Patterning of Porphyrin Molecules Using Micro-Contact Printing in Conjunction with Langmuir-Blodgett Deposition

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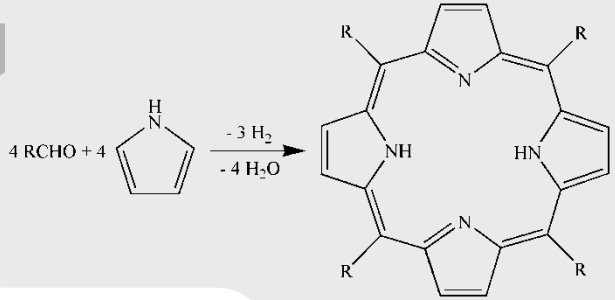
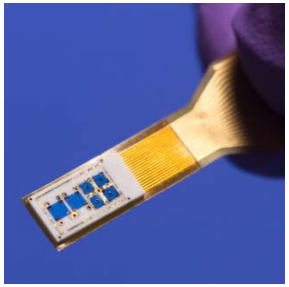
Introduction of porphyrin - Applications

Data Storage

Photonic and
Optoelectronic Materials



Photodynamic
Therapy



Chemical
Sensor

Photovoltaic
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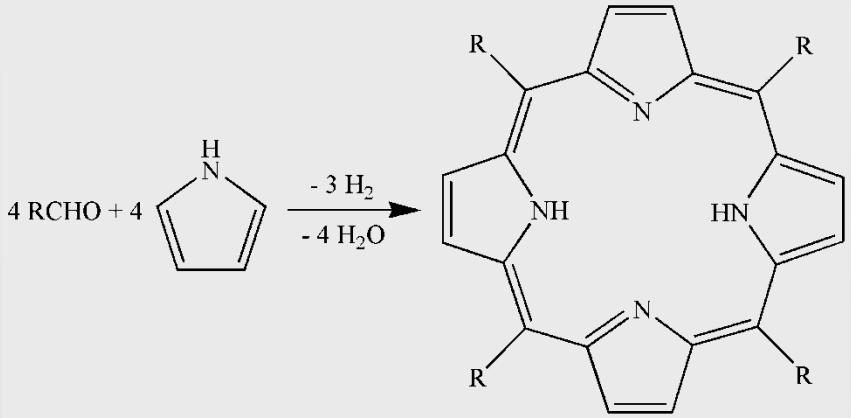
Introduction of porphyrin - Synthesis

Synthetic mechanism of porphyrin



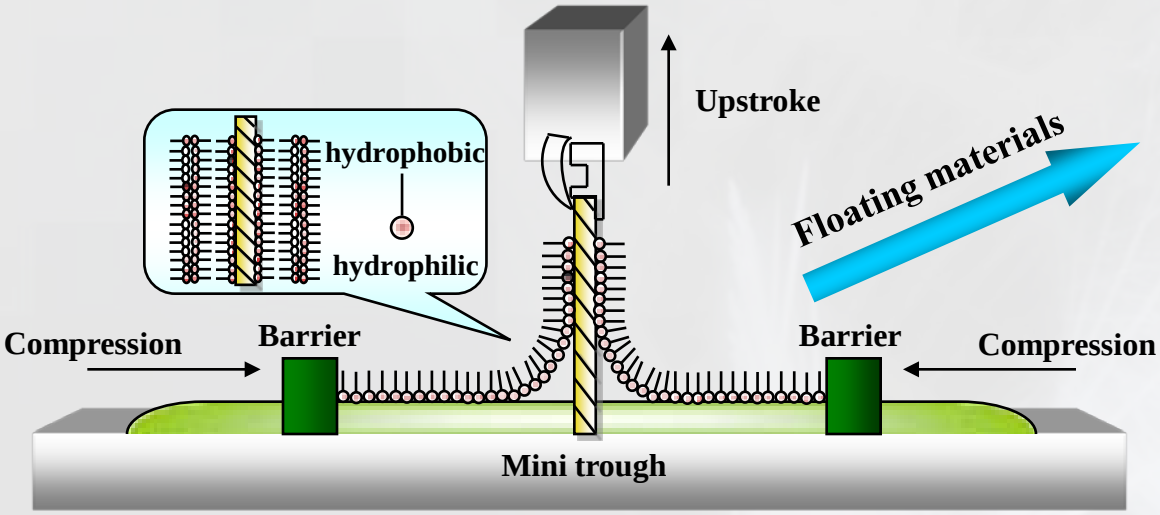
Porphyrin:
- **heterocyclic macrocycle composed of four pyrroles linked through methane bridges**

Applications of porphyrin derivatives

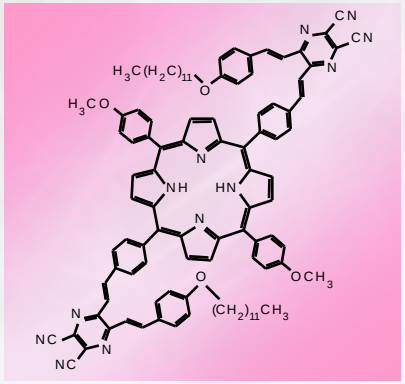
☞ Chemical sensor: Chromophoric systems of the dicyanopyrazine-linked porphyrin were investigated to validate the acid vapor sensing capability based on protonation of the porphyrin

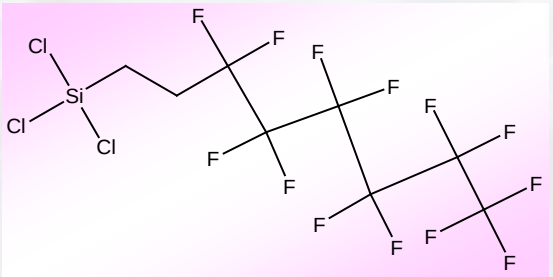
Langmuir-Blodgett film fabrication

KSV Minitrough Ⅱ(KSV instruments Ltd., Finland)



5,15-Di[5-{2-(4-alkoxyphenyl)-ethenyl}-6-{2-phenyl-ethenyl}-2,3-dicyano-pyrazino]-porphyrin (2-DCPP)



