

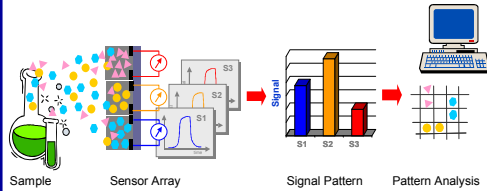
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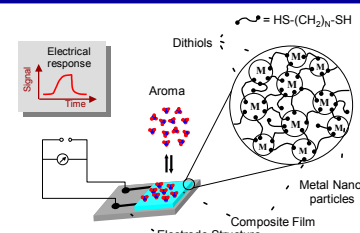
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## Introduction

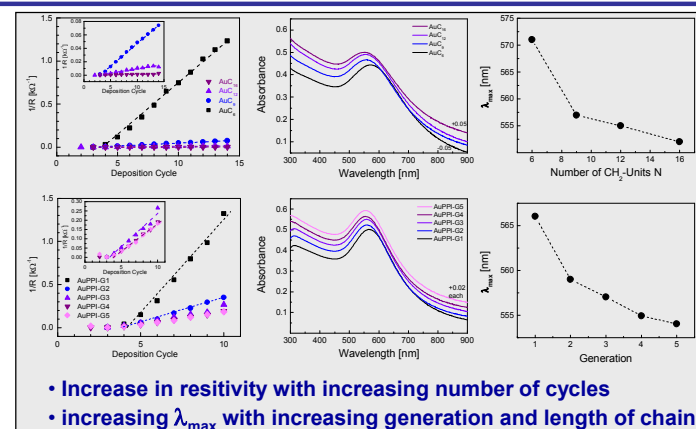
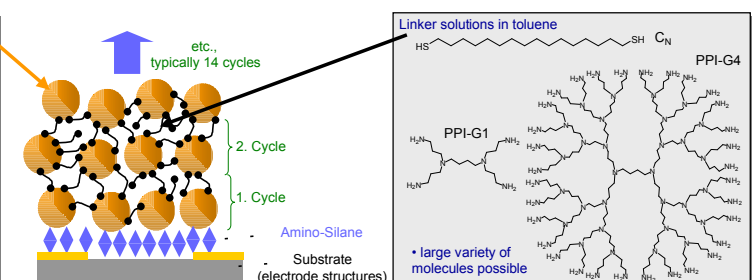
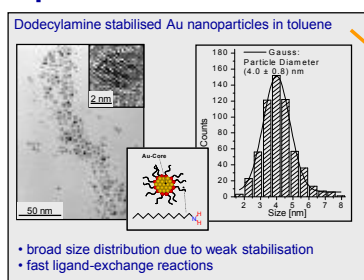


Recent efforts to control the physical and chemical properties of nanostructured materials through a molecular level design have generated enormous interest in thin films comprised of organically linked metal nanoparticles.<sup>[1]</sup> An interesting application of such metal nanoparticle/organic films is their use as chemiresistor-type or microgravimetric gas sensors.<sup>[2-4]</sup> In these films the nanoparticles provide electric conductivity, ensuring straightforward electrical signal transduction. The organic molecules ensure the mechanical stability of the film, while at the same time providing sites for interactions with vapour molecules. To study the structure and chemical composition of the films we employed AFM, FE-SEM, TEM, and XPS/UPS. The vapour sensitivity of the films at room temperature was investigated by dosing coated chemiresistors and quartz crystal microbalances (QCM) with different solvent vapours while monitoring their resistance and resonance frequency, respectively. In addition, the distribution of analyte molecules within the film material was investigated by neutron reflectometry.



## Preparation

By Layer-by-layer self-assembly from solutions of Au-nanoparticles and organic dithiols<sup>[5]</sup>



