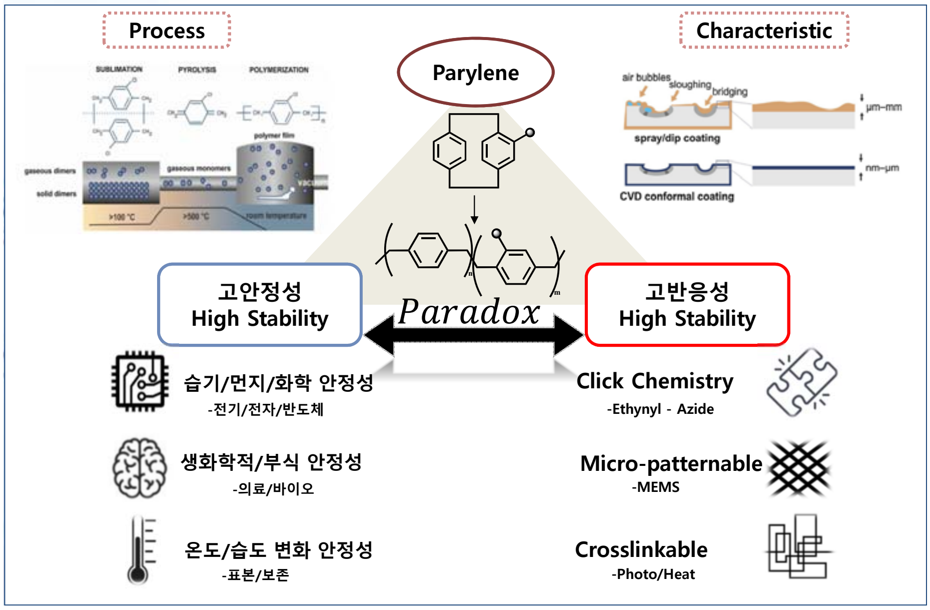
Paradox 형 Parylene 박막 필름



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