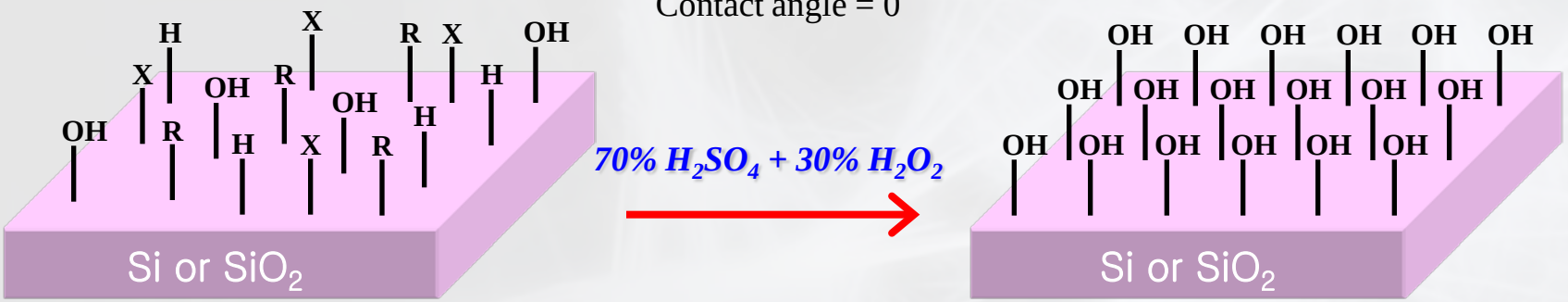


(Tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane

Langmuir-Blodgett film fabrication

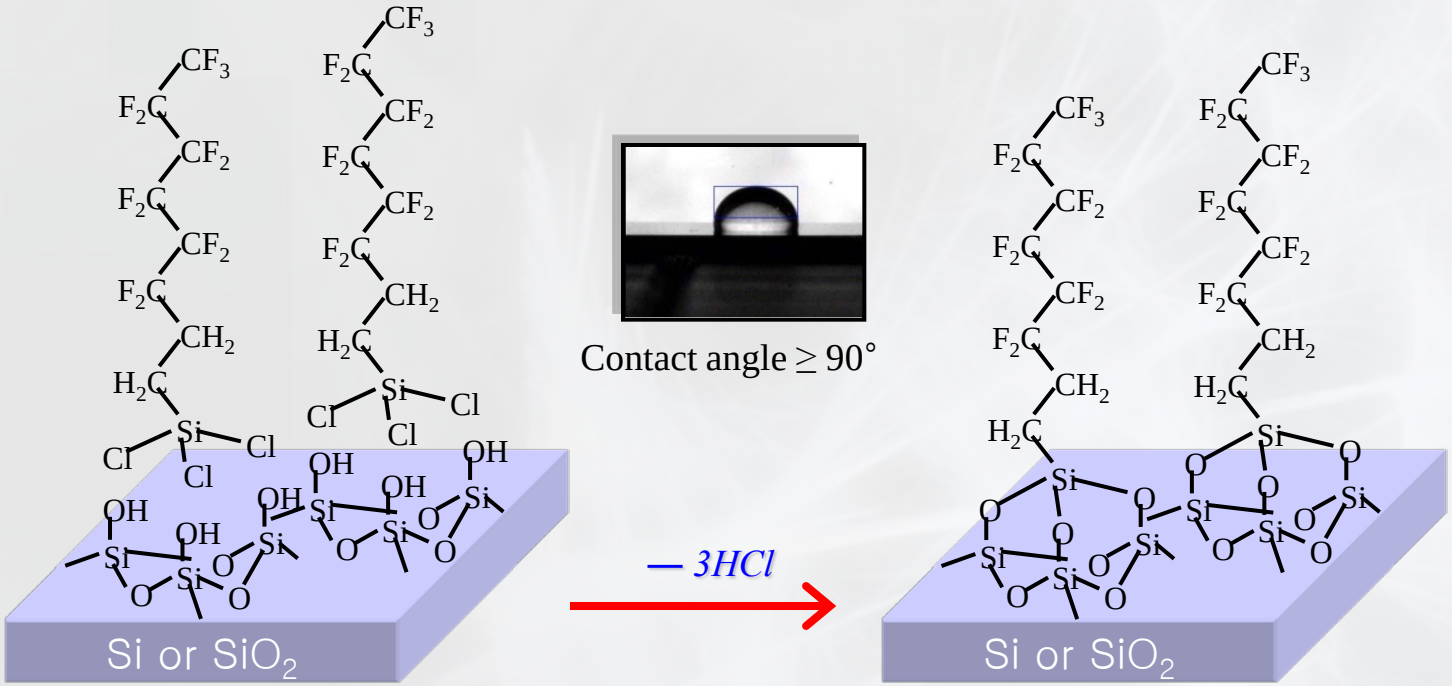
Piranha solution treatment of substrates