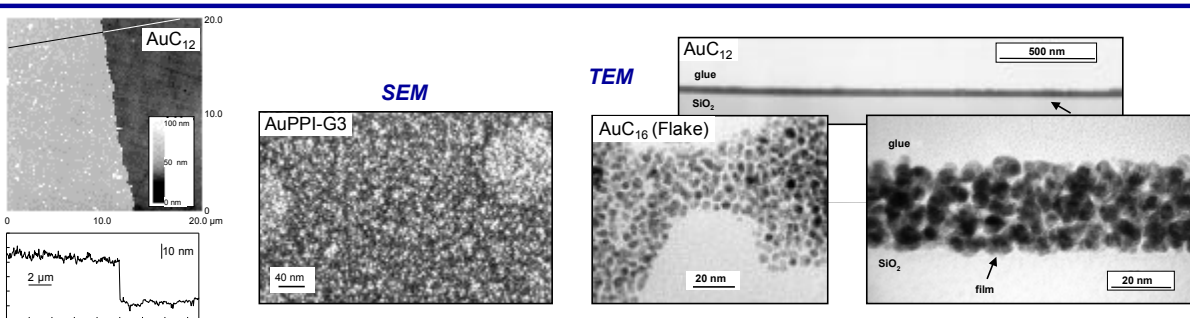
- Wide range of organic materials available
- Easy synthesis of starting materials
- Automated sensor preparation possible

- Increase in resistivity with increasing number of cycles
- increasing  $\lambda_{max}$  with increasing generation and length of chain

Well-controlled and reproducible film deposition

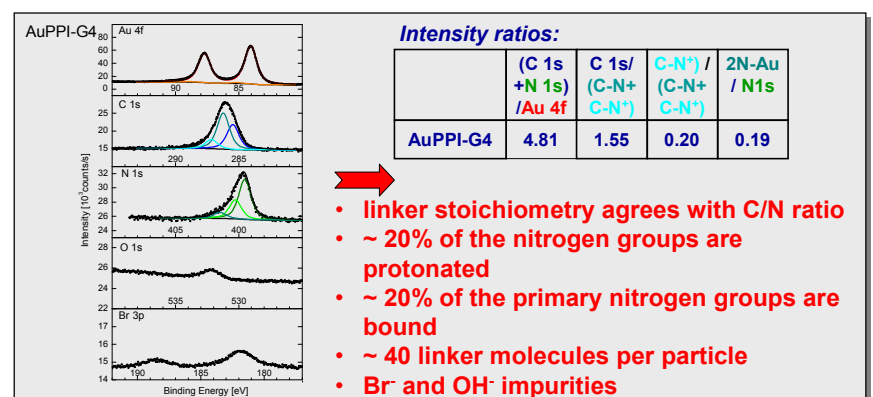
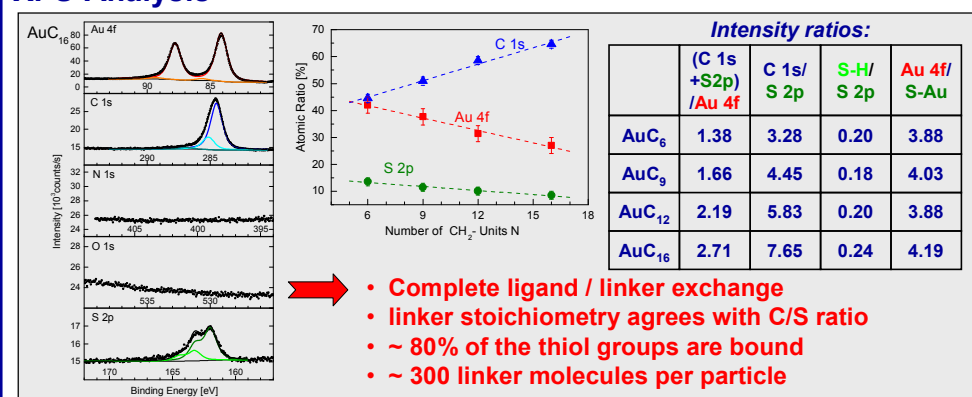
## Microscopy

Sensor	d [nm]	Sensor	d [nm]
AuC <sub>6</sub>	26.2	AuPPI-G1	19.1
AuC <sub>9</sub>	27.6	AuPPI-G2	22.1
AuC <sub>12</sub>	33.8	AuPPI-G3	22.3
AuC <sub>16</sub>	29.9	AuPPI-G4	23.1
		AuPPI-G5	32.1



- Homogeneous films
- Particles size and structure are stable during film assembly
- Porous and granular
- thin films (19 nm to 34 nm)