Contact angle = 0°



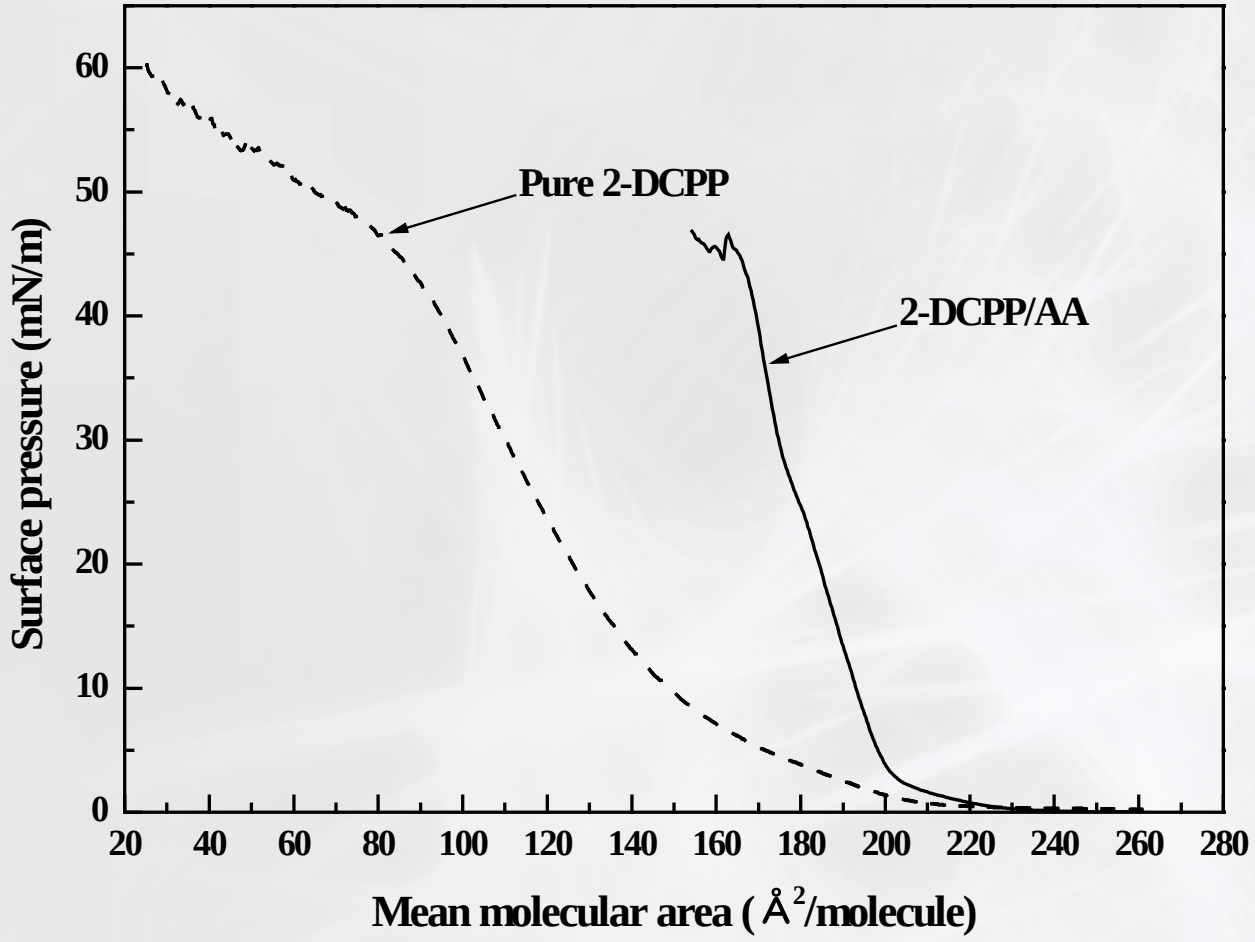
Langmuir-Blodgett film fabrication

Silanization treatment of substrates



Langmuir-Blodgett film fabrication

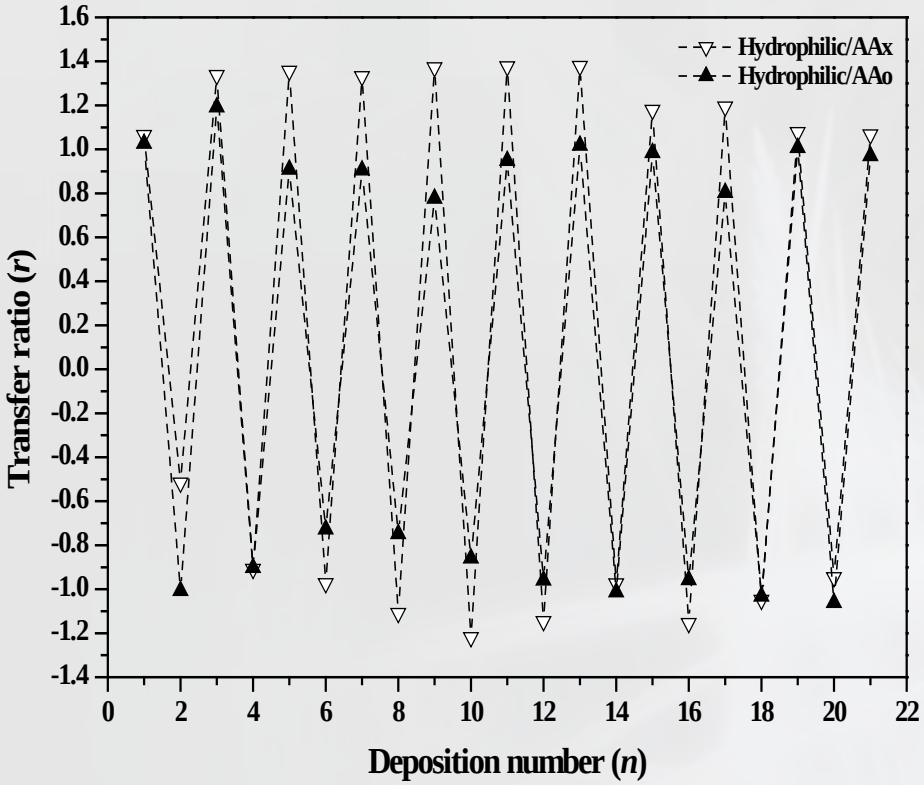
Isotherm graphs



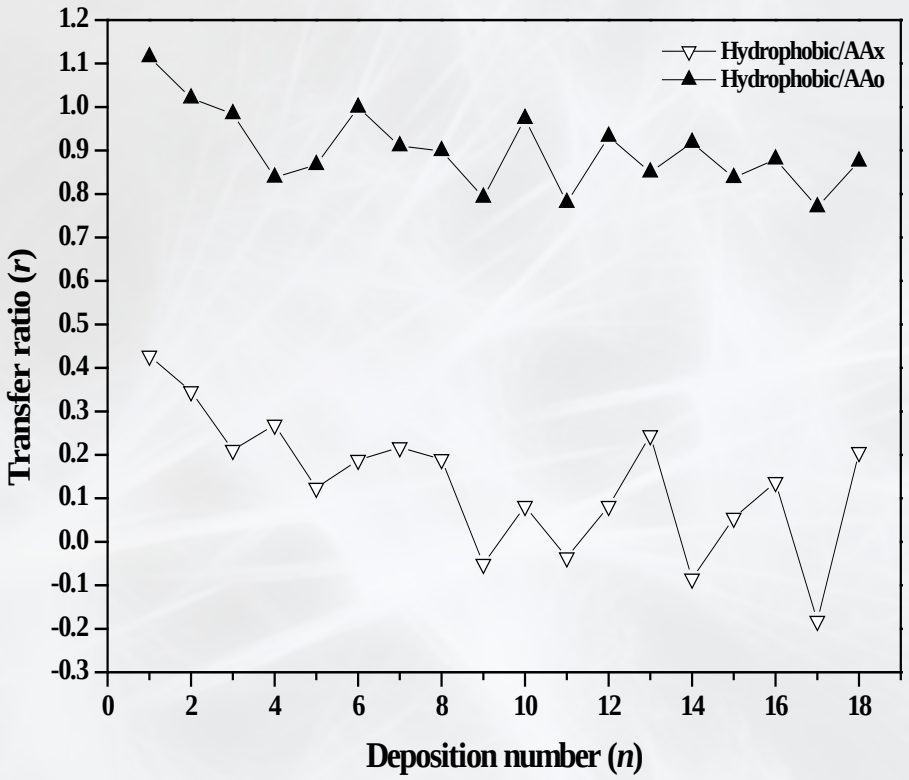
Langmuir-Blodgett film fabrication

Transfer ratio

2-DCPP LB films on hydrophilic substrate

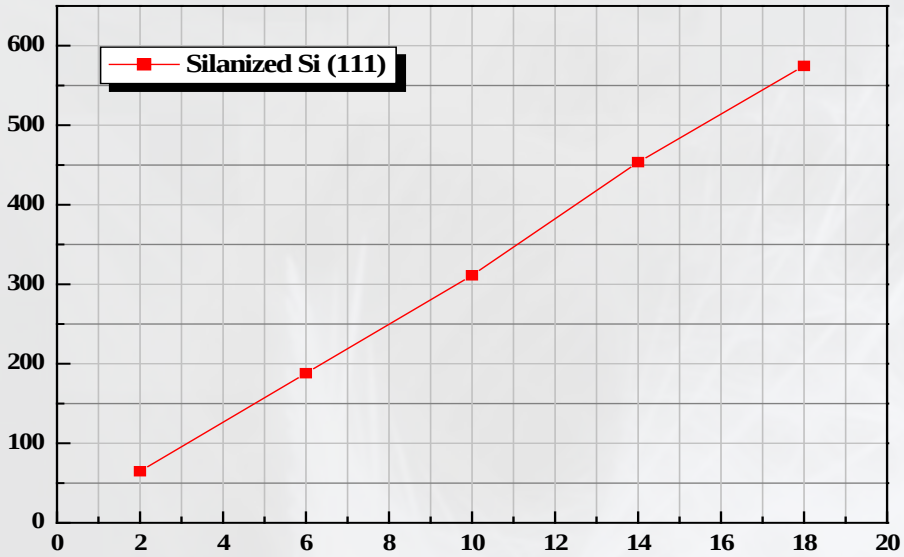


2-DCPP LB films on hydrophobic substrate



Langmuir-Blodgett film fabrication

Ellipsometric thickness

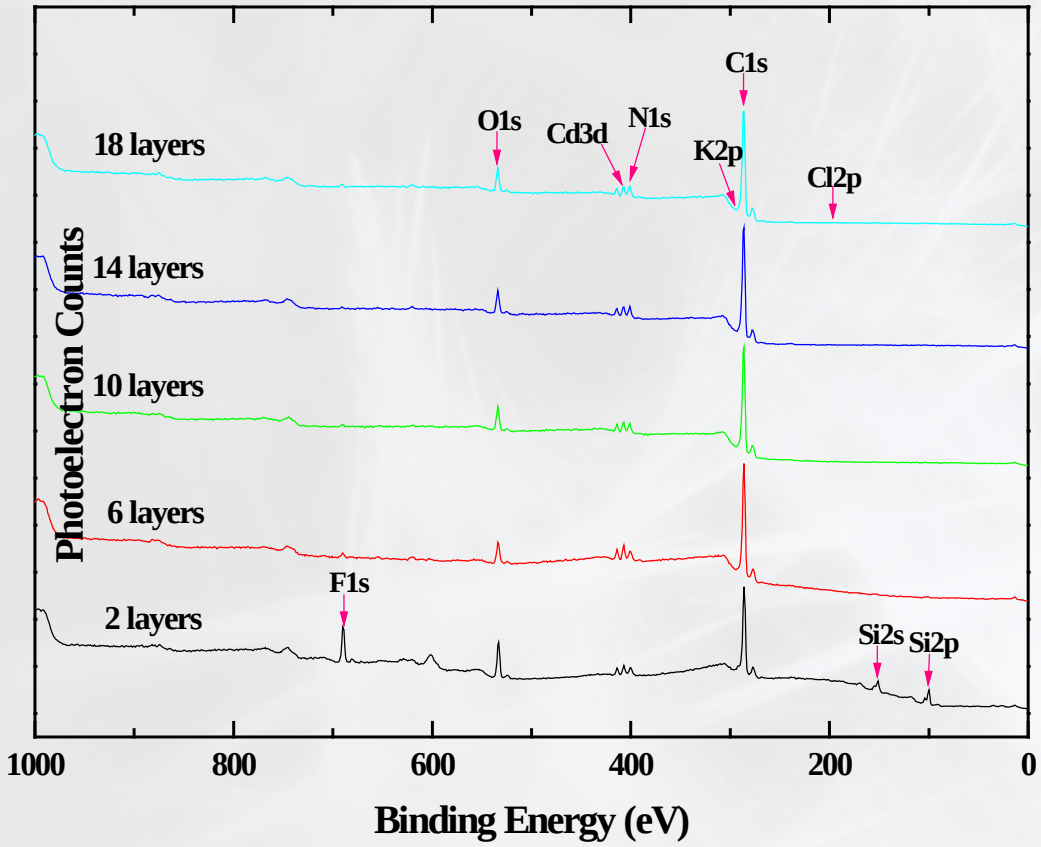


	Dicyanopyrazine-linked porphyrin (2-DCPP)				
	Silanized Si (111)				
Number of layers	2	6	10	14	18
Average thickness (Å)	64.8	188	311.2	453.6	574.6
Average thickness per layer (Å)	32.4	30.8	30.8	35.6	30.2

Langmuir-Blodgett film fabrication

X-ray photoelectron spectroscopy

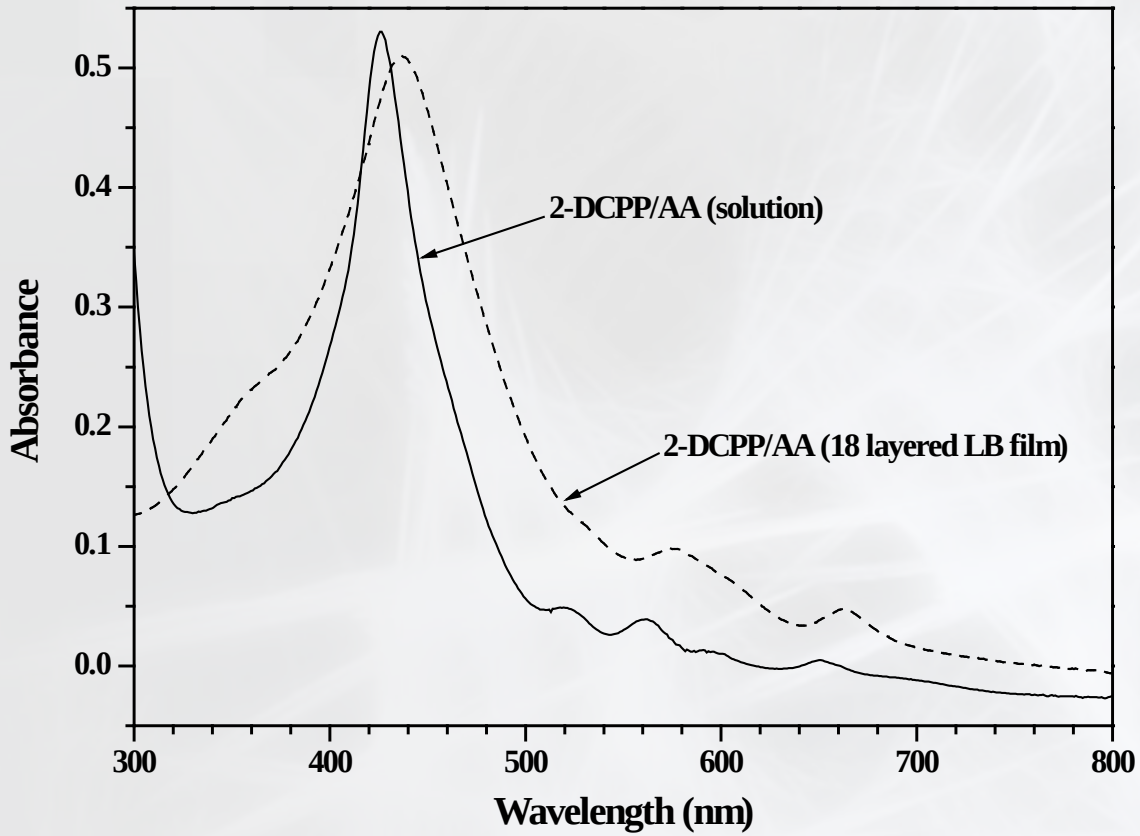
2-DCPP LB films on silanized Si (111) substrate



Langmuir-Blodgett film fabrication

UV-visible spectroscopy

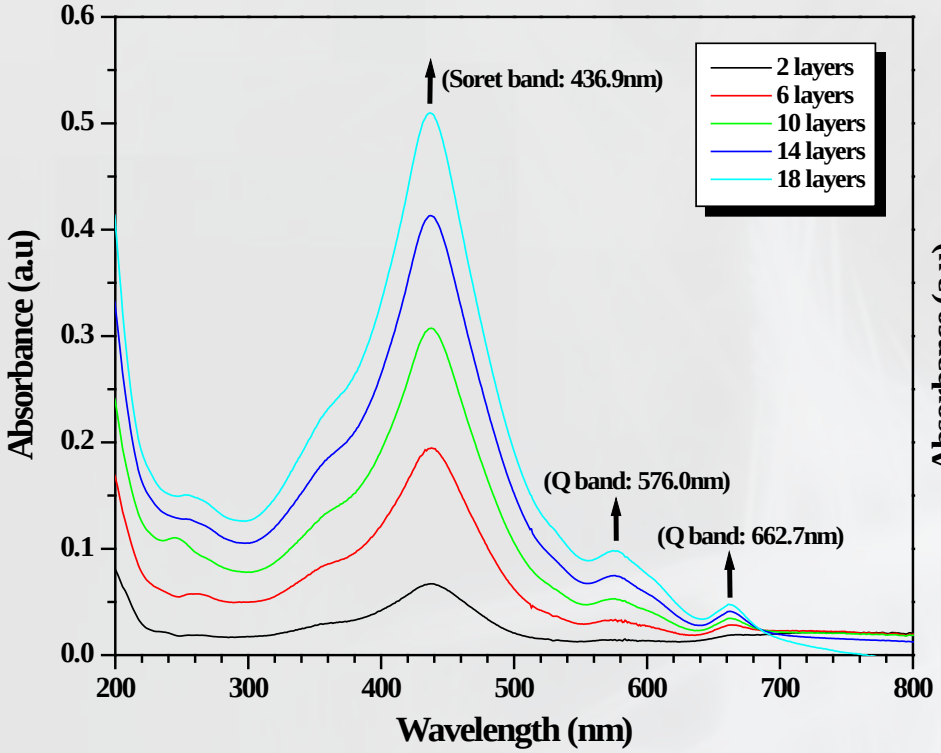
UV-visible spectra of 2-DCPP solution in chloroform and an 18-layered LB film

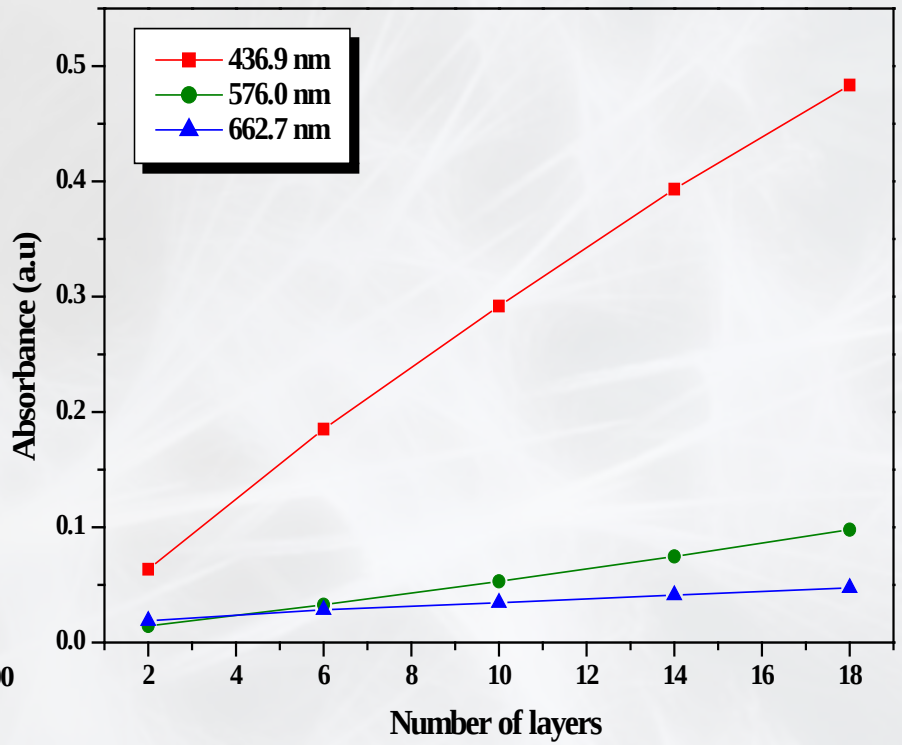


Langmuir-Blodgett film fabrication

UV-visible spectroscopy

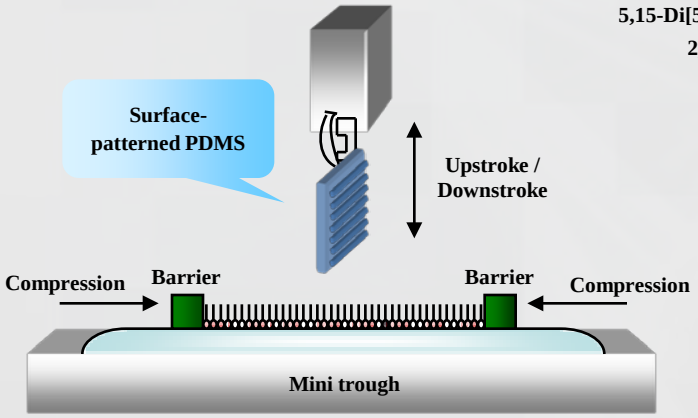
UV-visible absorption spectra of 2-DCPP LB films with various deposited layers