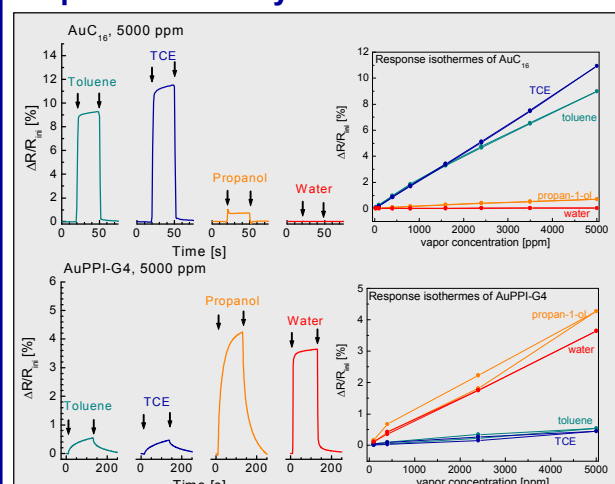
## XPS-Analysis



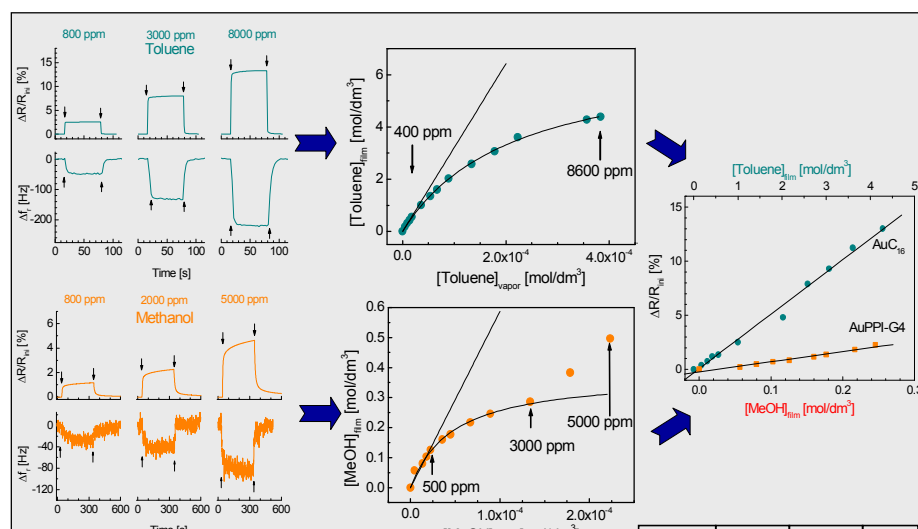
- linker stoichiometry agrees with C/N ratio
- ~ 20% of the nitrogen groups are protonated
- ~ 20% of the primary nitrogen groups are bound
- ~ 40 linker molecules per particle
- Br<sup>-</sup> and OH<sup>-</sup> impurities

- Complete ligand / linker exchange
- linker stoichiometry agrees with C/S ratio
- ~ 80% of the thiol groups are bound
- ~ 300 linker molecules per particle

## Vapour Sensitivity

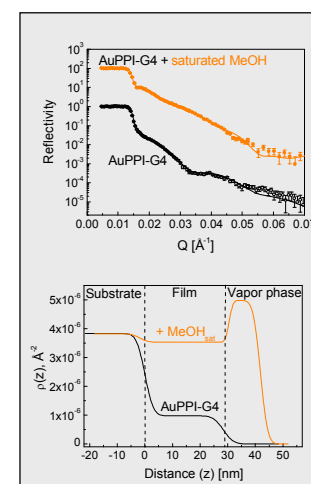


- Increase in the resistances
- Fast response and fast recovery ( $t_{90} < 300$  ms for alkylene dithiols)
- Tunable selectivity
- Selectivity is similar to the solubility properties of the organic molecules



- LANGMUIR-type adsorption isotherms
- Linear relation between mass uptake and electrical signal

	$K_p$	$K_b$ l/mol	$C_{sat}$ mol/l
AuC <sub>16</sub>	$3.2 \times 10^4$	$4.6 \times 10^3$	6.9
AuPPI-G4	$5.9 \times 10^3$	$2.1 \times 10^4$	0.4



- Analyte is distributed homogeneously in the film and condensed on top of it

## Conclusion

The high sensitivity, the fast response, and the well-controlled chemical selectivity make these materials promising candidates for chemical sensor applications

## References

- [1] A. N. Shipway et al.: *Chem. Phys. Chem.* **1** (2000) 18
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- [3] Y. Joseph et al.: *J. Phys. Chem. B*, (2003) in press, and references therein
- [4] Y. Joseph et al.: *Farad. Disc.*, (2003) in press, and references therein
- [5] D. Bethell et al.: *J. Electroanal. Chem.* **409** (1996) 137