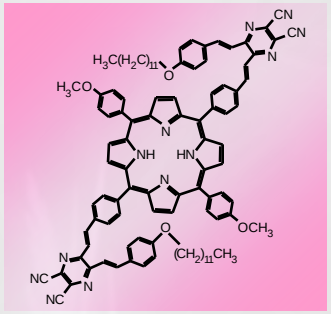


Pattering of porphyrin

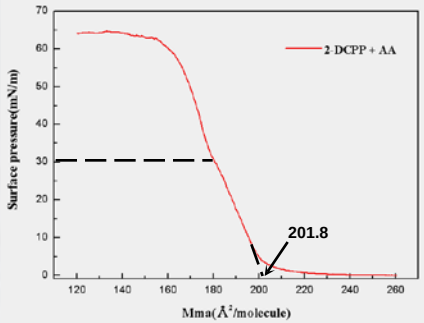
Langmuir-Blodgett technique



5,15-Di[5-{2-(4-alkoxyphenyl)-ethenyl}-6-{2-phenyl-ethenyl}-2,3-dicyano-pyrazino]-porphyrin (2-DCPP)



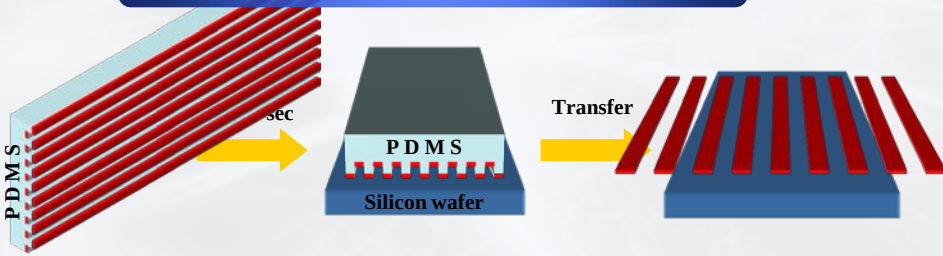
Isotherm of 2-DCPP monolayer



- ✓ Solvent : chloroform (99.0 %)
- ✓ Transfer promoter : arachidic acid (AA)
- ✓ Subphase : ultra pure water, cadmium chloride, potassium hydrogencarbonate
- ✓ Substrates : polydimethylsiloxane (PDMS)

- ✓ Ultra-pure water with a resistivity of ca. 18.2 MΩ and pH value of 5.8, purified by a Mili-Q ultra-pure water system, is used as the subphase.
- ✓ Concentration of dicyanopyrazine-linked porphyrin solution in chloroform is 0.77 × 10^{-4} M.
- ✓ Langmuir layer floating above the water surface is compressed at a speed of 10 mm/min.
- ✓ LB film is transferred onto PDMS at a surface pressure of 30 mN/m with a up/down stroke speed of 5 mm/min.

Micro-Contact Printing

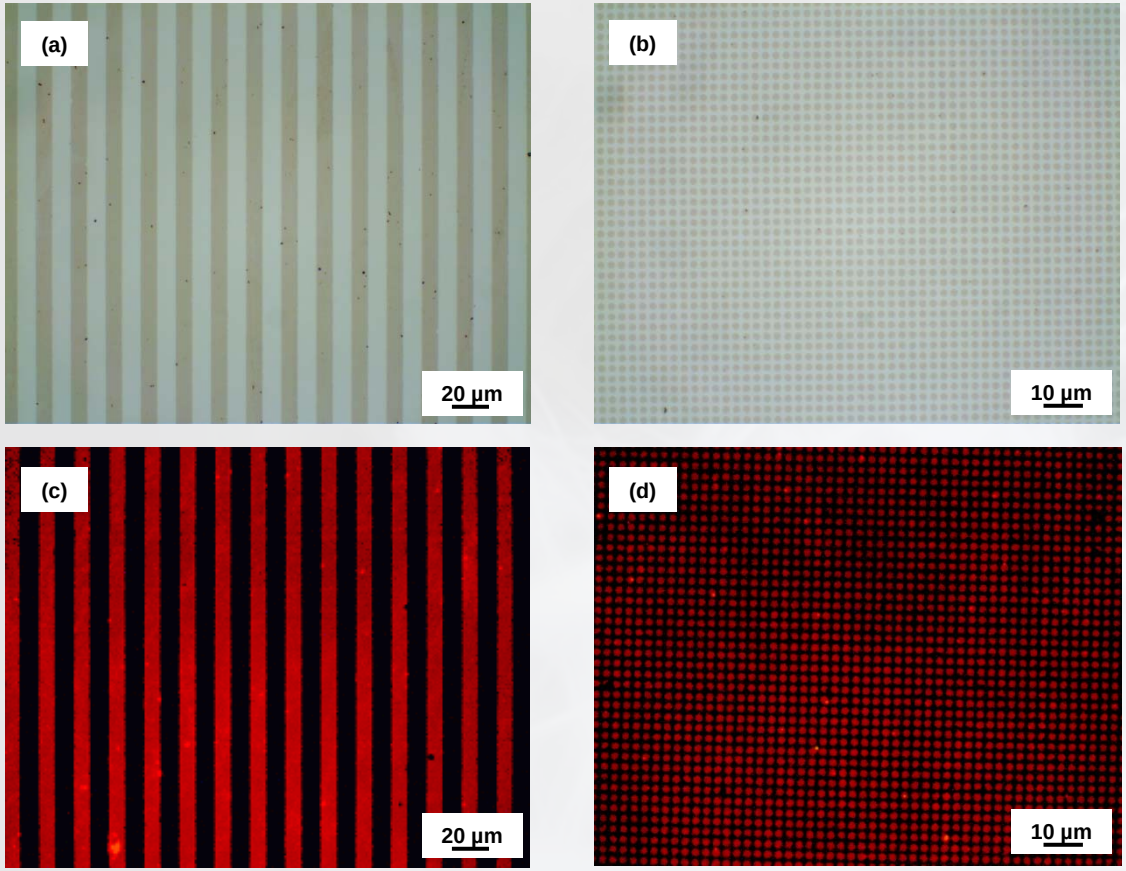


Porphyrin LB film | Stamping | Porphyrin patterns

Pattering of porphyrin

Optical / Fluorescence microscopy images

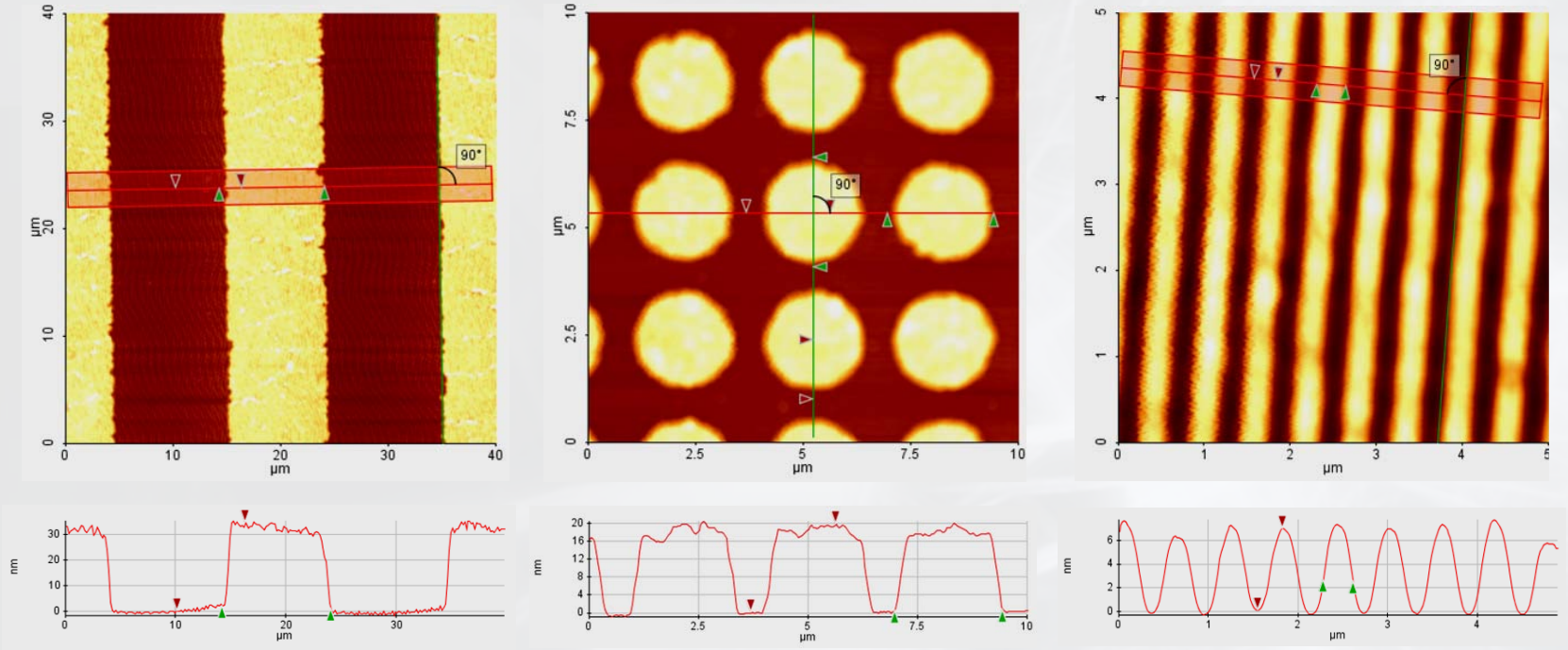
Optical and Fluorescence images of (a), (c) 10 μm line and (b), (d) 2 μm dot pattern of 10-layered 2-DCPP



Pattering of porphyrin

Atomic force microscopy images

AFM images of (a) 10 μm line pattern of 10-layered and (b) 2 μm dot pattern of 8-layered and (c) 300 nm line pattern of 6-layered 2-DCPP



(a) (b) (c)

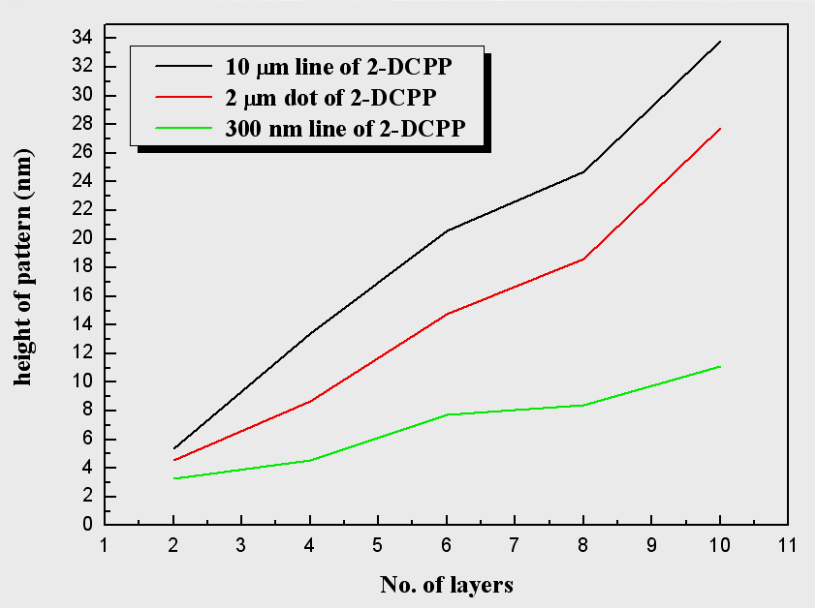
Pattering of porphyrin

Average height of patterns

(a) Table and (b) graph of average height of patterns in accordance with number of layers

No. of layers	Thickness (nm)			
	LB film on Si	10 μm line	2 μm dot	300 nm line
2	6.4	5.636	4.575	3.293
4	12.8	13.410	8.710	4.581
6	19.2	20.591	14.766	7.750
8	25.6	24.674	18.629	8.421
10	32	33.815	27.761	11.127

(a)

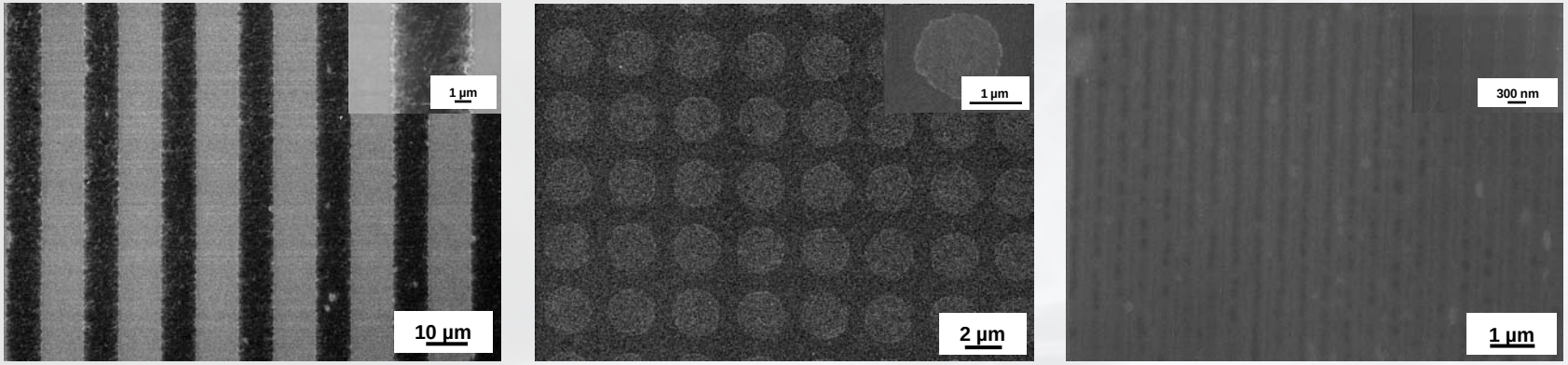


(b)

Pattering of porphyrin

Scanning electron microscopy images

SEM images of (a) 10 μm line and (b) 2 μm dot and (c) 300 nm line patterns of 10-layered 2-DCPP

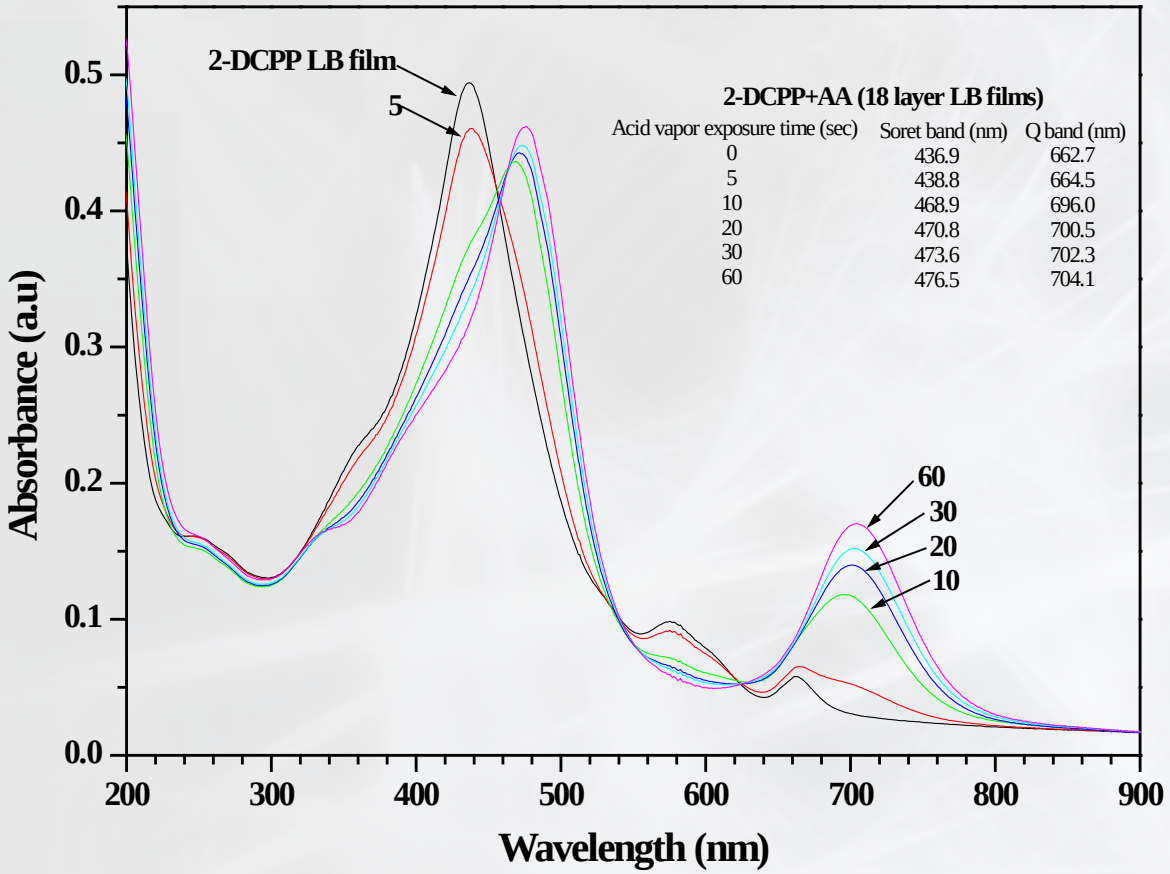


(a) (b) (c)

Acid-vapor sensing & fluorescent patterns

UV-visible spectroscopy

Acid vapor exposure to 18 layers LB film



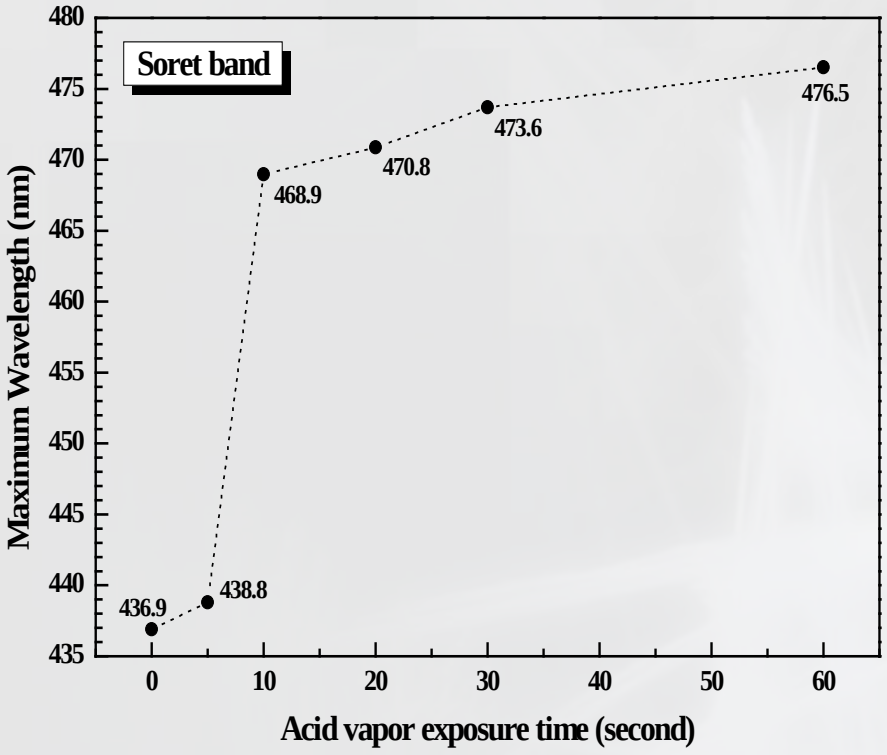
2-DCPP+AA (18 layer LB films)

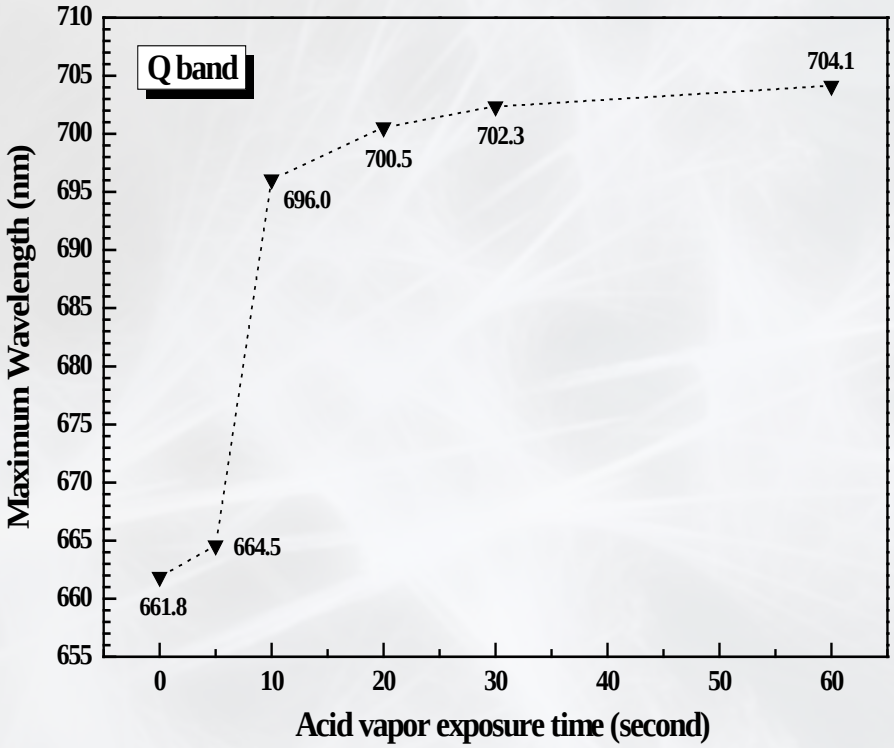
Acid vapor exposure time (sec)	Soret band (nm)	Q band (nm)
0	436.9	662.7
5	438.8	664.5
10	468.9	696.0
20	470.8	700.5
30	473.6	702.3
60	476.5	704.1

Acid-vapor sensing & fluorescent patterns

UV-visible spectroscopy

Exposure time (sec) dependence of the UV absorption spectra (18 layers LB film)

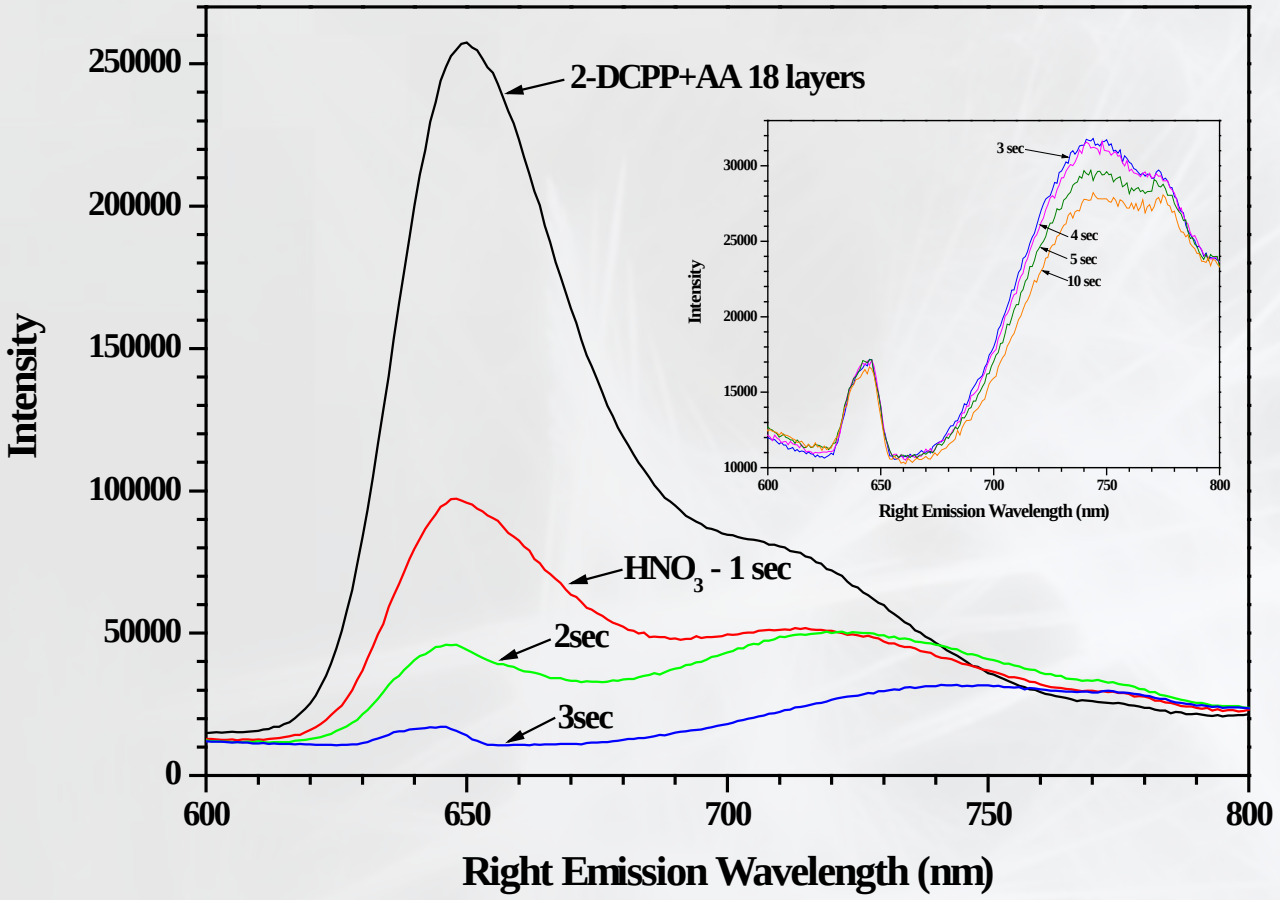




Acid-vapor sensing & fluorescent patterns

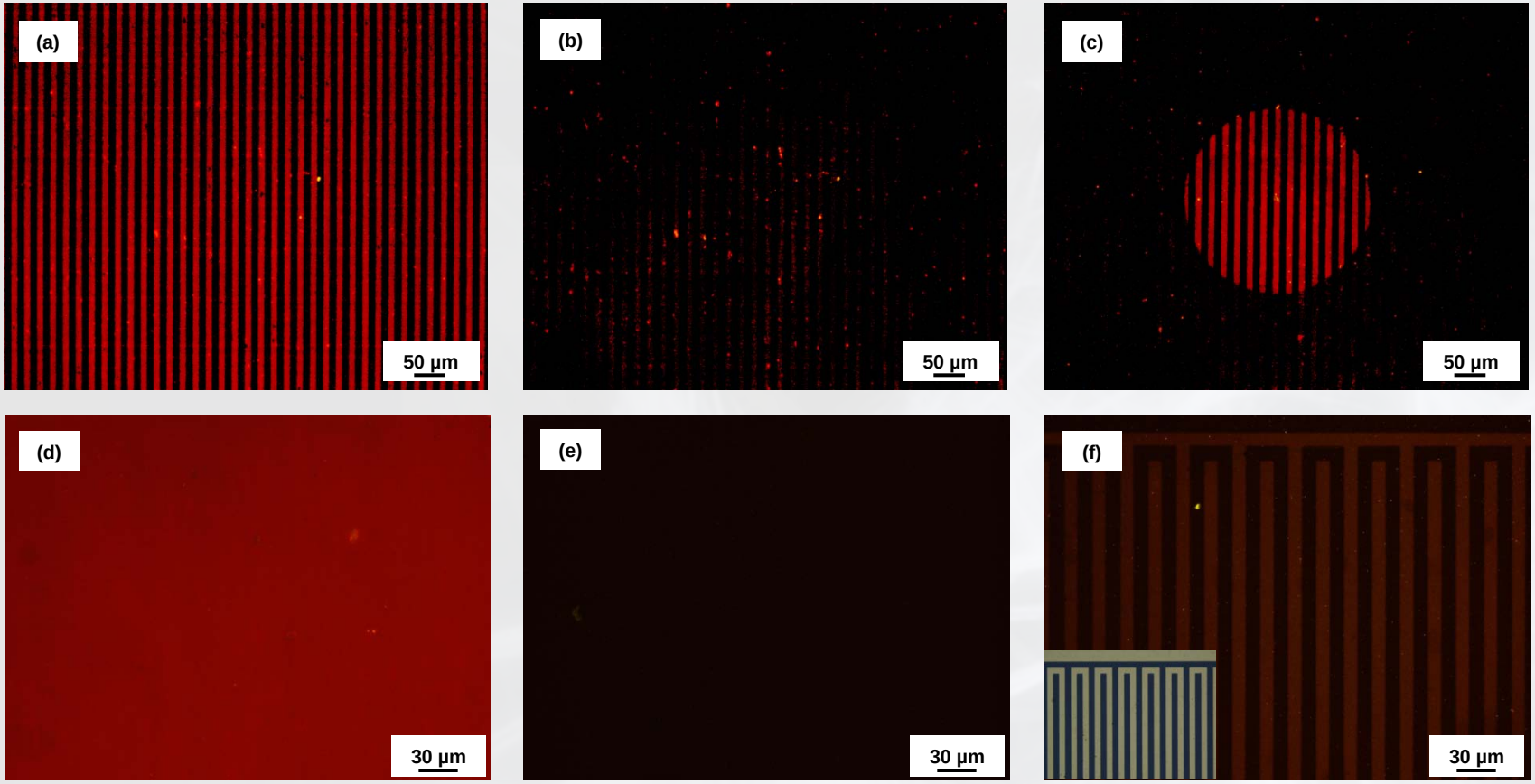
Photoluminescence spectroscopy

Acid vapor exposure to 18 layers LB film



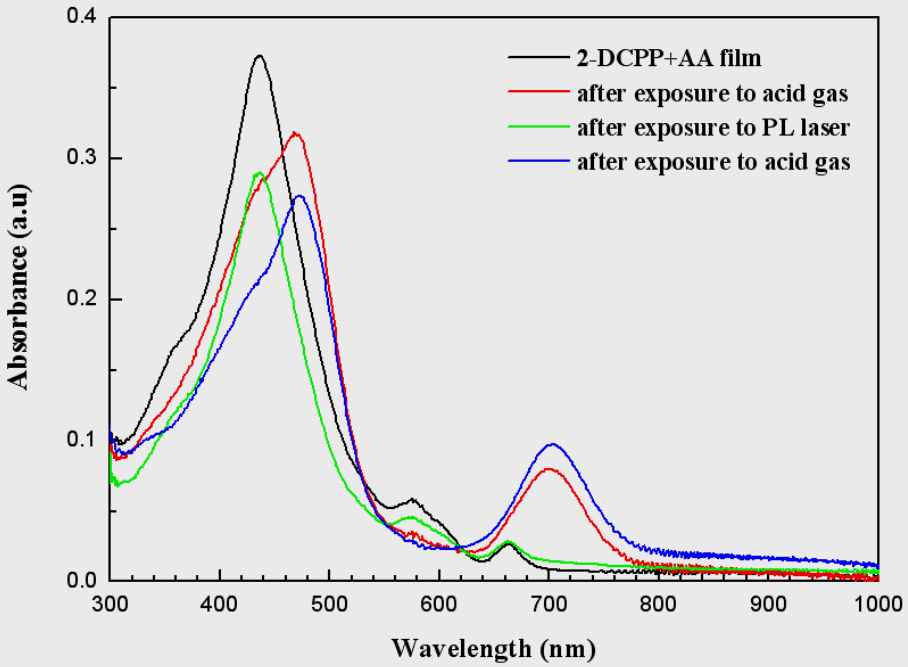
Acid-vapor sensing & fluorescent patterns

Fluorescence spectroscopy



Acid-vapor sensing & fluorescent patterns

UV-visible spectroscopy



Photoluminescence spectroscopy